

A SELF-CONTAINED GROUND-STATE
APPROACH FOR THE CORRECTION OF
SELF-INTERACTION ERROR IN
APPROXIMATE DENSITY-FUNCTIONAL
THEORY

Glenn Moynihan

THE UNIVERSITY OF DUBLIN
TRINITY COLLEGE



A DISSERTATION SUBMITTED FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY AT
THE UNIVERSITY OF DUBLIN
TRINITY COLLEGE

2018

DECLARATION

I DECLARE that this thesis has not been submitted as an exercise for a degree at this or any other university and it is entirely my own work. I agree to deposit this thesis in the University's open access institutional repository or allow the Library to do so on my behalf, subject to Irish Copyright Legislation and Trinity College Library conditions of use and acknowledgement. Except where otherwise stated, the contents of this thesis are the product of my own work carried out in the Condensed Matter Theory group at the School of Physics, Trinity College Dublin, supervised by Professor David D. O'Regan.

This dissertation does not exceed 60,000 words in length.

Glenn Moynihan
Trinity College Dublin
January 2018

SUMMARY

DENSITY-FUNCTIONAL THEORY (DFT), in its approximate Kohn-Sham formalism, is a highly-acclaimed computational tool that affords the practical and expeditious calculation of ground-state properties of molecules and solids, often with a very reasonable accuracy. It finds routine application in the fields of chemistry, physics, materials science, and biochemistry, where it now contributes in both a descriptive and predictive capacity.

It is not, in practice, without systematic errors such as those defined by self-interaction and static correlation. These errors undermine the accurate description of particular systems that are beyond the scope of the approximate exchange-correlation functionals, particularly for those comprising so-called *strongly-correlated* electrons. The effective treatment of these errors is laid down in a number of formative works now adopted within the canon of Kohn-Sham DFT. Many of the most popular and affordable correction schemes entail the calculation of external parameters to diagnose and treat these pervasive errors on a per-electron basis, such as the DFT+Hubbard U method.

A possibility that has not yet been explored, however, is the automation of these correction schemes for the provision of greater efficiency, versatility and comparability between DFT calculations. An automated procedure would enable the correction process to be self-contained, thereby circumventing the need for human input, and establish a standardised approach between the various softwares and electronic systems. Of particular interest is the application in high-throughput materials design, and the comparability of DFT+ U total-energies for the calculation of thermodynamical quantities.

In this dissertation, we present a comprehensive account of our work in pursuit of this goal. We motivate and describe an efficient self-contained approach for correcting the many-body self-interaction error in strongly-correlated systems from ground-state quantities within the DFT+ U framework. Moreover, we implement this procedure in a linear-scaling code, which extends its applicability to large-scale systems.

Specifically, we develop a highly accurate variational linear-response approach for calculating the Hubbard U and Hund's J parameters, for which a unique criterion for their self-consistency is identified. Our results demonstrate that this scheme is accurate and versatile, and facilitates the correction of many-body self-interaction error for various systems. Moreover, we propose the novel construction of a generalised DFT+ U functional that resolves Koopmans' condition exactly in a one-electron system when supplied with the appropriate self-consistent U value.

Our research provides insight into important questions about the practice and consequences of calculating corrective parameters for approximate DFT self-consistently, and opens up several new avenues for future developments.

ACKNOWLEDGMENTS

THE WORK DESCRIBED in this dissertation could not have been completed without the assistance and support from various people and institutions over the years, and it is a pleasure to take this opportunity to pay tribute to those who have aided in its completion.

I would first like to thank Science Foundation Ireland for providing the funding for this research through the AMBER program, as well as the Royal Irish Academy for facilitating the project collaboration with our colleagues at the University of Liverpool. I also wish to thank Trinity College for their generous support through the provision of the Non-Foundation Scholarship. I am grateful to the staff at the School of Physics for their assistance over the years, and to Trinity Research IT and ICHEC for providing computing resources, as well as the CRANN and AMBER support staff.

Much of this work would not be possible were it not for my esteemed colleagues. I would like to thank the members of the Computational Spintronics Group for their constructive feedback and discussions when presented with my work. I am deeply grateful in particular to my co-supervisor, Professor Stefano Sanvito, for all of his valuable help and guidance in my studies.

The members of the Chemical Physics of Low-Dimensional Nanostructures Group, Professor Johnny Coleman, Dr Damien Hanlon, Dr Conor Boland, and Dr Claudia Backes deserve a special thanks for expediting my first publication. I am grateful also to Emma Norton and Dr Karsten Fleischer of the Applied Physics Research Group for their helpful discussions and for contributing their experimental data. I also appreciate the helpful discussions with Fiona McCarthy, Mark McGrath, Thomas Wyse Jackson, and Edward Linscott.

The members of the ONETEP community were very helpful to me during the coding retreats. I appreciate their assistance very much.

My time in Dublin was frequently punctuated by visits to the University of Liverpool and I was incredibly fortunate to be placed in a safe pair of hands upon

arrival. I would therefore like to extend my warmest appreciation to the venerable Dr Gilberto Teobaldi for making each of these visits an absolute pleasure, even on those dark December days. His valuable assistance, inexhaustible patience, and excellent taste in hotels aided my stay immeasurably. Many thanks + cheer up.

I would like to give a special mention to my office-mates, who I have had the utmost pleasure of working beside: Dr James Lawlor, Dr Eric Mehes, Dr Pankaj Kumar, Dr Alessandro Lungi, Dr Claudia Rocha, Dr Linda Zotti, and last, but certainly not least, Okan Karaca Orhan. You have each made a valuable contribution to my postgraduate experience. I thank you all for the welcome distractions.

It would be remiss of me to fail to mention my distinguished flatmates, Izzy Kennedy, Lauren Boland, Naomi Beard and Niamh Ennis, whose company was the highlight of my years living on Trinity College campus.

I would like to extend my heartfelt gratitude to my supervisor, Professor David O'Regan, to whom I am truly indebted most of all, not least for taking a fellow Corkman under his wing. I have been extremely fortunate to be under his considerate mentorship the last four years. His continuous encouragement, attentive guidance, and meticulous work ethic are an example to aspire to.

I am especially privileged to have had Olivia Kerrigan by my side the last few years. I can only hope to repay the patience and devotion she has afforded me during these months of writing. She continues to brighten the otherwise anarchic days of the Ph.D. experience. I also humbly thank the Kerrigan family for graciously hosting me for the final push.

Finally, I would to thank my friends and family who have made my time here in Dublin over the past eight years very special. In particular, my parents, Karen and Michael, grandparents, and siblings who have all supported me relentlessly in the Big Smoke. I wouldn't be here without them.

LIST OF FIGURES

III.1	Crystal structure of orthorhombic black phosphorus	37
III.2	Phosphorus in-plane mechanical properties	46
III.3	Arsenic in-plane mechanical properties	47
III.4	Antimony in-plane mechanical properties	48
III.5	PVC:BP Young's modulus fit to rule-of-mixtures model	50
III.6	PVC:BP Young's modulus fit to Halpin-Tsai model	51
IV.1	Brillouin zone of orthorhombic phosphorus	55
IV.2	Electronic properties of monolayer phosphorus for in-plane strains .	57
IV.3	Electronic properties of bilayer phosphorus for in-plane strains . . .	58
IV.4	Predicted Dirac states of strained bilayer phosphorus	59
IV.5	Electronic properties of bulk phosphorus for in-plane strains	61
IV.6	Predicted Weyl states of strained bulk phosphorus	62
IV.7	Electronic properties of monolayer arsenic for in-plane strains . . .	63
IV.8	Predicted Dirac states of strained monolayer arsenic	64
IV.9	Electronic properties of bilayer arsenic for in-plane strains	65
IV.10	Predicted Dirac states of strained bilayer arsenic	66
IV.11	Electronic properties of bulk arsenic for in-plane strains	67
IV.12	Predicted Weyl states of strained bulk arsenic	68
IV.13	Electronic properties of monolayer antimony for in-plane strains . .	69
IV.14	Predicted Dirac states of monolayer antimony	70
IV.15	Electronic properties of antimony for in-plane strains	71
IV.16	Predicted Dirac states of bilayer antimony	72
IV.17	Strain-induced buckled phase in bilayer antimony	72
V.1	SIE of a H atom as the deviation from piece-wise linearity	77
V.2	Binding energy curve of H_2^+	78
V.3	Occupancy of H atom in dissociating H_2^+	79
V.4	Eigenvalue-derived binding energy of H_2^+	82

LIST OF FIGURES

V.5	Binding energy curve of H_2^+ with DFT+ U	89
V.6	Eigenvalue-derived binding energy of H_2^+ with DFT+ U	90
V.7	Binding energy curve of H_2 with DFT+ U	92
V.8	SCE of a H_2 molecule as the deviation from piece-wise constancy .	95
V.9	Binding energy curve of H_2 with DFT+ J	96
VI.1	Variational linear-response U values calculated for dissociating H_2^+ .	112
VI.2	PBE+ U binding curve of H_2^+ with linear-response U	113
VI.3	PBE+ U binding curve of H_2 with linear-response U	114
VI.4	$\text{Ni}(\text{CO})_4$ molecular structure and linear-response calculation	116
VI.5	NiO crystal structure and linear-response calculation	117
VI.6	Species-resolved DOS for NiO calculated with PBE	118
VI.7	Species-resolved DOS for NiO calculated with PBE+ U	119
VI.8	Cr_2O_3 crystal structure and linear-response calculation	120
VI.9	Species-resolved DOS for Cr_2O_3 calculated with LDA	122
VI.10	Species-resolved DOS for Cr_2O_3 calculated with LDA+ U	123
VI.11	Normalised XPS and UPS measurements of Cr_2O_3 compared to LDA+ U total DOS	124
VI.12	Normalised XPS and UPS measurements of Cr_2O_3 compared to LDA+ U species-resolved DOS	125
VI.13	Normalised absorption spectrum of Cr_2O_3 compared to LDA+ U joint DOS	126
VI.14	Stable and unstable magnetic potentials for H_2 at 1 a_0 and 4.8 a_0 bond-length	130
VI.15	Species-resolved DOS for NiO calculated with PBE+ U + J	132
VI.16	Species-resolved DOS for Cr_2O_3 calculated with PBE+ U + J	132
VII.1	Example of U_{in} vs U_{out} profile for H_2^+	142
VII.2	Self-consistent U_{out} schemes for H_2^+ vs best estimated U	145
VII.3	Binding energy of H_2^+ calculated with various U_{out} schemes	146
VII.4	Profiles of U_{out} , J_{out} , U_{eff} vs U_{in} for NiO	153
VII.5	Profiles of F_{Hxc} , F_J , $F^{\sigma\sigma}$, $F^{\sigma\bar{\sigma}}$ vs U_{in} for NiO	155

VII.6	Ranking of all self-consistency schemes for NiO	158
VII.7	NiO DOS with $U = 4.1$ eV and $J = 0$ eV	160
VII.8	NiO DOS with $U = 10.5$ eV and $J = 0$ eV	161
VII.9	NiO DOS with $U = 6.7$ eV and $J = 0.84$ eV	162
VII.10	NiO DOS with $U_{\text{eff}} = 5.2$ eV	163
VII.11	J_{in} vs J_{out} calculations for H_2 at 1 a_0 and 6 a_0 bond-length	165
VII.12	Calculated J_{out} schemes for dissociating H_2	166
VII.13	Binding energy of H_2 with PBE+ $J^{(2)}$	167
VII.14	The self-consistent U profile for H_2 at 2.8 a_0	168
VII.15	Approximated U_{eff} and J_{eff} for dissociating H_2	169
VIII.1	Total-energy of constrained H_2^+ vs Lagrange multiplier	178
VIII.2	Interacting response functions for H_2^+ vs Lagrange multiplier	179
VIII.3	Constraint energy landscape of H_2^+ vs Lagrange multipliers U_1 and U_2	185
VIII.4	DFT+ U_1+U_2 free energy landscape of H_2^+	188
VIII.5	Estimated U_1 and U_2 parameters to restore exact total-energy and Koopmans' condition in dissociating H_2^+	189
VIII.6	Total-energy and eigenvalue binding curves for H_2^+ calculated with generalised DFT+ U functional	192
B.1	Band structures of relaxed group-V phases	216
C.1	NiO DOS with $U = 4.1$ eV and $J = 2.82$	219
C.2	NiO DOS with $U = 10.5$ eV and $J = 5.9$	219
C.3	NiO DOS with $U = 4.1$ eV and $F_J = 0.78$	220
C.4	NiO DOS with $U = 10.5$ eV and $F_J = 0.69$	220
C.5	NiO DOS with $U - J = 1.3$ eV	221
C.6	NiO DOS with $U - J = 4.6$ eV	221
C.7	NiO DOS with $U - J = 5.9$ eV	222
C.8	NiO DOS with $U_{\text{eff}} = 5.2$ and $J = 3.48$ eV	222
C.9	NiO DOS with $U_{\text{eff}} = 5.2$ and $F_J = 0.84$ eV	223
C.10	NiO DOS with $U = 10.5$ and $J = 5.94$ eV including spin minority term	223

LIST OF FIGURES

C.11	Self-consistency profile for $\text{Ni}(\text{CO})_4$	224
C.12	Self-consistency profile for Cr_2O_3	225
C.13	Profiles of F_{Hxc} , F_J , $F^{\sigma\sigma}$ and $F^{\sigma\bar{\sigma}}$ vs U_{in} for Cr_2O_3	226

TABLE OF CONTENTS

DECLARATION	i
SUMMARY	iii
ACKNOWLEDGMENTS	v
LIST OF FIGURES	vii
I INTRODUCTION	1
1 Outline of dissertation	3
2 Associated publications	6
II QUANTUM MECHANICAL SIMULATION	7
1 The Schrödinger equation	8
2 The Hohenberg-Kohn theorems	9
3 The Kohn-Sham equations	13
4 Exchange-correlation functionals	16
5 Treatment of the ionic potential	18
5.1 Norm-conserving pseudopotentials	18
5.2 Projector-augmented wave method	21
6 An overview of linear-scaling DFT	24
6.1 Density matrix formalism in DFT	25
6.2 Psinc basis sets	26
6.3 Non-orthogonal generalised Wannier functions	27
6.4 Brillouin zone sampling in ONETEP	30
7 Conclusion	32
III MECHANICAL PROPERTIES OF TWO-DIMENSIONAL GROUP-V MATERIALS	35
1 Recent advances in black phosphorus	36

TABLE OF CONTENTS

2	Methodology	38
2.1	Calculation details	38
2.2	The Voigt-Reuss-Hill scheme	39
2.3	In-plane Voigt-Reuss-Hill average	40
2.4	Composite mixture models	40
3	Results	42
3.1	Calculated lattice constants	42
3.2	Isotropic bulk properties	43
3.3	In-plane elastic properties	44
3.4	Polymer-nano-flake composite	49
4	Conclusion	52
IV	ELECTRONIC PROPERTIES OF TWO-DIMENSIONAL GROUP-V MATERIALS	53
1	Weyl and Dirac semi-metals	54
2	Methodology	54
3	Electronic properties	56
4	Conclusion	70
V	THE NATURE AND ORIGIN OF PERVASIVE ERRORS IN APPROXIMATE DFT	75
1	Fractional charges	76
2	One-electron self-interaction correction	79
3	Koopmans' compliance	80
4	Strongly correlated systems	83
5	The DFT+ U method	84
5.1	A one-electron assessment of DFT+ U	88
6	Static Correlation Error	91
7	Conclusion	96

VI	CALCULATION OF HUBBARD PARAMETERS FROM VARIATIONAL LINEAR RESPONSE	99
1	Overview of the linear-response method	100
2	Construction of a variational linear-response approach	102
2.1	The non-interacting response	103
2.2	Choice of projection for the interacting kernel	104
2.3	Comparing the SCF and variational linear-response methods . . .	108
2.4	The subspace contribution to SIE: global vs local curvatures . . .	109
2.5	A one-electron test case: H_2^+	111
3	Application to multi-electronic systems	113
3.1	Dissociating H_2	113
3.2	Molecular $Ni(CO)_4$	114
3.3	Bulk NiO	115
3.4	Bulk Cr_2O_3	119
4	Calculating J using the variational linear-response method	126
4.1	Correcting static correlation error in H_2	128
4.2	Calculating J for NiO and Cr_2O_3	130
5	Conclusion	134
VII	CALCULATION OF SELF-CONSISTENT HUBBARD PARAMETERS	137
1	A note on the direct comparison of DFT+ U total-energies	139
2	A self-consistent U in a one-electron model	140
2.1	Which self-consistency scheme?: revisiting H_2^+	143
3	Coupled self-consistent parameters in multi-electronic systems	148
3.1	Generalised, self-consistent U and J formulae	149
3.2	Application to NiO	152
3.3	Comparison of self-consistency schemes	159
4	A self-consistent J applied to H_2	164
4.1	Correcting SCE with J	165
4.2	Will U_{eff} and J_{eff} improve H_2 ?	167

TABLE OF CONTENTS

	5 Choice of subspace projectors	169
	6 Conclusion	171
VIII	THE INVESTIGATION OF NON-LINEAR CONSTRAINTS AND A GENERALISED DFT+U FUNCTIONAL	173
	1 Constrained-DFT	175
	2 Non-linear constraints	176
	2.1 Proof of the inapplicability of non-linear constraints	179
	2.2 Construction of separable constraints	183
	3 A generalised DFT+ U formula	186
	3.1 Non-self-consistent estimates for U_1 and U_2	188
	3.2 Application to H_2^+	191
	4 Conclusion	192
IX	CONCLUDING REMARKS	195
	1 Synopsis	195
	2 Future work	199
A	Sample input files	203
	1 Sample QUANTUMESPRESSO input file	203
	2 Sample ONETEP input file	204
B	Supplemental data for group-V 2D materials	208
	1 Derivation of the Voigt-Reuss-Hill Equations	208
	2 Calculated elastic tensor elements	211
	3 Group-V in-plane elastic extrema	212
	4 Black phosphorus experimental data	213
	5 Summary of electronic properties	214
	6 Summary of electronic transitions	215
	7 Band structures figures	216
C	Further discussion on self-consistency schemes	217
	1 Alternative derivation for U_{out} and J_{out}	217

2 Supplemental DOS plots for NiO	219
2.1 Self-consistency calculations for Ni(CO) ₄	224
2.2 Self-consistency calculations for Cr ₂ O ₃	225

I

INTRODUCTION

All models are wrong but some are useful.

George E. P. Box [1]

THE PILLARS OF MODERN physics now comprise the well established fields of theory, experiment and simulation, where the latter addition has been made possible thanks to the technological advances of the 20th century, characterised by Moore’s law [2]. In the current ‘Age of Silicon’ [3] simulation and modelling have become indispensable tools that find cutting-edge application in the field of quantum physics, in particular for solving the complex many-body Schödinger equation [4]. Notwithstanding the significant progress made in micro-processors over the last five decades, it is only by the intelligent use of algorithms and suitable approximations that it is possible to quantitatively describe chemical processes and complex material properties with sufficient accuracy and efficiency.

Density-functional theory (DFT) conforms to all of these principles and is one of the most successful and highly acclaimed techniques in modern science. It affords a timely and accurate description of the ground-state properties of many atomic systems on an *ab initio* basis that is from an entirely deterministic standpoint with only minimal approximations and without the use of empirical models. It enables the straightforward calculation of properties derived from the ground-state total-energy, which includes, but is not limited to, elastic moduli, atomic forces, electromagnetic responses, cohesive binding energies, local magnetic moments, geometrically optimised structures, and charge transfer energies [5]. Its role in computational chemistry and materials science continues to flourish to this day.

Indeed, many systems pertinent to chemical, biological or technological applications, which typically comprise first-row transition metal or lanthanide ions, are often

largely spatially disordered and electronically complex. This special class of extensive system presents numerous challenges to DFT practitioners, as calculations on these so-called *strongly-correlated* materials often misrepresent, or directly contradict, experimental observations.

The first is simply a matter of computational economy; the study of these systems requires accurate large-scale simulation, which is unfortunately unattainable with current hardware. On the one hand, this is invariably due to the availability of finite resources, while on the other we are confronted with the uneconomical compute time of conventional algorithms for large systems, which scale cubically with system size. The design of linear-scaling methods, in which the computational cost scales linearly with system size, has provided considerable aid in this regard.

The second challenge pertains to the physically-relevant, yet poorly described, interactions between correlated electrons responsible for the exotic behaviour, which are demonstrably beyond the scope of the independent-particle approximation. The established, and computationally efficient, DFT+ U method is now routinely applied to these systems to restore the absent physical character, whereupon the strength of the corrective potential is determined by a set of Hubbard U parameters that must be determined.

The focus of this dissertation concerns the *ab initio* calculation of Hubbard parameters within linear-scaling DFT, and their subsequent application in an existing linear-scaling DFT+ U framework, in order to accurately describe strongly-correlated systems on a large-scale. Moreover, the ultimate goal of this body of research is to direct the design of automated first-principles methods for the description of strongly-correlated systems. We intend our work to contribute valuably to techniques involving high-throughput materials informatics, in particular for the provision of a mechanism for computing thermodynamical quantities, by availing ourselves of the computational utility afforded by a combined self-contained, linear-scaling DFT+ U procedure.

Notwithstanding this ambitious undertaking towards ever-more accurate and versatile computational techniques, as a minor player in this venture I am reminded of the words of the eminent statistician, George E. P. Box, whose famous aphorism prefaces this Chapter. I believe its lesson fittingly applies in the present context

of designing efficient *ab initio* practices, to which his words speak to our unending, insatiable pursuit to understand, and ultimately replicate, nature.

1 OUTLINE OF DISSERTATION

We begin in Chapter II by providing an overview of the key developments that have contributed to the formulation of contemporary Kohn-Sham DFT, such as the Hohenberg-Kohn theorems, the Kohn-Sham equations, the construction of approximate exchange-correlation (XC) functionals, and the treatment of the ionic cores with the pseudopotential approximation and projector-augmented wave method. We then motivate and outline the framework for enabling the computational expense to scale linearly with system size, which relies on the attenuation of non-local effects in a single-particle density matrix, and discuss some of the central features of the linear-scaling code ONETEP, in which our methods are implemented.

In Chapters III & IV we present the results of extensive calculations on the strained layers of phosphorus, arsenic, and antimony. We compare our results to the available experimental data for these materials and make qualitative predictions for the mechanical and electronic properties, which includes several electronic transitions and a number of states supporting ballistic conduction.

Following this discussion, we examine in detail the nature and origin of the self-interaction and static correlation errors in Chapter V, and highlight the role they play in undermining the accuracy of many DFT calculations. We discuss some of the notable methods developed over the years to effectively treat the inaccuracies affiliated with these errors, and emphasise the importance of restoring compliance with Koopmans' theorem. In particular, we outline the construction of the DFT+ U correction functional intended to treat the self-interaction error when it stems from highly-localised electrons. Finally, we briefly discuss a similar error arising from static-correlation of degenerate states, and suggest a possible mechanism for its treatment within the full DFT+ U + J framework.

We then proceed to discuss the *ab initio* calculation of Hubbard U parameters in Chapter VI, in which we address various methods utilised heretofore, in particular

the popular linear-response approach conceived by Coccocioni and de Gironcoli. We motivate and develop a variational approach modified from this method to be applied more conveniently in codes that employ total-energy direct-minimisation (as opposed to density self-consistency) to locate the DFT ground-state. We test this method on a variety of systems and consider the similarities and differences between the two approaches. Finally, we devise an equivalent scheme to calculate the exchange parameter J , and highlight some of the importance consequences of computing interaction parameters as ground-state quantities.

Our variational linear-response approach provides a convenient format to investigate the somewhat esoteric practice of parameter self-consistency in Chapter VII, for which numerous plausible schemes have been proposed. In doing so, we perform extensive calculations on dissociating H_2^+ to identify the self-consistency scheme that provides the appropriate correction to one-electron self-interaction, and then generalise the method to treat multi-electronic systems using rock-salt NiO as a case study. Moreover, we provide an original formulation for a self-consistent J and use this to correct the static-correlation error in dissociating H_2 beyond the Coulson-Fischer point.

Finally, in Chapter VIII we focus on the development of a generalised DFT+ U functional that can simultaneously target the total-energy SIE and the restoration of Koopmans' condition, which represents an original and novel construct. We first approach this challenge by investigating if the automated correction of systems prone to SIE is feasible within the framework of constrained-density-functional theory (cDFT). However, we provide a rigorous proof and stringent numerical calculations that verify that the non-linear constraints, including those required to enforce this condition, are impossible to satisfy. Rather than adding to the multitude of available approaches, here we make progress by limiting the scope for further proliferation of methods based on this strategy.

Nonetheless, we show that a generalised DFT+ U functional, wherein the Hubbard parameters may be determined from a self-consistent linear-response U parameter, is capable of correcting both the total-energy and eigenvalue of a one-electron system to the same precision. This work opens the door to new advances and possibilities

using a new class of generalised DFT+ U functionals.

We conclude in Chapter IX with a synopsis of the major findings of this work, and suggest possible new directions for future research. Finally, some appendices are provided to complement the primary text, which are intended to advance the discussion and provide further clarity, when necessary, with supplemental figures, tables, and derivations.

2 ASSOCIATED PUBLICATIONS

The Chapters that arise entirely, or in part, from previous publications or works intended to be published are as follows

Chapter III: Damien Hanlon, Claudia Backes, *et al.* “Liquid exfoliation of solvent-stabilized few-layer black phosphorus for applications beyond electronics.”

Nature Communications 6, 8563 (2015).

DOI: 10.1038/ncomms9563

Chapters III & IV: Glenn Moynihan, Stefano Sanvito, and David D. O’Regan. “Strain-induced Weyl and Dirac states and direct-indirect gap transitions in group-V materials.”

2D Materials 4 045018 (2017).

DOI: 10.1088/2053-1583/aa89d2

Chapters VI & VII: Glenn Moynihan, Gilberto Teobaldi, and David D. O’Regan. “A self-consistent ground-state formulation of the first-principles Hubbard U.”

In preparation. arXiv:1704.08076 [**cond-mat.str-el**]

Chapter VIII: Glenn Moynihan, Gilberto Teobaldi, and David D. O’Regan. “Inapplicability of exact constraints and a minimal two-parameter generalization to the DFT+ U based correction of self-interaction error.”

Physical Review B **94**, 220104(R) (2016).

DOI: 10.1103/PhysRevB.94.220104

II

QUANTUM MECHANICAL SIMULATION

RECENT TECHNOLOGICAL advances, in conjunction with an increasing community of active contributors, have succeeded in establishing Kohn-Sham density-functional theory (DFT) as one of the most widespread and utilised tools in modern science. DFT has evolved significantly since its inception over 50 years ago [6]; following the award of the Nobel prize in 1998 to Walter Kohn [7, 8] it has continued to flourish to this day under the auspicious stewardship of countless contributors. Presently, it sees routine application in academic and industrial research and has imparted immeasurable scientific [9–12] and economic [13] value. In this Chapter, we review the pioneering developments in condensed matter theory that have culminated in contemporary DFT, which is now routinely applied to electronic structure calculations.

We begin our discussion with the Schrödinger equation, central to all quantum mechanical calculations, and the seminal theorems of Hohenberg and Kohn [14] who pioneered the field. We then discuss how Kohn and Sham subsequently laid the foundations for the solution of the ground-state exactly via self-consistent field equations, incorporating an exchange-correlation (XC) functional [15]. The inaccessibility of the exact XC functional, however, prompted the development of approximate local functionals that enable the computational solution to the equations. These were originally based on the local-density of a uniform electron gas [15, 16], which was later extended to incorporate spin [17–19] and self-interaction corrections [20], with further development involving a generalised gradient [21, 22] approximation. These incremental improvements in theory were bolstered by simultaneous advances in hardware that preceded the proliferation of DFT applications across various fields [11, 23].

In spite of the theoretical and algorithmic breakthroughs that contributed to the popularity of DFT toward the end of the last century, calculations of very large sys-

tems remained decidedly out of reach [24]. The restrictive computational bottle-neck involved in diagonalising the dense Hamiltonian incurred a compute-time that scaled cubically with system size [25]. The quest for a linear-scaling formalism was marked by the proposal of Kohn himself to exploit the *near-sightedness* of quantum mechanical interactions [26] in the DFT procedure - thereby enabling the calculation of large-scale systems. In the final section, we outline the procedure for constructing a linear-scaling DFT, which has risen to prominence over the last 25 years [27, 28]. A suite of packages now boast linear-scaling functionality, which includes ONETEP [29–31], CONQUEST [32, 33], SIESTA [34, 35], BIGDFT [36], OPENMX [37, 38], and CP2K [39].

1 THE SCHRÖDINGER EQUATION

The basis of many quantum mechanical systems lies in the solution of the many-body, time-independent, Schrödinger equation [40]

$$\hat{H}\Psi(\mathbf{r}, t) = E\Psi(\mathbf{r}, t), \quad (\text{II.1})$$

where the complex-valued N -body wave function $\Psi(\mathbf{r}, t)$ encodes all information about the quantum state that is propagated in time by the Hamiltonian $\hat{H}$. In an organised configuration of N atoms in a crystal lattice or molecule, with nuclear positions $\mathbf{R}_\alpha$ and n electrons at positions $\mathbf{r}_i$, the governing non-relativistic, time-independent Hamiltonian is given by

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \left[\sum_{i=1}^n \nabla_i^2 + \sum_{\alpha=1}^N \frac{1}{m_\alpha} \nabla_\alpha^2 \right] - \sum_{i=1}^n \sum_{\alpha=1}^N \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \\ & + \frac{1}{2} \sum_{i=1}^n \sum_{j \neq i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{\alpha=1}^N \sum_{\beta \neq \alpha}^N \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}, \end{aligned} \quad (\text{II.2})$$

with nuclear masses and charges denoted by m_α and Z_α , respectively. Hartree units are invoked throughout this dissertation such that $\hbar = c = m_e = 1$.

For an atomic system that does not exchange energy with its environment, the wave function Ψ is the steady-state solution of a time-independent Hamiltonian, the Ansatz for which is constructed from a separation of variables

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}, t) = \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) \Theta(t) \quad (\text{II.3})$$

into a component that is time-dependent $\Theta(t)$ and one that is not $\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\})$. Thus the constituents are independently solvable by the Hamiltonian and coupled by the common energy eigenvalue ε

$$\hat{H}\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) = E\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}); \quad i\frac{\partial}{\partial t}\Theta(t) = \varepsilon\Theta(t). \quad (\text{II.4})$$

For low-temperature atomic systems, governed by a Hamiltonian such as Eq. (II.2), the time-scale of nuclear motion, tied to the available thermal energy, is generally orders of magnitude longer than that of the electrons due to the much heavier nuclear masses. Since the electrons relax into equilibrium on a time-scale much shorter than that of the nuclei, their behaviour is modelled by an electronically-relevant Hamiltonian $\hat{H}_{\text{el}}$

$$\hat{H}_{\text{el}} \approx \left(-\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \sum_{\alpha=1}^N \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{2} \sum_{i=1}^n \sum_{j \neq i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \quad (\text{II.5})$$

in which the nuclei are assumed to move so little that they can be effectively described as classical point charges. This renowned Born-Oppenheimer, or adiabatic, approximation [41], is invoked to make quantum mechanical calculations under Eq. (II.2) more feasible. However, advances in computational modelling, combined with the improved experimental apparatus [42], have permitted the application of Ehrenfest molecular dynamics for some time [43, 44].

Eigenvalue solutions to Eq. (II.2) span a multi-dimensional adiabatic potential energy surface parameterised by the nuclear coordinates $\{\mathbf{R}_\alpha\}$, which may be optimised classically using molecular dynamics methods [45, 46]. The neglect of explicitly nuclear-dependent terms leads to the failure to predict more complex phenomena such as superconductivity, photochemistry and vibrational spectroscopy, however, for most systems, the Born-Oppenheimer approximation is a very reasonable simplification.

2 THE HOHENBERG-KOHN THEOREMS

Despite the benefits of the adiabatic approximation, computationally solving the many-body Schrödinger equation for all but the simplest systems is practically impossible. Consider a real-valued, N -electron wave function discretised on a grid of

M points (ignoring spin). A full description of this wave function will require M^{3N} scalars [47] and is unquestionably beyond the scope of modern processing power for any realistic system of interest. Even if the exact wave function were known, the memory required to store it would present an impasse.

For an N -electron system, Hohenberg and Kohn [14] (HK) showed in their seminal work that the many-electron ground-state density distribution of a system $n_0(\mathbf{r})$ (subscript to denote ground-state) is sufficient for providing a full description of the ground-state properties, in principle. Thus, for a many-body quantum state vector $|\Phi\rangle$, the electron density is defined as

$$n(\mathbf{r}) = \langle \Phi | \hat{n} | \Phi \rangle = \int \prod_{i=2}^N d\mathbf{r}_i |\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2, \quad (\text{II.6})$$

where $|\Phi\rangle$ is assumed to be normalised $\langle \Phi | \Phi \rangle = 1$ and antisymmetric under particle exchange so as to obey the Pauli exclusion principle [48]. Furthermore, they proved that the ground-state was identified by variational minimisation of the total-energy with respect to the density [14]. Promoting the density to the central quantity of the theory drastically simplifies the problem of computationally solving Eq. (II.5), as the discretised wave function is now parameterised by only M^3 scalars.

Faithful to the motivation behind the HK formalism, the Hamiltonian in Eq. (II.5) may be re-expressed in terms of contributions stemming from potentials that are intrinsic and extrinsic to the system $\hat{H}_{\text{el}} = \hat{F} + \hat{V}$. Here $\hat{F}$ is sum of the kinetic energy operator and electron-electron Coulomb potential

$$\hat{F} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 + \frac{1}{2} \sum_{i=1}^n \sum_{j \neq i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (\text{II.7})$$

and is a universal function of the number of electrons n . The term $\hat{V}$ describes the static potential arising from the lattice of nuclei and defines the external potential specific to the system

$$\hat{V} = \sum_{i=1}^n V_{\text{ext}}(\mathbf{r}_i) = - \sum_{i=1}^n \sum_{\alpha=1}^N \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} \quad (\text{II.8})$$

but may also include other fields, such as the electromagnetic. The single-particle eigenstates $\{|\phi_i\rangle\}$ are found by solving Eq. (II.5), for which the eigenenergies $\{\varepsilon_i\}$

are the corresponding expectation values with the Hamiltonian

$$\varepsilon_i = \langle \phi_i | \hat{H}_{\text{el}} | \phi_i \rangle = \langle \phi_i | \hat{F} | \phi_i \rangle + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}). \quad (\text{II.9})$$

Thus, for a given number of electrons, the Hamiltonian is fully defined by the external potential $V_{\text{ext}}(\mathbf{r})$, on which the resultant ground-state density depends. The first theorem sets out to prove that the converse of this statement is also true, that is, that the ground-state density uniquely determines the potential up to an additive constant.

Hohenberg-Kohn Theorem 1. *There is a one-to-one correspondence between the ground-state charge density of an N electron system and the external potential acting upon it.*

We shall prove this statement by contradiction. Consider two potentials that differ by more than an arbitrary constant $\hat{V} - \hat{V}' \neq C$ with corresponding Hamiltonians $\hat{H}_{\text{el}}$ and $\hat{H}'_{\text{el}}$ that give rise to the eigenenergies E_0 and E'_0 , and eigenstates $|\phi_0\rangle$ and $|\phi'_0\rangle$, respectively. Suppose we assume $|\phi_0\rangle = |\phi'_0\rangle$. By considering the difference in the Hamiltonians

$$(\hat{H}_{\text{el}} - \hat{H}'_{\text{el}})|\phi_0\rangle = (\hat{V} - \hat{V}')|\phi_0\rangle = (E_0 - E'_0)|\phi_0\rangle \quad (\text{II.10})$$

we demonstrate that $\hat{V} - \hat{V}' = E_0 - E'_0$ and thus contradict our earlier assumption that the potentials differ by more than an additive constant. Thus we have shown that the mapping from the space of potentials to the space of ground-state densities is injective. It remains to be shown that the mapping from the space of densities to the space of eigenstates is also injective. Consider then that two ground-states $|\phi_0\rangle$ and $|\phi'_0\rangle$ both give rise to the same ground-state density $n_0(\mathbf{r})$. We may then write, using Eq. (II.9), that

$$\begin{aligned} E_0 &< \langle \phi'_0 | H | \phi'_0 \rangle = \langle \phi'_0 | H' | \phi'_0 \rangle + \langle \phi'_0 | H - H' | \phi'_0 \rangle \\ &= E'_0 + \int d\mathbf{r} [V(\mathbf{r}) - V'(\mathbf{r})] n(\mathbf{r}). \end{aligned} \quad (\text{II.11})$$

Similarly, by computing the converse, we find that

$$E'_0 < E_0 + \int d\mathbf{r} n(\mathbf{r}) [V'(\mathbf{r}) - V(\mathbf{r})]. \quad (\text{II.12})$$

Summing (II.11) and (II.12) leads to the second contradiction

$$E'_0 + E_0 < E'_0 + E_0, \quad (\text{II.13})$$

from which we conclude that the mapping from the space of eigenstates to the space of densities is also injective, thus proving the first HK theorem. We now proceed to the second theorem.

Hohenberg-Kohn Theorem 2. *For all V -representable ground-state densities $n(\mathbf{r})$, $E_0 \leq E_V[n]$, where $E_0 = E_V[n_0]$ is the ground-state energy for N electrons in the external potential $V(\mathbf{r})$ with corresponding ground-state density $n_0(\mathbf{r})$.*

By the first HK theorem, the ground-state density of a system $n(\mathbf{r})$ uniquely determines the potential $V_{\text{ext}}(\mathbf{r})$ and thus its wave function $|\phi[n(\mathbf{r})]\rangle$, where the class of V -representable densities are those generated by solving the Schrödinger equation with some external potential. A uniqueness criterion must also apply to the internal-energy operator $\hat{F}$, which we define as the minimum possible expectation value under a given density $n(\mathbf{r})$ by searching over the entire set of N -body anti-symmetric wave functions that give rise to that density. This is expressed mathematically as

$$F[n] = \min_{n[\phi] \rightarrow n} \langle \phi | \hat{F} | \phi \rangle = \langle \phi_n | \hat{F} | \phi_n \rangle. \quad (\text{II.14})$$

Thus, we may uniquely define the lowest total-energy of a given density $n(\mathbf{r})$ subject to an external potential $V(\mathbf{r})$, namely

$$E_V[n] = F_V[n] + \int d\mathbf{r} V(\mathbf{r})n(\mathbf{r}) = \langle \phi_n | \hat{F} + \hat{V} | \phi_n \rangle. \quad (\text{II.15})$$

For an external potential, there exists a ground-state wave function $|\phi_0\rangle$ that produces the ground-state energy E_V^0 and density $n_0(\mathbf{r})$, such that, by the variational principle, for any other N -representable densities, $E_V^0 \leq E_V[n]$. Furthermore, for the ground-state density $n_0(\mathbf{r})$ we find that, by definition, $F[n]$ can only be at most as large as the kinetic energy term of the ground-state total-energy that is determined by the ground-state wave function $|\phi_0\rangle$, such that

$$F_V[n] = \min_{n[\phi] \rightarrow n_0} \langle \phi | \hat{F} | \phi \rangle \leq \langle \phi_0 | \hat{F} | \phi_0 \rangle, \quad (\text{II.16})$$

which trivially implies the same for the total-energy

$$\begin{aligned}\langle \phi_{n_0} | \hat{F} + \hat{V} | \phi_{n_0} \rangle &\leq \langle \phi_0 | \hat{F} + \hat{V} | \phi_0 \rangle \\ \Rightarrow E_V[n_0] &\leq E_V^0.\end{aligned}\tag{II.17}$$

Since E_V^0 is the ground-state energy by definition, we have proven the second HK theorem, namely that is the ground-state density, subject to an external potential, is that which uniquely determines the minimum of the total-energy functional.

The Hohenberg-Kohn theorems illustrate that a full description of the ground-state of an interacting N electron system can be distilled to the knowledge of the ground-state density alone. Moreover, this ground-state density can be located via minimisation of the total-energy functional $E[n]$ with respect to the density, thus drastically reducing the complexity of the problem. In practice, however, no such formalism exists to carry out this variational procedure as the exact form of the universal internal energy functional described in Eq. (II.14) does not exist [47] and approximations must be used in its place. The formalism of Kohn and Sham, which we shall now describe, utilises intelligent approximations for the many-body effects contained in $\hat{F}$ in order to map the fully interacting N -particle system onto a fictitious system of N non-interacting particles immersed in an effective potential.

3 THE KOHN-SHAM EQUATIONS

Strategies for simplifying and then solving the many-body Schrödinger equation, which strive to simultaneously capture the qualitative features of the system of interest and avoid treating many-body interactions explicitly, precede the HK theorems by almost four decades. Indeed, soon after the formulation of the Schrödinger equation, Hartree established an approximate, self-consistent field procedure for iteratively solving it for the atomic wave functions in what was the first endeavour toward an *ab initio* approach [49]. Fock later contributed to the procedure [50, 51] by imposing the antisymmetry of the wave function explicitly in order to satisfy the Pauli exclusion principle [48], to form what is now known as the ‘Hartree-Fock’ (HF) approach. The exchange energy given in the HF theory, for particle exchange between pairs of

orbitals, is then

$$E_x[n] = -\frac{1}{2} \sum_{ij} \int d\mathbf{r} d\mathbf{r}' \frac{\psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}') \psi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (\text{II.18})$$

Despite neglecting electron correlation effects, which account for many of the discrepancies of the HF approach with experimental results, the scheme remains to this day a valuable tool in quantum chemistry.

A far more viable approach was developed by Kohn and Sham (KS) [15], who proposed mapping the interacting system onto a reference system comprising the same number of non-interacting particles whose ground-state density is identical to the interacting density by virtue of an effective potential $V_{\text{KS}}(\mathbf{r})$. The many-body problem is thereby circumvented by solving N one-particle Schrödinger equations instead of one N -particle equation.

Let us first consider the variational minimisation of the HK total-energy functional, subject to conservation of the particle number via

$$\delta \left[E[n] + \mu \left(N - \int d\mathbf{r} n(\mathbf{r}) \right) \right] = 0. \quad (\text{II.19})$$

This gives rise to the Euler-Lagrange equation in terms of the functional derivative of the internal energy functional $F[n]$ with respect to the density $n(\mathbf{r})$, the external potential $V_{\text{ext}}(\mathbf{r})$, and the chemical potential μ , namely

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} + V_{\text{ext}}(\mathbf{r}) = \mu. \quad (\text{II.20})$$

In the Kohn-Sham approach, the internal energy is expanded into its constituent single-particle terms

$$F[n] \equiv T_s[n] + E_H[n] + E_{\text{xc}}[n] \quad (\text{II.21})$$

comprising the non-interacting kinetic energy

$$T_s[n] = -\frac{1}{2} \sum_{i=1}^N \int d\mathbf{r} \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}), \quad (\text{II.22})$$

the classical Hartree energy

$$E_H[n] = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (\text{II.23})$$

and finally the exchange-correlation (XC) energy $E_{\text{xc}}[n]$, which encompasses all the quantum many-body effects ignored in the single-particle mapping, specifically the non-classical electron-electron interaction energy and the kinetic energy difference between the interacting and non-interacting systems¹. Substituting Eq. (II.21) into Eq. (II.20) generates the following non-interacting Euler-Lagrange equation

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + V_{\text{KS}}(\mathbf{r}) = \mu, \quad (\text{II.24})$$

which, by virtue of the first HK theorem, is guaranteed to reproduce the exact ground-state density of the interacting system subject to the effective *Kohn-Sham potential*

$$V_{\text{KS}}(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} + V_{\text{ext}}(\mathbf{r}) \quad (\text{II.25})$$

with the exchange-correlation potential given by

$$V_{\text{xc}}(\mathbf{r})[n] = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (\text{II.26})$$

The solution to the non-interacting Euler-Lagrange equation in Eq. (II.24) is achieved by resolving N independent Schrödinger equations

$$\hat{H}_{\text{KS}}\psi_i = \left[-\frac{1}{2}\nabla^2 + \hat{V}_{\text{KS}}(\mathbf{r}) \right] \psi_i = \epsilon_i\psi_i, \quad (\text{II.27})$$

acting on a set of non-interacting eigenfunctions $\{\psi_i(\mathbf{r})\}$ termed the *Kohn-Sham orbitals*. The KS orbitals then reconstruct the interacting ground-state density via

$$n(\mathbf{r}) = \sum_{i=1}^N \int d\mathbf{r} |\psi_i(\mathbf{r})|^2. \quad (\text{II.28})$$

Since the KS potential produces the KS orbitals, which construct the density, which in turn determines the potential, the solutions to (II.27) may be found by iteratively solving for the potential and orbitals until self-consistency is reached [5], or by direct-minimisation of the total-energy [29], which we will describe in greater detail in section 6. Furthermore, while the KS orbitals and eigenvalues may often provide an approximate representation of the physical electronic orbitals and related spectra, great care must be exercised in interpreting them as such, since they represent a fictitious system of non-interacting particles. We shall address this issue further in section 3.

¹ see section 4 for further discussion

4 EXCHANGE-CORRELATION FUNCTIONALS

Were the closed-form of $E_{\text{xc}}[n]$ known, then the KS approach described heretofore would be exact and resolve the ground-state density to arbitrary precision, thereby elevating approximate-DFT to the status of an exact theory. As the case may be, $E_{\text{xc}}(\mathbf{r})$ is unknown except for the simplest of systems [52–55], and the ability of the KS approach to reliably incorporate many-body effects and reproduce realistic ground-state properties lies in its appropriate approximation [15].

As the name suggests, $E_{\text{xc}}[n]$ may be partitioned into effects pertaining to exchange $E_{\text{x}}[n]$ and correlation $E_{\text{c}}[n]$ [47]. The exchange term is required to satisfy the Pauli exclusion principle [48] and lowers the Coulomb repulsion between like-spin electrons by keeping them spatially separated. The correlation energy, meanwhile, has many interpretations [47, 56], the most tangible of which is that given by Perdew and Zunger in Ref. [20]. Given the functional for exact exchange in Eq. (II.18), the correlation energy is uniquely defined as the remainder when all other energy terms have been removed from the total-energy, such that

$$E_{\text{c}} = E[n] - T_{\text{s}}[n] - E_{\text{H}}[n] - \int d\mathbf{r} V_{\text{ext}}n(\mathbf{r}) - E_{\text{x}}[n]. \quad (\text{II.29})$$

Initially, Kohn and Sham sought to use a *local-density approximation* (LDA) [15, 16] where the XC potential is approximated to that produced by a homogeneous electron gas (HEG), whose density is the same as the non-interacting system in each infinitesimal volume element $d\mathbf{r}$

$$E_{\text{xc}}^{\text{LDA}}[n] \equiv \int d\mathbf{r} \epsilon_{\text{xc}}^{\text{LDA}}(n(\mathbf{r}))n(\mathbf{r})$$

$$\Rightarrow V_{\text{xc}}^{\text{LDA}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}^{\text{LDA}}}{\delta n(\mathbf{r})} = \epsilon_{\text{xc}}^{\text{LDA}}[n(\mathbf{r})] + n(\mathbf{r}) \left. \frac{d\epsilon_{\text{xc}}^{\text{LDA}}[n(\mathbf{r})]}{dn} \right|_{n=n(\mathbf{r})}, \quad (\text{II.30})$$

where, $\epsilon_{\text{xc}}^{\text{LDA}}(n(\mathbf{r}))$ is the XC energy per-electron of the HEG with density $n(\mathbf{r})$. It was later extended to incorporate the local-spin density approximation (LSDA) [17–19], for which a commonly used functional is that developed by Perdew and Zunger [17, 20].

However, the LDA and LSDA suffer from systematic inaccuracies in insulating band gaps [57, 58], charge-transfer energies [59, 60], activation barriers [61], binding

and formation energies, as well as in spin-densities and their moments. The *generalised gradient approximation* (GGA) [22] is a semi-local extension to the LDA that takes into account spatial variations in the density

$$E_{\text{xc}}^{\text{GGA}}[n] = \int d\mathbf{r} \, \zeta(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \nabla^2 n(\mathbf{r}), \dots) \quad (\text{II.31})$$

and offers modest improvement of the LDA in many systems. Indeed, the Perdew-Burke-Ernzerhof (PBE) [22] functional is one that is widely used in calculations as it produces reliable results for a broad range of applications and is the XC functional primarily used in this dissertation.

Over the years there have been numerous other incremental improvements to the LDA functional, of which GGA was only the first, that offer increasingly accurate, albeit more computationally expensive, results. The next development were meta-GGA functionals [62], which depend on the density, its gradient and the kinetic energy density. These were followed by hybrid-functionals [63], which contain a linear combination of traditional XC functionals with exact exchange from HF and are orbital dependent, a popular choice of which is B3LYP. The next instalment admits functionals including non-local correlation effects [64], and finally, functionals currently in development include all occupied and unoccupied orbitals [65].

As of yet however, no such functional has been developed that can be universally employed that delivers reliable results for minimal computational cost. A reasonable balance between the two must be struck depending on the calculation to be performed. Notwithstanding the current selection of XC functionals available, the GGA remains widely popular due to its reasonable accuracy and minimal expense. While meta-GGAs and hybrid functionals provide superior accuracy, they do so at considerably more expense. The popular LDA and GGA functionals are also limited in their capacity to describe systems with exotic electronic behaviour, and are known to suffer from systematic self-interaction and static-correlation errors, which will be discussed in Chapter V.

5 TREATMENT OF THE IONIC POTENTIAL

In the process of chemical bonding, the role played by the valence electrons greatly outweighs that of the core electrons, whose contribution to the interaction is so little they may be regarded as effectively inert to the chemical environment [66]. Since the changes in energy are largely attributed to the valence electrons, the removal of the core states will allow these changes to be more accurately calculated, as they will constitute a larger proportion of the total-energy. Furthermore, the condition of orthonormality between all non-interacting KS eigenstates requires rapidly oscillating valence wave functions in the region of the spatially-localised core states. Satisfying this condition requires a large number of basis functions, and thus computational expense, to accurately describe them.

Motivated by the above observations, we now proceed to describe the two methods used in this dissertation for efficiently treating the ion core states, namely the *pseudopotential* approximation [67–69] and *projector-augmented wave* method [70, 71]. These techniques allow for greater accuracy in determining total-energy differences, and reduce the computational expense in treating the localised core states, while retaining the explicit treatment of the more chemically relevant valence states.

5.1 NORM-CONSERVING PSEUDOPOTENTIALS

The pseudopotential approximation is a method in which explicit treatment of the core states can be effectively avoided in the electronic structure problem. Instead, they may be considered part of the external nuclear potential. Consequently, the Coulomb potential is mitigated by a repulsive term that mimics the presence of the core electrons, and this effect produces a much weaker pseudopotential. The rapidly oscillating wave functions are thus replaced by smoothly varying *pseudo-wave functions* that can be resolved at a significantly reduced computational expense.

Following Ref. [72], let us suppose that a valence state $|\psi_{\text{val}}\rangle$, which is an eigenstate of the KS Hamiltonian $\hat{H}$ with eigenvalue E , may be transformed into a smoothly

varying pseudo-state $|\psi_{\text{ps}}\rangle$ by subtracting a linear combination of core states

$$|\psi_{\text{val}}\rangle = |\psi_{\text{ps}}\rangle + \sum_n^{\text{core}} a_n |\chi_n\rangle. \quad (\text{II.32})$$

The set of coefficients $\{a_n\}$ is then determined by the condition of orthogonality between the valence state and all core states

$$\langle \chi_n | \psi_{\text{val}} \rangle = 0 = \langle \chi_n | \psi_{\text{ps}} \rangle + a_n \quad (\text{II.33})$$

$$\Rightarrow a_n = -\langle \chi_n | \psi_{\text{ps}} \rangle \quad (\text{II.34})$$

thus, we arrive at

$$|\psi_{\text{val}}\rangle = |\psi_{\text{ps}}\rangle - \sum_n^{\text{core}} |\chi_n\rangle \langle \chi_n | \psi_{\text{ps}} \rangle. \quad (\text{II.35})$$

Solving the eigenvalue equation $\hat{H}|\psi_{\text{val}}\rangle = E|\psi_{\text{val}}\rangle$ we find that

$$\hat{H}|\psi_{\text{ps}}\rangle - \sum_n^{\text{core}} E_n |\chi_n\rangle \langle \chi_n | \psi_{\text{ps}} \rangle = E|\psi_{\text{ps}}\rangle - E \sum_n^{\text{core}} |\chi_n\rangle \langle \chi_n | \psi_{\text{ps}} \rangle, \quad (\text{II.36})$$

which may be conveniently re-written into an eigenvalue equation for the pseudo-state

$$\left[\hat{H} + \sum_n^{\text{core}} (E - E_n) |\chi_n\rangle \langle \chi_n| \right] \psi_{\text{ps}} = E|\psi_{\text{ps}}\rangle. \quad (\text{II.37})$$

Hence, the pseudo-state returns the same eigenvalue as the valence state when the Hamiltonian differs by a non-local potential, given by

$$\hat{V}_{\text{nl}} = \sum_n^{\text{core}} (E - E_n) |\chi_n\rangle \langle \chi_n|. \quad (\text{II.38})$$

This potential is repulsive in the region of the core and acts to partially cancel the Coulomb attraction. It thereby provides a net, smoothly-varying potential for the pseudo-valence states.

The energy argument E of the pseudopotential, the core states $\{|\chi_n\rangle\}$, and eigenenergies E_n are initially calculated for an isolated atom and generally assumed to be fixed. The validity of this assumption largely determines the *transferability* of a pseudopotential, that is, the accuracy with which it performs in various chemical environments. This greatly depends on the condition that any shift in the valence energy ΔE , when transferring from the atomic to chemical environment, satisfies $E - E_n \gg \Delta E$.

A widely used variety of pseudopotentials are those that preserve the scattering properties of the full atomic potential, up to leading order in the energy, by use of *norm-conservation*. We refer the reader to Refs. [73–76] for more details. These pseudopotentials must be independently computed for each of the angular momentum states l but, for spherically symmetric potentials, are independent of the azimuthal quantum number m . Suppose we then construct a pseudopotential where the contribution due to core electrons vanishes beyond a cutoff radius r_c such that $v_{\text{nl}}(r) = v(r)$ for $r < r_c$ and $v_{\text{nl}}(r) = 0$ otherwise. The valence wave functions may also be decomposed into radial R_l and spherical harmonic Y_{lm} terms, given by

$$\psi_{lm}(\mathbf{r}, E) = R_l(r, E)Y_{lm}(\theta, \phi) \quad (\text{II.39})$$

that are solutions of the atomic Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) \right] \psi_{lm}(\mathbf{r}, E) = E\psi_{lm}(\mathbf{r}, E). \quad (\text{II.40})$$

For $r > r_c$, the radial solution may be expressed in terms of Bessel $j_l(x)$ and von Neumann $n_l(x)$ functions

$$R_l^>(r, E) = A_l j_l(kr) + B_l n_l(kr) = A_l [j_l(kr) - \tan(\delta_l) n_l(kr)], \quad (\text{II.41})$$

where $k = \sqrt{2E}$ and the scattering phase shift δ_l is defined by $B_l/A_l = -\tan(\delta_l)$. Further stipulating that $R_l^>$ and its radial derivative match the solution of Eq. (II.40) at the boundary $r = r_c$, one can then show that

$$\left. \frac{d}{dr} \log [R_l(\mathbf{r}, E)] \right|_{r=r_c} = k \frac{j_l(kr_c) - \tan(\delta_l) n_l(kr_c)}{j_l(kr_c) - \tan(\delta_l) n_l(kr_c)} \quad (\text{II.42})$$

and, moreover, that the energy derivative is proportional to the norm of the wave function in the core region, i.e., that

$$\frac{d}{dE} \left[\frac{d}{dr} \log [R_l(\mathbf{r}, E)] \right] \sim \int_0^{r_c} dr \, r^2 R_l^2(r). \quad (\text{II.43})$$

Simultaneously satisfying Eqs. (II.42) & (II.43), such that

$$R_{l,\text{ps}}(l) = R_{l,\text{val}}(l) \quad \text{for } r > r_c, \quad (\text{II.44})$$

we can construct a pseudopotential that preserves the scattering properties of the full potential up to leading order in E .

In the construction of pseudopotentials, it is necessary to remove the contributions from the valence electron Hartree and XC potentials, as these will be accounted for in the DFT calculation according to the specific chemical environment. Thus, we leave behind only the XC of the core states

$$\hat{V}_{\text{xc}}^{\text{pseudo}} = \hat{V}_{\text{xc}}[n_v(\mathbf{r}) + n_c(\mathbf{r}), \zeta] - \hat{V}_{\text{xc}}[n_v(\mathbf{r}), \zeta_v] \quad (\text{II.45})$$

where $n_v(\mathbf{r})$ and $n_c(\mathbf{r})$ are the valence and core electron densities, respectively, which define the all-electron and valence magnetisations as

$$\zeta(\mathbf{r}) = \frac{n_v^\uparrow(\mathbf{r}) - n_v^\downarrow(\mathbf{r})}{n_v(\mathbf{r}) + n_c(\mathbf{r})} \quad \text{and} \quad \zeta_v(\mathbf{r}) = \frac{n_v^\uparrow(\mathbf{r}) - n_v^\downarrow(\mathbf{r})}{n_v(\mathbf{r})}. \quad (\text{II.46})$$

Thus, in the pseudopotential approximation, it is important to consider the degree of spatial overlap between the valence and core electron densities, especially for spin-polarised systems, such as the first-row transition-metals.

Since the V_{xc} functional is non-linear in the charge density and magnetisation, linear approximations, (such as those in Eq. (II.45)) although sufficient for many cases, will fail when ζ and ζ_v significantly differ. The non-linear core correction (NLCC), developed by Louie *et al.* [77], circumvents this problem in a DFT calculation by explicitly computing the XC of both the valence states and so-called *partial core* $\tilde{n}_c(\mathbf{r})$, which is identical to the core density outside some cutoff radius r_{NLCC} and a smoothly varying function within. Thus, the XC contribution from the pseudopotential and valence electrons can be effectively partitioned in an approximately linear fashion once again

$$\hat{V}_{\text{xc}}^{\text{pseudo}} = \hat{V}_{\text{xc}}[n_v(\mathbf{r}) + n_c(\mathbf{r}), \zeta] - V_{\text{xc}}[n_v(\mathbf{r}) + \tilde{n}_c(\mathbf{r}), \zeta_v]. \quad (\text{II.47})$$

5.2 PROJECTOR-AUGMENTED WAVE METHOD

The projector-augmented wave (PAW) method, devised by Blöchl [70], is a generalisation of the pseudopotential [67–69] and linear-augmented plane wave (LAPW) methods [78, 79], which combines the simple formalism of the former with the versatility of the latter. In this approach, instead of using a linear combination of core states,

the all-electron KS wave function² $|\Psi\rangle$ is derived from the pseudo wave function $|\Psi_{\text{ps}}\rangle$ by a linear transformation $\mathcal{T}$

$$|\Psi\rangle = \mathcal{T}|\Psi_{\text{ps}}\rangle. \quad (\text{II.48})$$

Expectation values of operators $\hat{A}$ can be obtained from either the all-electron states $\langle\hat{A}\rangle = \langle\Psi|\hat{A}|\Psi\rangle$ or, equivalently, from the pseudo-states $\langle\hat{A}\rangle = \langle\Psi_{\text{ps}}|\hat{A}'|\Psi_{\text{ps}}\rangle$ with $\hat{A}' = \mathcal{T}^\dagger \hat{A} \mathcal{T}$, when $\mathcal{T}$ is known.

In order to restrict the transformation to the regions of the ion core, we may expand $\mathcal{T}$ in terms of a sum of local contributions $\mathcal{T}_R$

$$\mathcal{T} = 1 + \sum_R \mathcal{T}_R, \quad (\text{II.49})$$

which only act within an *augmentation region* $\mathcal{V}_R$ enclosing the atom, analogous to the cutoff radius in the pseudopotential method. It is useful to re-cast the pseudo wave functions as a linear combination of partial-waves $\{|\phi_{i,\text{ps}}\rangle\}$ in $\mathcal{V}_R$

$$|\Psi_{\text{ps}}\rangle = \sum_i c_i |\phi_{i,\text{ps}}\rangle, \quad (\text{II.50})$$

which, themselves, may be a linear combination of polynomials or Bessel functions. These, in turn, are related to the all-electron partial-waves by the same linear transformation

$$|\phi_i\rangle = \mathcal{T}|\phi_{i,\text{ps}}\rangle, \quad (\text{II.51})$$

and are typically the solutions to the atomic Kohn-Sham Schrödinger equation. Thus, i is an index over the atomic labels R , angular momentum quantum numbers $\{l, m\}$, and partial-wave index n . Combining Eqs. (II.48), (II.50) and (II.51), the all-electron wave function can then be resolved from the pseudo wave function

$$|\Psi\rangle = |\Psi_{\text{ps}}\rangle - \sum_i |\phi_{i,\text{ps}}\rangle c_i + \sum_i |\phi_i\rangle c_i, \quad (\text{II.52})$$

and the expansion coefficients $\{c_i\}$, yet to be determined. Since the transformation $\mathcal{T}$ must be linear, the coefficients $\{c_i\}$ must be derived from a scalar product of $|\Psi_{\text{ps}}\rangle$ with some projector functions $\{|p_i\rangle\}$

$$c_i = \langle p_i | \Psi_{\text{ps}} \rangle \quad \text{with} \quad \langle p_i | \phi_{j,\text{ps}} \rangle = \delta_{ij} \quad (\text{II.53})$$

²not to be confused with the many-electron wave function.

that each have a corresponding pseudo partial-wave and satisfies the completeness condition $\sum_i |\phi_{i,\text{ps}}\rangle \langle p_i| = 1$. Thus, inserting the first term in Eq. (II.53) into Eq. (II.52) we arrive at the full expression for the all-electron wave function

$$|\Psi\rangle = |\Psi_{\text{ps}}\rangle + \sum_i (|\phi_i\rangle - |\phi_{i,\text{ps}}\rangle) \langle p_i | \Psi_{\text{ps}} \rangle, \quad (\text{II.54})$$

where we can now define the transformation as

$$\mathcal{T} = 1 + \sum_i (|\phi_i\rangle - |\phi_{i,\text{ps}}\rangle) \langle p_i|. \quad (\text{II.55})$$

The quantities that govern the transformation are

1. The set of all-electron partial-wave functions $\{|\phi_i\rangle\}$, which are solutions to the atomic Schrödinger equation,
2. the set of pseudo partial-wave functions $\{|\phi_{i,\text{ps}}\rangle\}$,
3. the set of projector functions $\{|p_i\rangle\}$ localised in the augmentation region, which satisfy $\langle p_i | \phi_{j,\text{ps}} \rangle = \delta_{ij}$.

There exists a variety of strategies to solve for each of these terms, which are discussed in Refs. [70, 80]

On a final note, we will briefly outline how the pseudopotential method may be derived from the PAW method. For a comprehensive derivation see Ref. [71]. By construction, the PAW method fulfils the same essential criteria as the pseudopotential approach, except for the condition of norm-conservation, although this can also be enforced. Using our definition of $\mathcal{T}$ in Eq. (II.55), it can be shown that a pseudo operator $\hat{A}_{\text{ps}}$ is given by

$$\hat{A}_{\text{ps}} = \hat{A} + \sum_{i,j} |p_i\rangle \left(\langle \phi_i | \hat{A} | \phi_j \rangle - \langle \phi_{i,\text{ps}} | \hat{A} | \phi_{j,\text{ps}} \rangle \right) \langle p_j|. \quad (\text{II.56})$$

However, there is the option to include an additional term of the form

$$\hat{B} - \sum_{i,j} |p_i\rangle \langle \phi_{i,\text{ps}} | \hat{B} | \phi_{j,\text{ps}} \rangle \langle p_j|, \quad (\text{II.57})$$

where $\hat{B}$ is an operator localised to the augmentation region, such that the expectation value of this new term with $|\Psi_{\text{ps}}\rangle$ is zero. This additional degree of freedom is useful

for constructing potentials that are difficult to express using a plane wave expansion, such as the nuclear Coulomb potential, due to the singularity inside the augmentation region. This new potential will inherently match the exact potential outside the core region and will be smoothly-varying inside, thus providing the framework for the pseudopotential approach in PAW. As a result of reducing the PAW method to the pseudopotential approach, a contribution from an additional non-local potential $\hat{V}_{nl}$ emerges during the process.

In summary, the PAW method offers numerous advantages over the pseudopotential approach, while requiring only a modest increase in computational resources, albeit larger memory requirements. It allows for increased computational accuracy and efficiency, larger core regions, and a reduced basis set if the norm-conserving condition is relaxed. Most importantly, by using both valence and core states in the self-consistency cycle and the construction of potentials, the PAW method bears a physical basis approaching that of more expensive ‘all-electron’ models, but at the price of a pseudopotential calculation. Moreover, for norm-conserving pseudopotentials without NLCC, the $\mathbf{k}$ -point grid-spacing for the density needs to be at least twice as fine as the grid-spacing for the wave function in order to guarantee adequate sampling and ensure that the two converge at a similar same rate. When NLCC or PAW are used, this equivalence is no longer guaranteed to hold because of the additional complexities introduced by the core electron density or augmentation regions.

6 AN OVERVIEW OF LINEAR-SCALING DFT

Despite the practicality of approximate DFT that has lead to its widespread adoption, there exists, within the electronic structure community, a growing repertoire of large-scale systems under study ($N_{\text{atoms}} \gtrsim 10^3$) that are computationally inaccessible by conventional codes and oblige a linear-scaling, so-called $\mathcal{O}(N)$, treatment. These include large biological molecules [29, 81–84], defect states [31, 85, 86], optical absorption [87, 88], molecular dynamics [89, 90], molecules in solution [91, 92], among many other examples [93–96].

In this section, we will proceed from the over-arching theory and techniques used in approximate DFT and discuss the motivation and technical details related to solving Eq. (II.25) within a linear-scaling regime. For this dissertation, we primarily used the Order- N Electronic Total-Energy Package (ONETEP) [29, 30, 94, 97–101], which employs direct-minimisation of the total-energy, rather than plane wave self-consistency, as a means to locate the ground-state energy. We will describe the optimisation procedure that occurs within ONETEP affording it $\mathcal{O}(N)$ functionality (with an accuracy comparable to that of plane wave codes [29, 30, 102, 103]), and define the central quantities of the calculations. For a comprehensive account of the ONETEP procedure, we refer the reader to Refs. [29, 30, 94, 97–101].

In this section, we shall invoke the Einstein summation convention over repeated indices [104], where we have denoted Greek suffixes to correspond to non-orthogonal quantities, and Latin suffixes to orthogonal ones.

6.1 DENSITY MATRIX FORMALISM IN DFT

The real-space single-particle density matrix is given in terms of the KS orbitals $\psi_i(\mathbf{r})$ with occupancies $\{f_i\}$ by

$$\rho(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r} | \hat{\rho} | \mathbf{r}' \rangle = \sum_i f_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}') \quad \text{where} \quad f_i = \{0, 1\}, \quad (\text{II.58})$$

with the single-particle density $n(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r})$. A physically meaningful density-matrix must abide by certain properties, namely, it must be

1. Hermitian $\rho(\mathbf{r}, \mathbf{r}') = \rho^\dagger(\mathbf{r}', \mathbf{r})$, to ensure real expectation values,
2. conserve (spin-)particle number $\int d\mathbf{r} \hat{\rho}^\sigma(\mathbf{r}, \mathbf{r}) = N^\sigma$,
3. idempotent $\rho(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}, \mathbf{r}')^2$, to ensure that $f_i = \{0, 1\}$.

In large DFT calculations comprising $N \gtrsim 10^2$ particles, enforcing orthogonality between the KS orbitals incurs an $\mathcal{O}(N^3)$ compute-time. Amid a growing appetite in the 1990s for solutions to surmounting this performance limitation [25, 103, 105–109], Kohn postulated a *near-sightedness* principle, based on the dependence of the one-particle density matrix on local-potentials, which forecast the development of

linear-scaling methods [26]. A corollary of this principle was that expectation values of local operators depend negligibly on spatially-distant density elements, which could be truncated accordingly beyond some cutoff distance r_{cut} (to be determined by total-energy convergence), such that

$$\rho(\mathbf{r}, \mathbf{r}') = 0 \quad \text{for} \quad |\mathbf{r} - \mathbf{r}'| > r_{\text{cut}}. \quad (\text{II.59})$$

The conditions presented above pose numerous challenges to direct-minimisation techniques invoking the density-matrix. We shall not discuss in detail the strategies employed by ONETEP to ensure a well-behaved density-matrix, but we refer the reader to Refs. [99, 109–113] for more information.

6.2 PSINC BASIS SETS

The tractable computation of the KS wave functions relies on the appropriate selection of a finite set of basis functions spanning the Hilbert space. This selection should be minimal, yet afford the efficient evaluation of ground-state densities, as well as the application of potentials and differential operators. Popular choices of basis set include Gaussian functions [114–116] in molecular systems, and plane waves [117–120] in periodic systems, which are efficiently transformed between representations via the Fast-Fourier Transform (FFT) [121].

ONETEP, on the other hand, adopts a variational basis set of *psinc* functions [122, 123], centred at positions $\mathbf{r}_{\{m\}}$, defined by

$$D_{\{m\}}(\mathbf{r}) = \prod_{k=1}^3 \frac{1}{N_k} \sum_{p_l=-J_k}^{J_k} e^{ip_l \mathbf{b}_k \cdot (\mathbf{r} - \mathbf{r}_{\{m\}})}, \quad (\text{II.60})$$

where the number of grid-points in each lattice direction then determines the grid-resolution as follows

$$N_k = 2J_k + 1; \quad J_k \in \mathbb{N}$$

$$\text{with} \quad \mathbf{r}_{\{m\}} = \sum_{i=1}^3 \frac{m_i}{N_i} \mathbf{a}_i; \quad m_i \in \{0, 1, \dots, N_i - 1\}. \quad (\text{II.61})$$

Here, $\{\mathbf{b}_k\}$ are the reciprocal lattice basis vectors³. The resolution of the grid then truncates the basis set and thus determines the maximum kinetic energy permissible.

³The reciprocal lattice is discussed further in section 6.4

The *psinc* functions are also periodic $D_{\{m\}}(\mathbf{r}) = D_{\{m\}}(\mathbf{r} + \mathbf{R})$, localised to a single grid-point each and real-valued everywhere⁴ [122]

$$D_{\{m_1, m_2, m_3\}}(\mathbf{r}_{\{\mu_1, \mu_2, \mu_3\}}) = \delta_{m_1 \mu_1} \delta_{m_2 \mu_2} \delta_{m_3 \mu_3}. \quad (\text{II.62})$$

As a result, they are an ideal basis for the construction of spatially-localised *representation support functions* [102] $\{\phi_\alpha(\mathbf{r})\}$, the choice of which we will now motivate.

6.3 NON-ORTHOGONAL GENERALISED WANNIER FUNCTIONS

In periodic systems, the real-space projection of the single-particle density-matrix may be generated from the integration of extensive periodic Bloch wave functions $\{\psi_{n,\mathbf{k}}^\sigma(\mathbf{r})\}$, labelled by band-index n and momentum-vector $\mathbf{k}$,

$$\rho(\mathbf{r}, \mathbf{r}') = \frac{1}{\Omega_{BZ}} \sum_n f_n \int_{BZ} d\mathbf{k} \psi_{n,\mathbf{k}}(\mathbf{r}) \psi_{n,\mathbf{k}}^*(\mathbf{r}'), \quad (\text{II.63})$$

where the $\mathbf{k}$ -vectors are restricted to the reciprocal-space primitive unit cell called the *first Brillouin zone* (BZ) with volume Ω_{BZ} ⁵. The principle of near-sightedness, advocated earlier by Kohn to facilitate linear-scaling functionality [26], prescribes that our set of support functions for the density-matrix be highly spatially-localised, a popular choice for which are Wannier functions [124–127]. The Wannier functions may be expressed as the Fourier transformations of the periodic Bloch wave functions restricted to a cell at the lattice-vector $\mathbf{R}$

$$w_{n,\mathbf{R}}^\sigma(\mathbf{r}) = \left(\frac{\Omega_{\text{cell}}}{2\pi} \right)^{\frac{1}{2}} \int_{BZ} d\mathbf{k} \psi_{n,\mathbf{k}}^\sigma(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{R}}, \quad (\text{II.64})$$

where Ω_{cell} is the real-space supercell volume. The Bloch functions may then be reconstructed from the discretised inverse-Fourier transform

$$\psi_{n,\mathbf{k}}^\sigma(\mathbf{r}) = \left(\frac{\Omega_{\text{cell}}}{2\pi} \right)^{\frac{1}{2}} \sum_{\mathbf{R}} w_{n,\mathbf{R}}^\sigma(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{R}}, \quad (\text{II.65})$$

which, when substituted into Eq. (II.63), returns the one-particle density-matrix in terms of the Wannier functions

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_n \sum_{\mathbf{R}} w_{n,\mathbf{R}}^\sigma(\mathbf{r}) f_n^\sigma w_{n,\mathbf{R}}^{\sigma*}(\mathbf{r}'). \quad (\text{II.66})$$

⁴As we will later demonstrate that $\mathbf{b}_{\mathbf{k}} \cdot \mathbf{r}_j = 2\pi n \delta_{kj}$ for $n \in \mathbb{Z}$

⁵See section 6.4.

Incidentally, it is often the case that the non-orthogonal representation of the Wannier functions is more local than its orthogonal equivalent as shown in Ref. [128]. This is because a set of orthogonal Wannier functions generated from orthogonal KS orbitals may require large oscillations in the former to ensure this condition is met, which increases their spatial spread characterised by the central second moment. Thus, if we relax the orthogonality condition, but conserve the particle number, we can then facilitate a more localised representation that avoids large oscillations. ONETEP implements a complete set of spatially-truncated non-orthogonal generalised Wannier functions (NGWFs) $\{\phi_\alpha(\mathbf{r})\}$, which are constructed from the KS orbitals by a unitary transformation $\mathbf{M}$

$$\psi_i(\mathbf{r}) = \phi_\alpha(\mathbf{r}) M_i^\alpha \quad \text{where} \quad M_i^\alpha = \langle \phi^\alpha | \psi_i \rangle. \quad (\text{II.67})$$

The grid-point representation of the NGWFs $\{\phi_\alpha^D(\mathbf{r})\}$, expanded in terms of the *psinc* basis functions over the simulation cell with dimension $N_{\text{cell}} = N_1 \times N_2 \times N_3$, is given by

$$\begin{aligned} \phi_\alpha^D(\mathbf{r}) &= \sum_{\{m\}} C_{\{m\},\alpha} D_{\{m\}}(\mathbf{r}); \\ \text{with } C_{\{m\},\alpha} &= \int d\mathbf{r} D_{\{m\}}(\mathbf{r}) \phi_\alpha(\mathbf{r}) = \frac{\Omega_{\text{cell}}}{N_{\text{cell}}} \phi_\alpha^D(\mathbf{r}_{\{m\}}). \end{aligned} \quad (\text{II.68})$$

The coefficients $C_{\{m\},\alpha}$ are determined by the integral overlap of the NGWFs with the *psinc* functions, which, in turn, are proportional to the approximate NGWFs $\{\phi_\alpha^D(\mathbf{r}_{\{m\}})\}$ evaluated at the corresponding grid-points. Therefore, since all spatial functions are evaluated at discrete grid-points, we henceforth suppress the superscript D for brevity and retain the original notation.

The NGWF overlap matrix $\mathbf{S}$ then defines the metric of the non-orthogonal basis spanned by the NGWFs

$$S_{\alpha\beta} = \langle \phi_\alpha | \phi_\beta \rangle = \int d\mathbf{r} \phi_\alpha^*(\mathbf{r}) \phi_\beta(\mathbf{r}) = \left(\frac{\Omega_{\text{cell}}}{N_{\text{cell}}} \right) \sum_{\{m\}} C_{\{m\},\alpha}^* C_{\{m\},\beta}, \quad (\text{II.69})$$

and arises in imposing orthogonality between Kohn-Sham orbitals

$$\delta_{ij} = \int d\mathbf{r} \psi_{i\mathbf{k}}^*(\mathbf{r}) \psi_{j\mathbf{k}}(\mathbf{r}) = \int d\mathbf{r} (M^\dagger)_i^\alpha \phi_\alpha^*(\mathbf{r}) \phi_\beta(\mathbf{r}) M_j^\beta = (M^\dagger)_i^\alpha S_{\alpha\beta} M_j^\beta. \quad (\text{II.70})$$

In the non-orthogonal regime, the dual functions $\{\phi^\alpha(\mathbf{r})\}$ are orthogonal to the NGWFs $\langle\phi_\alpha|\phi^\beta\rangle = \delta_\alpha^\beta$, and span the dual-space⁶, whereby we find, by the completeness relation, that

$$\phi^\alpha(\mathbf{r}) = \langle\mathbf{r}|\phi_\beta\rangle\langle\phi^\beta|\phi^\alpha\rangle = \phi_\beta(\mathbf{r})S^{\beta\alpha} \quad \Rightarrow \quad S^{\beta\alpha} = (S_{\beta\alpha})^{-1}. \quad (\text{II.71})$$

Finally, with Eqs. (II.64) - (II.71), it can be shown that the NGWFs depend on the aforementioned elements as follows

$$|\phi_{\alpha\mathbf{R}}\rangle = \left(\frac{\Omega_{\text{cell}}}{(2\pi)^3}\right)^{\frac{1}{2}} \int_{\text{BZ}} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_{i=1}^N |\psi_{i\mathbf{k}}\rangle \left[M_i^{\dagger\beta} S_{\beta\alpha}\right], \quad (\text{II.72})$$

in which the the expansion coefficients $C_{\{m\},\alpha}$ of the *psinc* basis set are one of the variational parameters optimised *in situ* in order to minimise the total-energy.

The other variational component in ONETEP procedure is the density-kernel $\mathbf{K}$ [110], which is found by substituting the transformation in Eq. (II.67) into the expression for the density-matrix in Eq. (II.58)

$$\rho(\mathbf{r}, \mathbf{r}') = \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta(\mathbf{r}'). \quad (\text{II.73})$$

The density-kernel is, therefore, a projection of the density-matrix onto the space of localised NGWF duals

$$K^{\alpha\beta} = \langle\phi^\alpha|\hat{\rho}|\phi^\beta\rangle = \sum_i \langle\phi^\alpha|\psi_i\rangle f_i \langle\psi_i|\phi^\beta\rangle = \sum_i M_i^\alpha f_i M_i^{\dagger\beta}. \quad (\text{II.74})$$

Invoking a cutoff radius r_{cut} on the spatial extent of the NGWFs, such that spatial overlap between them vanishes beyond a certain threshold, thus translates to truncating the density-matrix thereby making $\mathbf{K}$ a sparse matrix. The information contained in $\mathbf{K}$ then scales linearly with system size and enables the inexpensive computation of the density, the non-interacting band energy, as well as other quantities, by means of simple matrix operations

$$N = 2S_{\alpha\beta} K^{\beta\alpha} \quad \text{and} \quad E = 2K^{\beta\alpha} \langle\phi_\alpha|\hat{H}_{\text{KS}}|\phi_\beta\rangle. \quad (\text{II.75})$$

⁶The term ‘duals’ is perhaps a mathematical misnomer, but it is now part of the vocabulary since they were first proposed in Ref. [129]. Duals are discerned from the NGWFs by a superscript rather than a subscript.

Hence, total-energy minimisation according to the density-matrix is instead performed with respect to the auxiliary variables, namely the NGWFs, parameterised by the expansion coefficients $C_{\{m\},\alpha}$, and the density-kernel $\mathbf{K}$.

The `ONETEP` procedure thus comprises two nested optimisation loops, controlled by the conjugate-gradient algorithm [130], in which the ground-state total-energy is located via minimisation with respect to the NGWFs and density-kernel, such that the density-matrix remains idempotent, conserved and commutes with the Hamiltonian. The outer loop keeps the density-kernel fixed, while the real-space profile of the NGWFs is optimised by variational optimisation of the expansion coefficients $C_{\{m\},\alpha}$ [29, 94, 98, 100]. The inner loop, meanwhile, retains the form of the NGWFs while the energy is minimised with respect to the density-kernel matrix-elements using a variant of the LNV method [99]. The mathematical formalism underlying the optimisation procedure may be summarised by the following construction, adopted from Ref. [131],

$$\begin{aligned}
 E_0 &= \min_n E[n] = \min_\rho E[\rho] \\
 &= \min_\rho E[\rho(K^{\alpha\beta}, \{\phi_\alpha\})] \\
 &= \min_{K^{\alpha\beta}, \{C_{\{m\},\alpha}\}} E[K^{\alpha\beta}, \{C_{\{m\},\alpha}\}] \\
 &= \min_{\{C_{\{m\},\alpha}\}} \varepsilon[\{C_{\{m\},\alpha}\}]; \\
 \text{where } \varepsilon[\{C_{\{m\},\alpha}\}] &= \min_{K^{\alpha\beta}} E[K^{\alpha\beta}; \{C_{\{m\},\alpha}\}].
 \end{aligned} \tag{II.76}$$

6.4 BRILLOUIN ZONE SAMPLING IN ONETEP

In the final section of this Chapter, we will outline the Brillouin zone sampling procedure in `ONETEP`. A rapidly growing number of electronic structure simulations [11] now involve bulk or molecular crystals that are defined by an infinite, periodic, lattice. The primitive lattice vectors $\{\mathbf{a}_i\}$, which describe the primitive unit cell, are then repeated according to discrete translations generated by

$$\mathbf{R} = \sum_{i=1}^3 n_i \mathbf{a}_i; \quad \text{with } n_i \in \mathbb{Z}, \tag{II.77}$$

to form the underlying Bravais lattice. By construction, the Kohn-Sham potential also has the same periodicity [132], where

$$V_{\text{KS}}(\mathbf{r} + \mathbf{R}) = V_{\text{KS}}(\mathbf{r}). \quad (\text{II.78})$$

This inherent translational symmetry can be exploited to reduce the number of unique wave function solutions of Eq. (II.25). Indeed, it can be shown that, by virtue of the periodicity of the potential, the KS wave functions $\{\psi_n\}$ are simultaneous eigenstates of the Hamiltonian and translation operator $\hat{T}_{\mathbf{R}}$, with eigenvalue $c(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$, such that

$$\hat{T}_{\mathbf{R}}\psi(\mathbf{r}) = \psi_n(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_n(\mathbf{r}). \quad (\text{II.79})$$

Thus, we may label the eigenstates $\psi_n(\mathbf{r})$ by an additional set of quantum numbers $\mathbf{k}$, specifying the wave-vector. This forms the basis of Bloch's theorem [133], which states that, in a periodic crystal, the electron wave function can be written as the product of a plane wave, with momentum $\mathbf{k}$, and a periodic function $u_n(\mathbf{r})$ with the same periodicity as the lattice

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_n(\mathbf{r}) \quad \text{with} \quad u_n(\mathbf{r} + \mathbf{R}) = u_n(\mathbf{r}). \quad (\text{II.80})$$

The $\mathbf{k}$ -vector is constructed from a set of reciprocal lattice vectors $\{\mathbf{b}_i\}$ generated from the Fourier transform of the real-space Bravais lattice

$$\mathbf{k} = \sum_{i=1}^3 c_i \mathbf{b}_i; \quad c_i \in \mathbb{R} \quad \text{with} \quad \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}. \quad (\text{II.81})$$

It follows that wave functions that differ by integer multiples of reciprocal lattice vectors, which describe the first Brillouin zone (BZ),

$$\mathbf{G} = \sum_{i=1}^3 m_i \mathbf{b}_i; \quad m_i \in \mathbb{Z}, \quad (\text{II.82})$$

are equal modulo $\mathbf{G}$, and therefore redundant beyond the first BZ, as shown by

$$\begin{aligned} \psi_{n,\mathbf{k}+\mathbf{G}}(\mathbf{r}) &= e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}u_n(\mathbf{r}) = e^{i\mathbf{G}\cdot\mathbf{r}}e^{i\mathbf{k}\cdot\mathbf{r}}u_n(\mathbf{r}) \\ &= e^{i\sum_j \mathbf{a}_j \cdot \mathbf{b}_j} e^{i\mathbf{k}\cdot\mathbf{r}}u_n(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_n(\mathbf{r}) = \psi_{n,\mathbf{k}}(\mathbf{r}). \end{aligned} \quad (\text{II.83})$$

Thus, an infinite number of occupied wave functions in an infinite, periodic crystal may be represented by a finite number of occupied wave functions parameterised by the wave-vectors $\mathbf{k}$, confined to the first Brillouin zone.

The number of unique $\mathbf{k}$ -vectors, parameterising the solutions of the periodic system, scales with the number of unit cells, which become impossible to resolve in the bulk limit. However, since the eigenvalues and wave functions behave smoothly over the Brillouin zone [134], a weighted sampling of $\mathbf{k}$ -vectors is sufficient to approximate the continuous integration [135, 136]. The magnitude of the error introduced by the discrete sampling can be reduced, but not necessarily monotonically, by increasing the $\mathbf{k}$ -point resolution.

For aperiodic systems, such as molecules or defective crystals, in which translational symmetry is broken, Bloch’s theorem becomes inapplicable. To incorporate Bloch states in finite systems, it is a common practice to generate a periodic supercell, in which the molecule or defect is sufficiently separated (either by vacuum space or pristine crystal) from its periodic images [137]. The degree of electronic and orbital isolation is determined by an appropriate convergence of the total-energy with respect to the volume of the supercell Ω_{cell} .

Moreover, for sufficiently large supercells, such as those employed by ONETEP, the first Brillouin zone volume, given by

$$\Omega_{1^{\text{st}} \text{ BZ}} = \frac{(2\pi)^3}{\Omega_{\text{cell}}} \quad (\text{II.84})$$

is sufficiently shrunk such that the bands between BZ boundaries flatten and Γ -point sampling alone is adequate, i.e., $\mathbf{k} = 0$, whereby it is possible to use real-valued wave functions [99]. In this approach, repeating the unit cell by a factor of N_k along each Bravais lattice direction is analogous to sampling the original Brillouin zone on a regular grid of N_k vectors along each direction in reciprocal-space, as is the approach prescribed by most plane wave codes.

7 CONCLUSION

In this Chapter, we introduced the fundamental principles and incremental approximations underpinning the widely successful and highly versatile approximate density-

functional theory. We discussed the principle developments, namely, the founding Hohenberg-Kohn theorems; the subsequent Kohn-Sham equations, after which the development of approximate exchange-correlation functionals permitted the tractable solution of the Schrödinger equation; as well as the pseudopotential and PAW methods, which permit a more convenient treatment of the core states.

Furthermore, we highlighted the motivation for developing linear-scaling methods to facilitate large-scale electronic structure calculations, and outlined the theoretical framework behind the `ONETEP` code. We introduced the fundamental convergence parameters that govern the simulation process, namely the supercell dimension $N_1 \times N_2 \times N_3$, which effectively emulates $\mathbf{k}$ -point sampling; the grid-point resolution $\mathbf{r}_{\{m\}}$, related to the kinetic energy cutoff; and the NGWF cutoff radius r_{cut} .

Finally, we briefly introduced some important concepts that will be addressed in greater detail in later Chapters, such as the self-interaction error and the DFT+ U method, which plays an important role in increasing the accuracy and viability of commercial DFT.

Over the years, DFT has risen in prominence and become one of the most ubiquitous computational tools. Its widespread applicability is made possible due to the prevalence of efficient codes and powerful hardware, bolstered by timely, inexpensive and versatile methodologies, which strike a reasonable balance between accuracy and convenience to suit a wide variety of requirements.

DFT has benefitted from some of the best minds in science and continues to produce exciting developments in emergent technologies, such as high-energy storage materials [138, 139], superconductors [140, 141], topological insulators [142–144], and photovoltaic devices [145, 146], to name a few. It also features as a centre-piece to ambitious scientific projects such as the United States Materials Genome Initiative [147], and the Open Quantum Materials Database [148].

However, one of the fundamental difficulties that still limits the predictive capabilities of DFT, is the many-body self-interaction error [20, 149, 150], introduced in section 4, which is produced by the approximate nature of the XC functionals, and predominantly manifest in systems exhibiting strong electron correlation. We will explore this issue in detail in Chapter V and discuss some viable solutions. For a

7. Conclusion

comprehensive discussion on the history, development and future prospects of DFT, we refer the reader to Refs. [10, 11, 47, 150].

III

MECHANICAL PROPERTIES OF TWO-DIMENSIONAL GROUP-V MATERIALS

A PARADIGM SHIFT in materials science occurred in 2004 with the successful isolation of a stable sample of few-layer graphite by Novoselov and Geim [151]. Dubbed the ‘wonder material’ [152, 153], graphene quickly captured the imaginations of researchers and the public [154–156], boasting almost limitless potential - from revolutionising electronics [154, 157] to water desalination [158] - and was envisioned to be the answer to our material woes. The prowess of graphene lies in the extraordinary electronic and mechanical properties that it exhibits - most notably ballistic electron transport [157] and unrivalled mechanical strength [159]. However, enabling a viable band gap in graphene, without compromising on the conductive properties, has posed many challenges [160] and researchers have struggled to find a scalable, inexpensive method of producing quality samples [161].

During the interim, focus has shifted to the characterisation and synthesis of other two-dimensional (2D) structures derived from their, primarily layered, bulk analogues, such as boron-nitride (BN) [162–165], molybdenum-disulfide (MoS_2) [166–168] and, notably, black phosphorus (BP). Like graphene, the appeal of these materials lies in the emergence of exotic electro-mechanical phenomena, and a rapid increase in surface-area, with the reduction of a degree of freedom along one dimension. The technological impact of 2D materials is predicted to revolutionise existing practices and launch new innovations, with wide-ranging potential applications in photovoltaics [169–173], energy storage [174–180], composite materials [181, 182], and catalysis [183–185]. The successful simulation of these materials, in either a

predictive or analytical capacity, is therefore an important component of their exploration, and DFT calculations have provided an extensive and valuable complement to experiments.

In the following two Chapters, we provide a comprehensive analysis of DFT calculations performed on puckered (α -phase) phosphorus (P), arsenic (As) and antimony (Sb) in the monolayer, bilayer and bulk forms. We identify and compare the qualitative strain-related properties of each structure from a consistent set of calculations, thus treating each material on the same footing.

In this Chapter specifically, we compute the elastic properties, such as the Young's modulus Y ; shear modulus G ; bulk modulus $\mathcal{B}$; and Poisson ratio ν and present their in-plane and isotropic averages according to the Voigt-Reuss-Hill (VRH) averaging scheme, for which the relevant expressions are derived. In the following Chapter, we will continue the discussion and explore the qualitative electronic properties that are predicted to occur at various levels of strain. We shall observe that, while the mechanical behaviour of atomic systems is generally well reproduced by high-level DFT, the corresponding electronic properties, such as band structures and optical gaps, are typically not.

1 RECENT ADVANCES IN BLACK PHOSPHORUS

Two-dimensional black phosphorus (BP), or *phosphorene*, is one of several predicted stable allotropes of few-layer phosphorus [186–189]; it has attracted considerable attention since its recent successful synthesis [190–194], which is now possible with liquid phase exfoliation [181, 195]. The excitement behind BP is driven by the growing list of predicted technologically properties, which includes a tuneable band-gap [193, 196–201], a negative Poisson's ratio [202], anisotropic conduction [203, 204], and linear dichroism [205, 206]. So far, we have seen experimental verification of a high hole-mobility between 300 – 1000 cm²/Vs [192, 193, 205, 207], considerable mechanical flexibility [208], and a layer-dependent band gap [206, 209, 210] ranging from 0.3 eV in bulk to 2.0 eV in the monolayer. The anisotropic crystal structure of BP, as shown in Fig. III.1, is largely responsible for its wide range of exotic electro-

mechanical properties, which are predicted to be strongly directional-dependent and highly responsive to mechanical strain [181, 203].

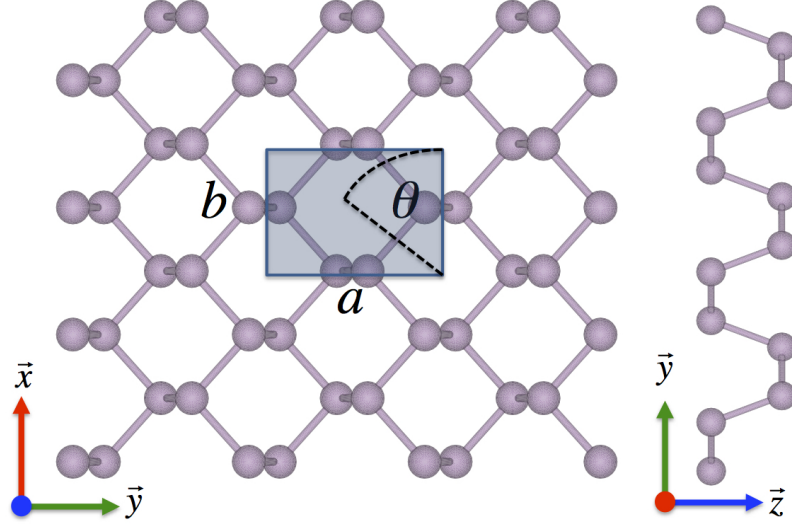


Figure III.1: Top and side view of the 2D orthorhombic puckered structure of the $Cmca$ space group and D_{2h} point group with the primary vectors along the zigzag ($\vec{x}$) and puckered ($\vec{y}$) directions shown. The unit cell, given by the shaded region, is described by the lattice parameters a and b with the in-plane angle θ also defined.

With this renewed interest in BP, attention has quickly turned to few-layer phases of the other pnictogen materials, namely arsenic (As) [211], antimony (Sb) [212], bismuth (Bi) [213, 214], and their alloys [169, 215–218]. In fact, many of the predicted strain-induced properties of these materials, such as direct-indirect band gap transitions [197, 211, 212, 219, 220], a negative Poisson’s ratio [202, 221], as well as electronic [187, 219, 222], structural [223], and topological [224–227] transitions, are already spurring emergent technologies in field-effect transistors [193, 204], gas sensors [228, 229], optical switches [230, 231], solar-cells [169], energy storage [174–176], reinforcing fillers [181, 182], and topological insulators [224–227, 232].

2 METHODOLOGY

2.1 CALCULATION DETAILS

The calculations in the following two Chapters were performed with the `QUANTUMESPRESSO` package¹ [233] using the Perdew-Burke-Ernzerhof (PBE) form of the generalised-gradient approximation (GGA) exchange-correlation functional [22]. An ultrasoft pseudopotential [234] from the SSSP Library² [235] (with 5 valence electrons) was used to represent the core electrons. Calculations in this Chapter were performed without spin-orbit coupling (SOC) for convenience but it was later included to confirm some aspects of their electronic behaviour (see Chapter IV). In all calculations, van der Waals (vdW) interactions were incorporated using the B97-D empirical dispersion correction functional [236]. In order to achieve an energy convergence of at least 1 meV/atom and force convergence of at least 1.3×10^{-4} eV/a₀, we found it sufficient to use a common plane-wave energy cutoff of 1100 eV with ‘cold’ Fermi-surface smearing [237] of 10^{-4} K for all elements. Meanwhile, the Brillouin zone sampling for bulk systems was $15 \times 15 \times 15$, and $15 \times 15 \times 1$ for monolayers and bilayers. Uniaxial and shear strains between $\pm 5\%$ were applied in increments of 1% to the unit cell with internal relaxation subject to the same force convergence criterion as above. A sample input file containing the preceding parameters is included in Appendix A.

The elements of the stiffness matrix C were computed from the gradients of the resultant stress-strain profiles $c_{ij} = \partial\sigma_i/\partial\varepsilon_j$, from which all elastic properties were derived. In practice, however, the calculated stiffness tensors are not exactly symmetric due to numerical noise but we make them so by taking the average of C and its transpose C^T as the *effective* stiffness tensor, which, henceforth, shall be referred to as C . We begin our discussion with a brief overview of the the VRH scheme, which is a popular model used for computing effective isotropic elastic properties.

¹QE is not linear-scaling and uses a plane-wave basis as discussed in section 6.

²<http://theosrv1.epfl.ch/Main/Pseudopotentials>

2.2 THE VOIGT-REUSS-HILL SCHEME

In order to effectively preserve, study and strain-engineer few-layer nano-structures, such as BP [238], or graphene [163], the nano-flakes are typically deposited onto a suitable substrate. The macroscopic elastic properties that are measured by experiment are the result of microscopic interactions between the nano-flakes dispersed on or within a bulk medium. The theoretical calculation of these elastic properties requires an appropriate mixture model, such as the rule-of-mixtures (ROM) [239] or the Halpin-Tsai (HT) [240, 241] models (see sections 2.4 & 3.4), which require the (typically averaged) elastic properties of the interstitial nano-flakes.

In the theory of effective media, isotropic bulk properties are computed by averaging the stiffness tensor C over all possible rotated reference frames [242–244], the approach for which is outlined in Appendix 1. The result is called the Voigt average [245, 246] and it gives isotropic averages for the bulk Young’s modulus Y_V , and shear modulus G_V , given in Eq. (B.10). The same scheme applied to the compliance tensor $S = C^{-1}$ results in the corresponding Reuss averages [247], Y_R and G_R , given in Eq. (B.12). The Voigt scheme assumes that the material is subject to homogeneous strain and tends to produce over-estimated elastic constants. Conversely, the Reuss scheme assumes homogeneous stress and it tends to under-estimate the elastic constants. The Hill averages [248], given by

$$Y_H = \frac{Y_V + Y_R}{2} \quad \text{and} \quad G_H = \frac{G_V + G_R}{2}, \quad (\text{III.1})$$

are widely considered as reliable estimates of the actual physical values [244] and from these, the isotropic Poisson’s ratio ν_H and bulk modulus $\mathcal{B}_H$ may also be calculated by means of

$$\nu_H = \frac{Y_H}{2G_H} - 1 \quad \text{and} \quad \mathcal{B}_H = \frac{Y_H G_H}{3(3G_H - Y_H)}. \quad (\text{III.2})$$

The VRH approach described above is used in the present work to determine the isotropic averages of the Young’s, shear and bulk moduli, and the Poisson ratio of the bulk structures using the computed elastic tensors. We will now discuss how the above approach may be adapted to derive the relevant equations for the specific case of two-dimensional materials.

2.3 IN-PLANE VOIGT-REUSS-HILL AVERAGE

If the interstitial nano-flakes in a bulk medium form high-quality planar sediments [181, 249–255], the random orientation is observed in the plane of the flakes and one must calculate isotropic-averages *in-plane*. Due to the weak vdW bonds between layers, strains related to out-of-plane directions can be consequently ignored, resulting in the reduced-stiffness tensor C_{2D} as in Eq. (B.4). In Appendix 1, we re-derive the angular dependence of the rotated tensor-elements $C_{ij}(\theta)$ and $S_{ij}(\theta)$ about the $\vec{z}$ -axis as a function of the elements in the original reference frame, similar to the isotropic VRH scheme. The angular dependence of the in-plane elastic constants are then expressed, from the elements in Eq. (B.9), as

$$\begin{aligned} Y_V(\theta) &= \frac{C_{11}^2 - C_{12}^2}{C_{11}}, & G_V(\theta) &= C_{66}, & \nu_V(\theta) &= \frac{C_{12}}{C_{11}}, \\ Y_R(\theta) &= \frac{1}{S_{11}}, & G_R(\theta) &= \frac{1}{S_{66}}, & \nu_R(\theta) &= -\frac{S_{12}}{S_{11}}, \end{aligned} \quad (\text{III.3})$$

with the Hill-average taken as in Eq. (III.1). The in-plane averages are then computed analogously by first integrating the elastic tensors $C_{ij}(\theta)$ and $S_{ij}(\theta)$ over 2π , before substituting back into Eqs. (III.3).

2.4 COMPOSITE MIXTURE MODELS

The successful simulation of the macroscopic elastic behaviour of a composite material requires an appropriate mixture model that strongly depends on the interplay between the dispersed filler and the bulk matrix material. In addition to the overt chemical interaction between the two constituents, the macroscopic response can also rely on the shape of the filler - for example planar, fibre or particulate - a feature which is predominantly governed, in the nano-scale, by the crystal structure. Here, we shall outline two simple models that could possibly describe a composite material composed of puckered group-V nano-flakes dispersed in a bulk polymer matrix.

The Rule-of-Mixtures model

The rule-of-mixtures (ROM) model [239] invokes a simple weighted mean to determine the properties of a macroscopic composite material, which, for our purposes,

is the Young's modulus Y . In the absence of any formal mathematical description of the underlying interactions between the filler and matrix, it may be regarded as an empirical, first-order approximation to the composite behaviour. Similar to the VRH scheme, the ROM defines a composite lower-bound Y_C^R and upper-bound Y_C^V in terms of the Young's modulus of the filler Y_f , the Young's modulus of the matrix Y_m , and the filler volume-fraction³ ϕ , where

$$Y_C^V = \phi Y_f + (1 - \phi) Y_m \quad \text{and} \quad Y_C^R = \left(\frac{\phi}{Y_f} + \frac{1 - \phi}{Y_m} \right)^{-1}. \quad (\text{III.4})$$

The true Young's modulus is thus predicted to lie somewhere between the two. Furthermore, since the ROM model has no explicit dependence on filler shape or orientation, it is unclear how to strictly define the Young's modulus of the filler, i.e. as an isotropic or in-plane average, thus the model parameters are likely to represent broad estimations.

The Halpin-Tsai model

The equations of Halpin and Tsai (HT) [240, 241] were developed as a simplified and extended form of earlier composite models derived by Hill [248] and Hermans [256]. Unlike the ROM model, the HT equations make explicit the dependence on the geometry and orientation of the filler, parameterised by the factor ζ . The particular alignment between filler and matrix can potentially augment their interaction, and thus the efficient transfer of stress, due, at least in part, to a large filler aspect ratio that provides a larger interfacial region. The HT equation for the Young's modulus of a composite material composed of a planar filler of length l and thickness t is given by

$$Y_{HT} = Y_m \left(\frac{1 + \zeta \eta \phi}{1 - \eta \phi} \right) \quad \text{with} \quad \eta = \frac{Y_f/Y_m - 1}{Y_f/Y_m + \zeta} \quad \text{and} \quad \zeta = \frac{2l}{t}. \quad (\text{III.5})$$

The HT equations provide an empirical extension to the ROM model, since the parameter ζ has no scientific basis and was determined by experimental fitting. In fact, it can be shown that the ROM model can be derived from the HT model by taking the limiting values of ζ . The first limit corresponds to the transverse

³These are formulated under similar assumptions of homogeneous strain and stress, respectively.

arrangement of fibres in a bulk matrix, i.e $\zeta \rightarrow 0$, such that

$$\begin{aligned} \lim_{\zeta \rightarrow 0} E_{HT}(\zeta) &= Y_m \left(\frac{1}{1 - \eta\phi} \right) = Y_m \left(\frac{1}{1 - (1 - \frac{Y_m}{Y_f})\phi} \right) \\ &= Y_m \left(\frac{1}{1 - \phi + \frac{Y_m}{Y_f}\phi} \right) = \left(\frac{1 - \phi}{Y_m} + \frac{\phi}{Y_f} \right)^{-1}, \end{aligned} \quad (\text{III.6})$$

which reproduces exactly the (iso-stress) ROM Reuss model.

The second limit assumes the longitudinal arrangement of fibres within the matrix, i.e $\zeta \rightarrow \infty$, such that

$$\begin{aligned} \lim_{\zeta \rightarrow \infty} E_{HT}(\zeta) &= \lim_{\zeta \rightarrow \infty} Y_m \left(\frac{\frac{Y_f}{Y_m} + \zeta + \zeta(\frac{Y_f}{Y_m} - 1)\phi}{\frac{Y_f}{Y_m} + \zeta + (\frac{Y_f}{Y_m} - 1)\phi} \right) \\ &= Y_m \left(1 + \left\{ \frac{Y_f}{Y_m} - 1 \right\} \phi \right) \quad (\text{by L'Hôpital's rule}) \\ &= Y_m(1 - \phi) + Y_f\phi, \end{aligned} \quad (\text{III.7})$$

which is precisely the (iso-strain) ROM Voigt estimate. Thus, for $0 < \zeta < \infty$, an intermediate value between that of the Voigt and Reuss estimates of the Young's modulus is attained.

3 RESULTS

In this section, we report the mechanical properties computed using plane-wave DFT, and compare them to the available experimental data. We begin with the lattice parameters of the fully-relaxed structures, and then discuss the isotropically averaged bulk properties, as well as the elastic properties as a function of in-plane orientation. Finally, we compare the aforementioned mixture models fitted to experimental data of a polymer-nano-flake composite, as described in our own Ref. [181], and with this confirm our DFT results.

3.1 CALCULATED LATTICE CONSTANTS

The lattice constants $\{a, b, c\}$ of the fully-relaxed structures are presented in Table III.1, where, in the monolayer and bilayer cases, we quote the layer thickness

c' instead of the unit cell height c . Our computed lattice parameters compare well with other recent theoretically predicted values [211, 212, 223, 224, 257–260] and the available experimental data [261, 262].

	a (Å)	b (Å)	c (Å)
P _{mono}	4.57	3.31	2.11
P _{bi}	4.51	3.31	7.34
P _{bulk}	4.43	3.32	10.47
Ref.[261]	4.37	3.31	10.47
As _{mono}	4.70	3.67	2.39
As _{bi}	4.64	3.69	7.86
As _{bulk}	4.56	3.71	10.94
Ref [262]	4.47	3.65	11.0
Sb _{mono}	5.02	4.23	2.79
Sb _{bi}	4.88	4.26	8.83
Sb _{bulk}	4.73	4.29	2.09
Ref [263]		4.3	11.2

Table III.1: Lattice parameters (Å) for monolayer, bilayer and bulk phases of P, As, and Sb compared to experimental data [261–263] quoted in parentheses. For the monolayers and bilayers the layer thickness c' is given.

For a given element, we find that the lattice parameter ‘ a ’ along the puckered direction, shortens as the number of layers increases. This is attributed to the increased vdW forces between layers leading to increased binding primarily in the softer puckered direction.

3.2 ISOTROPIC BULK PROPERTIES

The computed elements of the stiffness tensor of each structure are presented in Table B.1, where those pertaining to bulk P compare well to experiments [264, 265] and similarly computed values [257, 266]. For the elements related to in-plane strains $\{c_{11}, c_{22}, c_{66}, c_{12}\}$ we observe the expected increase in stiffness as the layer number

increases and for decreasing atomic number. However, for the other elements related to out-of-plane and shear stresses $\{c_{33}, c_{44}, c_{55}, c_{23}, c_{13}\}$ the stiffness is seen to, in general, increase with the atomic number.

The Hill-averaged bulk properties are presented in Table III.2, which compare well to other DFT values [257, 266], while our calculated bulk modulus for bulk P (37.2 GPa) is also within reasonable range of the experimental values (32.32 [261] - 36.02 GPa [267]). We also observe that the bulk properties remain largely comparable for all the species, but generally decrease from P to As to Sb (except for the Poisson's ratio and bulk modulus, which are largest for As). While bulk P has the largest in-plane responses, As and Sb have larger out-of-plane and shear responses, which enable the net isotropic properties for all three species to remain comparable overall.

	Y_H (GPa)	G_H (GPa)	ν_H	$\mathcal{B}_H$ (GPa)
P _{bulk}	61.1	24.9	0.23	37.2
As _{bulk}	60.0	23.8	0.26	41.4
Sb _{bulk}	52.5	21.1	0.24	33.8
Ref. [257]	70.3	29.4	0.30	38.5

Table III.2: The Hill-averaged Young's modulus Y_H , shear modulus G_H and bulk modulus $\mathcal{B}$ in GPa, and Poisson's ratio ν_H for bulk P, As and Sb compared to similarly calculated DFT values [257] and available experimental data [261, 267].

3.3 IN-PLANE ELASTIC PROPERTIES

In Appendix 1, we re-derive the equations for the elastic properties as a function of the in-plane orientation angle θ , defined in Fig. III.1, as outlined in Ref. [268]. The mechanical properties as functions of orientation angle are presented for P in Fig. III.2, As in Fig. III.3, and Sb in Fig. III.4, and illustrate the Young's modulus $Y(\theta)$ and its average $\langle Y(\theta) \rangle$, the shear modulus $G(\theta)$, and Poisson's ratio $\nu(\theta)$. We summarise this data in Table B.2. In contrast to the isotropic averages for the bulk properties in Table III.2, which remained largely similar for P, As and Sb, a much clearer trend across the species emerges once we have eliminated contributions from

the out-of-plane and shear stresses. In this instance, P clearly possesses superior in-plane mechanical strength in both moduli, which expectedly increase with increasing layers. Meanwhile, As and Sb are largely similar in the monolayer, though less so in the bilayer and bulk phases, where they are stronger in the $\vec{x}$ -direction. In contrast, the Poisson's ratio tends to remain relatively consistent aside from generally decreasing with increasing number of layers.

The anisotropy of the underlying crystal structure is clearly reflected in the mechanical profiles where the Young's modulus appears to have a 2-fold symmetry about the x -axis, in contrast to the shear modulus and Poisson's ratios, which display 4-fold symmetry about both the axes (except for the Poisson's ratio of P, which remains 2-fold symmetric). Indeed, for a given species, the general shape of each profile appears to remain relatively consistent with respect to the number of layers, while the range of each quantity tends to increase. This insight is advantageous in the strain-engineering of nano-flakes since one may forecast in advance the response of a material to in-plane strain, once the underlying profile and number of layers are known.

Another interesting feature is that the extrema of the elastic functions do not necessarily coincide with the coordinate-axes. For instance the Young's modulus for monolayer Sb is maximal at 22° . Table B.2 summarises the global minima and maxima of each function and the angles at which they occur. While most of the function extrema occur expectedly at 0° , 45° or 90° , many are incident away from the coordinate-axes. This result lends further insight into the mechanical anisotropy of the orthorhombic group- V materials of the $Cmca$ space group and D_{2h} point group.

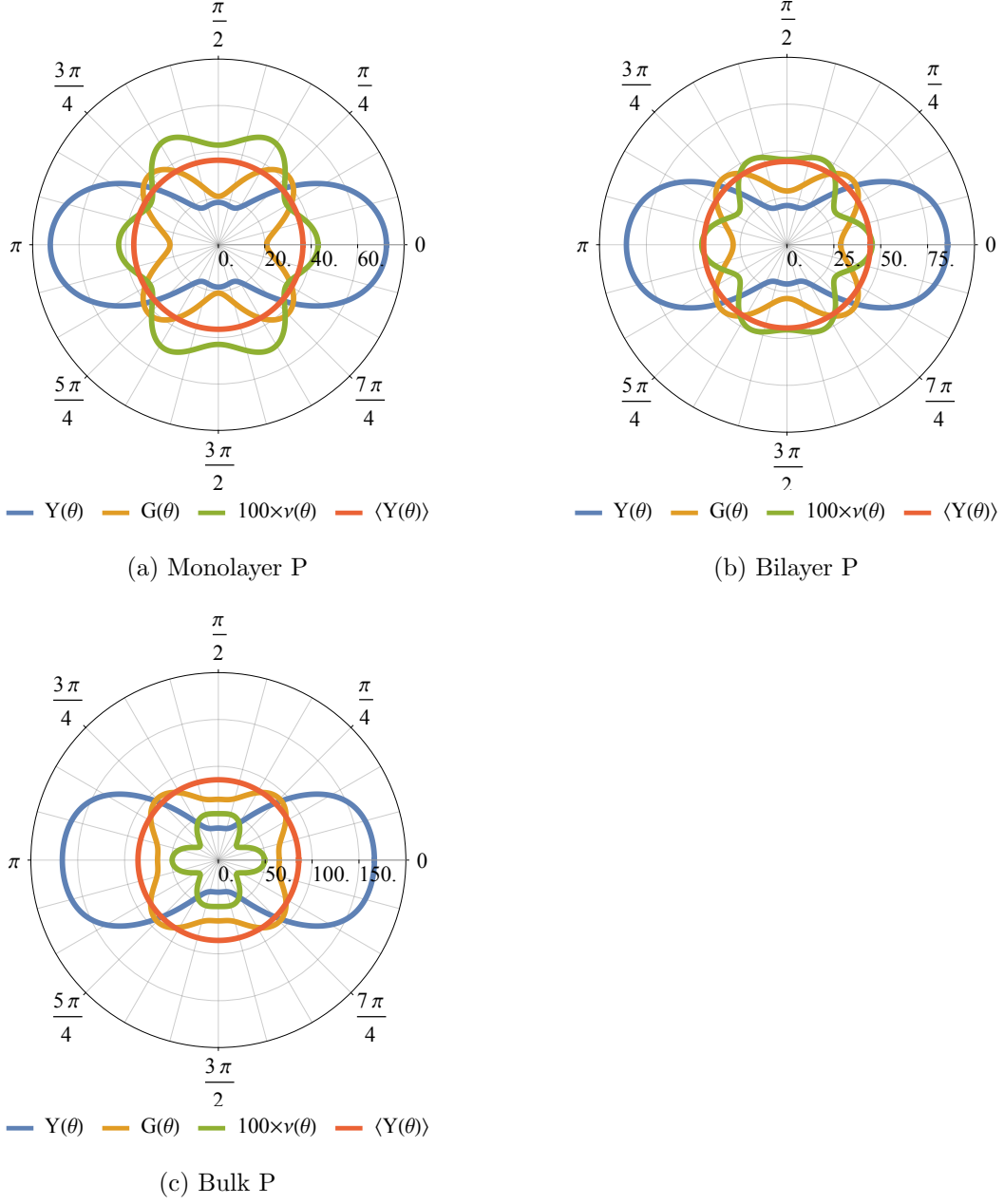


Figure III.2: In-plane functions for P Young's modulus $Y(\theta)$ (blue) and its isotropic average $\langle Y(\theta) \rangle$ (red) in units of GPa; shear modulus $G(\theta)$ in GPa (red); and Poisson's ratio $\nu(\theta)$ (scaled by 100).

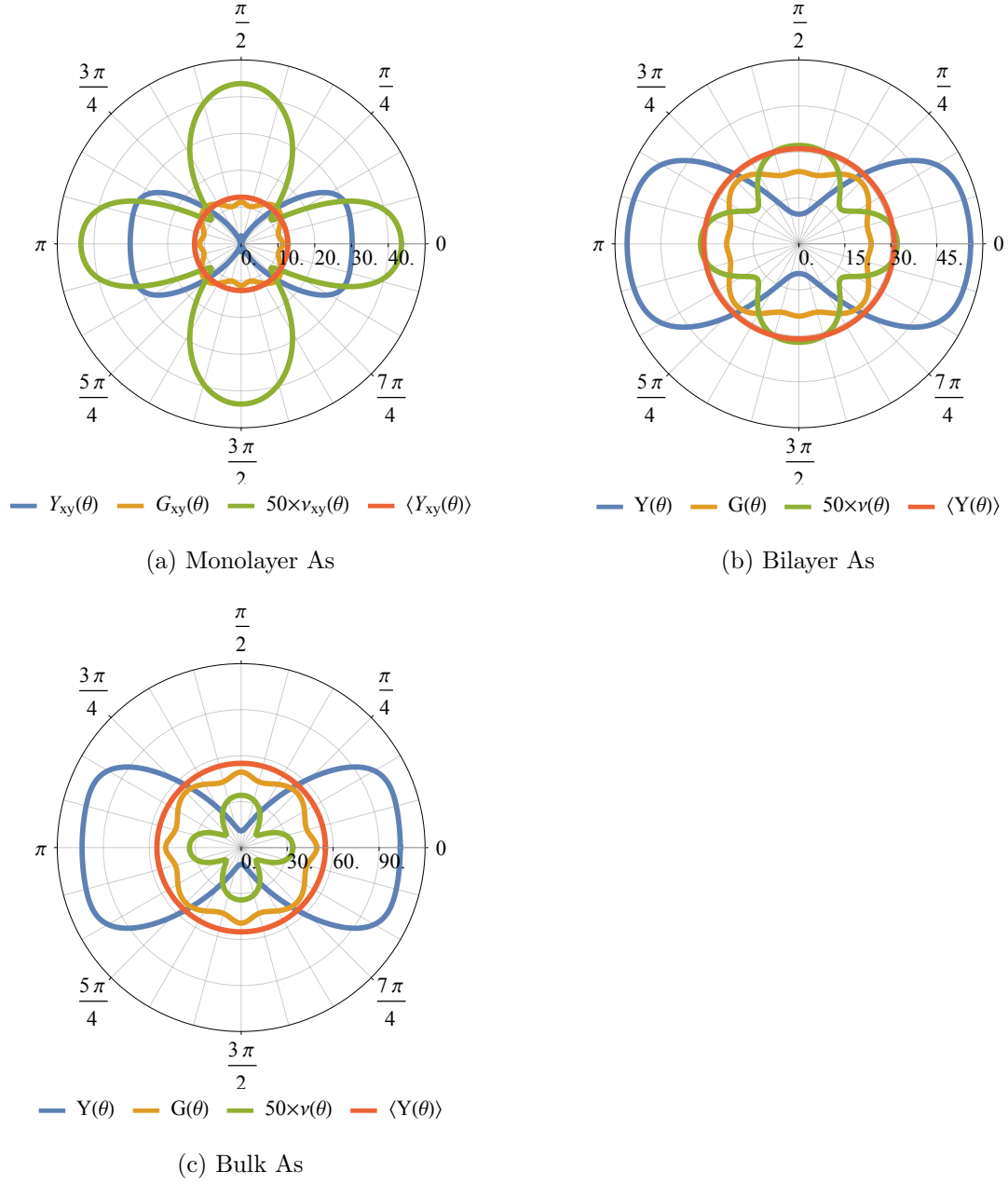


Figure III.3: In-plane functions for As Young's modulus $Y(\theta)$ (blue) and its isotropic average $\langle Y(\theta) \rangle$ (red) in units of GPa; shear modulus $G(\theta)$ in GPa (red); and Poisson's ratio $\nu(\theta)$ (scaled by 50).

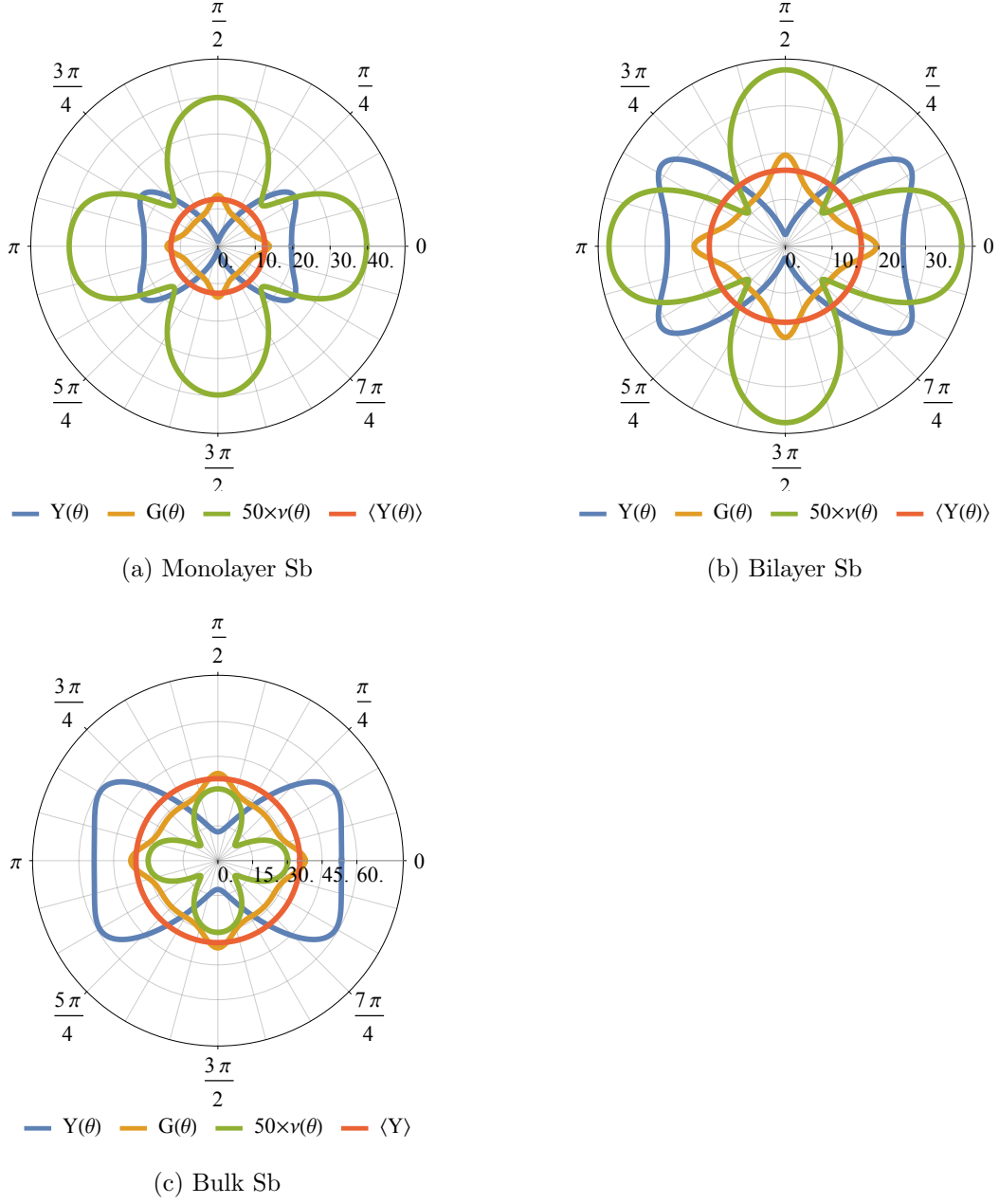


Figure III.4: In-plane functions for Sb Young's modulus $Y(\theta)$ (blue) and its isotropic average $\langle Y(\theta) \rangle$ (red) in units of GPa; shear modulus $G(\theta)$ in GPa (red); and Poisson's ratio $\nu(\theta)$ (scaled by 50).

3.4 POLYMER-NANO-FLAKE COMPOSITE

In our paper in Ref. [181], we demonstrated that the controlled production of large quantities of few-layer BP can be achieved by liquid-phase exfoliation (LPE) [269], in which the BP fragments are immersed in a solution of *N*-cyclohexyl-2-pyrrolidone (CHP), and separated into layers by sonication, or shearing. The particular choice of CHP as a solution is two-fold: to lubricate the exfoliation process, and to guard the produced samples from oxidation [190, 210, 270], a problem that has been reported to hinder the large-scale production of BP. The advantage of sonication is not only the effective mass-production of samples, but the means to control the size-dispersion of the produced stock, which varied from 50 nm to 2500 nm.

Our study focused in particular on two batches: one containing small samples with mean-length $L_s = 130 \pm 111$ nm and one containing large samples with mean-length $L_l = 2260 \pm 1000$ nm. A monolayer of BP was measured to be 2.06 ± 0.02 nm thick, which is a factor of 4 greater than the monolayer thickness estimated from the bulk value in Table III.1, however this was acknowledged to be overestimated. The samples were then determined to be 8 layers thick on average, which corresponds to a bulk calculation for our purposes. The nano-flakes were dispersed in PVC, up to 0.3% volume, and subject to mechanical stress to determine the composite PVC:BP Young's modulus. The pristine PVC Young's modulus was measured to be $Y_m = 511 \pm 118$ MPa. The experimental data in this section was provided by the experiments conducted by our colleagues, Damien Hanlon, Conor Boland, and Johnny Coleman and may be found in Table B.3.

Since the ROM models in Eq. (III.4) make no distinction between flake sizes, they may be fit to all the data simultaneously, as shown in Fig. III.5. The upper-bound BP Young's modulus, given by the Voigt ROM model, is determined as $Y_f^V = 184 \pm 38$ GPa, and is in excellent agreement with the calculated DFT values. In fact, the Young's modulus coincides precisely with the elastic stiffness in the zigzag direction $c_{11} = 187.9$ GPa (Table B.2), and, thus, supports our earlier assumption that the flakes are naturally aligned in-plane. On the other hand, the Reuss model cannot be feasibly extrapolated to a Young's modulus at 100% volume fraction since

the fit quickly diverges beyond the limited range of the data. Nonetheless, the PVC Young's modulus was determined by both models to be $Y_m^V = 541 \pm 44$ MPa, as expected.

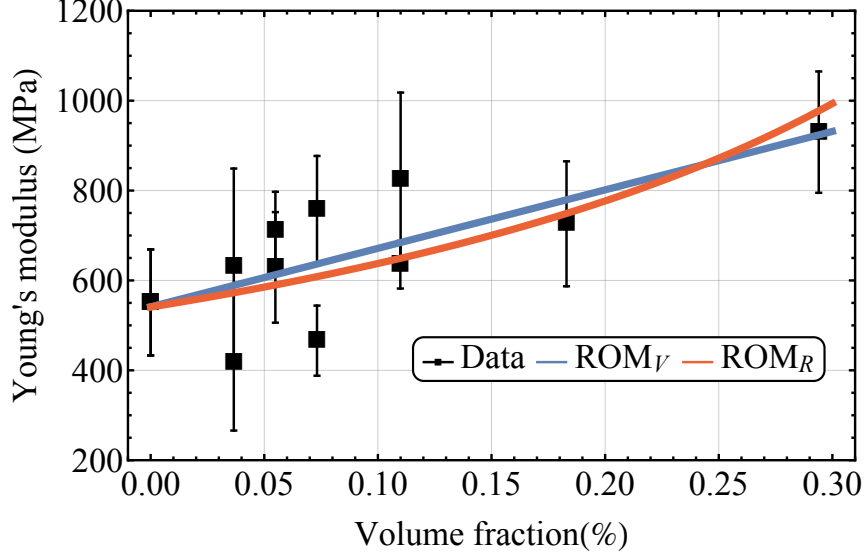


Figure III.5: Young's modulus of PVC:BP composite (MPa) against BP nano-flake volume fraction (%) fit to the Voigt (blue) and Reuss (red) ROM models.

The HT model, meanwhile, must accommodate the flake sizes according to the parameter $\zeta = 2l/t$, which, for small flakes, is $\zeta_S = 15.8$ and for large flakes is $\zeta_L = 274.3$. The models were then fit to the corresponding data where the matrix Young's modulus $Y_m = 511$ MPa is kept fixed, and are shown by the solid lines in Fig. III.6, keeping all other variables fixed. The resulting Young's modulus for the small flakes is $Y_S = 117 \pm 71$ GPa, and for the large flakes is $Y_L = 215 \pm 28$ GPa, which are very reasonable indeed and closely resemble the values we obtained in the VRH model.

Furthermore, if we allow the model to be simultaneously optimised according to Y_f and Y_m shown by the dashed lines in Fig. III.6, we can find the best fit for Y_m as well. In this instance, the model parameters for the small flakes were calculated as $Y_S = 140 \pm 148$ GPa and $Y_m = 494 \pm 84$ MPa. While Y_S has a large associated uncertainty, Y_m is at least close enough to the margin of experimental uncertainty. Meanwhile, the model parameters for the large flakes, given by $Y_L = 167 \pm 26$ GPa and $Y_m = 622 \pm 41$ MPa are slightly larger but have smaller uncertainties and are

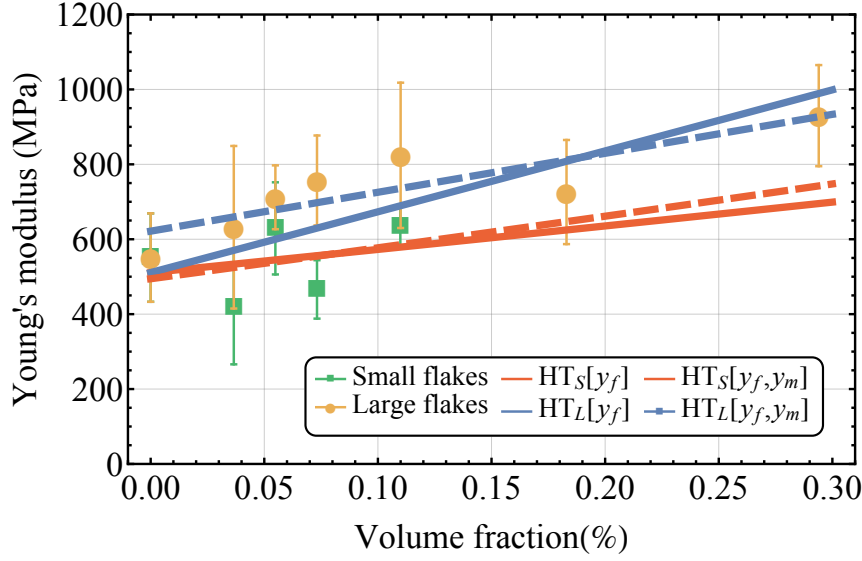


Figure III.6: Young's modulus of PVC:BP composite (MPa) against BP nano-flake volume fraction (%) for large (orange) and small (green) flakes. Halpin-Tsai models are shown for the large (blue) and small (red) flakes, where the parameters in parentheses indicate which variables are optimised in the models. The solid line indicates the model where just Y_f is optimised while the dashed lines indicate where Y_f and Y_m are optimised.

also broadly in line with all other results up to now.

A summary of the model results is presented in Table III.3, where it is clear that the Voigt ROM and HT models are in very reasonable agreement with experimental and theoretical data. Moreover, with the various models we can estimate the Young's modulus of BP to be approximately between 120 GPa and 200 GPa.

Model	Y_f (GPa)	Y_m (MPa)	ζ
ROM Voigt	184 ± 38	541 ± 44	-
ROM Reuss	-	541 ± 44	-
HT _S [Y_f]	117 ± 71	(511)	(15.8)
HT _L [Y_f]	215 ± 28	(511)	(273.9)
HT _S [Y_f, Y_m]	140 ± 148	494 ± 84	(15.8)
HT _L [Y_f, Y_m]	167 ± 26	622 ± 41	(273.9)

Table III.3: ROM and HT model results for the Young’s moduli of BP (GPa) and PVC (MPa), and ζ parameter. Variables in parentheses are not optimised by the model.

4 CONCLUSION

In this Chapter, we have quantified the qualitative mechanical properties of puckered phosphorus, arsenic and antimony, in the few-layer and bulk phases, from comprehensive DFT calculations. We have found that these materials exhibit a broad range of elastic properties and in-plane behaviour that are reflective of the underlying anisotropic crystal structure, which potentially provide for widespread technological application. Moreover, the calculated mechanical properties, from lattice constants to Young’s moduli, are in excellent agreement with experimental observations. We have provided further confirmation of these values from the experimental measurements of a PVC:BP composite material and appropriate mixture models, which place the Young’s modulus between 120 GPa and 200 GPa.

This work, detailing the macroscopic physical behaviour of mono-crystalline, alloyed, or composite structures, is a typical example of the utility DFT provides. While the predictive capability of DFT is largely dependent on the system under consideration, the quality of the pseudopotential and, crucially, the choice of exchange-correlation functional, quantities such as lattice constants and mechanical properties are generally well reproduced [271]. However, DFT suffers from inherent, systematic failures, which, as we shall discuss in the next Chapter, can lead to qualitative miscalculation of electronic properties, in particular the band gap.

IV

ELECTRONIC PROPERTIES OF TWO-DIMENSIONAL GROUP-V MATERIALS

THE SEARCH FOR GRAPHENE alternatives that are capable of supporting ballistic electron transport has driven intense research toward the development of a new class of materials termed Weyl and Dirac semi-metals [272–282, 282, 283, 283–285]. Weyl and Dirac states in semi-metals result from the manifestation of massless quasi-particle states in bulk or low-dimensional condensed matter systems, respectively. These states lead to unique topological properties characterised, primarily, by ballistic conduction.

In this Chapter, we continue our analysis of the calculation results of puckered phosphorus (P), arsenic (As) and antimony (Sb) in relation to the electronic properties, with particular emphasis on the identification of qualitative electronic transitions. Specifically, we investigate the Kohn-Sham band gaps and charge-carrier effective masses from the computed electronic band structures, insofar as the Kohn-Sham eigenvalues are physically relevant, which, strictly speaking, they are not. Nonetheless, reasonable confidence can be afforded in the reproduction of electronic trends [9, 286] and, thus, we make tentative predictions of strain-induced Dirac and Weyl states in particular cases, numerous band gap transitions, one-dimensional conductivity, and a structural phase-transition for moderate in-plane stresses. Our predicted results contribute to the mounting evidence for the utility of these materials, as outlined in the previous Chapter, but are undermined by the failure of DFT to accurately resolve specific electronic properties which, as we shall observe, can differ dramatically from experimental observations.

1 WEYL AND DIRAC SEMI-METALS

In 1929, Herman Weyl derived a solution to the Dirac equation [287] that proposed the existence of relativistic, massless fermions [284], which have come to bear his name. As of yet, Weyl fermions have not been observed as fundamental particles in nature, but persistent breakthroughs in topological insulators have lead to their recent discovery by Xu *et al.* [272] as emergent quasi-particles in tantalum arsenide (TaAs), among other predicted candidates [275, 288, 289]. Weyl semi-metals are primarily characterised by the crossing of linearly-dispersive energy bands through nodes at the Fermi energy, termed Weyl *points* or *cones*, which support ballistic charge transport [285]. Weyl points emerge as the result of underlying symmetries of the crystal lattice, namely time-reversal and inversion or reflection symmetries [283], but can also be produced by mirror symmetries [290], which affect the solutions of the Hamiltonian. As such, Weyl cones are highly robust and always occur in pairs of opposite chirality [285].

A Dirac semi-metal, on the other had, is the two-dimensional analogue of a Weyl semi-metal, the most famous exhibition of which is seen in graphene [291]. The particular difficulty in attaining Dirac points in two-dimensional materials is well documented [282, 283] and is due to the difficulty attaining the required symmetry-protection mechanisms in reduced dimensions. Nonetheless, a Dirac semi-metal in few-layer BP was observed experimentally by Kim *et al.* [292], while arsenic [293], antimony [224, 232, 294], and bismuth [224] are also predicted candidates. The ambitious development of Weyl and Dirac semi-metals is driven by highly anticipated applications in high-speed electronics and computing. We refer the reader to Refs. [272, 279, 282–285] for further information on Weyl and Dirac semi-metals.

2 METHODOLOGY

The run-time calculation parameters and straining procedure for this Chapter were the same as those outlined in section 2.1. Calculations without SOC were initially performed for convenience and those strains that exhibit potential Dirac or Weyl states were reassessed at representative strains including non-perturbative SOC [295].

Electronic band structures were calculated along the high-symmetry points of the Brillouin zone $\{\Gamma, X, S, Y, Z\}$, shown in Fig. IV.1 below, from which the Kohn-Sham band gaps were determined.

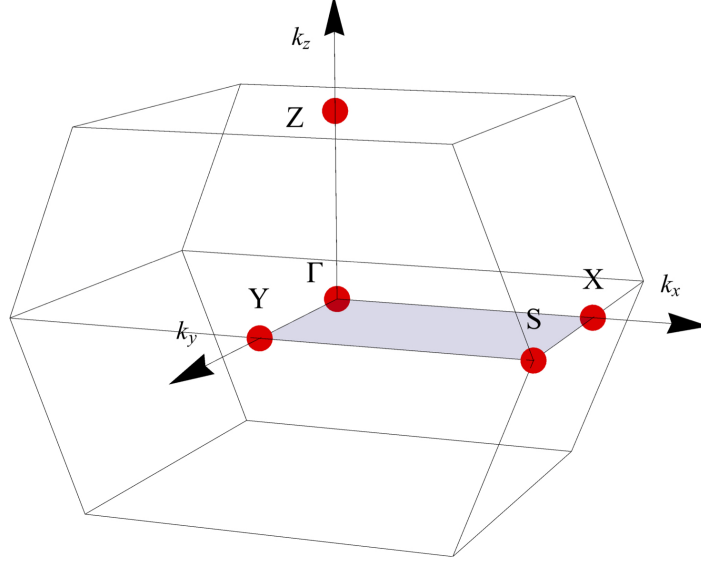


Figure IV.1: The Brillouin zone for orthorhombic phosphorus of the Cmca space group and D_{2h} point group with high-symmetry points $\{\Gamma, X, S, Y, Z\}$ labelled.

Under shear strain, the Brillouin zone deforms into an asymmetric honeycomb in the x - y plane, yet we retained sampling along the original path since the deformation up to 5% strain is negligible and the effective masses were all calculated at the Γ -point. We determined charge-carrier effective masses according to the nearly-free electron model $m_{ij}^* = \hbar^2 (\partial^2 E / \partial k_i \partial k_j)^{-1}$ using a cubic spline fit to 9 data points about the Γ -point. The charge velocities were similarly determined according to the dispersion relation $v = \hbar^{-1} dE(k)/dk$ from the linear fit to the Dirac and Weyl states. To confirm the existence of linear-dispersion, we also plotted three-dimensional band structures in the region of the Dirac and Weyl points with SOC, as well as lines intersecting the points at 0° , 30° , 60° , and 90° with respect to the $\Gamma - X$ line. Following the convention of terminology found in the Refs. [274, 292, 296], and other sources, we henceforth classify Dirac or Weyl states as those associated with regions of sustained linear dispersion in the band structure, at or near the Fermi level, in at least one direction.

3 ELECTRONIC PROPERTIES

All of the band structures pertaining to the following analysis are presented in the supplemental material of Ref. [297]. This section is divided into nine parts detailing the electronic properties derived from the plane-wave DFT calculations for each species at each layer-number. We discuss the trends in Kohn-Sham band gaps and charge carrier effective masses, and identify the qualitative transitions that occur, which are summarised in Table B.5. Where applicable, we discuss the predicted existence of Dirac and Weyl states and reassess those examples with high resolution two- and three-dimensional band structures, including SOC.

In the following discussion, directions along $\Gamma - Y$ pertain to the zig-zag direction in the crystal structure, while those along $\Gamma - X$ pertain to the puckered direction.

Monolayer Phosphorus

For the relaxed P monolayer, our calculations produced a direct band gap of 0.88 eV at the Γ -point, as shown in Fig. IV.2a, which falls within range of other gaps determined by DFT: 0.7 eV from DFT-PBEsol [196] and 1.0 eV from DFT-HSE06 [193]. On the other hand, quasi-particle calculations [206], which treat electronic addition and removal events on an explicit footing, predict a larger band gap of 2 eV with significant exciton binding [298] (between 0.4 eV to 0.83 eV).

This discrepancy is a classic example of the systematic band gap problem inherent to approximate semi-local functionals such as PBE [299]. These errors not only misrepresent band gaps and other electronic properties, but may also adversely affect the critical strains of the identified transitions and, thus, must be treated cautiously. Nevertheless, it is important to emphasise that band alignments and rates of change are quite often reliably reproduced [300].

While absolute band gaps are therefore not expected to be accurate, we can expect reasonable agreement with trends in electronic and mechanical behaviour [9, 286]. While discussing the remaining results, we shall omit further discussion of these errors until section 4.

The application of uniaxial in-plane strain was found to open the band gap

for tensile strain and diminished it for compressive strain, while shear strain had a negligible effect. The electron and hole effective masses (Figs. IV.2b & IV.2c), compare well to the figures computed in Ref. [266], where, at $\varepsilon_{xx} = +5\%$ tensile strain, the electron and hole effective masses coincide at $0.9 m_0$ while, for compressive strains, the hole effective mass along $\Gamma - X$ rises significantly.

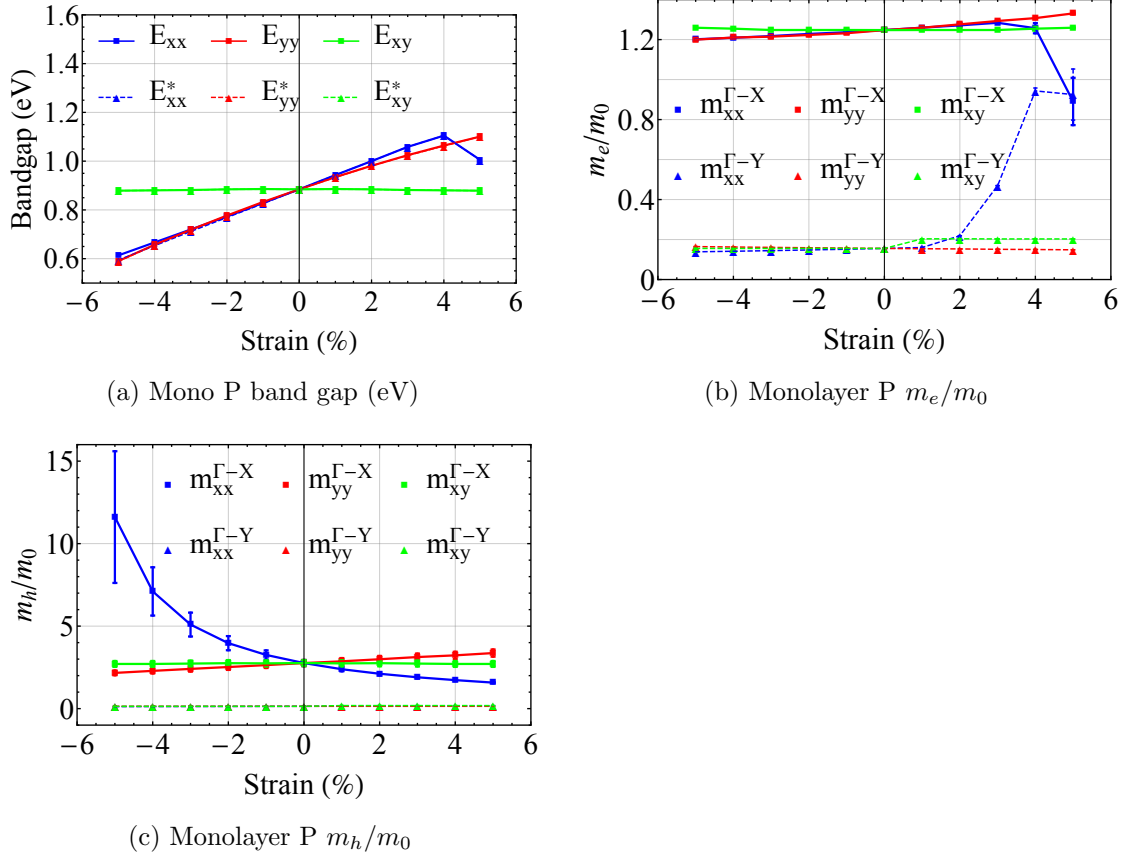


Figure IV.2: The relationships for monolayer P between the applied in-plane strains ε_{xx} (blue), ε_{yy} (red) and ε_{xy} (green) against (a) the direct E (solid squares) and indirect E^* (dashed triangles) band gaps (eV); (b) the effective electron masses m_e/m_0 along $\Gamma - X$ (solid squares) and $\Gamma - Y$ (dashed triangles); (c) the effective hole masses m_h/m_0 along $\Gamma - X$ (solid squares) and $\Gamma - Y$ (dashed triangles).

Bilayer Phosphorus

Relaxed bilayer P was also found to have a direct band gap of 0.43 eV (Fig. IV.3a), and exhibits broadly the same electronic behaviour as the monolayer. This includes the convergence of the electron effective masses (Fig. IV.3b) at +4% strain, and

increasing hole effective masses (Fig. IV.3c) for compressive strains. A direct-indirect band gap transition was also observed at +2% uniaxial tensile strain.

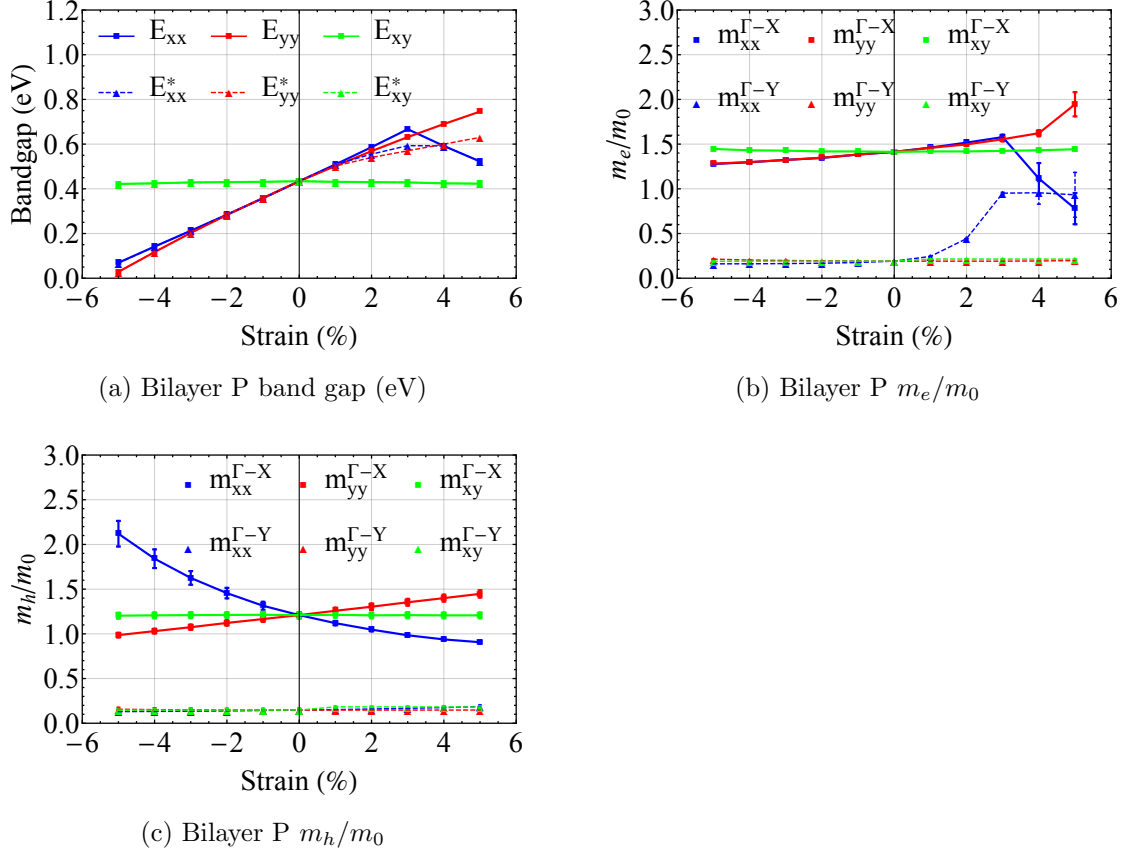


Figure IV.3: The relationships for bilayer P between the applied in-plane strains ε_{xx} (blue), ε_{yy} (red) and ε_{xy} (green) against (a) the direct E (solid squares) and indirect E^* (dashed triangles) band gaps (eV); (b) the effective electron masses m_e/m_0 along $\Gamma-X$ (solid squares) and $\Gamma-Y$ (dashed triangles); (c) the effective hole masses m_h/m_0 along $\Gamma-X$ (solid squares) and $\Gamma-Y$ (dashed triangles).

Incidentally, the band gap closes around -5% uniaxial compressive strain, at which point a Dirac state emerges at the Γ -point. The effect of SOC on the band structure (Fig. IV.4a) induces no qualitative difference in the bands and the three-dimensional bands plotted about the Dirac points (Fig. IV.4b) confirm the linear-dispersion, albeit in only one direction. A linear fit to the surface of the bands (Fig. IV.4c) returns a maximum charge velocity of $v = 3.80(1) \times 10^6 \text{ ms}^{-1}$ along $\Gamma-Y$, while, in the orthogonal direction, the bands are flat with a charge velocity that is relatively negligible. This high anisotropy in charge velocities, dominated by

ballistic conduction along $\Gamma-Y$, is indicative of effective one-dimensional conductivity that is supported by the large disparity in effective masses at $\varepsilon_{xx} = -5\%$, evident in Figs. IV.3b & IV.3c. The Dirac state for $\varepsilon_{yy} = -5\%$, which is due to band inversion, occurs off the $\Gamma-Y$ symmetry line at a point X' , as illustrated in Figs. IV.4a - IV.4c. Here the maximum charge velocity is $v = 3.22(1) \times 10^6 \text{ ms}^{-1}$. These results are supported by the work of Doh *et al.* [301], who demonstrated the effect of strain on hopping parameters can lead to a Dirac semi-metallic state in bilayer P. Similarly, Baik *et al.* [296] found that the SOC did not induce a band gap in potassium-doped multi-layer P, but did lift the spin-degeneracy of the Dirac points.

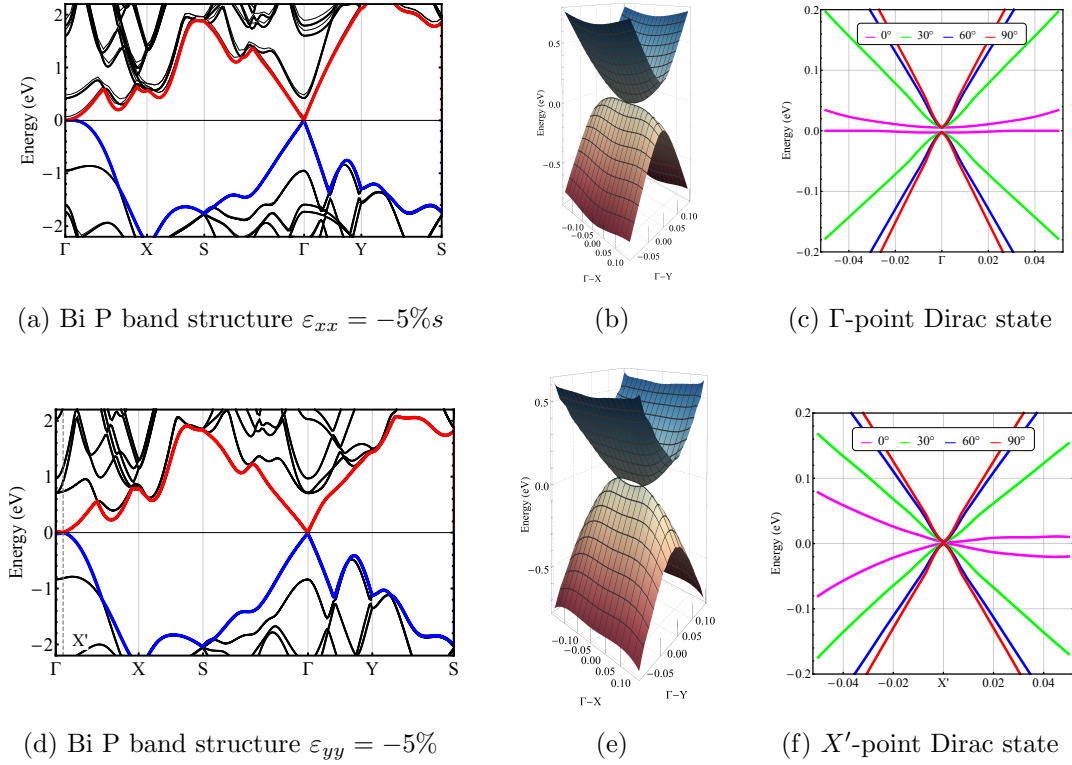


Figure IV.4: (a) Band structure of bilayer P at $\varepsilon_{xx} = -5\%$ with SOC (thick lines), and without SOC (thin lines) (b) three-dimensional bands about the predicted Dirac point at Γ (c) slices through the Dirac point at 0° , 30° , 60° and 90° relative to the $\Gamma-X$ line that indicate highly anisotropic conduction. [(d) - (f)] Illustrates the same for bilayer P at $\varepsilon_{yy} = -5\%$, where the Dirac state occurs at the non-symmetry point X' along $\Gamma-X$.

Bulk Phosphorus

In the bulk, however, we found the band gap to be completely closed (Fig. IV.5a), and therefore the system is predicted to be metallic, in contrast to numerous experiments [302–305], which have measured a direct gap in the range of 0.31–0.36 eV. We concluded after investigation that this was, in part, due to an effect of the Fermi surface smearing functionality [237] in the ionic geometry relaxation procedure. When relaxed under fixed-occupancy conditions, instead, a band gap of 0.35 eV was produced.

The electron effective masses were found to be quite responsive to strain (Fig. IV.5b), where those along $\Gamma - Y$ rose for both tensile strain along ε_{xx} , due to falling conduction bands, and compressive strain along ε_{yy} , due to flattening bands along $\Gamma - Y$. In comparison, the hole effective masses were found to vary to a lesser extent (Fig. IV.5c). The effective masses along $\Gamma - X$ were not computed once the band gap closed below +2% strain. Finally, shear strain was seen to have a negligible effect on the gap.

While the PBE gap remained incorrectly closed in the relaxed state, a possible Weyl state was observed at 2% uniaxial strain (Fig. IV.6a), before a direct gap opened that subsequently transitioned to an indirect gap at +3%. The SOC slightly reduced the band gap by approximately 0.05 eV but did not qualitatively affect the overall results. The three-dimensional band structure with SOC is shown in Fig. IV.6b, in which a pair of potential Weyl points occur on an off-symmetry point X' along $\Gamma - X$. The maximum charge velocity, computed from Fig. IV.6a, is $v = 2.40(1) \times 10^6 \text{ ms}^{-1}$ for both $\varepsilon_{xx} = +2\%$ and $\varepsilon_{yy} = +2\%$ (Figs. IV.6d - IV.6f) and occurs along a line parallel to $\Gamma - Y$. This band-inversion may also lead to further Weyl states under greater compression, which have been predicted at similar pressures [225–227].

To summarise, we predict the onset of Γ -point Dirac states in bilayer P at -5% uniaxial compression, which is supported by previous studies [296, 301]. We also predict effective one-dimensional conductivity at $\varepsilon_{xx} = -5\%$, and a direct-indirect band gap transition at +2% tensile strain. We observe possible Weyl states at +2% tensile strain in bulk P, followed by a direct-indirect band gap transition at +3%. Finally, effective masses are found to vary widely between phases and strain directions

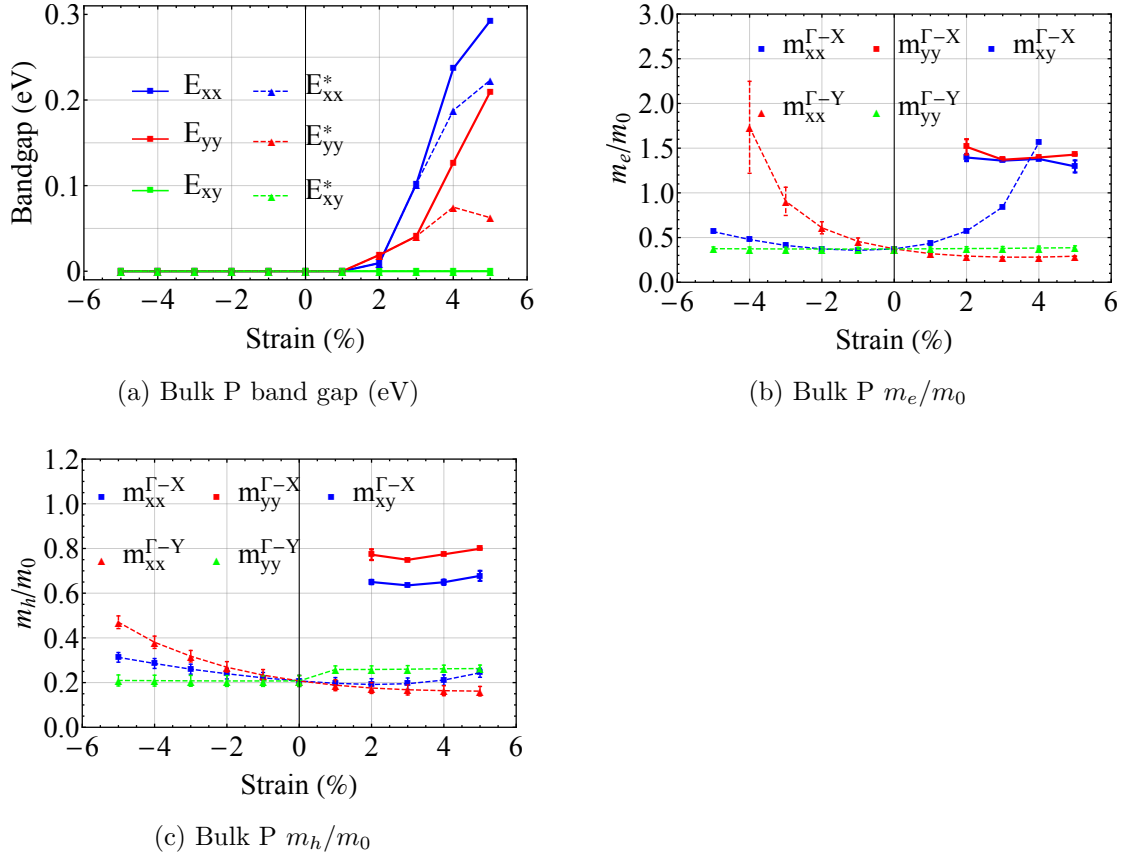


Figure IV.5: The relationships for bulk P between the applied in-plane strains ε_{xx} (blue), ε_{yy} (red) and ε_{xy} (green) against (a) the direct E (solid squares) and indirect E^* (dashed triangles) band gaps (eV); (b) the effective electron masses m_e/m_0 along $\Gamma-X$ (solid squares) and $\Gamma-Y$ (dashed triangles); (c) the effective hole masses m_h/m_0 along $\Gamma-X$ (solid squares) and $\Gamma-Y$ (dashed triangles).

and seem strongly susceptible to tuning.

Monolayer Arsenic

In contrast to P, we identified an indirect band gap of 0.15 eV along the $\Gamma-Y$ direction in the relaxed As monolayer (Fig. IV.7a), which was significantly lower than the predicted DFT-HSE06 gap of 0.83 eV [259]. However, the relaxed band structure and band gap profiles closely resemble the band structures in Refs. [211, 293].

The band gap diminishes for tensile strain along ε_{xx} and at +2% the material becomes semi-metallic with a Dirac state at the Γ -point emerging at $\varepsilon_{xx} = +5\%$ accompanied by an electron pocket above the Fermi-level (Fig. IV.8), which is unaf-

3. Electronic properties

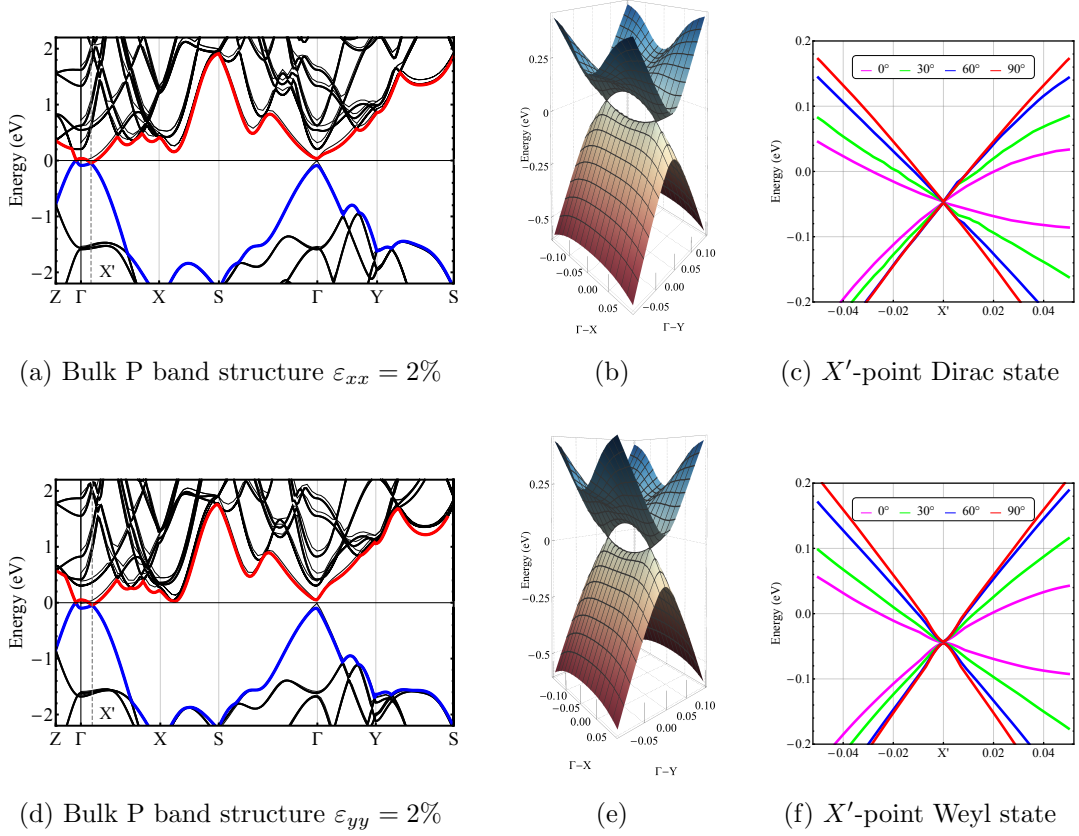


Figure IV.6: (a) Band structure of bulk P at $\varepsilon_{xx} = +2\%$ with SOC (thick lines), and without SOC (thin lines) where the off-symmetry point X' , located along $\Gamma - X$, is indicated by the dashed vertical line (b) three-dimensional bands with SOC about the potential Weyl points (c) slices through one Weyl point at 0° , 30° , 60° and 90° relative to the $\Gamma - X$ line, also with SOC. [(d) - (f)] The same is illustrated for $\varepsilon_{yy} = +2\%$.

ected by the SOC. The maximum charge velocity here is $v = 3.01(1) \times 10^6 \text{ ms}^{-1}$ and lies along $\Gamma - Y$. In the orthogonal direction the bands are flat, similarly to monolayer P, with a relatively small charge velocity. This high anisotropy in charge velocities, dominated by the ballistic conduction along $\Gamma - Y$, is again indicative of effective one-dimensional conductivity and is further supported by the large disparity in effective masses at $\varepsilon_{xx} = 5\%$, shown in Figs. IV.7b & IV.7c.

For compressive strain along ε_{xx} an indirect-direct transition occurs [211] at $\varepsilon_{xx} = -2\%$. For tensile strain along ε_{yy} the band gap opens, where at $\varepsilon_{yy} = -3\%$, the indirect band gap closes along $\Gamma - Y$. Similar to monolayer phosphorus, there is no

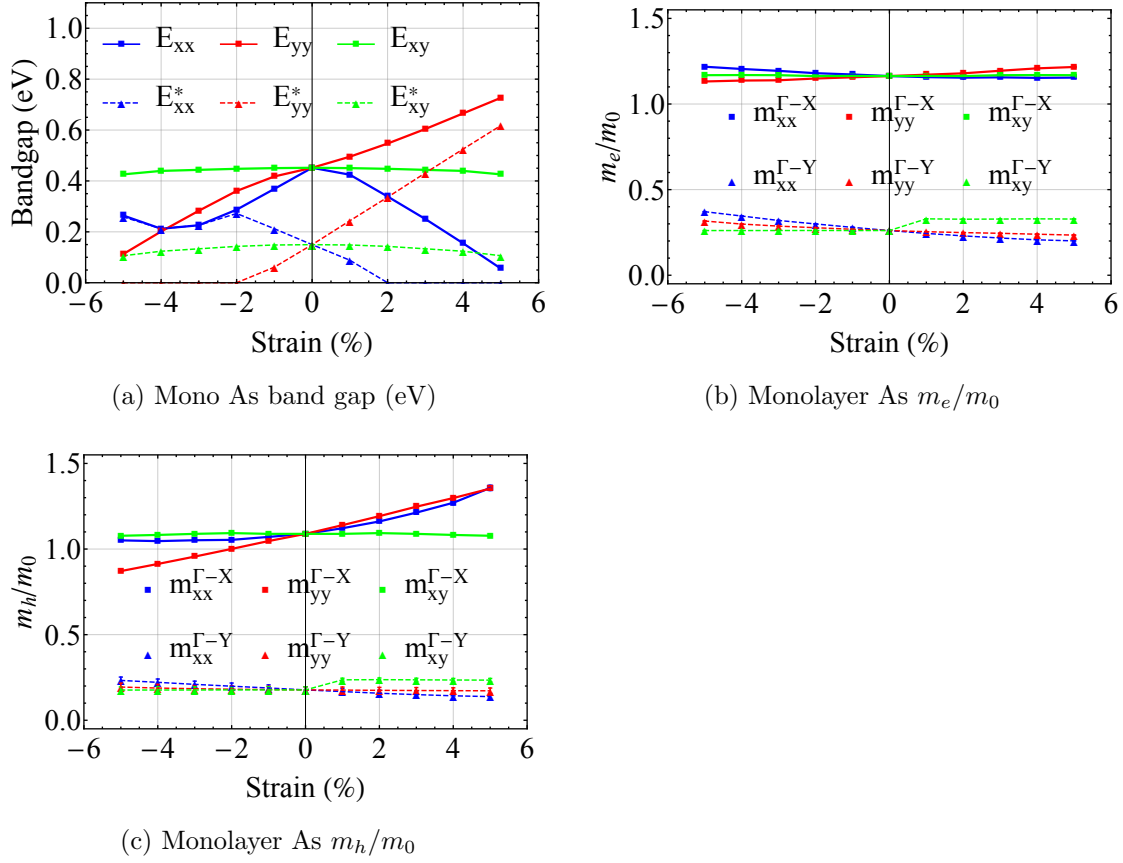


Figure IV.7: The relationships for bulk As between the applied in-plane strains ε_{xx} (blue), ε_{yy} (red) and ε_{xy} (green) against (a) the direct (solid squares) and indirect (dashed triangles) band gaps (eV); (b) the effective electron masses m_e/m_0 along $\Gamma - X$ (solid squares) and $\Gamma - Y$ (dashed triangles); (c) the effective hole masses m_h/m_0 along $\Gamma - X$ (solid squares) and $\Gamma - Y$ (dashed triangles).

appreciable effect due to shear-strain. Meanwhile, the charge-carrier effective masses (Figs. IV.7b & IV.7c) respond linearly to uniaxial strain and compare well to other works [262], where, in particular valence band broadening along $\Gamma - X$ leads to an increasing hole effective mass.

Bilayer Arsenic

For bilayer As, we identify a direct band gap of 0.45 eV (Fig. IV.9a), in contrast to the indirect band gap observed in the monolayer. Here, the band gap opens for uniaxial tensile strain and diminishes for compressive strain. The direct band gap transitions to an indirect gap at both $\varepsilon_{yy} = -3\%$ and $\varepsilon_{yy} = +2\%$, while at $\varepsilon_{xx} = +2\%$ it also

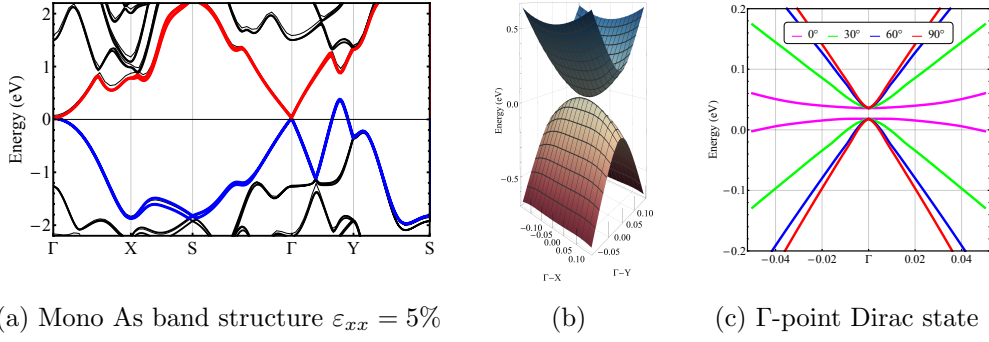


Figure IV.8: (a) Band structure of monolayer As at $\varepsilon_{xx} = +5\%$ with SOC (thick lines), and without SOC (thin lines) (b) three-dimensional bands with SOC about the predicted Dirac point at Γ (c) slices through the Dirac point at 0° , 30° , 60° and 90° relative to the $\Gamma-X$ line, also with SOC.

transitions to an indirect gap before resuming to a direct gap again at $\varepsilon_{xx} = +3\%$.

Moreover, we predict a Dirac state at the Γ -point at $\varepsilon_{xx} = -4\%$ compression (Fig. IV.10), for which the maximum charge velocity is $v = 2.62(2) \times 10^6 \text{ ms}^{-1}$ along $\Gamma-Y$. The bands are also flat along $\Gamma-X$, similar to the monolayer, and have a relatively negligible charge velocity. The high anisotropy in charge velocities, again suggests effective one-dimensional conductivity, dominated by the ballistic conduction along $\Gamma-Y$, and is further supported by the large disparity in effective masses at $\varepsilon_{xx} = 5\%$, shown in Figs. IV.9b & IV.9c. Here again, the SOC has no appreciable effect on the bands. The electron and hole effective masses (Figs. IV.9b & IV.9c) respond approximately linearly to the applied strain, where conduction band broadening leads to increased effective electron masses, and valence band flattening at Γ leads to increasing hole effective masses.

Bulk Arsenic

Finally, no band gap is determined in the relaxed bulk phase (Fig. IV.11a), again contrary to experiments [306], where a small direct band gap of approximately 0.3 eV is observed. The electron and hole effective masses along $\Gamma-Y$ (Figs. IV.11b & IV.11c) are found to increase rapidly for compressive strains, as the band peaks rapidly flatten at the Γ -point.

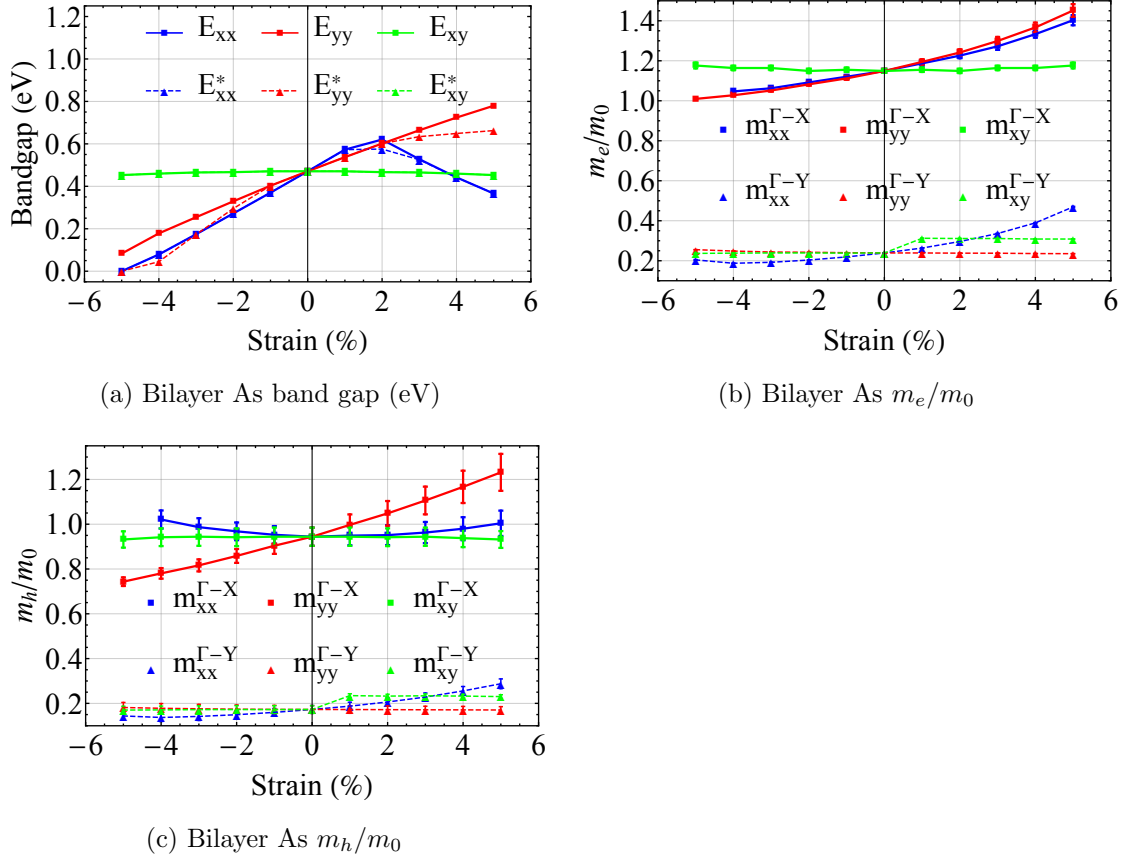


Figure IV.9: The relationships for bulk As between the applied in-plane strains ε_{xx} (blue), ε_{yy} (red) and ε_{xy} (green) against (a) the direct (solid squares) and indirect (dashed triangles) band gaps (eV); (b) the effective electron masses m_e/m_0 along $\Gamma - X$ (solid squares) and $\Gamma - Y$ (dashed triangles); (c) the effective hole masses m_h/m_0 along $\Gamma - X$ (solid squares) and $\Gamma - Y$ (dashed triangles).

At $\varepsilon_{xx} = +1\%$ strain, a potential Weyl state is briefly observed on an off-symmetry point X' (Fig. IV.12) before a direct gap opens that subsequently transitions to an indirect one at $\varepsilon_{xx} = +3\%$, after which it reduces again. Another potential Weyl state around the same off-symmetry point X' is also predicted to occur between $+1\% \leq \varepsilon_{yy} \leq +2\%$, after which a direct band gap also appears. The recalculated band structure with the SOC for $\varepsilon_{yy} = +1\%$ (Fig. IV.12) confirms the linear-dispersion, where the maximum charge velocity in both cases occurs along a line parallel to $\Gamma - Y$ and is $v = 1.38(1) \times 10^6 \text{ ms}^{-1}$.

In summary, we predict Γ -point Dirac states in the monolayer and bilayer of As, which support one-dimensional ballistic conduction, as well as possible Weyl states

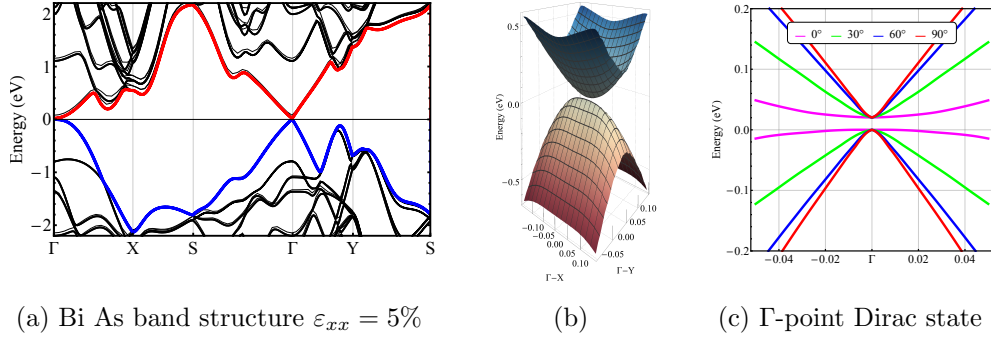


Figure IV.10: (a) Band structure of bilayer As at $\varepsilon_{xx} = +5\%$ with SOC (thick lines), and without SOC (thin lines) (b) three-dimensional bands with SOC about the predicted Dirac point at Γ (c) slices through the Dirac point at 0° , 30° , 60° and 90° relative to the $\Gamma - X$ line, also with SOC.

on off-symmetry points in the bulk at moderate levels of in-plane stress. These states were found to be unaffected by SOC. We also observe several band gap transitions, in particular in the monolayer phase, which also include semi-conducting-metallic transitions. Finally, the effective masses respond approximately linearly with respect to uniaxial strain, except in the bulk, which exhibits quadratic behaviour.

Monolayer Antimony

The relaxed Sb monolayer is found to possess an indirect band gap of 0.21 eV along $\Gamma - Y$ (Fig. IV.13a), which is reasonably comparable to other PBE values 0.28 [212] and 0.37 [307] eV, where these values were obtained including SOC. For tensile strain along ε_{yy} the band gap opens, suggesting an indirect-direct transition for strains above 6 – 7%, and it diminishes for compressive strains before finally closing at $\varepsilon_{yy} = -2\%$, where the material becomes a semi-metal. Similarly, the indirect gap closes along $\Gamma - X$ at a compressive strain of $\varepsilon_{xx} = -2\%$ at which monolayer Sb again becomes semi-metallic.

The indirect gap transitions to a direct gap at $\varepsilon_{xx} = +1\%$ tensile strain and remains so until finally closing at $\varepsilon_{xx} = +4\%$, at which point we predict a potential Dirac state along $\Gamma - Y$ at an off-symmetry point [273] Y' (Fig. IV.14a) that has also been predicted in Ref. [224]. Fig. IV.14a depicts the calculated band structure,

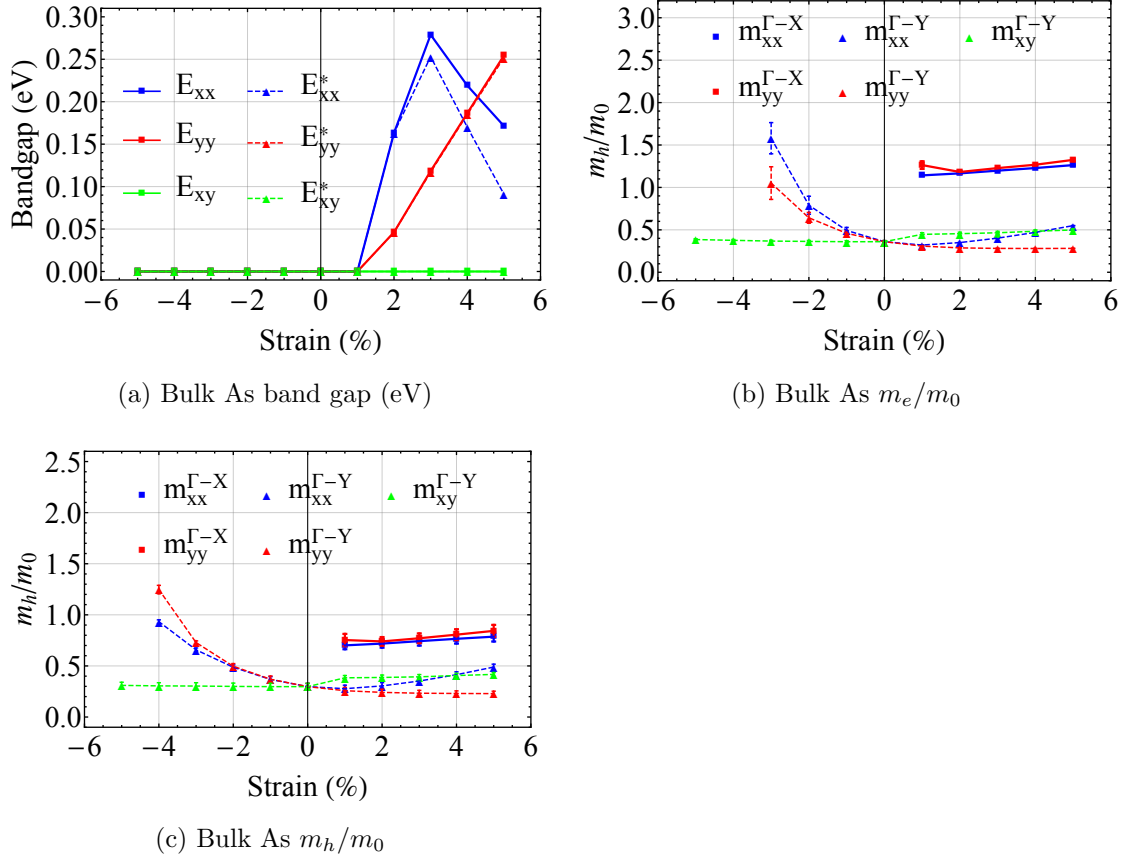


Figure IV.11: The relationships for bulk As between the applied in-plane strains ε_{xx} (blue), ε_{yy} (red) and ε_{xy} (green) against (a) the direct (solid squares) and indirect (dashed triangles) band gaps (eV); (b) the effective electron masses m_e/m_0 along $\Gamma - X$ (solid squares) and $\Gamma - Y$ (dashed triangles); (c) the effective hole masses m_h/m_0 along $\Gamma - X$ (solid squares) and $\Gamma - Y$ (dashed triangles)

in which it is shown that SOC preserves the Dirac state but not does not open the band gap. The three-dimensional band structure about the Dirac point is shown in Fig. IV.14b in which the maximum charge velocity is $v = 4.31(1) \times 10^6 \text{ ms}^{-1}$ and occurs along a line parallel to the $\Gamma - Y$ direction (Fig. IV.14c). Moreover, the valence band at the X -point undergoes a Rashba splitting [308] due to SOC, which is also predicted to occur in the monolayers of α -P [309], and β -Sb [294, 310]. Finally, the electron effective masses experience a weak linear-response to strain (Figs. IV.13b & IV.13c), while the hole effective masses along $\Gamma - X$ respond much more strongly to a rapid broadening or flattening of the valence band.

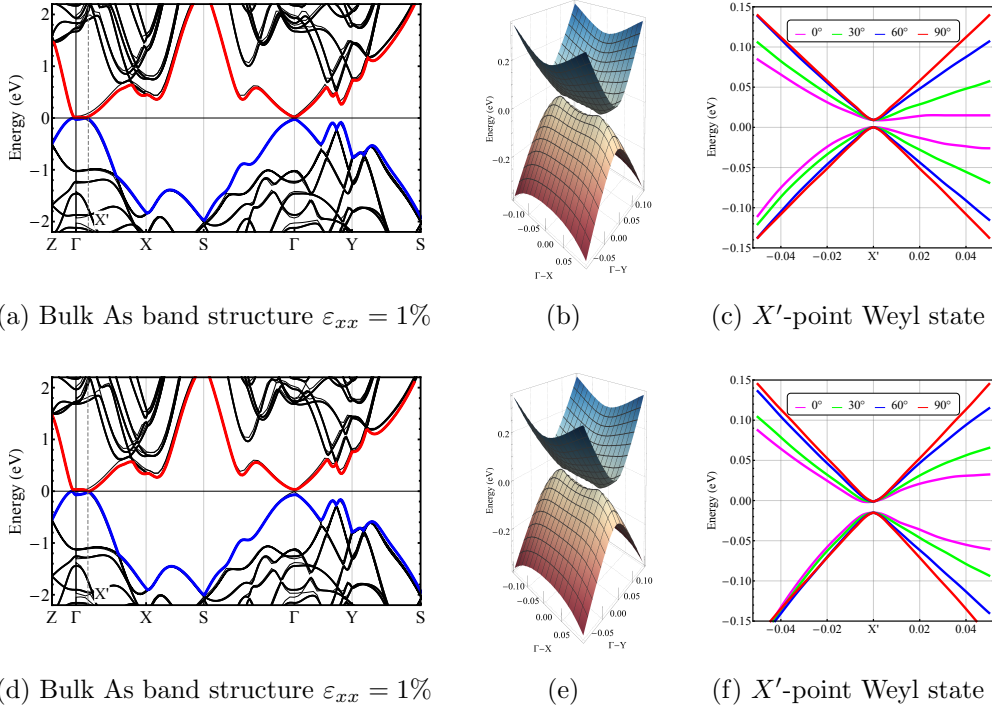


Figure IV.12: (a) Band structure of bulk As at $\varepsilon_{xx} = +1\%$ with SOC (thick lines), and without SOC (thin lines) where the off-symmetry point X' , located along $\Gamma - X$, is indicated by the dashed vertical line (b) three-dimensional bands with SOC about the potential Weyl points (c) slices through one Weyl point at 0° , 30° , 60° and 90° relative to the $\Gamma - X$ line, also with SOC. [(d) - (f)] The same is illustrated for $\varepsilon_{yy} = +1\%$.

Bilayer Antimony

The relaxed bilayer phase is found to be semi-metallic, where an indirect band gap opens at $\varepsilon_{yy} = +3\%$ tensile strain, and band-inversion at the Γ -point leads to a fully-metallic state for uniaxial strains $< -1\%$. The effective masses (Figs. IV.15b & IV.15c) experience soft linear-response to strains prior to the transition to full metallicity, at which point a rapid flattening of the bands at the Γ -point suggesting strong electron localisation.

In addition, a possible Dirac state emerges at a non-symmetry-point Y' along $\Gamma - Y$ for $\varepsilon_{xx} = +2\%$ tensile strain (Fig. IV.16) and remains in place up to at least $+5\%$ strain. The maximum charge velocity $v = 4.47(3) \times 10^6 \text{ ms}^{-1}$ is also along $\Gamma - Y$ and is approximately the same as that of the monolayer.

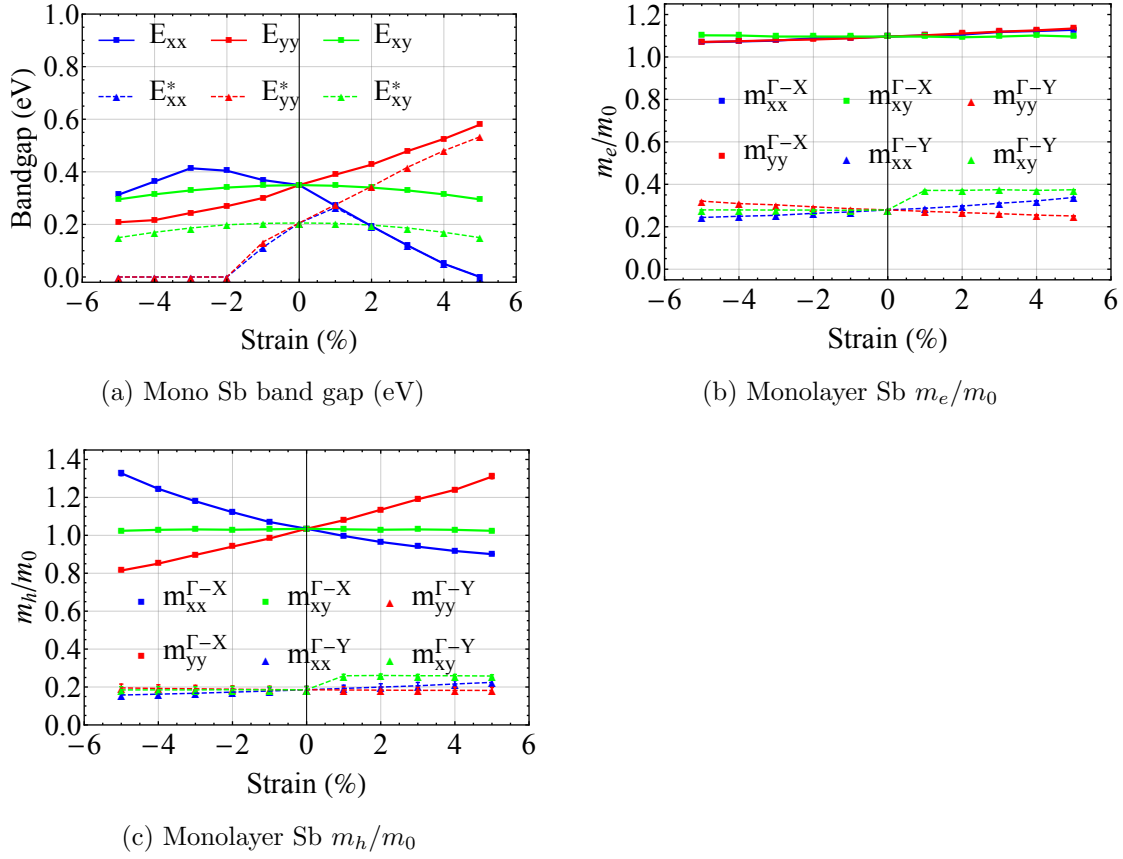


Figure IV.13: The relationships for monolayer Sb between the applied in-plane strains ε_{xx} (blue), ε_{yy} (red) and ε_{xy} (green) against (a) the direct (solid squares) and indirect (dashed triangles) band gaps (eV); (b) the effective electron masses m_e/m_0 along $\Gamma-X$ (solid squares) and $\Gamma-Y$ (dashed triangles); (c) the effective hole masses m_h/m_0 along $\Gamma-X$ (solid squares) and $\Gamma-Y$ (dashed triangles).

Finally, beyond a compressive strain of $\varepsilon_{yy} = -3\%$, at a stress of approximately 0.3 GPa, we observed a structural phase-transition in the bilayer, which buckled in the puckered ($\vec{y}$) direction. This buckled structure has a total-energy 1.7 meV/atom lower than that of the relaxed state of the unperturbed α -bilayer and 3.0 meV/atom lower when allowed to fully-relax, as shown in Fig. IV.17. This suggests the possible existence of a new phase of Sb that is attainable via strain.

Bulk Antimony

Finally, bulk Sb is found to be completely metallic for all levels of strain explored in this work. However, shear strains in this case do appear to have a significant effect

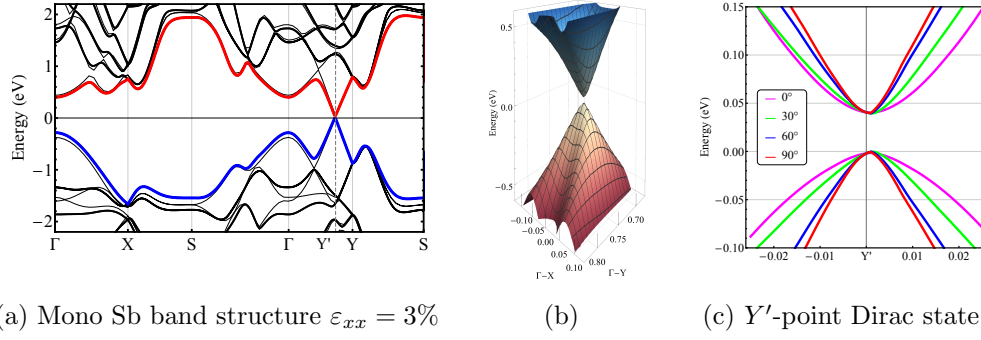


Figure IV.14: (a) Band structure of monolayer Sb at $\varepsilon_{xx} = -5\%$ with SOC (thick lines), and without SOC (thin lines) (b) three-dimensional bands about the predicted Dirac point at Γ (c) slices through the Dirac point at 0° , 30° , 60° and 90° relative to the $\Gamma - X$ line that indicate highly anisotropic conduction.

on the bands despite not opening a gap.

In summary, we predict possible non-symmetry-point Dirac states in the strained monolayer and bilayer of Sb, which are qualitatively unaffected by SOC, as well as Rashba splitting at the X -point in the monolayer. We also predict indirect-direct and indirect-semi-metallic transitions in the monolayer phase and a band gap opening in the bilayer phase. Finally, we observe a buckled phase induced in bilayer Sb at -4% compressive strain. Bulk Sb was found to be metallic at all levels of strain explored.

We provide a brief summary of the band gaps and qualitative phase-transitions in Table B.5, and in Table B.4 we outline the calculated band gaps and effective charge carrier masses for the relaxed phases of each structure.

4 CONCLUSION

Continuing the discussion in the previous Chapter, we have provided the accompanying electronic properties from the extensive calculations of few-layer and bulk P, As and Sb, where we have compared and contrasted these results with experimental studies. Our findings predict several band gap transitions, numerous Dirac and Weyl states, one-dimensional conductivity driven by ballistic conduction on the order of 10^6 ms^{-1} , and a notable strain-induced buckled phase in bilayer Sb. We also note that the critical stresses at which these transitions occur are expected to be experi-

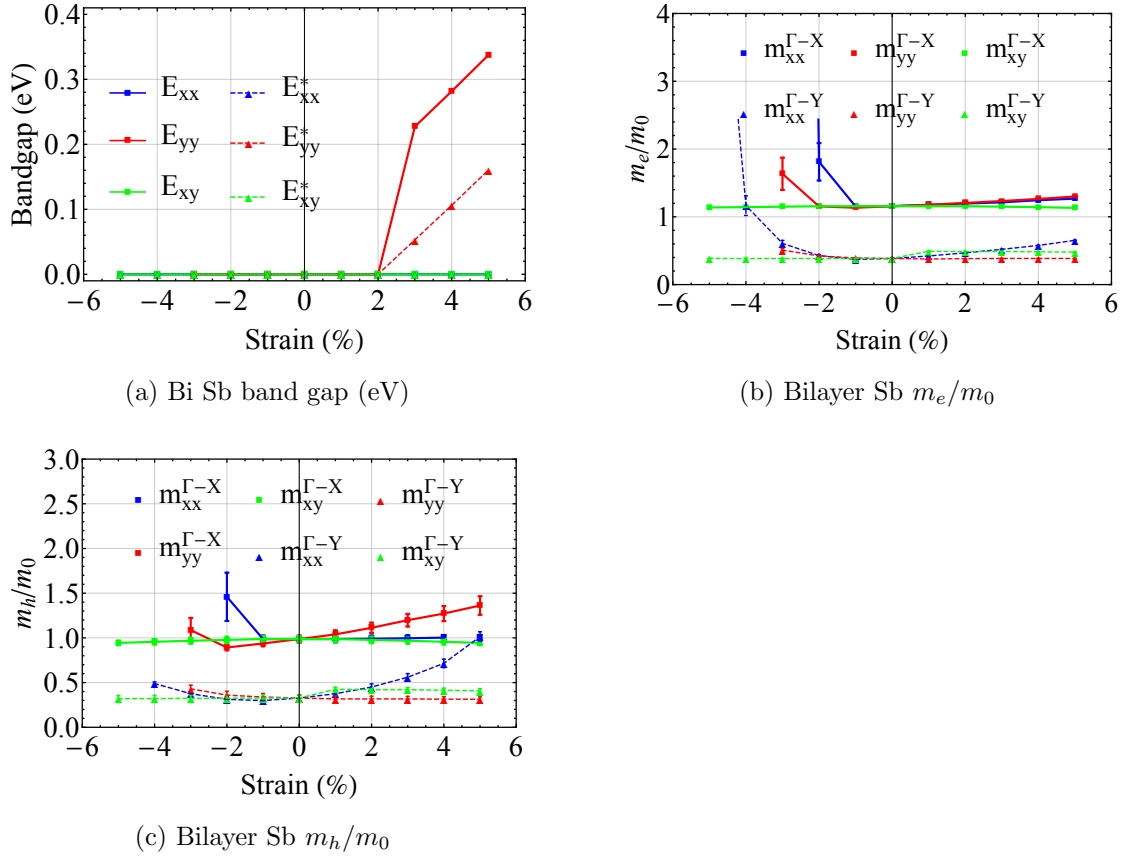


Figure IV.15: The relationships for bilayer Sb between the applied in-plane strains ε_{xx} (blue), ε_{yy} (red) and ε_{xy} (green) against (a) the direct (solid squares) and indirect (dashed triangles) band gaps (eV); (b) the effective electron masses m_e/m_0 along $\Gamma - X$ (solid squares) and $\Gamma - Y$ (dashed triangles); (c) the effective hole masses m_h/m_0 along $\Gamma - X$ (solid squares) and $\Gamma - Y$ (dashed triangles).

mentally accessible and highly switchable, paving the way for possible verification. With the ongoing enthusiastic research in group-V layered materials, they are poised to become central to the development of next generation materials comprising a vast portfolio of applications.

We would like to conclude this work on 2D materials with a brief note on the conclusions of these calculations within a wider context, in particular with regards to the general predictive power of Kohn-Sham DFT. For this work, we used the PBE exchange-correlation functional supplemented by vdW corrections and, where warranted, spin-orbit coupling, which form a highly robust computational framework. Nonetheless, throughout this Chapter, we made note of several instances where com-

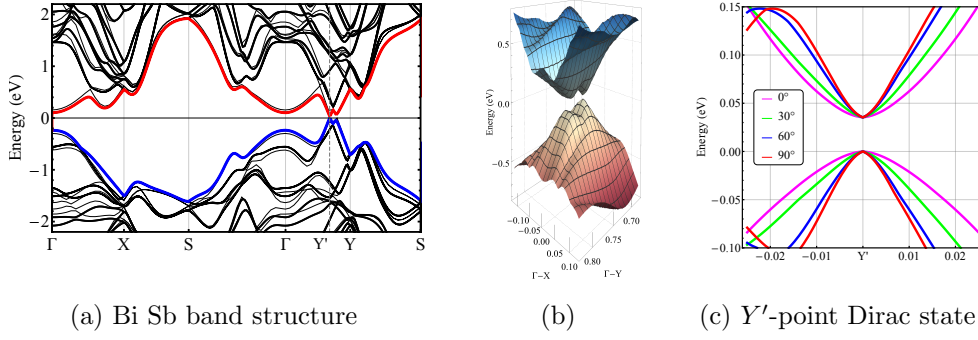


Figure IV.16: (a) Band structure of bilayer Sb at $\varepsilon_{xx} = +3\%$ with SOC (thick lines), and without SOC (thin lines) where the off-symmetry point Y' , located along $\Gamma - Y$, is indicated by the dashed vertical line (b) three-dimensional bands with SOC about the predicted Dirac point (c) slices through the Dirac point at 0° , 30° , 60° and 90° relative to the $\Gamma - X$ line, also with SOC.

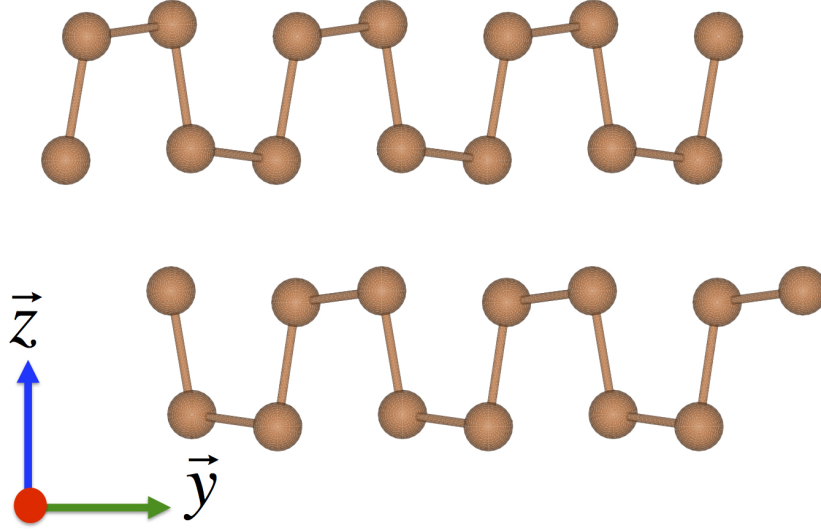


Figure IV.17: Side-view of the strain-induced buckled phase of Sb at $\varepsilon_{yy} = -4\%$ compression.

puted properties differed, or even outright contradicted, experimental observations, for example in the band gaps of bulk phosphorus [302–305] and bulk arsenic [306]. Ostensibly, the best agreement one can reasonably expect to obtain from conventional DFT calculations are in band alignments [300], lattice constants, and general trends in mechanical and electronic properties [197, 311]. However, the accurate computation of specific electronic properties is, patently, not guaranteed.

This lack of agreement with basic experimental measurements for relatively simple structures is concerning, and draws attention to a pressing issue pervading approximate DFT - that of the self-interaction error (SIE). Despite decades of theoretical, algorithmic and computational advances, the SIE, to this day, leads to qualitative inaccuracies in some of the most basic DFT calculations. This SIE originates from the approximation of exchange-correlation functionals, and requires that calculation results be interpreted with caution to avoid coming to erroneous conclusions. Rather than depend on one's own intuition or experience to decide if SIE might be present in a system (and in absence of relevant experimental data), there exist strategies with which one can quantify and treat it, at least approximately. In the next Chapter, we shall explore the SIE in detail, and discuss some techniques developed over the years toward its correction.

V

THE NATURE AND ORIGIN OF PERVASIVE ERRORS IN APPROXIMATE DFT

IN THE PRECEDING CHAPTERS, we extensively explored a set of calculations on puckered, two-dimensional materials, and classified broad trends in electro-mechanical properties while making comparison to experimental and computational data. However, specific quantities, particularly those derived from electronic band structures, were found to be significantly miscalculated and, in some instances, in direct contradiction to experiments. These erroneous findings are not just limited to the group-V materials but are a pervasive feature of all DFT electronic structure calculations when performed with commonplace exchange-correlation (XC) functionals.

In spite of the numerous, yet justifiable, approximations introduced in the formulation of Kohn-Sham DFT in Chapter II, none affect the qualitative reliability of calculations more so than the approximation to the XC functional. Although DFT is, in principle, an exact theory, the semi-empirical determination of the XC functional used in practical calculations fails to fully account for the nuanced many-body effects found in various chemical environments. The infamous many-body self-interaction error (SIE) [20, 312–315], or delocalisation error [9, 150, 316], and static correlation error (SCE) [9, 150, 299, 314, 317–322] are extensively documented. They are responsible for the systematic inaccuracies in electronic and optical band gaps [323]; charge transfer excitation energies [324]; chemical reaction barriers [325–327]; binding energies [313, 328]; and electric field responses [329]. In fact, the SIE is arguably the largest obstacle preventing DFT from attaining the superior level of accuracy possible in quantum chemistry calculations. Understanding the origin of the SIE is

therefore crucial to the construction of better XC functionals and the development of practical remedies.

In this Chapter, we shall describe the nature and origin of the SIE and SCE as they relate to the violation of conditions on the exact XC functional pertaining to fractional occupancies and fractional spins, respectively [150]. We shall employ the examples of the dihydrogen cation H_2^+ and hydrogen molecule H_2 as test models in order to understand the effect of these errors in strongly-correlated systems.

Moreover, we will outline corrective procedures developed to ameliorate these errors, beginning with the formative work of Perdew and Zunger [20], in constructing self-interaction corrections. We will also emphasise the efforts of Dabo and co-workers [330–333] to restoring compliance with the generalised Koopmans’ condition [330, 331, 334, 335]. We will then discuss the establishment of the widely successful DFT+ U (DFT + Hubbard U) method [149, 336–343] for treating one-electron SIE, which finds its roots in the treatment of strongly-correlated Mott-Hubbard systems, drawing from the work of Anisimov [336–339], Dederichs [339, 344, 345], and Gunnarsson [336, 346–350], and later revised by Liechtenstein and Dudarev [340, 351–353], and Himmetoglu and Cococcioni [342, 354]. We find that DFT+ U may be well placed to correct one-electron SIE, when supplied with a sufficient U parameter and under the appropriate population analysis. However, it fails entirely to restore Koopmans’ compliance. Finally, we propose that the generalised DFT+ U + J functional may potentially be used to correct the SCE.

1 FRACTIONAL CHARGES

Perdew [355], Zhang [312], and Ayers [356], cumulatively demonstrated that the SIE is best understood from the perspective of non-integer particle numbers $E(N+q)$. This formalism stems from the well-known failure of the XC energy $E_{\text{xc}}[n]$ to sufficiently cancel the Hartree energy $E_H[n]$ in fractionally occupied orbitals [316]. A somewhat heuristic argument can also be made by noting that the Hartree energy in Eq. (II.23) is incorrectly non-zero for one electron, as noted by Fermi and Amaldi [357]. The exact energy of a fractional-charge system was proven in Ref. [355] to be a piece-wise

linear interpolation between the adjacent integer values (Fig. V.1)

$$E(N + q) = (1 - q)E(N) + qE(N + 1) \quad \text{for } 0 \leq q \leq 1. \quad (\text{V.1})$$

Deviations from this *linearity condition* are, therefore, indicative of a residual SIE that is affiliated with a spurious curvature in the total-energy vs particle number profile, as illustrated in Fig. V.1.

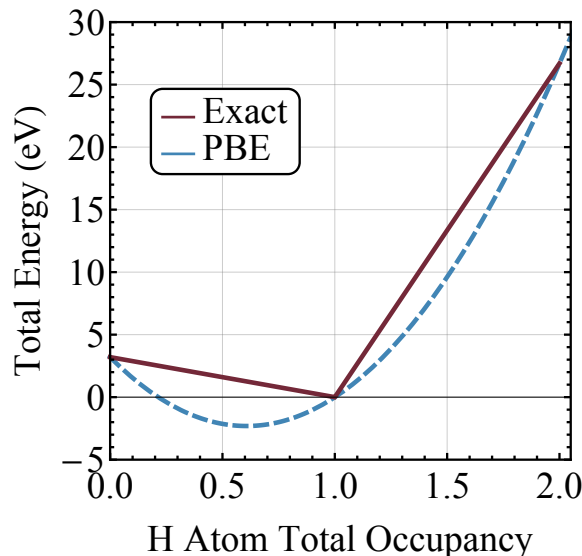


Figure V.1: The calculated SIE of a H atom is shown by the deviation of the PBE total-energy (dashed) from the correct piece-wise linearity (solid) between integer particle number.

The concept of non-integer electrons makes very little sense from a chemical perspective, as no fractionally-charged systems exist in nature, yet they provide a useful contrivance for the diagnosis of XC functionals. The study of SIE, therefore, is often constructed from the dissociation of homo-nuclear diatomic ions. While H_2^+ is not a strongly-correlated system, it is the simplest one-electron system lacking in any extraneous multi-reference and static correlation error effects, and thus permits a systematic analysis of the SIE relevant only to the underlying XC functional. Moreover, the exact binding curve can be calculated with the same code and pseudopotential by omitting contributions from the Hartree and XC potentials, and therefore allows a direct comparison between energies.

The binding curve of H_2^+ , calculated in ONETEP with a hard (0.65 a_0 cutoff)

norm-conserving pseudopotential [76], a PBE XC functional, 10 a_0 NGWF cutoff radius, and open boundary conditions [358], is presented in Fig. V.2. We note that any attempt to extend our bond-length interval beyond 8.5 a_0 , in this and subsequent calculations, resulted in numerical instabilities due to the near-degeneracy of the Kohn-Sham σ and σ^* eigenstates, and shown here are the results only of well-converging calculations.

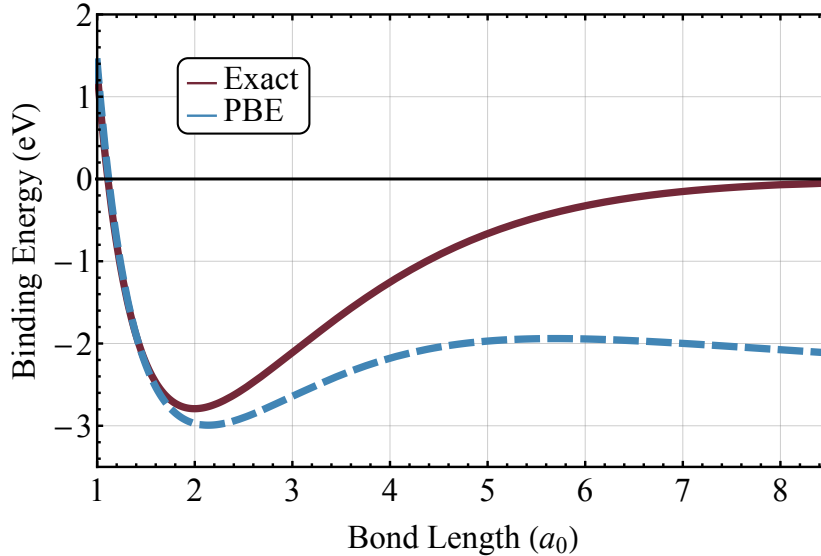


Figure V.2: Binding energy of H_2^+ calculated with exact (solid) and PBE (dashed) XC functionals. The reference energy for each curve is that of the isolated H atom calculated with the corresponding XC functional. The significant failure of PBE functional is evident in the dissociation limit.

The occupancy of each H atom, calculated respectively from the exact and PBE 1s orbital subspace projectors, closely match the KS orbitals and are reasonably well described as seen in Fig. V.3. The subspace occupancy acquires values greater than one half due to the overlap of the orbitals, which results in double-counting of the occupancy. Furthermore, when the KS density is not completely enclosed by the subspace orbitals, particularly for the exact calculations, the resulting charge spillage causes the subspace occupancy to be less than one half.

The spurious repulsion between the symmetrically charged ions is then caused by the semi-local PBE XC functional (since $E_{xc}[n] \leq 0$), which significantly lowers the total-energy. The superfluous repulsion imposes artificial electron delocalisation,

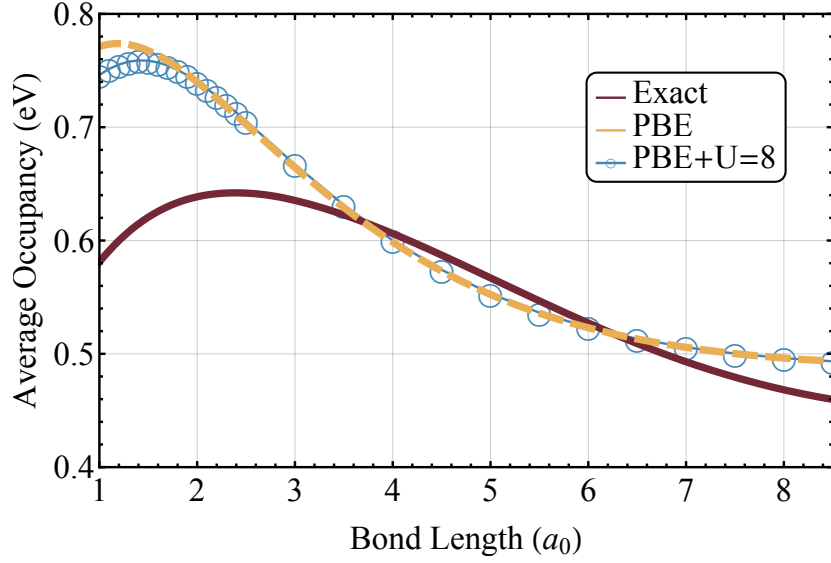


Figure V.3: Average total occupancy of the H atoms in dissociating H_2^+ calculated with exact (solid) and PBE (dashed) and PBE+ U (open circles) XC functionals. The population analysis was performed on the $1s$ orbital subspace projectors, which closely match the KS orbitals.

manifested by the curvature of the total-energy vs occupancy profile, shown in Fig. V.1, and is the reason for an incorrect total-energy. Moreover, the importance of fractional charges in chemical processes such as charge transfer, molecular binding and spectroscopic properties, alludes to the effect of SIE in these scenarios as well, for which many remedies have been proposed.

2 ONE-ELECTRON SELF-INTERACTION CORRECTION

Over the years, a number of methods have been devised for correcting many-body SIE [316, 320, 330, 342, 359–369], many of which take direct inspiration from that proposed by Perdew and Zunger (PZ) [20]. PZ first laid out a formalism for a self-interaction correction (SIC) based on the individual removal of one-electron SIE from fully-occupied spin-polarised KS-orbitals $\{\psi_{i\sigma}\}$, with occupancies $n_{i\sigma} = |\psi_{i\sigma}|^2$,

via a correction term to the total-energy given by

$$E_{\text{PZ}} = E_{\text{DFT}} + \sum_{i\sigma} \Delta_{i\sigma}^{\text{SIC}}$$

$$\text{with } \Delta_{i\sigma}^{\text{SIC}} = E_H[n_{i\sigma}] + E_{\text{xc}}^{\text{approx}}[n_{i\sigma}, 0]. \quad (\text{V.2})$$

Here, $E_{\text{xc}}^{\text{approx}}[n_{i\sigma}, 0]$ is the approximate exchange energy functional where one spin-channel has an occupation $n_{i\sigma}$ and the other is empty. This corrective approach, based on the removal of single-orbital SIE from a system, became a popular precept for the treatment of many-body SIE [370, 371]. The PZ SIC produced remarkable improvements for single atoms, but tended to over-correct the SIE in polyatomic systems, leading to inaccurate binding energies and under-estimated bond-lengths [9, 330, 372]. This result prompted the development of several modifications [365, 370, 371, 373] that scaled down the correction term by a factor α

$$E_{\alpha\text{PZ}} = E_{\text{PZ}} + \alpha (E_{\text{PZ}} - E_{\text{DFT}}), \quad (\text{V.3})$$

which yielded modest improvements. Regardless, an initial drawback of orbital-dependent SIC, such as those used by PZ, is that the Hamiltonians are no longer invariant under unitary transformations, and so precluded the treatment of periodic systems, such as crystals and extensive molecules [362]. Later work by Svane and Gunnarsson [347–350], and Szotek and Temmerman [374–379], extended the method to include the treatment of solids.

3 KOOPMANS' COMPLIANCE

The basis of all chemical reactions relies on the addition and removal of electrons in a system. The chemical potential¹ μ quantifies the difficulty of this process and is defined as the derivative of the total-energy $E(N)$ with respect to particle number N for a fixed external potential v

$$\mu_N = \left(\frac{\partial E(N)}{\partial N} \right)_v. \quad (\text{V.4})$$

¹ μ also acts as the Lagrange multiplier conserving particle number in Eq. (II.19)

For exact functionals, the chemical potential assumes constant values between adjacent integer particle numbers (shown in Fig. V.1), given by the first ionisation energy I_N and electron affinity A_N , respectively, for a neutral atom

$$\mu_N = \begin{cases} -I_N = E(N) - E(N-1) \\ -A_N = E(N+1) - E(N) \end{cases} . \quad (\text{V.5})$$

Mulliken's electronegativity is defined as the average chemical potential at a given occupancy

$$\chi_N = \frac{I_N + A_N}{2} = \frac{E(N-1) - E(N+1)}{2} \quad (\text{V.6})$$

and dictates the tendency of the atom to gain or lose electrons in chemical reactions. Meanwhile, the fundamental gap for extended solids is the difference of these quantities

$$\begin{aligned} \epsilon_N^{\text{gap}} &= I_N - A_N \\ &= [E(N-1) - E(N)] - [E(N) - E(N+1)] \\ &= E(N-1) + E(N+1) - 2E(N) \end{aligned} \quad (\text{V.7})$$

and plays a key role in charge transfer, electronic structure and the energetics of defects and surfaces. In molecules, the corresponding quantity is the Pearson hardness [380].

A critical, and perhaps defining, characteristic of a system free from SIE is its compliance with the generalised Koopmans' theorem [330, 331, 334, 335], which states that, for a given system, the energy of the highest occupied molecular orbital (HOMO) is precisely the negative of the ionisation energy $\epsilon_{\text{HOMO}} = -I$. In a one-electron system, such as H_2^+ , this implies that the total-energy and the occupied Kohn-Sham eigenvalue ϵ should differ only by the ion-ion energy. Thus, the binding curve of H_2^+ should be equivalently accessible by calculating either the total-energy directly, or by using the occupied eigenvalue with the expression $E = \epsilon + E_{\text{ion-ion}}$. Fig. V.4 illustrates the strikingly poor compliance of KS DFT with Koopmans' condition and is, yet another, well-documented consequence of SIE [320, 330, 331, 360, 381].

Motivated by the explicit restoration of Koopmans' condition as a remedy for SIE, Dabo *et al* [330–333] constructed a PZ-type SIC, termed αNK . Instead of

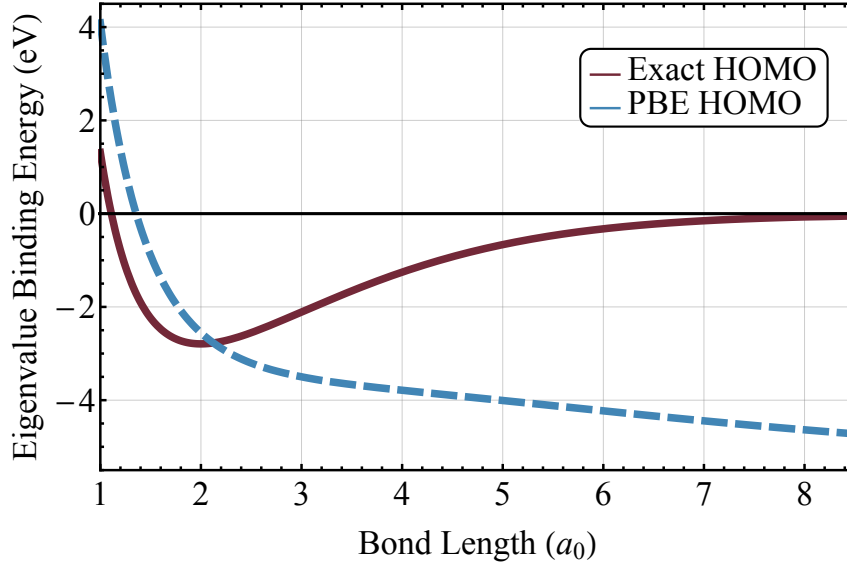


Figure V.4: Binding energy of H_2^+ derived from the KS occupied HOMO eigenvalue calculated with exact (solid) and PBE (dashed) XC functionals, relative to total-energy of an isolated H atom with the respective functional. The inability of the PBE functional to replicate the exact HOMO is another effect of the SIE.

removing single-orbital SIE, the αNK correction to the total-energy is a measure of the unphysical occupation dependence of the orbital eigenvalue energies in the frozen-orbital approximation

$$E_{\alpha\text{NK}} = E_{\text{DFT}} + \alpha_{\text{NK}} \Pi_{i\sigma}^u(f)$$

$$\text{with } \Pi_{i\sigma}^u(f) = \int_0^{f_{i\sigma}} df' [\epsilon_{i\sigma}^u(f) - \epsilon_{i\sigma}^u(f')], \quad (\text{V.8})$$

for which they define their generalised Koopmans' condition as

$$\Pi_{i\sigma}^u(f) = 0 \quad \text{where} \quad 0 \leq f \leq 1. \quad (\text{V.9})$$

Here, the orbital screening is accounted for by the coefficient α^{NK} . The αNK method offers significant improvement in atomic and molecular ionisation energies, photoemission energies, binding energies and molecular bond-lengths, avoiding the over-binding tendency of PZ [330], and has recently been extended to solids [333].

4 STRONGLY CORRELATED SYSTEMS

In addition to the practical application of a single-particle SIC in atoms and finite molecules, the emergence of SIE in extended systems, comprising first-row transition-metals or lanthanide ions, warrants a similarly measured treatment. Indeed, many of these compounds boast considerable technological and biological significance in photovoltaics [382, 383], high-temperature superconductors [384], energy storage [179, 385], and biochemistry [81, 386], where much of the chemically-relevant interactions concern the highly-localised $3d$ or $4f$ valence electrons. These states tend to exhibit strong correlation as a result of their spatial confinement, and are hence very much outside the scope of approximate XC functionals.

While there is no strict definition for strongly correlated systems, they are typically characterised by a correlation energy comparable with the kinetic or Hartree energies $E_c[n] \sim U_H[n]$ or $E_c[n] \sim T_s[n]$. Meanwhile, Rahm and Hoffman have recently proposed a useful metric for quantifying different types of chemical bonds [56], which may prove to be a plausible measurement of correlation energy in solids.

As a result of invoking approximate XC functionals, the incurred electron delocalisation often produces results that are both quantitatively and qualitatively inconsistent with experiments, including underestimated local moments, misclassified Mott-Hubbard insulators and inaccurate electric field responses. The treatment of the many-body SIE in these cases is concerned with the restoration of piece-wise linearity in the total-energy functional with respect to the localised-orbital occupancy, much in the spirit of PZ SIC. The modification of PZ-SIC to the treatment of solids was later enabled [347–350, 374–379, 387], where Stengel and Spaldin [368] advocated the implementation of Wannier functions, and rotationally invariant correction functionals in general. In the following section, we will discuss one such correction that is widely renowned, known as the DFT+ U method, which seeks to correct SIE when it is attributed to such highly-localised regions.

5 THE DFT+ U METHOD

A widely established and computationally efficient [101] scheme for correcting SIE, when it may be appropriately attributed to highly-localised orbitals, is the DFT+ U method [149, 336–343], which we have adopted in this dissertation as the preferred approach for correcting SIE. Initially formulated by Anisimov and co-workers [336–339] from the tight-binding Anderson model [388], its initial purpose was to restore the Mott-Hubbard effects absent in the LDA description of transition-metal oxides.

In order to confine the electron charge-density to the localised-orbitals, in which it is assumed the correlated electrons interact more strongly compared to the electrons in the surrounding bath, the DFT total-energy is supplemented by an explicit on-site $d-d$ Coulomb energy term, given by

$$E_{\text{Hub}} = \frac{U}{2} \sum_{i \neq j}^{\text{sites}} n_i n_j \quad \text{where} \quad \hat{n}_i = \hat{c}_i^\dagger \hat{c}_i. \quad (\text{V.10})$$

The d -shell occupancies $\{n_i\}$ are the number operators defined by the creation and annihilation operators on the subspace [388], $\hat{c}_i^\dagger$ and $\hat{c}_i$, respectively. The on-site interactions described by E_{Hub} , however, are already present in an average sense in the total-energy E_{DFT} , stemming from the cumulative interaction between the total number of d electrons present $N = \sum n_i$. The proto-DFT+ U functional was therefore constructed from the addition of subsidiary $d-d$ interaction energies to the KS total-energy functional, mitigated by the removal of the average on-site Coulomb energy in terms of the double counting correction E_{dc}

$$\begin{aligned} E[n(\mathbf{r})] &= E_{\text{DFT}}[n(\mathbf{r})] + E_{\text{Hub}} - E_{\text{dc}} \\ &= E_{\text{DFT}}[n(\mathbf{r})] + \frac{U}{2} \sum_{i,j \neq i}^{\text{sites}} n_i n_j - \frac{U}{2} N(N-1). \end{aligned} \quad (\text{V.11})$$

Here $n(\mathbf{r})$ represents the conventional KS electron density. The resulting functional in Eq. (V.11) invariably awarded better experimental agreement to the calculation of transition-metal oxides [337, 338], and transition-metal impurities [339, 345]. Nonetheless, the functional was still orbital dependent and sensitive to the choice of basis representing the localised electrons.

A rotationally-invariant form was later established by Liechtenstein *et al* [340, 352, 353] in terms of the elements of a subspace occupancy matrix of the localised orbitals $\{n_{mm'}^{I\sigma}\}$, given by

$$E_U[\{n_{mm'}^{I\sigma}\}] = E_{\text{Hub}}[\{n_{mm'}^{I\sigma}\}] - E_{\text{dc}}[\{n^{I\sigma}\}]. \quad (\text{V.12})$$

The occupancy matrix, for Hubbard site I , is constructed from the projection of the KS density matrix onto the manifold of localised orbitals $\{\varphi_m^I\}$,

$$n_{mm'}^{I\sigma} = \langle \varphi_m^I | \hat{\rho}^\sigma | \varphi_{m'}^I \rangle \quad \text{with} \quad \hat{P}_{mm'}^I = |\varphi_m^I\rangle \langle \varphi_{m'}^I|, \quad (\text{V.13})$$

which also defines the idempotent Hubbard projection operator $\hat{P}^I$, where $\hat{P}^I = \hat{P}^{I2}$. The localised subspaces are usually pre-defined for corrective treatment, having been deemed responsible for the dominant SIEs on the basis of physical intuition and experience, although a further level of self-consistency over subspaces is also possible [389].

The Hubbard energy correction is then evaluated from the sum over the screened Coulomb interactions V between all on-site orbitals, and is evaluated as follows

$$\begin{aligned} E_{\text{Hub}}[\{n_{mm'}^{I\sigma}\}] = & \frac{1}{2} \sum_{\{m\}, I\sigma} \{ V_{mm''m'm'''}^I n_{mm'}^{I\sigma} n_{m''m'''}^{I\bar{\sigma}} \\ & + (V_{mm''m'm'''}^I - V_{mm''m''m'}^I) n_{mm'}^{I\sigma} n_{m''m'''}^{I\sigma} \}. \end{aligned} \quad (\text{V.14})$$

The terms in Eq (V.14) respectively correspond to spin off-diagonal Coulomb repulsion, spin on-diagonal Coulomb repulsion, and spin on-diagonal exchange. The Coulomb matrix elements of a given site I are expressed in terms of renormalised Slater integrals

$$V_{mm''m'm'''}^I = \sum_{k=0}^{2l} a_k(m, m', m'', m''') F^k \quad (\text{V.15})$$

for angular momentum quantum number l and magnetic quantum number m where a_k are given by

$$a_k(m, m', m'', m''') = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle lm | Y_{kq} | lm' \rangle \langle lm'' | Y_{kq}^* | lm''' \rangle. \quad (\text{V.16})$$

The Slater integrals over the spherical harmonics are then defined as follows [390]

$$\langle lm | Y_{kq} | lm' \rangle = \int Y_{lm}^*(\mathbf{r}) Y_{kq}(\mathbf{r}) Y_{lm'}(\mathbf{r}) d\mathbf{r}. \quad (\text{V.17})$$

Following the procedure in Refs. [342] & [354], to simplify matters, we concern ourselves only with the lowest-order non-zero polar terms between m and m' , i.e. $V_{mm'mm'}$ and $V_{mm'm'm}$. Thus, the sum over interaction terms in Eq. (V.14) may be approximated by the expansion

$$E_{\text{Hub}} \approx \frac{1}{2} \sum_{I\sigma} \sum_{mm'} \{ V_{mm'mm'}^I n_{mm}^{I\sigma} n_{m'm'}^{I\bar{\sigma}} + V_{mm'm'm}^I n_{mm'}^{I\sigma} n_{m'm}^{I\bar{\sigma}} \\ + (V_{mm'mm'}^I - V_{mm'm'm}^I) (n_{mm}^{I\sigma} n_{m'm'}^{I\sigma} - n_{mm'}^{I\sigma} n_{m'm}^{I\sigma}) \}. \quad (\text{V.18})$$

For d -electrons, the sum over k in Eq. (V.15) runs over F^0 , F^2 and F^4 (and F^6 for f -electrons), hence, the average on-site Coulomb and exchange interactions are

$$U^I = \frac{1}{(2l+1)^2} \sum_{m,m'} V_{mm'mm'}^I = F^0 \\ \text{and } J^I = \frac{1}{2l(2l+1)} \sum_{m \neq m', m'} V_{mm'm'm}^I = \frac{F^2 + F^4}{14}. \quad (\text{V.19})$$

Using these definitions, we construct the aforementioned double-counting correction in terms of the total subspace occupancy $N^{I\sigma} = \sum_m n_{mm}^{I\sigma}$ for site I and spin σ ,

$$E_{\text{dc}} = \frac{1}{2} \sum_I U^I N^I (N^I - 1) - \frac{1}{2} \sum_{I\sigma} J^I N^{I\sigma} (N^{I\sigma} - 1) \\ = \frac{1}{2} \sum_{I\sigma} \{ (U^I - J^I) [N^{I\sigma} (N^{I\sigma} - 1)] + U^I N^{I\sigma} N^{I\bar{\sigma}} \}. \quad (\text{V.20})$$

Finally, substituting Eqs. (V.18) & (V.20) into Eq. (V.12), we arrive at the full expression for the Hubbard correction

$$E_U = \frac{1}{2} \sum_{I\sigma} \sum_{mm'} \{ V_{mm'mm'}^I n_{mm}^{I\sigma} n_{m'm'}^{I\bar{\sigma}} + V_{mm'm'm}^I n_{mm'}^{I\sigma} n_{m'm}^{I\bar{\sigma}} \\ + (V_{mm'mm'}^I - V_{mm'm'm}^I) (n_{mm}^{I\sigma} n_{m'm'}^{I\sigma} - n_{mm'}^{I\sigma} n_{m'm}^{I\sigma}) \} \\ - \frac{1}{2} \sum_{I\sigma} \{ (U^I - J^I) [N^{I\sigma} (N^{I\sigma} - 1)] + U^I N^{I\sigma} N^{I\bar{\sigma}} \}. \quad (\text{V.21})$$

We may simplify this equation further by re-expressing the total occupancy $N^{I\sigma}$ in

terms of the constituent matrix elements

$$\begin{aligned}
 E_U = & \frac{1}{2} \sum_{I\sigma} \sum_{mm'} \{ V_{mm'mm'}^I n_{mm}^{I\sigma} n_{m'm'}^{I\bar{\sigma}} + V_{mm'm'm}^I n_{mm'}^{I\sigma} n_{m'm}^{I\bar{\sigma}} \\
 & + (V_{mm'mm'}^I - V_{mm'm'm}^I) (n_{mm}^{I\sigma} n_{m'm'}^{I\sigma} - n_{mm'}^{I\sigma} n_{m'm}^{I\sigma}) \\
 & - (U^I - J^I) (n_{mm}^{I\sigma} n_{m'm'}^{I\sigma} - n_{mm'}^{I\sigma} \delta_{mm'}) - U^I n_{mm}^{I\sigma} n_{m'm'}^{I\bar{\sigma}} \}, \quad (V.22)
 \end{aligned}$$

and grouping terms according to their dependence on such

$$\begin{aligned}
 E_U = & \frac{1}{2} \sum_{I\sigma} \sum_{mm'} \{ (V_{mm'mm'}^I - U^I) n_{mm}^{I\sigma} n_{m'm'}^{I\bar{\sigma}} \\
 & + (V_{mm'mm'}^I - U^I + V_{mm'm'm}^I - J^I) n_{mm}^{I\sigma} n_{m'm'}^{I\sigma} \\
 & + (U^I - J^I) n_{mm}^{I\sigma} \delta_{mm'} \\
 & - (V_{mm'mm'}^I - V_{mm'm'm}^I) n_{mm'}^{I\sigma} n_{m'm}^{I\sigma} \\
 & + V_{mm'm'm}^I n_{mm'}^{I\sigma} n_{m'm}^{I\bar{\sigma}} \}. \quad (V.23)
 \end{aligned}$$

Finally, we may simplify the expression again by replacing the orbital-dependent terms $V_{mm'mm'}^I$ and $V_{mm'm'm}^I$ by their respective scalar averages U^I and J^I , which yields

$$\begin{aligned}
 E_U = & \frac{1}{2} \sum_{I\sigma} \sum_{mm'} \{ (U^I - J^I) (n_{mm'}^{I\sigma} \delta_{mm'} - n_{mm'}^{I\sigma} n_{m'm}^{I\sigma}) + J^I n_{mm'}^{I\sigma} n_{m'm}^{I\bar{\sigma}} \} \\
 = & \frac{1}{2} \sum_{I\sigma} \{ (U^I - J^I) \text{Tr} [\hat{n}^{I\sigma} - \hat{n}^{I\sigma} \hat{n}^{I\sigma}] + J^I \text{Tr} [\hat{n}^{I\sigma} \hat{n}^{I\bar{\sigma}}] \}, \quad (V.24)
 \end{aligned}$$

and completes the full DFT+ U + J functional for Hubbard site I in terms of the spin-dependent occupancy matrices $\hat{n}^{I\sigma}$.

To simplify the utilisation and transparency of the Hubbard functional, many practitioners tend to ignore unlike-spin interactions by setting the exchange term J^I to zero [391] (thereby omitting magnetic interaction), or equivalently, incorporating J^I into the U -term to compose an effective parameter [149, 342, 391] $U_{\text{eff}}^I = U^I - J^I$, which simplifies Eq. (V.24) even more

$$E_U[\{\hat{n}^{I\sigma}\}] = \sum_{I\sigma} \frac{U^I}{2} \text{Tr} [\hat{n}^{I\sigma} - \hat{n}^{I\sigma} \hat{n}^{I\sigma}], \quad (V.25)$$

²Alternatively, it is not uncommon for J^I to be set to ~ 1 eV.

resulting in the functional most commonly implemented in the DFT+ U formalism. The intended effect of Eq. (V.25) becomes more clear if it is represented in a basis that diagonalises the occupancy matrix

$$\hat{n}^{I\sigma} v_i^{I\sigma} = q^{I\sigma} v_i^{I\sigma} \quad \text{with} \quad 0 \leq q_i^{I\sigma} \leq 1, \quad (\text{V.26})$$

such that the correction becomes

$$E_U[\{\hat{n}^{I\sigma}\}] = \sum_{I\sigma} \sum_i \frac{U^I}{2} q^{I\sigma} (1 - q^{I\sigma}), \quad (\text{V.27})$$

which is ensured because $\hat{n}$ is also idempotent³. Here, Eq. (V.25) is clearly imposing a penalty on non-integer occupancies in the localised orbitals $q^{I\sigma}$, the strength of which is tuned by the magnitude of the U parameter, in order to restore the linear behaviour of the exact XC functional. The correction thus favours orbitals that are either fully occupied $q^{I\sigma} = 1$, or fully depleted $q^{I\sigma} = 0$, and contributes a non-zero correction to the potential when $q^{I\sigma} \neq 1/2$, which counteracts the SIE.

This effect can be further examined by constructing the DFT+ U potential

$$\begin{aligned} \hat{V}_U &= \frac{\delta E_U}{\delta \hat{\rho}} = \sum_{I\sigma} \frac{U^I}{2} \left(\hat{P}^I - 2\hat{P}^I \hat{\rho}^\sigma \hat{P}^I \right) \\ &= \sum_{I\sigma} \sum_{mm'} \frac{U^I}{2} |\varphi_m^I\rangle \left(\hat{1} - 2\hat{n}_{mm'}^{I\sigma} \right) \langle \varphi_{m'}^I |, \end{aligned} \quad (\text{V.28})$$

which is repulsive for occupancies less than one half, and attractive for occupancies greater than one half, thus incentivising idempotency in the subspace occupancy matrix. This re-localisation process opens a gap on the order of U between occupied and unoccupied KS states, thereby restoring the desired Mott-Hubbard behaviour. In practice, however, the individual subspace occupancy matrices do not attain binary eigenvalues, and are only partially enforced, since it competes with the idempotency condition in the ground-state KS density-matrix $\hat{\rho}$, which is strictly enforced.

5.1 A ONE-ELECTRON ASSESSMENT OF DFT+ U

It has been repeatedly stated [337, 338, 342, 392–396], or at least inferred, that DFT+ U provides a sufficient correction to one-electron SIE. This claim, however, has

³This is for the same reason the Kohn-Sham density matrix $\hat{\rho}$ is, see section 6.1

not been explicitly verified to our knowledge, despite forming the basis for DFT+ U as an SIE correction scheme. In Chapter VI, we provide the first demonstration of this claim, but for now let us explore the effect of the DFT+ U functional on dissociating H_2^+ , which we saw provided an emphatic example of one-electron SIE, and investigate the effect of DFT+ U on this system.

Following the same procedure described in section 1, we calculated the binding curve using the DFT+ U functionality in ONETEP [101]. The + U correction was applied simultaneously to each atom, using a separate $1s$ pseudoatomic orbital (PAO) subspace centred on each, generated from the occupied KS state of the pseudopotential for neutral hydrogen with the PBE XC functional. The effect of the correction on the binding energy is evident in Fig. V.5, where the Hubbard U parameter required to correct the PBE total-energy to the exact value, ranges over approximately 8 eV from the fully bonded to dissociated limits. This result highlights the importance of the chemical environment, and not just the atomic species, in determining the U parameters, as was previously shown in Refs. [397–399].

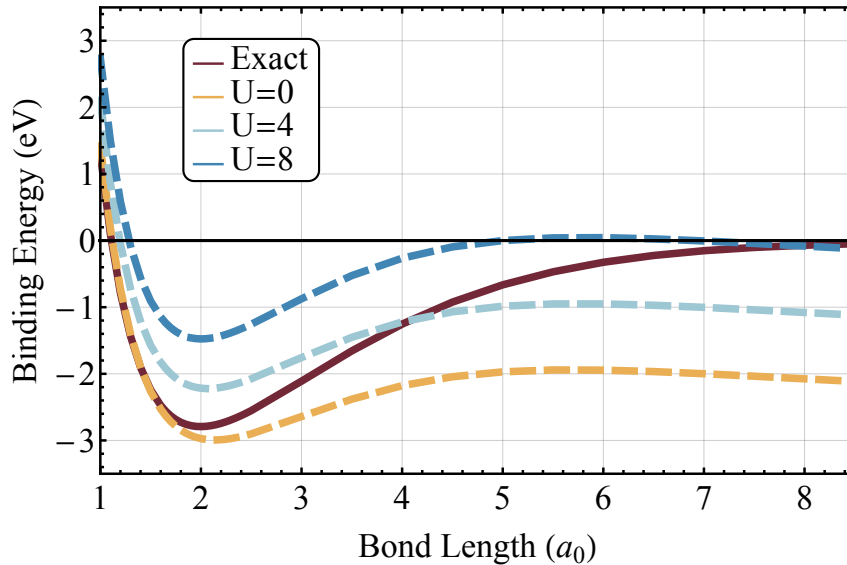


Figure V.5: Binding energy of H_2^+ calculated with exact XC functional (solid) and DFT+ U with $U = 0, 4, 8$ eV (dashed), relative to energy of isolated H atom. DFT+ U successfully resolves the SIE in the total-energy, albeit for a bond-length dependent Hubbard U .

If we instead explore the efficacy of DFT+ U at restoring Koopmans’ compliance,

we can inspect the eigenvalue-derived total-energy as before, but where we now concern ourselves with the treatment of only the HOMO. In Fig. V.6, we observe the egregious failure of the DFT+ U scheme when charged with the latter condition. The non-compliance with Koopmans' condition broadly increases both with bond-length and, to one's surprise, with the Hubbard U . In fact, the effect of DFT+ U on the eigenvalue is lost entirely in the dissociated limit, where both factors drive the subspace occupancy to $1/2$, at which point the + U potential vanishes.

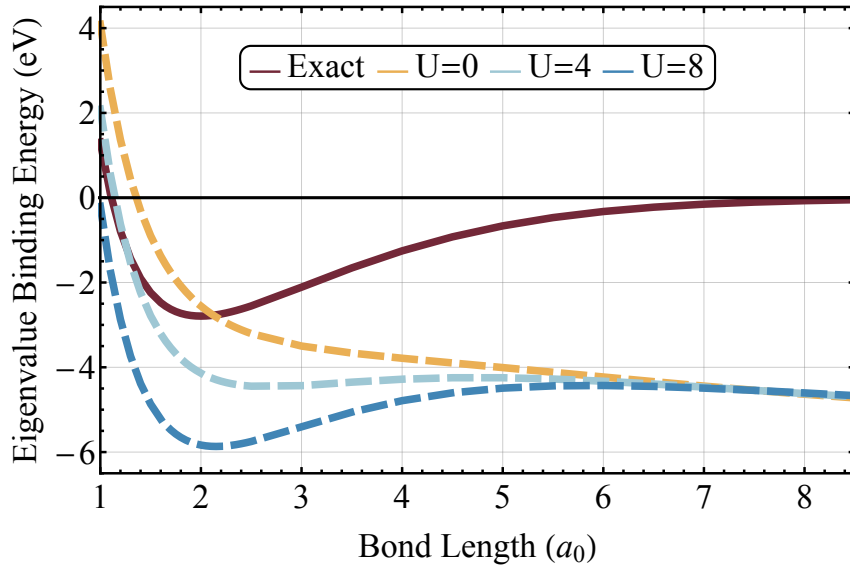


Figure V.6: Binding energy of H_2^+ derived from the KS HOMO eigenvalue calculated with exact XC functional (solid) and DFT+ U with $U = 0, 4, 8$ eV (dashed), relative to energy of isolated H atom. DFT+ U does not address the inaccuracy in the Kohn-Sham eigenvalue, or non-compliance with Koopmans' condition.

Across the binding curve, we see that the Hubbard U required to enforce compliance with Koopmans' condition, and that needed to attain the exact total-energy typically differ substantially. The facile correction of the total-energy of this system with DFT+ U , albeit with a varying but reasonable U value, is in sharp contrast with the qualitative failure to correct the occupied eigenvalue. Indeed, the vanishing eigenvalue correction at dissociation suggests an insufficiency in the linear term of the DFT+ U formalism, the root of which lies in the symmetric treatment of the linear and quadratic terms in the double-counting correction in Eq. (V.20). Going forward, H_2^+ will serve as a useful tool for benchmarking the performance of the DFT+ U

methodologies, since we have by now accumulated a commanding understanding of the behaviour of SIE and Koopmans' condition in this model system.

6 STATIC CORRELATION ERROR

Another important source of error that also permeates approximate DFT calculations is the *static correlation error* (SCE). The SCE is known to arise in DFT when performing calculations on systems with degenerate states [9, 150, 314, 317, 318], such as those found in strongly correlated systems, transition-metal oxides, and chemical dissociation, where it plays an equally pivotal role as the SIE in their accurate description. The SCE becomes particularly dominant in DFT when the single Slater determinant wave function is no longer a valid approximation. For example, the closed-shell dissociation of H_2 [150, 317, 318, 400, 401] is often used to illustrate SCE [9, 150, 319], which we shall now explore.

We performed non-spin-polarised calculations of the dissociating H_2 molecule in ONETEP using the DFT+ U functional for $U = 0, 2, 4$ eV, with the same calculation parameters as before in sections 1 & 5.1. We then compared these results against highly accurate binding energies calculated in Ref. [402], which in turn used the full configuration interaction (FCI) method described in Ref. [403]. Presented in Fig. V.7 are the resulting binding curves where it is demonstrated that the conventional PBE functional performs reasonably well for short bond-lengths, but overestimates the total-energy in the dissociation limit. Furthermore, positive U values serve only to make matters worse by increasing the total-energy⁴.

To understand what is happening in this instance, let us consider the H_2 wave function as constructed in Hartree-Fock theory using molecular orbitals. Around equilibrium, the H_2 bonding and anti-bonding orbitals are constructed from a basis of $1s$ atomic orbitals centred on the atoms labelled A and B (up to a constant of

⁴ Although, it appears that selectively invoking negative U values, which would instead *encourage* delocalisation, could correct the SCE by haphazardly increasing the level of SIE.

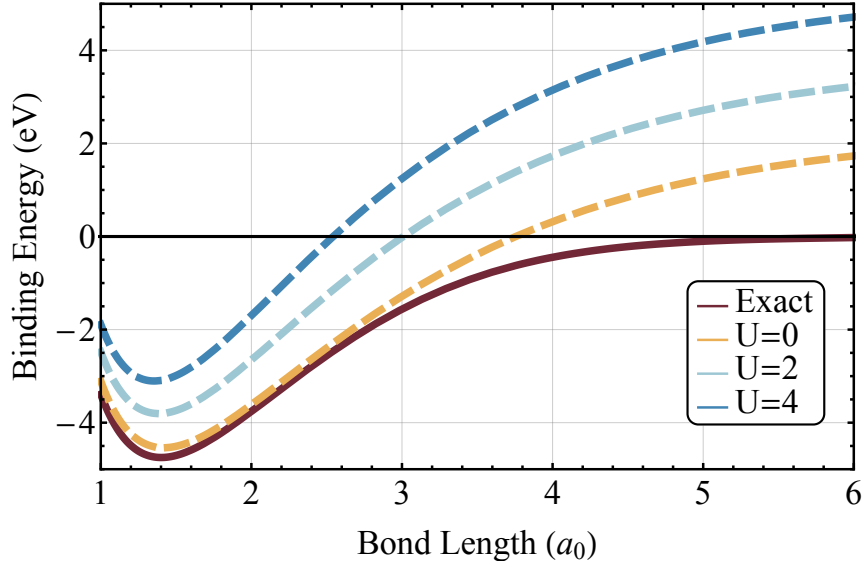


Figure V.7: Binding energy of closed-shell H_2 calculated with FCI [402] (solid) and DFT+ U with $U = 0, 2, 4$ eV (dashed), relative to energy of isolated H atoms, with the respective functionals. Positive U values exacerbate the SCE for all bond-lengths, in which case, negative U values may be required.

normalisation) respectively given as follows

$$\sigma_{1s}(i, \alpha) \sim (1s_A(i) + 1s_B(i)) \chi(\alpha) \quad (\text{V.29})$$

$$\text{and } \sigma_{1s}^*(i, \alpha) \sim (1s_A(i) - 1s_B(i)) \chi(\alpha), \quad (\text{V.30})$$

where $\chi(\alpha)$ denotes the spin component of the wave function for electron i . Thus, the ground-state $^1\Sigma_g^+$ wave function Ψ_0 may be built from a single Slater determinant of σ_{1s} bonding orbitals with an anti-symmetric spin component

$$\Psi_0 \sim \sigma_{1s}(1)\sigma_{1s}(2) [\chi(\uparrow)\chi(\downarrow) - \chi(\downarrow)\chi(\uparrow)]. \quad (\text{V.31})$$

If we now expand the spatial component of this expression we find that the wave function comprises terms attributed to both ionic and covalent states

$$\Psi_0 \sim \underbrace{1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)}_{\text{ionic}} + \underbrace{1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)}_{\text{covalent}}, \quad (\text{V.32})$$

in which the electrons simultaneously occupy one or both atoms, respectively.

Around equilibrium, this single Slater determinant wave function produces a more or less reasonable approximation to the exact wave function and, depending on the

level of theory, i.e., Hartree-Fock or DFT [9], it determines the binding energy to a very reasonable accuracy as shown in Fig. V.7.

As the bond-length increases, however, this approximation clearly breaks down as the ionic terms contribute as much to the construction of the wave function as the covalent terms. In other words, the independent-particle approximation maintains that the two electrons have equal probability of occupying the same atom, even as the bond-length increases to infinity. Physically, we know this to be false as the electrons should be correlated in such a way that they avoid each other and localise on one atom each into dissociation. The single Slater determinant approximation in Hartree-Fock therefore neglects a large component of the correlation that exists between the two electrons.

In the FCI, this correlation is explicitly considered as the wave function is built from a linear combination of all allowed single determinants $\Psi_{\text{CI}} = \sum_{I=0} a_I \Psi_I$, where the coefficients $\{a_I\}$ are optimised by a variational procedure. In the case of the $^1\Sigma_g^+$ state of H_2 , it suffices to consider only the bonding singlet state Ψ_0 and doubly-excited anti-bonding singlet state Ψ_1 [404], given by

$$\Psi_1 \sim \sigma_{1s}(1)^* \sigma_{1s}(2)^* [\chi(\uparrow)\chi(\downarrow) - \chi(\downarrow)\chi(\uparrow)]. \quad (\text{V.33})$$

Thus, the FCI wave function (expressed in terms of the $1s$ orbitals only) is simply expressed in terms of the adaptive mixing of the ionic and covalent contributions

$$\begin{aligned} \Psi_{\text{CI}} &= a_0 \Psi_0 + a_1 \Psi_1 \\ &= (a_0 + a_1) \underbrace{(1s_A(1)1s_A(2) + 1s_B(1)1s_B(2))}_{\text{ionic}} \\ &\quad + (a_0 - a_1) \underbrace{(1s_A(1)1s_B(2) + 1s_B(1)1s_A(2))}_{\text{covalent}}, \end{aligned} \quad (\text{V.34})$$

which is optimised according to a_0 and a_1 . Around equilibrium, one finds that $a_1 \approx 0$, while towards dissociation $a_1 \approx -a_0$ such that the exact binding energy is calculated at all bond-lengths [9, 402]. The Ψ_1 state therefore introduces the so-called *left-right correlation* between the two electrons that is inherently absent in the single determinant construction.

While electron correlation is entirely absent in HF theory, it is included to some extent in DFT via the PBE XC functional, which is used to generate Fig. V.7, in

spite of the latter also utilising a single Slater determinant wave function. Evidently, the PBE binding energy still exhibits SCE and to understand its origins in DFT in terms of the *density* it is instructive to approach from the perspective of fractional spins [9, 299, 319–322], similar to the diagnosis of SIE in terms of fractional occupancy.

Let us consider therefore H_2 hypothetically stretched to infinity, at which point each atom accommodates one electron in total that is equally split between spin-up and spin-down states. This configuration, in which only the covalent terms in Eq. (V.34) feature, must in principle be equal in energy to two fully spin-polarised H atoms at infinite bond-length, as proven in Ref. [319].

Approximate XC functionals, such as the PBE functional in Fig. V.7, fail to comply with this so-called *constancy condition*, which states that, for fixed occupancy, the total-energy of a system with g degenerate states is independent of the distribution of spin-density among those states. The violation of this condition is thus responsible for the SCE and is expressed mathematically in Ref. [319] as follows

$$E \left[\sum_{i=1}^g c_i \rho_i \right] = E[\rho_j] = E_0(N),$$

$$\text{with } j = \{1, \dots, g\} \quad \text{and} \quad \sum_{i=1}^g c_i = 1, \quad (\text{V.35})$$

which is illustrated in Fig. V.8 to be maximised at half-spin occupancy.

As we have previously shown, the correction of SCE is possible with multi-determinant FCI wave functions. While the recent work of Alavi *et al* have helped extend its application to quite large systems [405, 406] it is nonetheless desirable to have at hand a first-principles DFT correction scheme. The unsuitability of the DFT+ U functional, while correctly targeting fractional occupancies, ultimately lies with the U parameter itself, which is a measure of the curvature with respect to total occupancy and *not* magnetisation. As such, it will not be conducive to correcting SIE and other options must be explored.

Indeed, the J parameter that couples occupancy matrices of opposite spin in Eq. (V.24) has been linked to the curvature of the total-energy with respect to magnetisation in Ref. [354], and acts to penalise non-magnetic ordering [354, 391]. Given this connection between J , the SCE, and the parabolic deviations from the

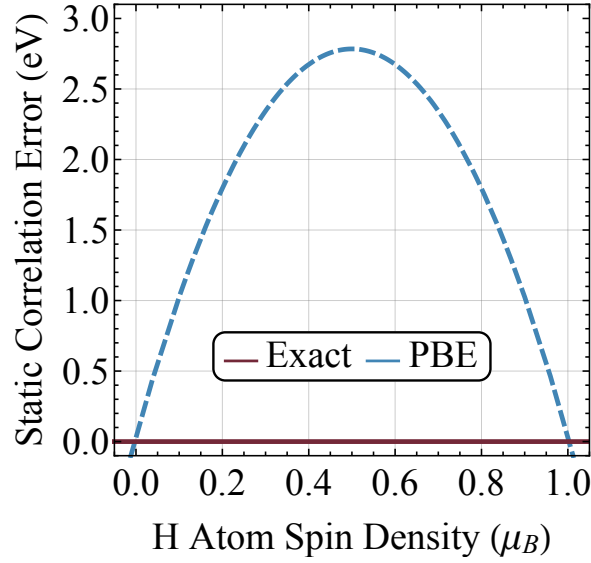


Figure V.8: The calculated SCE of a the H_2 molecule is shown by the deviation of the PBE total-energy (dashed) from the correct piece-wise constant behaviour (solid) between integer spin-density .

constancy condition, as in Fig. V.8, we postulate that J may be the parameter we desire to correctly restore the H_2 total-energy, while retaining the physical spin-density.

Let us therefore restrict our treatment to un-like spin interactions only, for which the DFT+ J functional takes the form

$$E_{\text{DFT}+J} = E_{\text{DFT}} + \sum_{I\sigma} \frac{J^I}{2} \text{Tr} [\hat{n}^{I\sigma} \hat{n}^{I\bar{\sigma}}] . \quad (\text{V.36})$$

The spin-polarised calculations of the H_2 binding curve, for $J = 0, 2, 4$ eV, are presented in Fig. V.9, in which it is evident that positive J values again worsen the total-energy at all bond-lengths, albeit in a slightly different way to the DFT+ U functional in Fig. V.7.

This outcome can be understood when J is interpreted as the negative of the energy curvature with respect to magnetisation [354], in which case applying a positive J will only increase the level of curvature present and consequently increase the error. Although a range of negative J values over the binding curve could hypothetically alleviate the SCE by removing this spurious curvature, we desire the means to calculate the necessary J values from first-principles analogous to how the U values

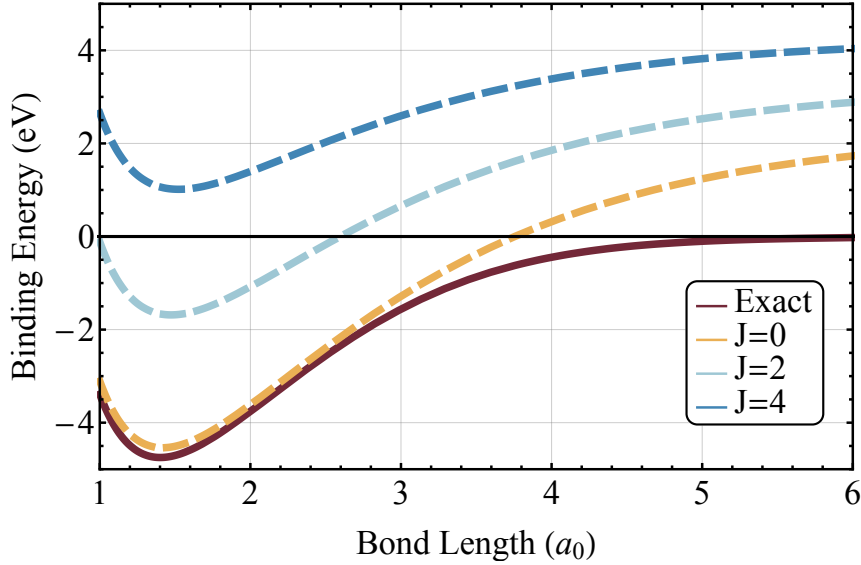


Figure V.9: Binding energy of closed-shell H_2 calculated with CI (solid) and DFT+ J with $J = 0, 2, 4$ eV (dashed), relative to energy of isolated H atoms. Positive J values also worsen the SCE for all bond-lengths, but negative J values may alleviate the error.

may be computed to treat SIE.

Based on our discussion heretofore, however, we would argue that the SIE and SCE of a given system are likely to be intricately linked, as both relate to the violation of physical conditions pertaining to fractional orbital occupations. Consequently, we are unable to determine, as of yet, exactly how the treatment of one error may affect the other [9, 407], e.g., favourably, adversely, or not at all as the case may be, prior to the analysis of the particular system. This will become an important matter to consider when we pursue a ground-state that is simultaneous free of SIE and SCE.

7 CONCLUSION

In this Chapter, we have outlined the origins of the most pervasive errors in approximate DFT, namely the self-interaction error (SIE) and static-correlation error (SCE), which may be respectively attributed to violations in the linearity and constancy conditions obeyed by exact XC functionals. In particular, we have discussed how the SIE is manifest in a spurious curvature in the total-energy vs occupancy pro-

file which is attributed to fractional occupancies. In the same context, we explored how the incorrect energy-derivatives between integer occupancies is related to the non-compliance of Koopmans' condition of the HOMO eigenvalue.

We then outlined the motivation and subsequent development of the rotationally-invariant $\text{DFT}+U+J$ functional and its potential for effectively correcting single and many-body SIE in strongly-correlated systems, a claim which is widely accepted but has not been explicitly verified. However, we found $\text{DFT}+U$ to be remarkably unsuitable for restoring Koopmans' compliance due to an insufficient linear-term. It appears that $\text{DFT}+U$, in its current form, is limited to the treatment of either the total-energy or the eigenspectrum, since it cannot achieve both for a one-electron system. The choice of the Hubbard subspace in the $\text{DFT}+U$ approach is also non-incident but, for our purposes in this dissertation, we have restricted ourselves to using the well-known pseudoatomic orbitals (PSA).

Finally, we illustrated how SCE arises from using a single Slater determinant wave function and that explicit treatment of electron correlation found in the FCI are required for it to be adequately resolved. In DFT, the SCE arises in systems with degenerate valence states, which tends to increase the total-energy, and is quantified in terms of the spurious curvature in the total-energy with respect to subspace magnetisation.

To conclude, we have presented the motivation and theoretical framework for the $\text{DFT}+U$ method, which is known to be an efficient and highly effective many-body SIE correction scheme that now finds routine application in a diverse range of systems [81, 343, 408–410]. The versatility of the method grants it widespread applicability in a variety of software packages [393, 394, 396], including `ONETEP` [101, 131, 389, 411–413]. Furthermore, it attains the status of an automated, first-principles method when it is provided with calculated Hubbard U parameters [341–343, 351, 414] (particularly at their self-consistency [396, 410, 415]), the calculation of which, from first-principles, will be addressed in the following Chapters.

VI

CALCULATION OF HUBBARD PARAMETERS FROM VARIATIONAL LINEAR RESPONSE

THE EFFECTIVENESS OF METHODS intended to correct inherent inaccuracies in approximate DFT, either by DFT+ U , constrained-DFT [416–418] or hybrid functionals [63, 419] etc., depends largely on the accurate calculation of parameters controlling the strength of the corrective potentials. In this Chapter, we will describe the process of computing the Hubbard U and J parameters from first principles in ONETEP, using an adaptation of the acclaimed linear-response (LR) approach of Cococcioni and de Gironcoli [342, 354].

To date, there exists in the literature a variety of methods for determining the Hubbard U parameter in strongly-correlated systems. Originally, the Hubbard U was determined via semi-empirical fitting to experimental data, which was typically spectral [311, 420–422], structural [311, 394, 421], or energetic [393, 423], and is a practice that continues in many studies to this day.

This method, while reasonably motivated, is rather unfavourable in practice as it interprets the Hubbard U parameter as an adjustable variable and not as an intrinsic property of the system. Moreover, tuning the U parameter to reproduce the electronic or optical gaps exactly is precarious, since the KS eigenvalues are not intended for this purpose and there is no guarantee that the SIE will have been adequately resolved. This approach becomes particularly unviable when the experimental data is insufficient or difficult to measure. If instead the Hubbard U was calculated as a variational ground-state density-functional property, even implicitly, then DFT+ U becomes elevated to the status of a fully variational first-principles method.

Early attempts to compute an *ab initio* U for use in the Anderson-type Hubbard functional in Eq. (V.11), began with taking the difference in the energy eigenvalues of ionic states, for example [336]

$$U \approx \varepsilon_{3d\uparrow} \left(\frac{N+1}{2}; \frac{N}{2} \right) - \varepsilon_{3d\uparrow} \left(\frac{N+1}{2}; \frac{N}{2} - 1 \right). \quad (\text{VI.1})$$

From this perspective, the U parameter is determined via a constrained-LDA (cLDA) calculation [336, 337, 344–346, 416, 424–426], where the correlated subspace occupancy is constrained while artificially decoupled from the surrounding atom. This method remained popular for estimating Coulomb parameters for many years but tended to drastically over-estimate the U values because it neglected the screening effects of the surrounding environment.

The random-phase approximation (RPA) [426–432], was later used and circumvented this by allowing for responses in both on-site and off-site electrons as well as permitting a frequency-dependent $U(\omega)$ to be calculated. This later evolved into the more accurate constrained-RPA (cRPA) approach [433–436], which excluded on-site transitions from contributing to the U .

Other methods for calculating U include the local density supercell impurity approach [437] and the calculation of on-site Coulomb matrix elements from maximally-localised Wannier functions [438, 439].

1 OVERVIEW OF THE LINEAR-RESPONSE METHOD

The linear-response (LR) approach to calculating U was initially conceived by Pickett *et al* [341], and later developed by Coccocioni and de Gironcoli [342] (who also extended the method the exchange parameter J [354]), as an inexpensive method to be implemented within the rotationally invariant DFT+ U functional given in Eqs. (V.25) & (V.24). In this formulation, a uniform external potential shift $\hat{V}_{\text{ext}} = \alpha \hat{P}$ is applied to the electrons in the localised subspaces and the U parameter is determined from the corresponding response functions, including the effects of screening.

As noted by the authors in Ref. [342], the SIE in strongly-correlated systems, representative of an open quantum system that does not interact with its bath for

particle exchange, is illustrated by the spurious curvature in the total-energy with respect to subspace occupancy, which we discussed at length in Chapter V. Consequently, their interpretation of the Hubbard U parameter is that of the measure of unphysical curvature exhibited in a system, which is in keeping with its implementation in Eq. (V.25), given by (suppressing site and spin index)

$$\frac{d^2 E_U}{dn^2} = -U. \quad (\text{VI.2})$$

The authors in Ref. [342] make an important distinction between the *interacting* and *non-interacting* curvatures present in a system. The latter is a superfluous feature that has nothing to do with the interacting curvature, and so must be removed to enable the reliable calculation of U values for both solids and molecules. This observation was alluded to, but initially absent, in the original formulation [341].

Inspired by the cLDA approach, Cococcioni and de Gironcoli postulated that the spurious curvature can be accessed by cDFT calculations on the local subspace responsible for SIE, in accordance with target occupancies $\{q_I\}$ and Lagrange multipliers $\{\alpha_I\}$

$$E[\{q_I\}] = \min_{n(\mathbf{r}, \alpha_I)} \left\{ E[n(\mathbf{r})] + \sum_I \alpha_I (n_I - q_I) \right\}. \quad (\text{VI.3})$$

In practice, however, it is more feasible to re-parameterise Eq. (VI.3) in terms of the Lagrange multipliers $\{\alpha_I\}$, and avoid performing cDFT calculations altogether

$$E[\{\alpha_I\}] = \min_{n(\mathbf{r})} \left\{ E[n(\mathbf{r})] + \sum_I \alpha_I (n_I - q_I) \right\}. \quad (\text{VI.4})$$

The second derivative of Eq. (VI.4) thus corresponds to a value of U that is consistent with its definition as the curvature of the of total-energy with respect to occupation

$$\frac{d^2 E[\{\alpha_I\}]}{dq_J dq_I} = -\frac{d\alpha_I}{dq_J} = -\chi_{IJ}^{-1}, \quad (\text{VI.5})$$

where we have introduced the *interacting* response function χ . However, the expression in Eq. (VI.5) is inclusive of the curvature associated with the re-hybridisation of the KS orbitals in response to the applied potential. We must therefore subtract this curvature, given in terms of the *non-interacting* response χ_0 corresponding to the KS system E_0 , to ensure a U value that accurately reflects the magnitude of on-site

Coulomb and XC interaction. Hence, U is evaluated according to the following Dyson equation

$$U = +\frac{d^2 E_0[\{q_I\}]}{dq_I^2} - \frac{d^2 E[\{q_I\}]}{dq_I^2} = (\chi_0^{-1} - \chi^{-1})_{II}. \quad (\text{VI.6})$$

The non-interacting response present in Eq. (VI.6) is a, hitherto, ambiguous, yet crucial, quantity in determining the calculation of U . In Ref. [342], it is interpreted as the reorganisation of charge subject to the potential shift on the subspace without allowing the self-consistent screening to take effect. In practice then, it is then acquired after the first iteration in the self-consistent calculation; subsequent to the initial response of the density, but prior to the Hamiltonian being updated.

The LR method just described has become a widely popular approach [343, 394, 440–443] to calculating Coulomb interaction parameters as it allows the parameters to be evaluated from a small set of inexpensive DFT calculations. The mathematical elegance and practical simplicity of the LR approach therefore presents an ideal foundation on which to construct the evaluation of U parameters in a direct-minimisation code such as ONETEP. However, as we will discuss in the following section, this type of formalism can not be directly accommodated in codes that utilise direct-minimisation as a means to locate the KS ground-state, and an appropriate adaptation to the LR method must be made to generalise its application.

2 CONSTRUCTION OF A VARIATIONAL LINEAR-RESPONSE APPROACH

The most problematic aspect of extending the LR approach to direct-minimisation codes lies in the calculation of the non-interacting response function χ_0 . Given that codes like these do not update the density and Hamiltonian iteratively¹, but do so simultaneously throughout the calculation, it is inefficient and extraneous to calculate χ_0 in the fashion described above. We are therefore motivated to seek a linear-response formalism for the Hubbard U that is readily compatible with direct-minimisation DFT solvers, particularly for linear-scaling DFT+ U [101].

¹ That is, within nested loops in which the density is optimised while the Hamiltonian is kept fixed, followed by the optimisation of the Hamiltonian where the density is fixed.

The principal challenge lies in the evaluation of the non-interacting response, the derivation of which we shall now outline.

2.1 THE NON-INTERACTING RESPONSE

If we perturb the subspace of a given system by an external potential $\delta V_{\text{ext}}(\mathbf{r})$, the resulting variation in the density is given, to first order, in terms of the response function $\chi(\mathbf{r}, \mathbf{r}')$, such that

$$\delta n(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \delta V_{\text{ext}}(\mathbf{r}') d\mathbf{r}' \quad \text{where} \quad \chi(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta V_{\text{ext}}(\mathbf{r}')} \quad (\text{VI.7})$$

For the same perturbation, we can define a second response function $\chi_{\text{KS}}(\mathbf{r}, \mathbf{r}')$ in terms of the change in the KS potential $V_{\text{KS}}(\mathbf{r})$

$$\delta n(\mathbf{r}) = \int \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}') \delta V_{\text{KS}}(\mathbf{r}') d\mathbf{r}' \quad \text{where} \quad \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta V_{\text{KS}}(\mathbf{r}')} \quad (\text{VI.8})$$

Following the discussion in Chapter II, the change in KS potential may be conveniently expressed, to first order, as the sum of changes in its interacting constituents, namely the Hartree, XC, and the external potential $\delta V_{\text{KS}} = \delta V_{\text{Hxc}} + \delta V_{\text{ext}}$. Moreover, any perturbation to the potential may be expressed in terms of the interaction kernel, given by

$$F_{\text{Hxc}}(\mathbf{r}', \mathbf{r}'') = \frac{\delta V_{\text{Hxc}}(\mathbf{r}')}{\delta n(\mathbf{r}''}),$$

$$\text{such that} \quad \delta V_{\text{Hxc}}(\mathbf{r}') = \int F_{\text{Hxc}}(\mathbf{r}', \mathbf{r}'') \delta n(\mathbf{r}'') d\mathbf{r}'' \quad (\text{VI.9})$$

Combining Eqs. (VI.9) & (VI.8) then yields the variation in the density in terms of KS quantities

$$\begin{aligned} \delta n(\mathbf{r}) &= \int \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}') [\delta V_{\text{Hxc}}(\mathbf{r}') + \delta V_{\text{ext}}(\mathbf{r}')] d\mathbf{r}' \\ &= \iint \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}''') F_{\text{Hxc}}(\mathbf{r}''', \mathbf{r}'') \delta n(\mathbf{r}'') d\mathbf{r}'' d\mathbf{r}''' + \int \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}') \delta V_{\text{ext}}(\mathbf{r}') d\mathbf{r}', \end{aligned} \quad (\text{VI.10})$$

where in the double integral we have relabeled the dummy variables $\mathbf{r}' \rightarrow \mathbf{r}'''$ for later convenience. We can now equate this expression to Eq. (VI.8), where the variation in the density is given in terms of the interacting quantities, and substitute the same

relation for $\delta n(\mathbf{r}'')$ in the double integral. We then remove the integral over $d\mathbf{r}'$ and divide across by $\delta V_{\text{ext}}(\mathbf{r}')$ for brevity, thereby giving

$$\chi(\mathbf{r}, \mathbf{r}') = \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}') + \iint \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}''') F_{\text{Hxc}}(\mathbf{r}''', \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' d\mathbf{r}''' \quad (\text{VI.11})$$

which relates χ , χ_{KS} and F_{Hxc} by a Dyson-like equation where we identify the non-interacting response function as none other than the KS response

$$\chi_0(\mathbf{r}, \mathbf{r}) \equiv \frac{\delta n(\mathbf{r})}{\delta V_{\text{KS}}(\mathbf{r})}. \quad (\text{VI.12})$$

This interpretation of χ_0 , in terms of the KS response to the perturbation, can now be readily computed in a variational procedure as easily as the interacting response χ . Let us now proceed to constructing a definition of U in accordance with the desired properties, which will require an appropriately projected interaction kernel.

2.2 CHOICE OF PROJECTION FOR THE INTERACTING KERNEL

In this work, our definition of U for a given subspace is derived from its original interpretation, given in Eq. (V.19), i.e., that of the net on-site Coulomb and XC interactions acting within it. More specifically, we seek terms coupling to the subspace density matrices in Eq. (V.25) up to order $(n_i^I)^2$, and therefore only consider an interacting kernel like $\hat{f}_{\text{int}} = \delta^2 E_{\text{int}} / \delta \hat{\rho}^2$, and not terms related to $\hat{g}_{\text{int}} = \delta^3 E_{\text{int}} / \delta \hat{\rho}^3$, or higher. Here, E_{int} comprises the Hartree, XC, and any other electronic interaction terms.

Crucially, we require only the interactions that arise due to density variations within a subspace to contribute to $\hat{f}_{\text{int}}$, and so an appropriate projection must be chosen. Finally, our formulation of U must comply with the convention of correcting the many-body SIE by subtracting the individual one-electron SIE of each eigenstate of the subspace density-matrix. It should therefore not scale extensively with the subspace eigenvalue count $\text{Tr}[\hat{P}]$ and must be appropriately averaged. In order to illustrate the above requirements, let us consider some candidate formulae for Hubbard U parameters which do not meet them.

Simple curvature from total derivatives of the energy

Immediately, we may rule out the formulation proposed by Pickett and co-workers [341], in which the U parameter is calculated from the curvature of the total-energy with respect to total occupancy²

$$\mathcal{U} = \frac{d^2 E}{dN^2} = -\frac{d\alpha}{dN} = -\chi \quad \text{where} \quad N = \text{Tr} [\hat{n}]. \quad (\text{VI.13})$$

As discussed in Ref. [342], this term fails to account for the non-interacting contribution arising from hybridisation of charge and is thus an inappropriate starting point.

Consider instead the curvature of just the interaction energy

$$\mathcal{U} = \frac{d^2 E_{\text{int}}}{dN^2} \quad \text{where} \quad E_{\text{int}} = E_{\text{Hxc}} \equiv E_H + E_{\text{xc}}. \quad (\text{VI.14})$$

However, the reasons for its non-suitability are quite subtle, which relate to the fact that the Hellman-Feynman theorem cannot be applied to E_{int} alone. Therefore, the first total derivative of E_{int} with respect to N is given by

$$\frac{dE_{\text{int}}}{dN} = \frac{\partial E_{\text{int}}}{\partial N} + \text{Tr} \left[\frac{\delta E_{\text{int}}}{\delta \hat{\rho}} \frac{d\hat{\rho}}{dN} \right] = \text{Tr} \left[\hat{V}_{\text{int}} \frac{d\hat{\rho}}{dN} \right], \quad (\text{VI.15})$$

yielding a vanishing partial derivative (due to no explicit N -dependence in E_{int}), but also a term proportional to the interaction potential $\hat{V}_{\text{int}}$. This term is screened with respect to the bath, since $d\hat{\rho}/dN$ is coupled to the external potential $\hat{V}_{\text{ext}} = \alpha \hat{P}$. The second total derivative

$$\frac{d^2 E_{\text{int}}}{dN^2} = \text{Tr} \left[\frac{d\hat{V}_{\text{int}}}{dN} \frac{d\hat{\rho}}{dN} + \hat{V}_{\text{int}} \frac{d^2 \hat{\rho}}{dN^2} \right] \quad (\text{VI.16})$$

incorporates screening again, and the resulting twice-screened objects have no physical interpretation and so this formulation is also omitted.

Curvature from functional derivatives of the energy

One may then suggest taking the curvature of the interaction kernel projected onto the subspace instead, which is denoted by

$$\mathcal{U} = \hat{P} \frac{\delta^2 E_{\text{int}}}{\delta \hat{n}^2} \hat{P} = \hat{P} \hat{f}_{\text{int}} \hat{P}. \quad (\text{VI.17})$$

² $\mathcal{U}$ is used to distinguish incorrect formulae from the correct one, which are denoted U .

However, this interaction is now bare of potentially substantial screening of density-matrix variations outside the subspace, and also makes an unsuitable starting point for measuring of many-body SIE.

This problem is the opposite, in a sense, to that of $d^2 E_{\text{int}}/dN^2$, from which one may surmise the correct definition is an intermediate case, where screening effects due to the complement of the subspace at hand should be incorporated, but only once. In other words, we require that U should be screened with respect to the bath, yet remain bare within the subspace. This motivates us to work not from the interacting energy, but from the interacting potential, i.e., to start from the unscreened functional derivative of the interacting energy, and to then differentiate that object by N .

Total derivative of the unscreened potential

Since the functional derivative is defined as a generalised partial derivative, the interaction term in the KS potential

$$\hat{V}_{\text{int}} = \frac{\delta E_{\text{int}}}{\delta \hat{\rho}} \quad (\text{VI.18})$$

is bare of screening, as is its subspace projection

$$\hat{P} \hat{V}_{\text{int}} \hat{P} = \hat{P} \left(\frac{\delta E_{\text{int}}}{\delta \hat{n}} \right) \hat{P}. \quad (\text{VI.19})$$

The object is then described by the average total derivative of the interacting potential, given by

$$\mathcal{U} = \text{Tr} \left[\hat{P} \frac{d \hat{V}_{\text{int}}}{d \hat{n}} \hat{P} \right] / \text{Tr} [\hat{P}]^2, \quad (\text{VI.20})$$

seems to fulfil many of the requirements of a valid Hubbard parameter, in that it is once-screened, non-extensive and subspace-averaged.

In practice, however, the screened kernel $d \hat{V}_{\text{int}}/d \hat{n}$ is arduous to calculate, even in orbital-free density-functional theory. More importantly, it includes screening effects due to density-matrix fluctuations within the subspace, which makes it unsuitable for quantifying the bare subspace interaction we intend to correct with DFT+ U .

This is easily remedied by instead taking the derivative with respect to the total occupancy N , and finally defining

$$U \equiv \frac{dV_{\text{int}}}{dN}, \quad \text{where} \quad V_{\text{int}} \equiv \frac{\text{Tr}[\hat{V}_{\text{int}}\hat{P}]}{\text{Tr}[\hat{P}]} \quad (\text{VI.21})$$

as the conveniently calculated, non-extensive, subspace-averaged interaction potential. To illustrate this interpretation, it is instructive to represent U in terms of approximations to the scalar *subspace-screened* parallel and anti-parallel interactions, denoted $F^{\sigma\sigma}$ and $F^{\sigma\bar{\sigma}}$, respectively³. Let us expand Eq. (VI.21) in terms of the total derivatives over the spin-dependent densities

$$\begin{aligned} U \equiv \frac{dV_{\text{int}}}{dN} &= \frac{1}{2} \left(\frac{dV_{\text{int}}^{\uparrow}}{dN} + \frac{dV_{\text{int}}^{\downarrow}}{dN} \right) \\ &= \frac{1}{2} \left(\frac{dV_{\text{int}}^{\uparrow}}{dn^{\uparrow}} \frac{dn^{\uparrow}}{dN} + \frac{dV_{\text{int}}^{\uparrow}}{dn^{\downarrow}} \frac{dn^{\downarrow}}{dN} + \frac{dV_{\text{int}}^{\downarrow}}{dn^{\downarrow}} \frac{dn^{\downarrow}}{dN} + \frac{dV_{\text{int}}^{\downarrow}}{dn^{\uparrow}} \frac{dn^{\uparrow}}{dN} \right) \\ &= \frac{1}{2} \left(F_{\text{int}}^{\uparrow\uparrow} \frac{dn^{\uparrow}}{dN} + F_{\text{int}}^{\uparrow\downarrow} \frac{dn^{\downarrow}}{dN} + F_{\text{int}}^{\downarrow\downarrow} \frac{dn^{\downarrow}}{dN} + F_{\text{int}}^{\downarrow\uparrow} \frac{dn^{\uparrow}}{dN} \right) \\ &\Rightarrow F_{\text{Hxc}}^{\hat{P}} = \frac{1}{4} \left(F_{\text{int}}^{\uparrow\uparrow} + F_{\text{int}}^{\uparrow\downarrow} + F_{\text{int}}^{\downarrow\downarrow} + F_{\text{int}}^{\downarrow\uparrow} \right). \end{aligned} \quad (\text{VI.22})$$

In the last line we have defined the interaction kernel $F_{\text{Hxc}}^{\hat{P}}$ as the approximation to the screened, net, average electronic interaction acting within the subspace due to *all* spin interactions, using the expressions

$$n^{\uparrow} = \frac{1}{2}(N + M) \quad \text{and} \quad n^{\downarrow} = \frac{1}{2}(N - M) \quad \Rightarrow \quad \frac{dn^{\uparrow}}{dN} = \frac{dn^{\downarrow}}{dN} = \frac{1}{2}. \quad (\text{VI.23})$$

Thus, U may be similarly defined as the net, average electronic interaction acting within the subspace due to *all* spin interactions. Finally, since the uniform potential α used in the linear-response method induces no density-variations within the subspace to first-order except for the uniform shift, the screening within the subspaces is effectively suppressed, similar to the cRPA approach [433–435].

In practice, the external potential is applied by a uniform shift of magnitude α to all electrons in the subspace, such that

$$dV_{\text{ext}} = \frac{\text{Tr}[d\hat{V}_{\text{ext}}\hat{P}]}{\text{Tr}[\hat{P}]} = \frac{\text{Tr}[d\alpha\hat{P}\hat{P}]}{\text{Tr}[\hat{P}]} = d\alpha. \quad (\text{VI.24})$$

³The distinction is made to avoid confusion with the subspace-bare interaction kernels denoted by $F^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \delta V^{\sigma}(\mathbf{r})/\delta n^{\sigma'}(\mathbf{r}')$.

Therefore, for a single-site model incorporating a scalar U , Eq. (VI.21) may be derived using the Dyson equation in Eq. (VI.6) as follows

$$U \equiv \chi_0^{-1} - \chi^{-1} = \left(\frac{dN}{dV_{\text{KS}}} \right)^{-1} - \left(\frac{dN}{d\alpha} \right)^{-1} = \frac{dV_{\text{Hxc}}}{dN} = F_{\text{Hxc}}, \quad (\text{VI.25})$$

using the interacting and non-interacting response functions

$$\chi = \frac{d\alpha}{dN} \quad \text{and} \quad \chi_0 = \frac{dV_{\text{KS}}}{dN} \quad \text{where} \quad V_{\text{KS}} \equiv \frac{\text{Tr}[\hat{V}_{\text{KS}}\hat{P}]}{\text{Tr}[\hat{P}]}. \quad (\text{VI.26})$$

Hence, we have derived the relevant expression for the Hubbard U to be determined from a variational procedure. Moreover, the Dyson equation above in Eq. (VI.25), may be readily extended to calculate long-range, inter-subspace parameters V [441], and their corresponding Hubbard U values, by constructing the matrix response functions [341] χ^{IJ} and χ_0^{IJ} .

2.3 COMPARING THE SCF AND VARIATIONAL LINEAR-RESPONSE METHODS

In this section, we shall digress for a moment to discuss the technical differences between the SCF LR method introduced in Ref. [342], and the variational adaptation just described.

Insofar as the LR method has been applied in both scenarios, the SCF [342] and variational methods are identical in terms of their applied external perturbation α , the use of the Dyson equation, and issues surrounding DFT+ U population analysis choice and convergence. They are also equally convenient for use with SCF-type codes, however, the variational approach is much more convenient for use with direct-minimisation solvers. They are also perfectly identical in their calculation of the interacting response χ , with the primary difference relating to the calculation of the non-interacting response χ_0 (at least formally, but the mathematical differences are as yet unexplored).

In the SCF LR procedure, χ_0 is calculated following the first step of the SCF cycle, which relies, by construction, upon a non-ground-state density for each given external parameter α . An important consequence of this practice is that the SCF non-interacting response $\chi_0 = -dV_{\text{ext}}/dn_0$ is calculated from the total-derivative of

the external potential with respect to the non-converged density n_0 , which does not correspond to the ground-state of the system. Consequently, the SCF Hubbard U is not a property that can be derived from the ground-state density as a function of the external potential, without reference to the eigensystem of the KS Hamiltonian. Thus, since the SCF Hubbard U cannot be regarded as a purely ground-state density-functional property, the total-energies computed from the DFT+ U calculations are not necessarily so either. This has important consequences for the comparability of total-energies between various crystallographic or molecular structures with differing Hubbard U values, and the validity of thermodynamic calculations based on DFT+ U , which remains a challenging endeavour [399, 444–448].

Conversely, in the variational procedure above, *both* χ and χ_0 , given in Eq. (VI.25), are calculated at the end of the minimisation procedure from the same set of constrained ground-state densities defined by α . As a result, χ , χ_0 , and the corresponding U value are all derived from the ground-state density of the system. This is a promising first step towards implementing DFT+ U with the calculation of thermodynamical properties and we will return to address this issue further in the next Chapter.

2.4 THE SUBSPACE CONTRIBUTION TO SIE: GLOBAL VS LOCAL CURVATURES

A further point to address is the important distinction between the total many-body SIE of a system, and that stemming from a localised subspace. The former pertains to the addition or removal of electrons in a system, while the latter is measured as a result of redistribution of charge in a system, albeit with the caveat that the local subspace weakly interacts with the surrounding environment. In both cases, it relates to the deviation in piece-wise linear behaviour in total-energy, either with respect to total particle number, or subspace occupancy, respectively.

With the application of the DFT+ U functional, the aim is to correct the former as much as possible by treatment of the latter on a per-electron basis, and is assumed to be precise in the atomic limit, based on the conservation of total particle number and dominance of local interactions. It is therefore most effective when the subspace, or *local*, SIE composes a large portion of the *global* SIE, adopting the terminology

from Ref. [395].

Consider for a moment the local SIE arising from a strongly-correlated subspace, which may be computed from the integral of the interacting potential over the subspace occupancy up to its ground-state value N_0

$$E_{\text{local}}^{\text{SIE}} = \int_0^{N_0} dN' V_{\text{int}}(N'). \quad (\text{VI.27})$$

A change of variables allows us to compute this instead as the energy expended in depleting the subspace of charge from its ground-state

$$\begin{aligned} E_{\text{local}}^{\text{SIE}} &= - \int_0^\infty d\alpha V_{\text{int}}(N'(\alpha)) \frac{dN'}{d\alpha} \\ &= \int_0^\infty d\alpha V_{\text{int}}(N'(\alpha)) \left(\frac{d^2 E_{\text{total}}}{dN'^2} \Big|_{N'(\alpha)} \right)^{-1}, \end{aligned} \quad (\text{VI.28})$$

where in the last line we have used the relation in Eq. (VI.5), to connect the expression with the global curvature of the constrained total-energy E_{total} .

The curvature of $E_{\text{local}}^{\text{SIE}}$ in a single-site model, while not implemented in practice, is the term measured by U

$$\frac{d^2 E_{\text{local}}^{\text{SIE}}}{dN^2} = U \quad (\text{VI.29})$$

and not, as we have discussed, the curvature of the total-energy

$$\frac{d^2 E_{\text{total}}}{dN^2} = -\chi^{-1}. \quad (\text{VI.30})$$

It follows that the difference between these quantities returns the positive-definite non-interacting inverse response χ_0^{-1}

$$\begin{aligned} \frac{d^2 (E_{\text{total}} - E_{\text{local}}^{\text{SIE}})}{dN^2} &= -\chi^{-1} - U = -\chi_0^{-1} \geq 0 \\ \Rightarrow \frac{d^2 E_{\text{total}}}{dN^2} &\geq \frac{d^2 E_{\text{local}}^{\text{SIE}}}{dN^2}. \end{aligned} \quad (\text{VI.31})$$

Thus, the global energy curvature with respect to subspace occupancy, is shown to be at least as large as the local energy curvature, subject to particle number conservation. The above result is heuristically analogous to the comprehensive study by Kulik *et al.* in Ref. [395], in which it was rigorously proven that a $+U$ correction, while intended to mitigate the local SIE, cannot, at the very least, increase the global SIE.

2.5 A ONE-ELECTRON TEST CASE: H_2^+

To illustrate the efficacy of the variational LR approach described above, let us consider its application in treating the SIE present in the binding energy of H_2^+ . Calculations to determine the U values were performed using the calculation parameters outlined in Chapters II & V. The external potential α was varied between ± 0.1 eV in intervals of 0.05 eV and applied to one atom only, while the other acted as the electronic bath. The U values were then computed according to Eq. (VI.21) for all bond-lengths, as shown in Fig. VI.1, and compared to the values required to correct the PBE total-energy U_{int} , which were estimated from the linear interpolation of the various PBE+ U binding energies presented in Fig. V.5 with the exact binding energy.

We see from Fig. VI.1 that the calculated U parameters span a large range of values between -5 eV and 8 eV and broadly match the behaviour of U_{int} , particularly in the dissociation limit. For short bond-lengths, however, the comparison breaks down due to large subspace overlap, charge spillage and inappropriate population analysis. Remarkably, we also see that U attains negative values for $r < 2 a_0$, which implies that the charge in this regime is over-localised according to the response functions.

Furthermore, the calculations to determine U were found to remain highly linear across all bond-lengths for this particular system and methodology. A typical example of such a calculation, at a bond-length of $4 a_0$, is presented in the inset of Fig. VI.1, which shows a clear linear relationship between V_{int} and N with only 5 data points. The slope of the resulting linear fit dV_{int}/dN , corresponding to the variational LR formula for U , results in $U = 4.840 \pm 0.006$ eV, which is accompanied by very small fitting errors.

We then applied the calculated U values to both atoms and, maintaining a symmetric charge density, we computed the PBE+ U binding curve shown in Fig. VI.2 below. Here, we see a marked improvement over the bare PBE curve, for which the DFT+ U functional resolves the total-energy to appreciable accuracy across all bond-lengths and provides qualitative agreement with the exact curve, thereby

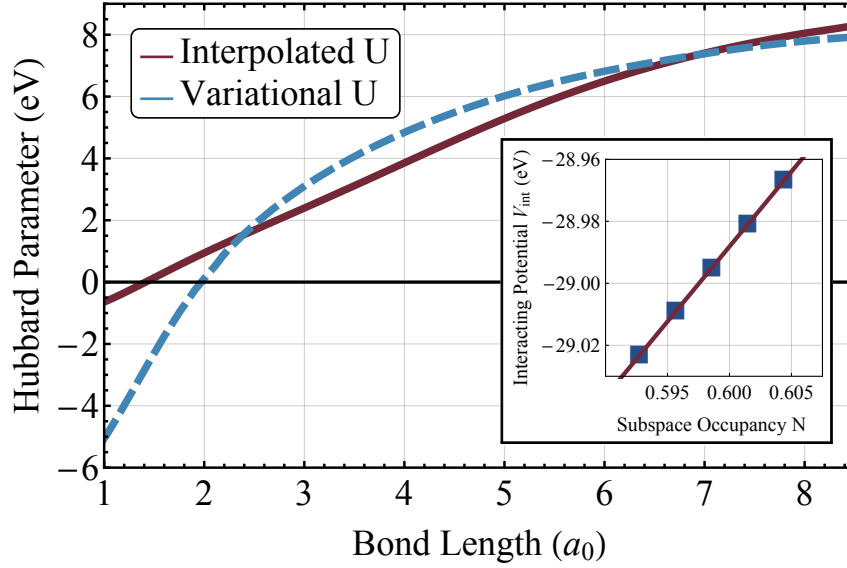


Figure VI.1: Variational linear-response U values calculated for dissociating H_2^+ compared to the U_{int} values required to correct the PBE binding energy estimated from interpolating with the exact binding energy.

demonstrating that DFT+ U is an effective scheme for the treatment of one-electron SIE.

Crucially, the improvement continues into the dissociation limit, at which point the two $1s$ orbitals, used to define the Hubbard subspaces, overlap and spill charge minimally, such that the population analysis becomes ideal. Furthermore, the weakening inter-atomic interaction becomes increasingly ideal for the application of DFT+ U in this limit. This shows that our method for calculating U values corresponds sufficiently with the necessary correction.

Our results show, therefore, that DFT+ U , when supplied with the U values calculated from variational linear-response, is capable of adequately correcting the total-energy SIE of a one-electron system under ideal population-analysis conditions, and is the first explicit confirmation of such to our knowledge. It is then clear that DFT+ U provides an efficient and effective correction to the SIE in the total-energy, as discussed in detail in Refs. [395, 396, 440]. In the following section, we shall apply our variational approach to more challenging, multi-electronic systems.

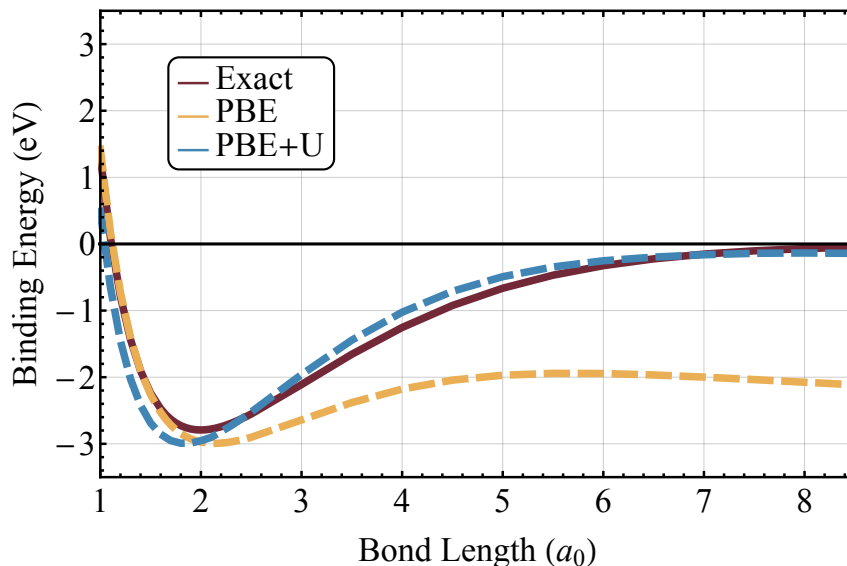


Figure VI.2: The calculated PBE+ U binding curve of H_2^+ (blue dashed) with U calculated from variational linear-response, compares well to the exact total-energy (red), and shows a remarkable improvement over the bare PBE curve (orange, dashed) in the dissociation limit.

3 APPLICATION TO MULTI-ELECTRONIC SYSTEMS

The treatment of SIE in dissociating H_2^+ has so far served the important purpose of testing our variational method to ensure the intended behaviour and adequate treatment of one-electron SIE. We now wish to extend this methodology to consider multi-electronic systems and certify that the variational LR method is robust and applicable to ameliorating many-body SIE.

3.1 DISSOCIATING H_2

We shall first return to the H_2 molecule, which is the simplest multi-electronic structure to consider, and demonstrate that DFT+ U is unsuitable to correct the static-correlation error (SCE) characteristic of the system.

As we discussed in section 6, it may be possible to formulate a viable correction to the SCE exhibited in dissociating H_2 if DFT+ U is provided with the appropriate (negative) U values. To this end, and as a demonstration of the inapplicability of DFT+ U in correcting SCE, we calculated the U parameters along the dissociating

curve, as with H_2^+ , for $\alpha = \pm 0.05$ eV, and recalculated the total-energy with the DFT+ U functional, presented in Fig. VI.3.

From this plot it is very clear that the U values act counter to the intended result, and that DFT+ U increases the error in the total-energy. The reason for this is because U is a measure of SIE manifest in spurious *positive* curvature deviating from piece-wise linear behaviour, whereas SCE is exhibited by a *negative* curvature, deviating from piece-wise constancy with respect to total spin magnetisation. The calculated U values are positive and therefore inapplicable to systems dominated by SCE in this regard, thereby illustrating that DFT+ U cannot be applied in an *ad hoc* manner. Let us now consider a molecule for which the error *is* dominated by SIE.

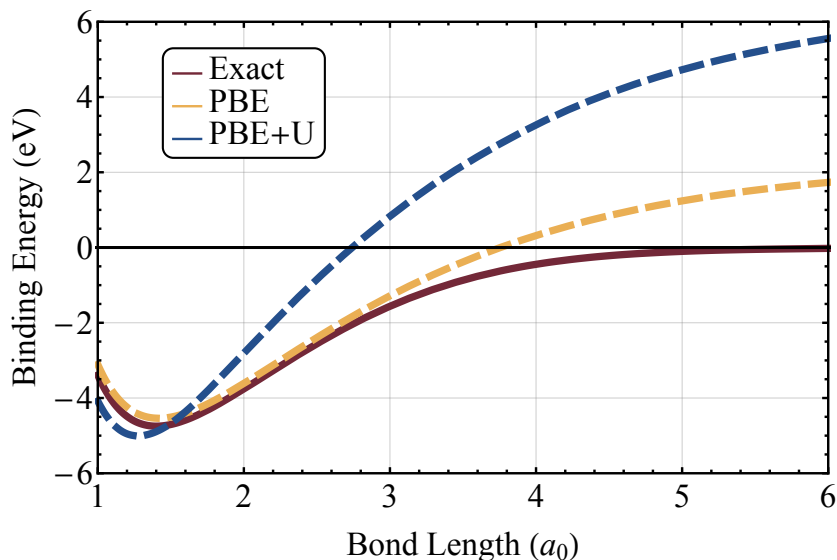


Figure VI.3: Binding curve of H_2 calculated with CI (red) and PBE (orange) and PBE+ U (blue). The U values calculated with variational LR exacerbate the SCE for all bond-lengths, as expected, and are therefore an inappropriate remedy for SCE.

3.2 MOLECULAR $\text{Ni}(\text{CO})_4$

The following work was conducted in collaboration with Okan Karaca Orhan, Fiona McCarthy, Mark McGrath, and Thomas Wyse Jackson, whom we thank for their valuable contributions.

Let us now turn our attention to a transition metal complex nickel tetracarbonyl ($\text{Ni}(\text{CO})_4$), which we selected based on its simple molecular structure centred around

a Ni atom with almost full $3d$ subshells [449]. This ensures the dominant error on the Ni atom is attributed to SIE rather than SCE [150, 299].

The relaxed geometry for $\text{Ni}(\text{CO})_4$ was acquired from Ref. [450], and entails a tetragonal structure with equal bond angles of 109.48° between all Ni and C atoms, as shown in Fig. VI.4a. The Ni–C bond-length is $1.85 \text{ \AA}$, while the C–O bond-length is slightly shorter at $1.15 \text{ \AA}$.

Calculations were performed with a hard ($2.10 a_0$ cutoff) norm-conserving pseudopotential [76], an LDA was used for the XC functional, and open boundary conditions [358] were employed. The kinetic energy cutoff was 900 eV, 9 NGWFs were chosen for the Ni atom and 4 each for the C and O atoms with a cutoff radius of $16 a_0$. The HOMO-LUMO gap in $\text{Ni}(\text{CO})_4$, as measured by experiment [451], is 4.83 eV, while the gap determined from a PBE calculation with $U = 0$ is 3.87 eV, which is ~ 1 eV below the experimental value.

To calculate U , in which the atomic positions are fixed, the potential shift α is chosen to be on the order of approximately 1 – 2% of the unperturbed interacting potential V_{int} . This ensures as broad a range of perturbations as possible are applied, while remaining in the linear-response regime. Here, α was varied between ± 0.1 eV in intervals of 0.05 eV, from which we calculated $U = 10.8 \pm 0.1$ eV quite accurately, as shown below in Fig. VI.4b. Taken in isolation, this value seems excessively large, however, we argue that by perturbing the charge density in such a spatially confined molecule, it is unsurprising that the response is larger than usual. Indeed, the HOMO-LUMO gap with the $+U$ correction applied in this case yields a relatively modest increase to 4.56 eV, but it is much more agreeable with the experimental figure and is accurate to within 6%. Furthermore, under this correction, the occupancy of the Hubbard subspace only increased from 9.09 e to 9.31 e. The correct treatment of SIE in this simple molecule, using our variational method, is therefore an encouraging preliminary result.

3.3 BULK NiO

We shall investigate our first bulk structure, nickel oxide (NiO), which is a particularly challenging system for approximate DFT and one that has been the subject

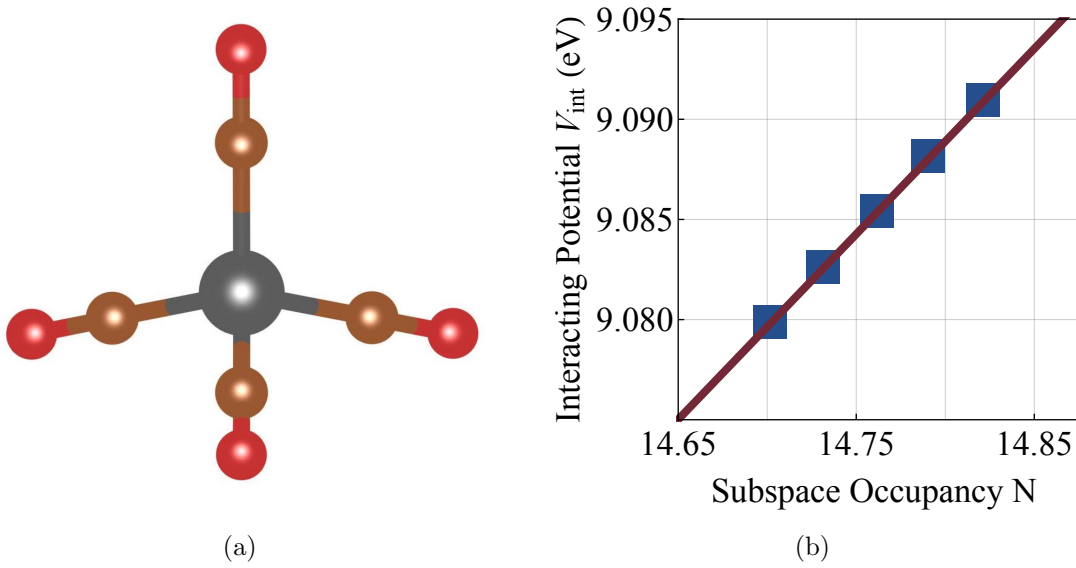


Figure VI.4: (a) The tetragonal $\text{Ni}(\text{CO})_4$ molecular structure. (b) The interacting response V_{int} against subspace occupancy N , the slope of which gives $U = 10.8 \pm 0.1$ eV.

of repeated testing for novel methods such as periodic unrestricted Hartree-Fock theory [452], the self-interaction corrected local density approximation [349], the GW approximation [453], LDA + DMFT [454] and first-principles methods for the original calculation of the Hubbard U parameter via linear-response [341, 342]. It has a rock-salt crystal structure, as shown in Fig. VI.5a, with a lattice constant of 4.16 Å [149] and a Néel temperature of 523 K [455], below which it is an anti-ferromagnetic type-II insulator with alternating magnetic moments, ranging from 1.64 μB [456] to 1.9 μB [457], between adjacent Ni atoms, as measured by neutron diffraction.

DFT+ U has also been successfully employed with NiO [149, 338, 341, 342, 458] when supplied with a sufficient U parameter.

The majority of studies to date have observed a band gap of ~ 4 eV arising from charge-transfer-type $p - d$ transitions [459, 460], however recent BIS spectral data [461], supported by calculations invoking GW quasiparticle [462, 463] and screened-exchange LDA [464], report a highly dispersive s -like state as low as 3 eV that accounts for very weak optical absorption [458, 465, 466].

Spin-polarised calculations of NiO were performed using a norm-conserving PBE pseudopotential with a PBE exchange-correlation functional, a sample input file

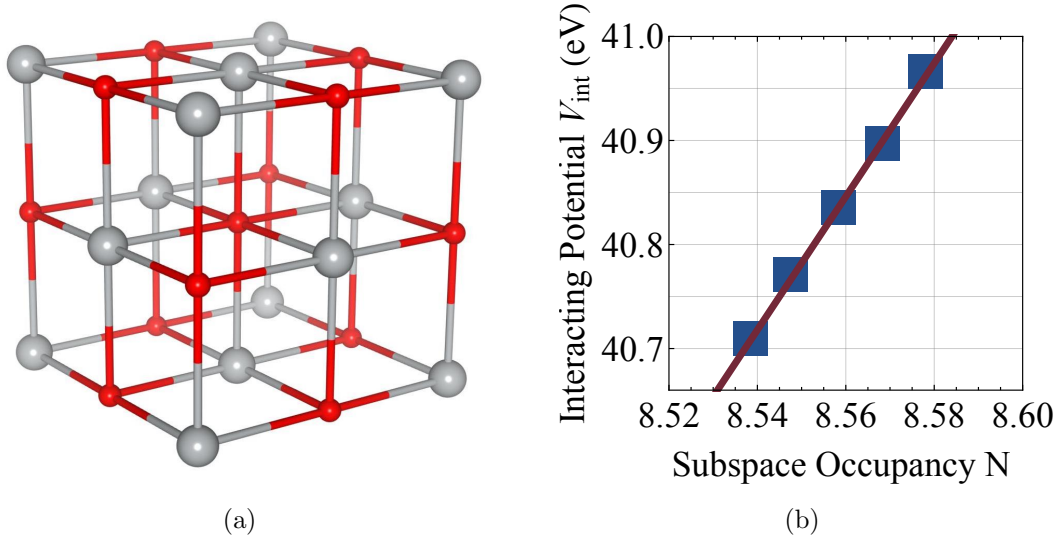


Figure VI.5: (a) The NiO rock-salt crystal structure. (b) The interacting response V_{int} against subspace occupancy N , the slope of which gives $U = 6.7 \pm 0.1$ eV.

is available in Appendix A. A plane-wave energy cutoff of 1170 eV was chosen with a $4 \times 4 \times 4$ supercell with Γ -point sampling, and an NGWF cutoff radius of $11 a_0$ such that total-energy convergence was achieved to within 2×10^{-6} Ha per atom. Values of α between ± 0.2 eV in intervals of 0.1 eV were applied here, for which we calculated $U = 6.4 \pm 0.1$ eV, as shown in Fig. VI.5b. This is within reasonable range of the U values used in other studies, which vary between 4.6 eV and 8 eV [337, 342, 458, 467, 468]. The parameters and results of this study, as well as those from various other DFT+ U works, are summarised in Table VII.4 in Chapter VII along with the experimental data.

Unsurprisingly, the PBE calculation qualitatively underestimates both the local magnetic moment, measured here to be $1.37 \mu_B$, and the band gap, which is 1.66 eV, in accordance with other studies [20]. Moreover, it incorrectly attributes the valence band edge states to nickel $3d$ -orbitals, as indicated by the density of states (DOS) plot in Fig. VI.6. Given that the system is fully compensated, we inspect only the spin-up channel, for which we depict the contributions from Ni spin-up sub-lattice (green), Ni spin-down sub-lattice (blue), the O atoms (red), and finally the total spin-up DOS (black). We note that in this, and subsequent, DOS profiles the conduction states beyond a few eV are likely to be unreliable [87], which is due to the limited

resolution provided by the valence-optimised NGWFs for states beyond the valence band edge.

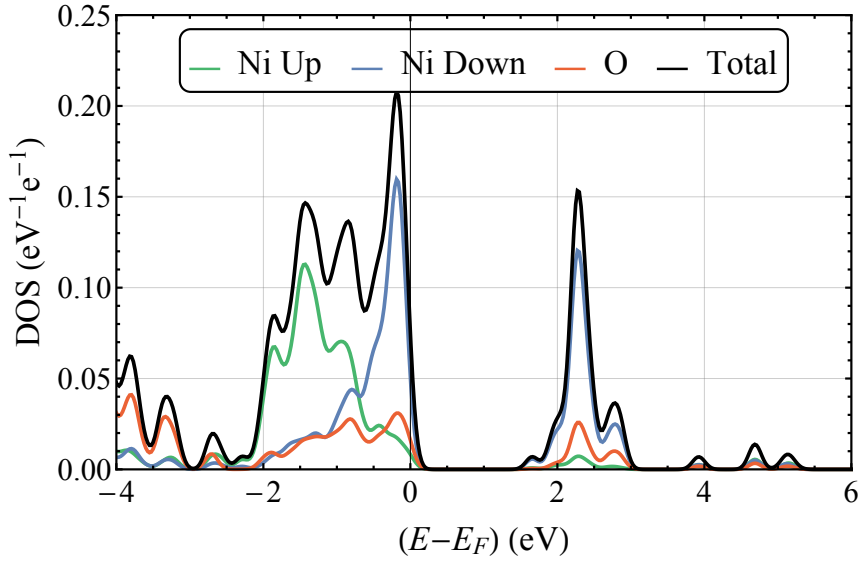


Figure VI.6: The species-resolved DOS for NiO with half-width Gaussian smearing of 0.1 eV and the zero-energy set to the Fermi level (eV) for unperturbed PBE. The DOS is plotted for the up-spin channel stemming from Ni spin-up atoms (green), Ni spin-down atoms (blue), O atoms (red), and total (black).

The DOS computed from applying $U = 6.7$ eV to all Ni atoms in the crystal is presented in Fig. VI.7, in which the band gap is increased to 3.04 eV. Here, the grey dashed line, labeled as the Hubbard DOS, describes the DOS stemming from the localised subspace, i.e., the localised Ni $3d$ states. The conduction band edge (shown in the inset) is assigned to a dispersive s -state, which is unaffected by the $+U$ correction, in line with experimental results [458, 465, 466]. This is evident from the lack of contribution of this state arising from the localised subspace, as indicated by the total Hubbard DOS. The sharp peak in the conduction states lies 4.44 eV above the Fermi level and likely relates to the experimentally observed band gap. The magnetic moment for this state is $1.62 \mu_B$ and within reasonable range of the experimental values [456, 457].

Finally, the constituent states of the valence band from -1.5 eV up to the Fermi level are 25% Ni and 75% O, whereas the conduction band is composed of 90% Ni and 10% O up to 5 eV above the Fermi level. These figures corroborate experimental

observations [459, 460] that categorise NiO as a charge transfer type semi-conductor. We therefore conclude that our computed Hubbard U value, from variational LR, is also applicable to extensive solids and yields sufficient agreement with experimental data.

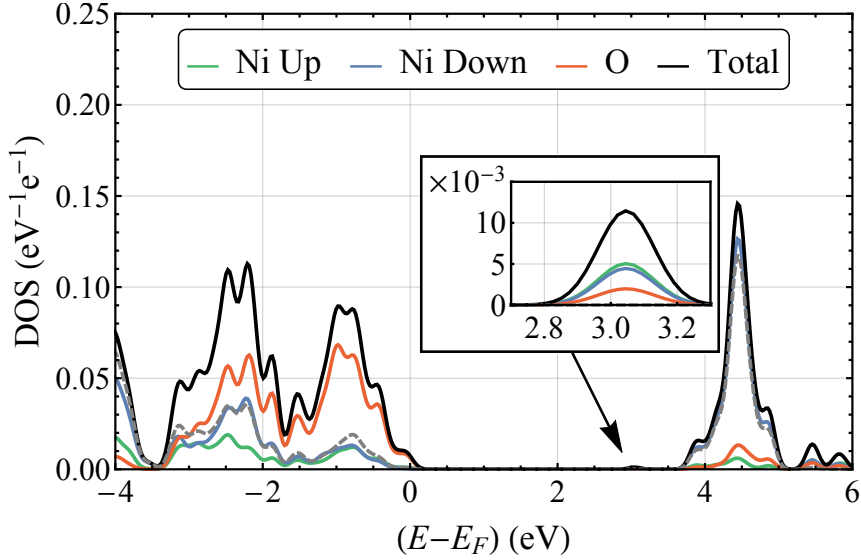


Figure VI.7: The species-resolved density-of-states of NiO with half-width Gaussian smearing of 0.1 eV and the zero-energy set to the Fermi level (eV) for $U = 6.7$ eV. The lines depict the same as in Fig. VI.6, with the Hubbard total given in dashed grey. Inset illustrates the conduction band minimum is not attributed to the localised Hubbard states but a dispersive s -state, giving a band gap of 3.04 eV.

3.4 BULK Cr_2O_3

Finally, we shall consider chromium(III) oxide (Cr_2O_3), or *chromia*, which is a Mott-Hubbard material when computed with DFT+ U but, until now, has not benefited from the calculation of the Hubbard U from LR approach. The following work was conducted with Emma Norton and Karsten Fleischer, and provides a welcome opportunity to showcase the first novel application of our variational LR method.

The search for a viable p -type transparent semiconducting oxide (TCO) has seen growing interest in magnesium-doped chromia $\text{Mg}:\text{Cr}_2\text{O}_3$, which has demonstrated potential as such [469–472]. The host matrix, Cr_2O_3 , possesses a corundum crystal structure with lattice constants $a = b = 4.96$ Å and $c = 13.60$ Å in the $R\bar{3}c$ space

group [473]. The Néel temperature is 307 K [474, 475], below which it is an antiferromagnetic insulator with alternating magnetic moments of $2.76 \mu\text{B}$, determined via neutron diffraction [476], on each Cr atom along the c -axis.

The excitation mechanism in chromia is deemed to be between that of a charge-transfer and Mott-Hubbard type [311, 477] with an optical band gap of 3.0-3.4 eV [471, 476, 478–480]. However, several experiments [471, 478, 481, 482] have observed transition energies at 2.1 eV and 2.7 eV, but no computational study to date has successfully reproduced them, despite their being experimentally attributed to spin-allowed transitions [483].

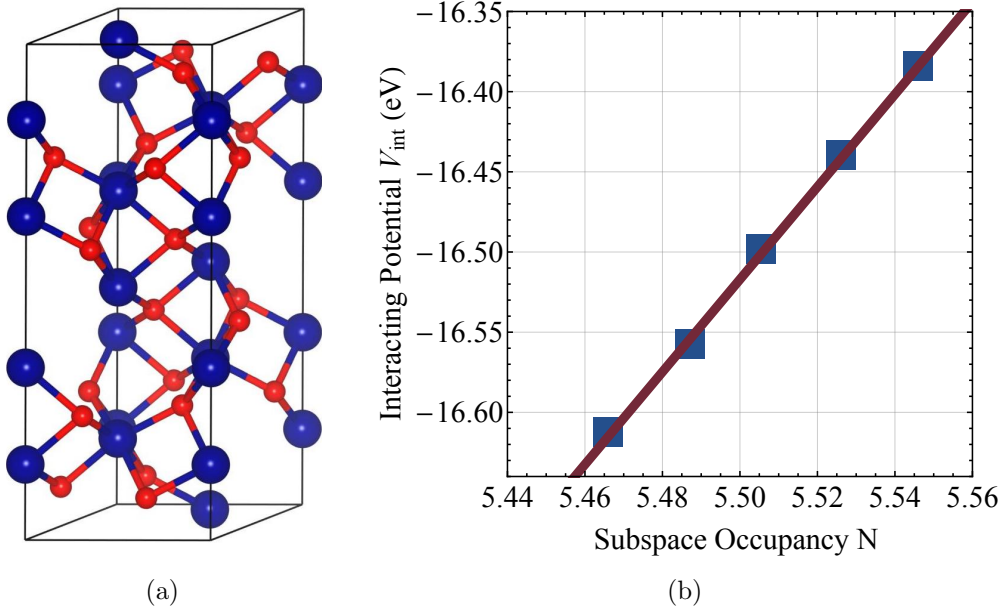


Figure VI.8: (a) The Cr_2O_3 corundum crystal structure. (b) The interacting response V_{int} against subspace occupancy N , the slope of which gives $U = 2.8 \pm 0.1$ eV.

Chromia has been the focus of many DFT+ U computational studies to date, the first of which was performed by Catti *et al.* [477] using unrestricted Hartree-Fock (UHF), in which they calculated an excessively large band gap of ~ 15 eV. Progress later came when Dobin and co-workers [484] performed LSDA calculations but found an underestimated band gap of 1.5 eV. The first attempt to address the poorly resolved electromagnetic behaviour came when Rohrbach *et al* [311, 485] invoked the DFT+ U functional of Dudarev and Liechtenstein [352] with $U = 5$ eV and $J = 1$ eV, determined via fitting to experimental data. Nevertheless, the band gap

and magnetic moment they calculated, 2.6 eV and 3.01 μB , respectively, were in much better agreement with experiment and have been widely used since [486, 486, 487].

Mosey and co-workers [487–490], were the first to calculate U from *ab initio* methods and used UHF to calculate $U = 3.3$ eV and $J = 0.1$ eV, which they also implemented in Dudarev’s DFT+ U functional [352]. The band gap they resolved was 2.9 eV while the magnetic moment was 2.9 μB , which were in reasonable agreement with experiment.

Shortly thereafter, Shi *et al.* [491], in pursuit of resolving the magnetic properties, determined $U \approx 4$ eV, for a fixed $J = 0.58$ eV, from the full-potential linear augmented plane-wave (FLAPW) method described in Ref. [492]. They implemented the rotationally invariant DFT+ U functional [340, 342, 353] and computed a 2.88 eV band gap and 3.26 eV magnetic moment. In more recent years, U and J values have been determined via fitting to experimental data [393, 470, 493–496], for which a range of values have been derived. A summary of the parameters and results of this study, as well as those from other selected DFT+ U reports, and the experimental data are presented in Table VI.1 in Chapter VII.

For this study, spin-polarised calculations were performed using the projector-augmented wave (PAW) method and an LDA for the XC functional. A plane-wave energy cutoff of 1100 eV was chosen with a $3 \times 3 \times 2$ supercell, Γ -point sampling, and a NGWF cutoff radius of 12 a_0 such that total-energy convergence was achieved to within 2×10^{-5} Ha per atom. Values of α between ± 0.2 eV in intervals of 0.1 eV were again applied, for which we calculated $U = 2.8 \pm 0.1$ eV, as shown in Fig. VI.8b. To our knowledge, this is the first instance of the Hubbard U calculated from LR (variational or otherwise) for this material.

We again plot the DOS for the spin-up sub-lattice and present the contributions from Cr spin-up atoms (green), Cr spin-down atoms (blue), O atoms (red), and the total spin-up DOS (black). As expected, the traditional LDA calculation underestimates the local magnetic moment, here calculated as 2.30 μB , and the band gap, which is 1.27 eV, in line with Ref. [484]. Fig. VI.9 demonstrates that the valence and conduction band edge states are heavily attributed to the Cr 3*d*-states.

The LDA+ U calculation on the other hand, provided with $U = 2.8$ eV on all Cr

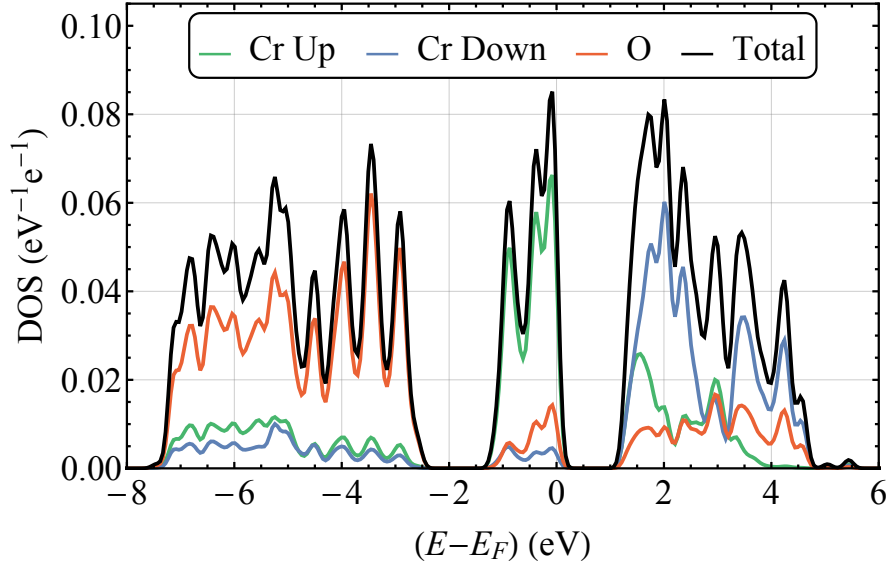


Figure VI.9: The species-resolved DOS of Cr_2O_3 calculated with LDA, with half-width Gaussian smearing of 0.1 eV and the zero-energy set to the Fermi level (eV). The lines depict Ni majority-spin (green), Ni minority-spin (blue), O (red), and total (black)

atoms, returns a DOS depicted in Fig. VI.10, in which the band gap is increased to 2.10 eV, and a magnetic moment of $2.56 \mu\text{B}$, which are both in excellent agreement with experimental observations [471, 476, 478, 481, 482]. Excitations are now expected to be governed by $d-d$ like-spin transitions up to 2.8 eV above the Fermi level. The constituent states of the valence band from -1.5 eV up to the Fermi level are, on average, 70% Cr and 30% O, whereas the conduction band is composed of 80% Cr and 20% O up to 4 eV above the Fermi level, which confirms the Mott-Hubbard character [491].

Comparison to spectroscopic measurements

Our experimentalist colleagues, Emma Norton and Karsten Fleischer, obtained high resolution (0.58 eV) X-ray and ultraviolet photoelectron spectroscopy measurements, termed XPS and UPS respectively, which probe the valence DOS of bulk chromia. Furthermore, ultraviolet-visible spectroscopy (UV-Vis) data were provided, which measures the optical absorption according to the method described in Ref. [471]. In this section, we compare their measurements with computational data. A 0.29 eV

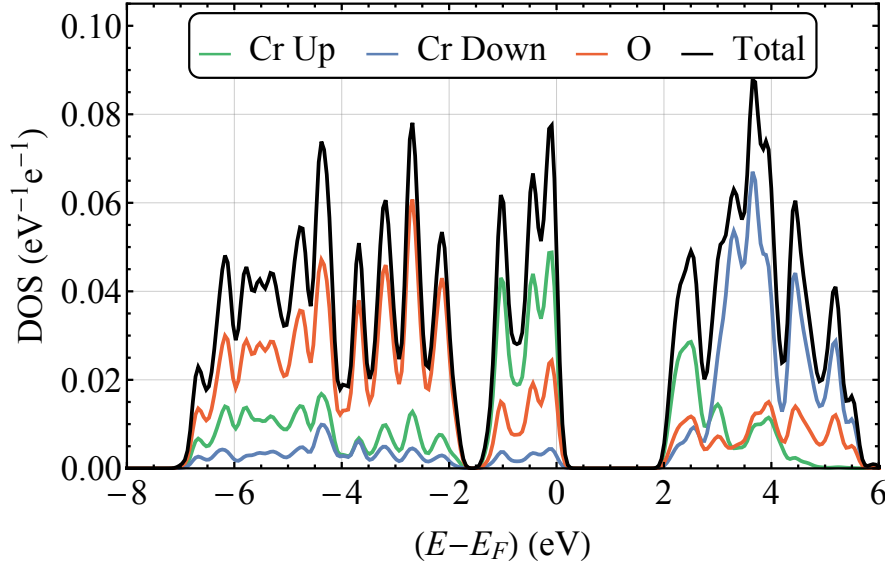


Figure VI.10: The species-resolved DOS of Cr_2O_3 , calculated with $\text{LDA}+U = 2.8$ eV with half-width Gaussian smearing of 0.1 eV and the zero-energy set to the Fermi level (eV). The lines depict the same as in Fig. VI.9, with the Hubbard total given in dashed grey.

half-width Gaussian smearing was applied to all $\text{LDA}+U$ DOS given in Fig. VI.10, in order to provide a consistent comparison to the all experimental data.

Plotted in Fig. VI.11 are the Gaussian smeared total (solid red line) and Hubbard (blue solid line) DOS along with the XPS (dashed orange line) and UPS (dashed blue line) measurements. In order to assist in their comparison, we have normalised the DOS plots such that the integral over the binding energy E returns the total number of electrons in the unit cell (432). From the graph it is clear that the total DOS reproduces very well the large peak in the XPS between -2.5 eV and 0 eV. Furthermore, between -8 eV and -2.5 eV, the total DOS qualitatively reproduces the behaviour in the UPS data. Meanwhile, the Hubbard DOS broadly follows the behaviour of the XPS across all energies, and accounts for approximately 50% of the total contribution.

To further aid this analysis, in Fig. VI.12, we present the species-resolved DOS in comparison to the XPS and UPS data. Here, we observe that the profile of the Cr up DOS (green solid line) contributes heavily to the sharp peak in the XPS data at ≈ -2 eV. Moreover, the trend in the UPS data seems to be reliably matched by

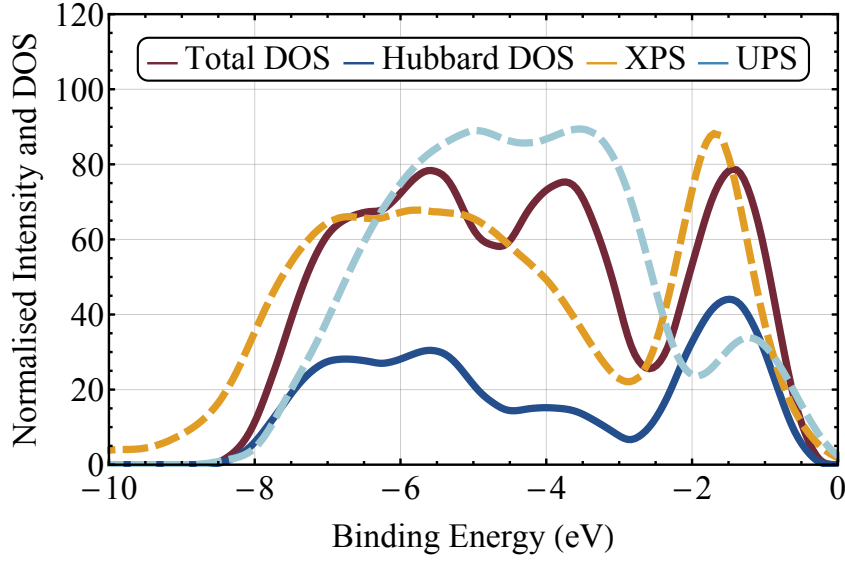


Figure VI.11: Comparison of XPS (orange, dashed) and UPS (blue, dashed) measurements of Cr_2O_3 against the total (red, solid) and Hubbard (blue, solid) DOS calculated with LDA+ U . All data are normalised such that the integral under the curves equals the number of electrons in the unit cell. A Gaussian smearing of 0.29 eV has been applied to the DOS to ensure consistent comparison. The total DOS reproduces the peak in the XPS, and matches the broad trend in the UPS for lower binding energies very well. The Hubbard DOS, which is attributed to the localised states, contributes $\sim 50\%$ toward the XPS data across all energies.

that of the O DOS (solid red line), from 0 eV, where there exists a small peak, to the large spectral feature present from -2 eV to -8 eV. The Cr down DOS (blue solid line), however, does not contribute appreciably to the total DOS.

Finally, in Fig. VI.13, we present the absorption spectrum truncated to 5 eV above the conduction band edge, which has been normalised such that the integral under the curve is equal to one. The absorption spectrum may be approximated from the joint DOS (assuming fixed optical matrix elements)

$$\alpha(\omega) \sim \int d\omega' \rho_v(\omega - \omega') \rho_c(\omega'), \quad (\text{VI.32})$$

and we plot the joint DOS evaluated from the summed convolution of the species-resolved valence and conduction DOS, given by $\rho_v(\omega)$ and $\rho_c(\omega)$, respectively. This has been similarly normalised to aid in the visual comparison.

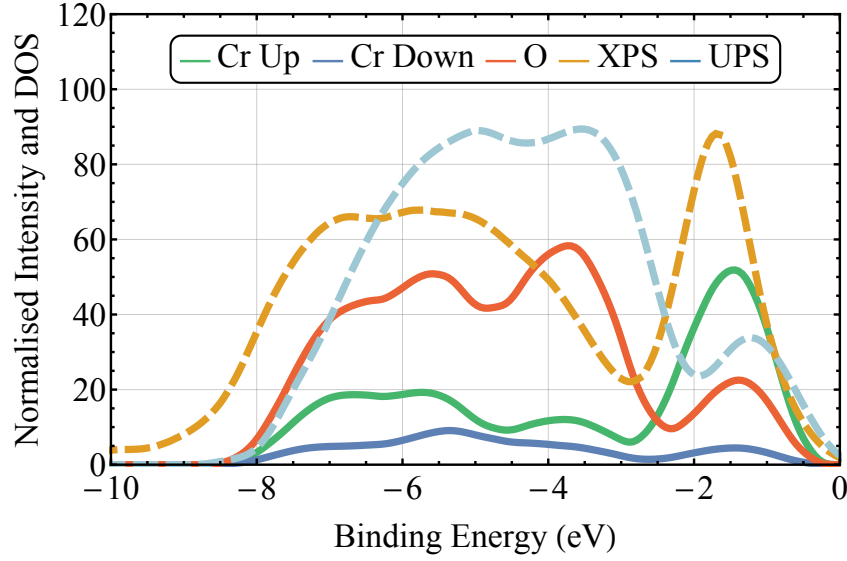


Figure VI.12: Comparison of XPS (orange, dashed) and UPS (blue, dashed) measurements of Cr_2O_3 against the Cr up (green, solid), Cr down (blue solid), and O (red, solid) DOS calculated with LDA+ U . All data are normalised and a Gaussian smearing of 0.29 eV has been applied to the DOS. The Cr up DOS contributes heavily to the sharp peak in the XPS data at high binding energies. The O DOS reproduces the broad trend in the UPS data at all energies. The Cr down DOS contributes very little.

Although the predictive capabilities of the calculated joint DOS is limited (see our above comment regarding conduction states) we nonetheless observe some similar features present in both profiles. For instance the onset of absorption coincides at ≈ 2 eV, whereupon the peak values at 5 eV are of similar magnitude. Furthermore, the excitation present at ≈ 2.5 eV corresponds to a similar feature in the joint DOS.

To produce a more reliable comparison between the joint DOS and UV-vis data, one could incorporate more NGWFs in the calculation to provide more conduction states, or optimise the energy with respect to the conduction states (with which it would be cumbersome to converge the total-energy), however, neither approach is guaranteed to significantly improve results.

Regardless, these combination of the present results provide further support for the validity of our variational LR method, as we have now reliably calculated both qualitative and quantitative electronic properties to reasonably precision, without

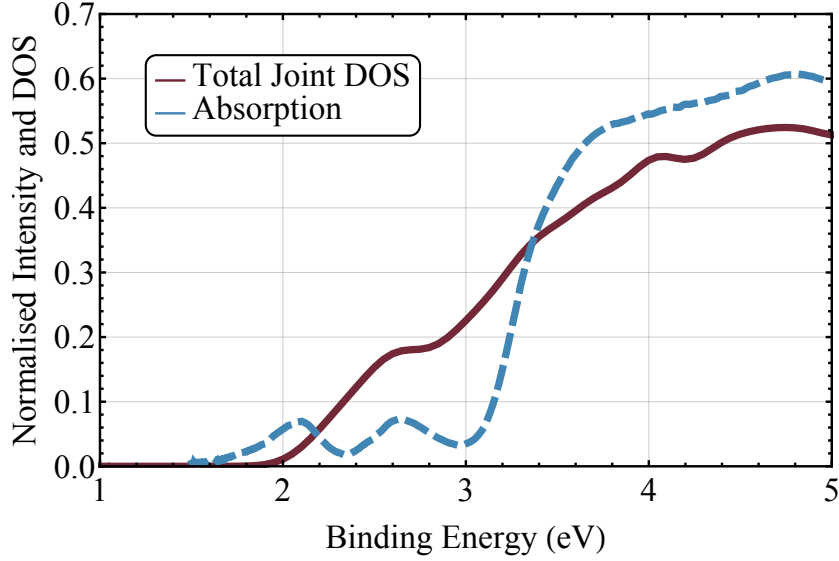


Figure VI.13: Comparison of UV-Vis (dashed) measurements of Cr_2O_3 of the optical absorption against the joint DOS calculated with LDA+ U . All data are normalised and a Gaussian smearing of 0.29 eV has been applied to the DOS.

invoking fitting of any kind.

4 CALCULATING J USING THE VARIATIONAL LINEAR-RESPONSE METHOD

Let us now extend our variational approach to the calculation of the Hund's exchange parameter J , which is utilised in Eq. (V.24) to penalise anti-parallel spins occupying the same site and thereby encourages magnetic ordering. While the full expression given in Eq. (V.24) is not frequently employed, it is common practice [391], dating back to the Dudarev model [149], to combine U and J to create an effective Coulomb repulsion between like-spins only $U_{\text{eff}} = U - J$ for use in Eq. (V.25).

Similar to U , the J term has historically been determined by fitting [311], or calculated by cLDA [337], LAPW [491, 497, 498], linear muffin-tin orbitals (LMTO) [337], linear combination of atomic orbitals (LCAO) [499], or by configuration interaction (CI) [500, 501]. Computed J values are typically ≈ 1 eV in magnitude [337] and are often absorbed into U , or sometimes ignored altogether.

Himmetoglu and co-workers in Ref. [354] formulated an extension to the LR

approach outlined in section 1, in which J is calculated from the *magnetic* response functions and is related to the curvature of the energy with respect to magnetisation $M = n^\uparrow - n^\downarrow$, given by

$$J \sim \frac{\partial^2 E}{\partial M^2}. \quad (\text{VI.33})$$

Let us outline the formulation required to calculate the J term from a variational approach in the same spirit as we did for U in section 2, by computing the total-energy curvature with respect to magnetisation. We start by defining a constrained energy parameterised by a target magnetisation M_I , enforced by a set of Lagrange multipliers $\{\beta_I\}$, whereby

$$E[\{\beta\}] = \min_{n(\mathbf{r})} \left\{ E[n(\mathbf{r})] + \sum_I \beta_I (n_I^\uparrow - n_I^\downarrow - M_I) \right\}. \quad (\text{VI.34})$$

For a single site model, the difference between the spin up and spin down potentials in this system is then defined by the spin-splitting β_I as follows

$$\begin{aligned} \hat{V}^\uparrow - \hat{V}^\downarrow &= \frac{\delta E}{\delta \hat{\rho}^\uparrow} - \frac{\delta E}{\delta \hat{\rho}^\downarrow} = \hat{V}_{\text{ext}}^\uparrow - \hat{V}_{\text{ext}}^\downarrow = 2\beta \hat{P} \\ \Rightarrow \quad \beta &= \frac{1}{2} \left(V_{\text{ext}}^\uparrow - V_{\text{ext}}^\downarrow \right), \end{aligned} \quad (\text{VI.35})$$

where $\hat{P}$ is the usual projection operator and $V_{\text{ext}}^\sigma \equiv \text{Tr} [\hat{V}_{\text{ext}}^\sigma \hat{P}]$.

In keeping with the subspace-bare potential prescribed in section 2, we take the partial derivative of Eq. (VI.34) with respect to M which, according to the Hellman-Feynman theorem presented in Ref. [502], yields

$$\frac{\partial E}{\partial M} = -\beta = -\frac{1}{2} \left(V_{\text{ext}}^\uparrow - V_{\text{ext}}^\downarrow \right). \quad (\text{VI.36})$$

The total derivative of this expression follows to give the inverse of the bath-screen interacting on-site magnetic response χ_M

$$\frac{d}{dM} \left(\frac{\partial E}{\partial M} \right) = -\frac{d\beta}{dM} = -\chi_M^{-1} = -\frac{1}{2} \frac{d}{dM} \left(V_{\text{ext}}^\uparrow - V_{\text{ext}}^\downarrow \right). \quad (\text{VI.37})$$

The non-interacting equivalent is then computed as before

$$\chi_{M,0}^{-1} = \frac{1}{2} \frac{d}{dM} \left(V_{\text{KS}}^\uparrow - V_{\text{KS}}^\downarrow \right), \quad (\text{VI.38})$$

such that we may define J as the difference between interacting and non-interacting magnetic responses as before, giving the net, subspace-averaged exchange interaction

$$J = \chi_{M,0}^{-1} - \chi_M^{-1} = -\frac{1}{2} \frac{d(V_{\text{int}}^{\uparrow} - V_{\text{int}}^{\downarrow})}{d(n^{\uparrow} - n^{\downarrow})}. \quad (\text{VI.39})$$

Moreover, we may expand the expression for J in terms of the spin-dependent interactions, as we did for U , as follows

$$\begin{aligned} J &= -\frac{1}{2} \left(\frac{dV_{\text{int}}^{\uparrow}}{dM} - \frac{dV_{\text{int}}^{\downarrow}}{dM} \right) \\ &= -\frac{1}{2} \left(\frac{dV_{\text{int}}^{\uparrow}}{dn^{\uparrow}} \frac{dn^{\uparrow}}{dM} + \frac{dV_{\text{int}}^{\uparrow}}{dn^{\downarrow}} \frac{dn^{\downarrow}}{dM} - \frac{dV_{\text{int}}^{\downarrow}}{dn^{\downarrow}} \frac{dn^{\downarrow}}{dM} - \frac{dV_{\text{int}}^{\downarrow}}{dn^{\uparrow}} \frac{dn^{\uparrow}}{dM} \right) \\ &= -\frac{1}{2} \left(F_{\text{int}}^{\uparrow\uparrow} \frac{dn^{\uparrow}}{dM} - F_{\text{int}}^{\uparrow\downarrow} \frac{dn^{\downarrow}}{dM} + F_{\text{int}}^{\downarrow\downarrow} \frac{dn^{\downarrow}}{dM} - F_{\text{int}}^{\downarrow\uparrow} \frac{dn^{\uparrow}}{dM} \right) \\ \Rightarrow F_J^{\hat{P}} &= -\frac{1}{4} \left(F_{\text{int}}^{\uparrow\uparrow} - F_{\text{int}}^{\uparrow\downarrow} + F_{\text{int}}^{\downarrow\downarrow} - F_{\text{int}}^{\downarrow\uparrow} \right). \end{aligned} \quad (\text{VI.40})$$

In the last line we have defined the interaction kernel $F_J^{\hat{P}}$ as the average *difference* between subspace-screened parallel and anti-parallel spin interactions, using

$$n^{\uparrow} = \frac{1}{2}(N + M) \quad \text{and} \quad n^{\downarrow} = \frac{1}{2}(N - M) \quad \Rightarrow \quad \frac{dn^{\uparrow}}{dM} = -\frac{dn^{\downarrow}}{dM} = \frac{1}{2}. \quad (\text{VI.41})$$

The connection between the definitions of U , presented in Eq. (VI.22), and J now becomes clear, where the former is a measure of the average on-site interaction between all spins, and the latter is the average on-site difference between parallel and anti-parallel spin interactions. We also remind the reader that the DFT+ U functional, presented in Eq. (V.25), only explicitly affects like-spin interactions. Thus, the practice of incorporating $U - J$ now makes sense as a correction for the average like-spin interaction, as seen by the role of the DFT+ U functional in Eq. (V.25),

$$U_{\text{eff}}^I = U^I - J^I = \left(F_{\text{Hxc}}^{\hat{P}} - F_J^{\hat{P}} \right)^I = \frac{1}{2} \left(F_{\text{int}}^{\uparrow\uparrow} + F_{\text{int}}^{\downarrow\downarrow} \right)^I. \quad (\text{VI.42})$$

4.1 CORRECTING STATIC CORRELATION ERROR IN H_2

While SCE has not been directly treated by DFT+ J , at least to our present knowledge, the association of J with the curvature of the constrained energy with respect to

magnetisation in Eq. (VI.33), alludes to an intriguing prospect. If we consider Fig. V.8, we observe that the SCE is expressed by a deviation from piece-wise constancy [319] with respect to total spin magnetisation in the form of a spurious curvature. We therefore surmise that SCE may be effectively treated by an energy correction that vanishes at integer values of the spin-density and contributes a non-zero correction otherwise, which may be expressed in the form

$$E_J = \frac{1}{2} \sum_{I\sigma} J^I n^{I\sigma} (n^{I\sigma} - 1). \quad (\text{VI.43})$$

This expression is precisely the double-counting term present in Eq. (V.20) (up to a minus sign). It therefore begs the question if a DFT+ J functional can be used effectively to this end.

We applied the variational method to calculate J in spin-polarised calculations of dissociating H_2 , with the intention of treating the SCE. The resulting values were again calculated with excellent precision, within 10^{-3} eV, where it transpired that for short bond-lengths, an excessively high exchange term was computed, e.g, $J \approx 150$ eV at $1.0 a_0$, due to the large responses induced by strongly overlapping $1s$ orbitals. These values quickly decayed with the internuclear separation, however, as the orbital overlap reduced and measured $J = 4.3$ eV at $2.8 a_0$.

However, beyond the Coulson-Fischer point [503] at $\approx 3.2 a_0$, J can not be computed since the magnetic potential, given by $V_{\text{KS}}^\uparrow - V_{\text{KS}}^\downarrow$, switches from a stable to an unstable equilibrium. This is illustrated below in Fig. VI.14 where we have computed the potential at $1 a_0$, which clearly exhibits a stable equilibrium with respect to the magnetisation of a H atom. Meanwhile, the system is clearly unstable at $4.8 a_0$. Hence, any magnetic perturbation that is applied beyond $\approx 3.2 a_0$ immediately causes the system to fully polarise, wherein we depart from the linear-response regime, thereby making a calculation of J infeasible with this method.

To effectively calculate J for larger bond-lengths, and toward the dissociation limit, it will be necessary to supplement the system with an external potential to impose a stable equilibrium and mitigate this tendency to polarise. The potential we will require to do this is none other than the second term in Eq. (V.24), or just Eq. (V.36), in conjunction with a *negative* J . Crucially, this additional potential can

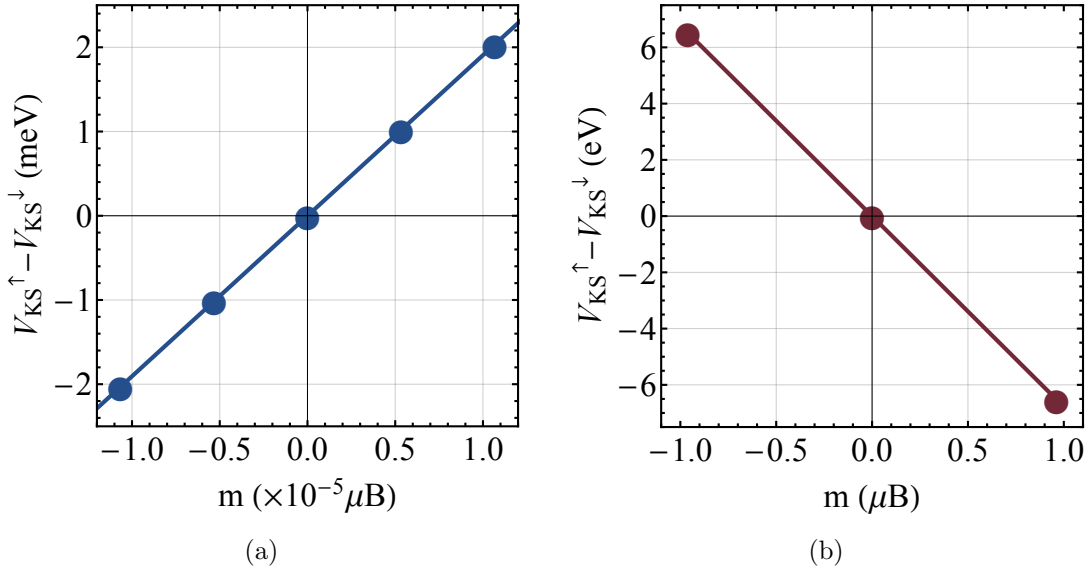


Figure VI.14: The stable and unstable magnetic potentials for H₂ at (a) 1 a₀ and (b) 4.8 a₀ bond-length illustrating the transition from a stable to an unstable equilibrium beyond the Coulson-Fischer point.

penalise the polarisation and therefore increase the slope of the magnetic potential with respect to magnetisation to ensure a stable equilibrium once more.

This proposed strategy likens to that of the incipient practice of calculating self-consistent Hubbard U parameters [396, 441, 504, 505], which has aided in providing an improved description of many systems. This method entails computing U_{out} values in a system for incremental values of an applied U_{in} until some pre-defined self-consistency condition has been met. The self-consistency procedure will therefore feature prominently in our attempt to effectively calculate the J parameter in dissociating H₂, and will be a central aspect of the following Chapter.

4.2 CALCULATING J FOR NiO AND Cr₂O₃

For now, let us revisit NiO and Cr₂O₃ and calculate the J term for these systems. At the start of this section, we outlined how to calculate J via magnetic perturbations of the form $\hat{V}_{\text{ext}}^{I\sigma} = \pm\beta\hat{P}^{I\sigma}$. However, for spin-polarised systems, we may also calculate J from the magnetic perturbations induced from the uniform perturbation $\hat{V}_{\text{ext}}^I = \alpha\hat{P}^I$, since nowhere in Eq. (VI.39) does β feature explicitly. In other words, while the uniform external potential will not yield the lowest-energy states consistent with a

given non-trivial magnetisation [502], the magnetisation induced can nonetheless be used as a proxy. This convenient workaround to evaluate J , from the same set of calculations we previously performed to determine U , approximates the result of the variational linear-response calculations we would otherwise have to perform.

NiO DFT+ U + J results

Using the same set of calculations from the previous section, we determined $J = 0.84 \pm 0.01$ eV and applied it in conjunction with $U = 6.7$ eV in the full DFT+ U + J functional in Eq. (V.24). In comparison to the previous DFT+ U calculation, the resulting band gap reduced slightly to 2.95 eV, while the magnetisation increased to 1.66 μB . We again refer the reader to the summary of results presented in Table VII.4.

In Fig. VI.15 we present the resulting DOS, where the combined $U + J$ treatment has increased the contribution of Hubbard states in the valence bands between -4 eV and -1.75 eV, which now feature as much as the O states. Moreover, there seems to be no qualitative difference in the conduction bands, however they have migrated upwards in energy, where the peak now lies at 4.87 eV above the Fermi energy. The profile of the dispersive s -states, meanwhile, seems relatively unaffected.

Cr₂O₃ DFT+ U + J results

Similarly, we calculated $J = 0.435 \pm 0.004$ eV and applied it with $U = 2.8$ eV from the same calculations in the DFT+ U + J functional. Here the band gap is 2.06 eV and the magnetic moment is 2.59 μB which only provides a marginal improvement in the latter compared to the DFT+ U results presented in Fig. VI.10.

We therefore conclude that the J -term computed in this alternative fashion, when implemented in the DFT+ U + J functional, does not produce any new qualitative features. In fact, the band gaps, magnetic moments and DOS profiles remained largely comparable between the different regimes. But without the relevant and experimental data, or the explicit evaluation of J from magnetic perturbations, it is difficult to precisely ascertain the difference. However, given that J is essentially free to compute from the U calculations, we maintain that there is still an advantage to

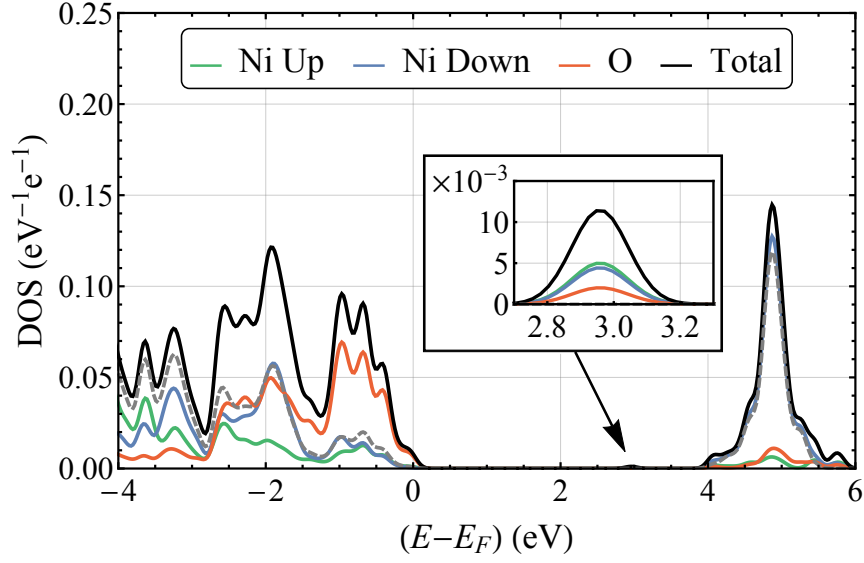


Figure VI.15: The species-resolved density-of-states of NiO for $U=6.7$ eV and $J=0.84$ eV. The lines depict the same as in Fig. VI.7. The J term has marginally decreased the band gap, and increased the magnetisation. The conduction bands, along with deep valence states, have migrated upwards in energy, where the peak now occurs at 4.87 eV, while the dispersive s -state remains unaffected.

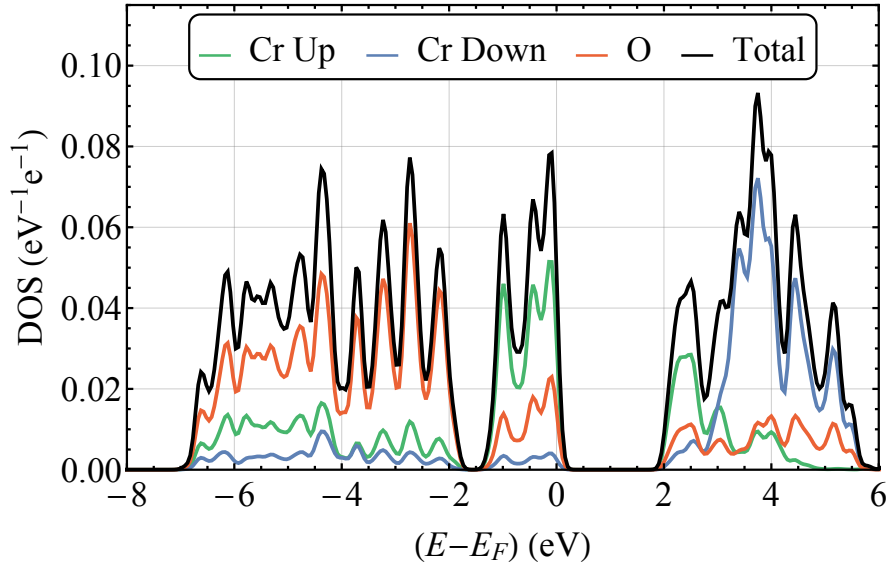


Figure VI.16: As in Fig. VI.10. The species-resolved DOS of Cr_2O_3 , calculated with $\text{LDA}+U = 2.8+J = 0.44$. There exists little discernible difference between these two regimes.

be gained from computing it, such as the knowledge of its approximate magnitude.

Finally, in Table VI.1, we present a summary of the results for Cr_2O_3 obtained in this and other studies, in comparison to experimental data.

Calculation	U (eV)	J (eV)	E_g (eV)	m (μB)
Experiment	-	-	2.1 ^[471]	2.76 ^[476]
Refs. [311, 485, 486, 486, 487]	5.0	1.0	2.6	3.01
Ref. [487–490]	3.3	0.1	2.9	2.9
Ref. [342]	4.0	0.58	2.88	3.26
LDA	0.0	0.0	1.27	2.30
LDA+ U	2.8	0.0	2.10	2.56
LDA+ $U+J$	2.8	0.44	2.06	2.59

Table VI.1: Summary of experimental and computational results of Cr_2O_3 , including band gap E_g (eV) and magnetic moment m (μB), and the U (eV), J (eV), where applicable.

5 CONCLUSION

In this Chapter, we developed a modification to the linear-response method for calculating the Hubbard U and Hund’s J parameters from a variational approach, such that it is equally applicable in direct-minimisation and SCF codes alike. We outlined the technical similarities and stated the key differences between the two methods, which amounted to the evaluation of the non-interacting response function from the ground-state density. The variational framework thus enables DFT+ U to be placed on a first-principles footing within the context of direct-minimisation DFT solvers. This prospect has important consequences for the calculation of DFT+ U total-energy differences featured in high-throughput calculations [506–510], phase diagrams [444, 447, 511], heterogeneous catalysis [512], thermodynamical properties [394, 399, 444–448, 513–515], and spin-triplet splittings [516–518].

We tested our method extensively on dissociating H_2^+ and successfully corrected the total-energy curve to remarkable accuracy, thereby demonstrating for the first time that DFT+ U is capable of correcting one-electron SIE under ideal conditions. We proceeded to calculate highly accurate U values for multi-electronic systems, $\text{Ni}(\text{CO})_4$, NiO , and Cr_2O_3 , with which we achieved broad agreement with experimental

measurements of the HOMO-LUMO and optical gaps, magnetic moments, and DOS profiles. For both NiO, and Cr₂O₃, we also successfully calculated a J term from the same set of calculations that produced a marginal difference. Finally, we compared our numerical results for Cr₂O₃, with high-resolution XPS, UPS and absorption measurements obtained from experimental colleagues, for which our calculations successfully reproduced the qualitative features.

The successful employment of our variational method in testing conventional and novel structures therefore demonstrates that it is versatile, robust and effective. It enables the reliable reproduction of both quantitative and qualitative features in solids and molecules that systemically suffer from many-body SIE.

However, we illustrated with dissociating H₂ that DFT+ U is an inappropriate correction scheme for systems dominated by SCE. We postulated, however, that a correction of the form presented by DFT+ J may be an adequate remedy. Unfortunately, this hypothesis could not be confirmed, since stable magnetic perturbations were intractable beyond the Coulson-Fischer point. We proposed a possible solution to this problem that consists of supplementing the subspace orbitals with a J_{in} correction in order to calculate a J_{out} . This goal, and the pursuit of a self-contained mechanism for performing thermodynamics within the DFT+ U framework, provides the motivation for the development of a self-consistency scheme, presented in the next Chapter.

VII

CALCULATION OF SELF-CONSISTENT HUBBARD PARAMETERS

IN THE PREVIOUS CHAPTER, we outlined the construction of a variational linear-response (LR) approach to calculate the Hubbard U and Hund's J parameters in linear-scaling DFT, with the added advantage that these quantities are computed as strict ground-state properties. To progress, it is our intention to now address the open question of the rigorous comparability of DFT+ U total-energies that are generated by calculations with different U values, which ordinarily represent external parameters with the same status as ionic positions. This question is of considerable contemporary relevance, as demonstrated by recent progress in calculating thermodynamic quantities [394, 399, 444–448, 513–515], in high-throughput materials informatics [506–510], catalysis [512, 519–522], and in the study of ion-migration in battery materials [410, 422, 423, 523–528] by means of DFT+ U .

Currently, the calculation of U as an external, albeit ground-state, parameter of the system does not uniquely determine a ground-state density and therefore prohibits the comparability of the resulting DFT+ U total-energies. If the U parameter is instead calculated as an implicit functional of the ground-state density $E[n(\mathbf{r}), U[n(\mathbf{r})]] \equiv E[n(\mathbf{r})]$, which can be uniquely defined, then DFT+ U as a whole becomes a fully self-contained, variational first-principles method. Only under the latter condition could we expect the fully rigorous direct comparability of the total-energies, and their derived thermodynamic observables, calculated from different DFT+ U calculations with different system-specific U parameters. As a result, any external parameters, such as ionic positions, may then be varied simultaneously with their corresponding first-principles U values.

In this Chapter, we argue that the self-consistent calculation of the U and J parameters as properties of the respective DFT+ U and DFT+ J ground-states may

be a solution toward this goal. Calculating Hubbard U parameters self-consistently in this fashion is a recent and rather esoteric practice, however its application bears significant theoretical and conceptual consequences in this context. Hence, we shall first give a brief outline of its operation.

In Ref [396], Kulik *et al.* first outlined the scheme for the self-consistent calculation of Hubbard U parameters that was later adopted by other works [441, 504, 505]. The motivation for this approach arose from the observation that, for certain systems, the nature of the electronic states (and response properties) in the DFT+ U ground-state differed qualitatively from those of the DFT ground-state [149, 354, 524], i.e., insulating vs metallic, thereby requiring a U that is consistent with the state in which it is applied.

In self-consistency schemes generally, incremental values of U_{in} are applied to the subspace at hand, with varying ground-state orbitals and densities as a result, and a new first-principles U_{out} is computed for each U_{in} . The numerical relationship $U_{\text{out}}(U_{\text{in}})$ is then used to select the self-consistent U , using a pre-defined criterion. Its conceptual implications aside, a self-consistent U has been shown to provide improvements in transition-metal chemistry [354, 440, 443, 529–534], biological systems [415], photovoltaics [535–537], and high-density energy storage [410].

While many practitioners have used the original, linear-extrapolation type U_{scf} in their studies [415, 440, 529, 531–538], others have used the equality between U_{in} and U_{out} as an alternative self-consistency condition [354, 410, 415, 441, 443, 539, 540]. The majority of published first-principles U calculations involve no self-consistency over the parameter at all, however, and there may even be a case to be made that none is ordinarily warranted. While approaching this concept from a different motivation and perspective, we find the resolution of this ambiguity, in itself, an intriguing open challenge in abstract DFT. In particular, it demands investigation in the present context of the variational linear-response U since, ideally, the optimal scheme to match that method should be established from the outset.

In this Chapter, we shall demonstrate that our variational approach provides a convenient framework in which to analyse a number of different self-consistency criteria that have been proposed, and address this partially-unresolved question. We

will again utilise H_2^+ as a model system, as we have repeatedly done so far, as it will allow us to study and draw firm conclusions regarding the numerous plausible, yet different, strategies currently in use for defining self-consistency over the Hubbard U . For the particular case of the variational LR Coulomb parameters at least, we identify a well-defined best choice of self-consistency criterion supported by numerical results. We will then extend this methodology to the treatment of multi-electronic systems, which, in the process, will necessitate the inclusion of a self-consistent J . We will then test a variety of possible multi-electronic self-consistency schemes with NiO, incorporating both U and J . As a final demonstration, we will use the self-consistent J , which is itself a relatively unexplored concept [540], as a means to correct the static-correlation error (SCE) beyond the Coulson-Fischer point in dissociating H_2 .

1 A NOTE ON THE DIRECT COMPARISON OF DFT+ U TOTAL-ENERGIES

Before we commence our analysis of parameter self-consistency, we would like to outline our argument in favour of adopting this approach for the purposes of comparing the ground-state total-energies of DFT+ U calculations.

The variational LR definition $U = dv_{\text{int}}/dN$, so-called as it is based on the variational response of the ground-state density, demands that the subspace-averaged non-interacting response $\chi_0 = dN/dv_{\text{KS}}$ is calculated using the same set of ground-state densities as that used for calculating the interacting response $\chi = dN/d\alpha$, which are parameterised by the external perturbation strength α . If we take the limit of small perturbations around the unperturbed KS ground-state density matrix $\hat{\rho}_0$, we may write

$$U_{\text{out}} = \chi_0^{-1} - \chi^{-1} = \left. \frac{dv_{\text{KS}}[\hat{\rho}]}{dN[\hat{\rho}]} \right|_{\hat{\rho}_0} - \left. \frac{dv_{\text{ext}}}{dN[\hat{\rho}]} \right|_{\hat{\rho}_0}. \quad (\text{VII.1})$$

From this, it is clear that $U_{\text{out}}[\hat{\rho}_0]$ is a ground-state density-functional, albeit not one of an explicit algebraic form. This illustrates why the comparability of DFT+ U total-energies, using a U determined from the unperturbed density, breaks down.

If we instead perform a variational LR calculation for a given U_{in} , it follows that the resulting U_{out} may be thought of as a functional of the ground-state density pa-

parameterised by U_{in} such that $U_{\text{out}} \equiv U_{\text{out}}[\hat{\rho}(U_{\text{in}})]$. If we can then uniquely determine a particular U'_{in} , by applying a self-consistency criterion, we will thereby uniquely determine the self-consistent ground-state DFT+ U density-matrix (up to unitary transformations) $\hat{\rho}_{\text{DFT}+U}(U'_{\text{in}})$. The same then can also be said for its derived properties, such as the total-energy, in terms of the remaining parameters, i.e., the ionic positions. In this respect, the DFT+ U ground-state energy is thus a functional of the DFT+ U ground-state density alone. The comparability then of total-energies between various crystallographic or molecular structures with differing self-consistent Hubbard U values directly follows, as does the validity of thermodynamic calculations based on DFT+ U .

In this way, given the underlying explicit algebraic XC functional, such as PBE, together with the choice of a set of subspaces to target for SIE correction, DFT+ U is elevated to the status of a self-contained orbital-dependent density-functional in its own right, which incorporates the Hubbard U as a non-algebraic but readily computable auxiliary ground-state variable. The task at hand is then to apply the correct self-consistency scheme to all relevant systems to facilitate their direct comparison.

2 A SELF-CONSISTENT U IN A ONE-ELECTRON MODEL

In order to compute a variational linear-response U_{out} for a single subspace already subject to a DFT+ U term of strength U_{in} , the subspace-averaged interaction potential V_{int} must incorporate the spin-dependent DFT+ U potential $\hat{V}_U^\sigma$ as well as the usual Hartree and exchange-correlation (XC) terms $\hat{V}_{\text{Hxc}}$. Furthermore, as described in Chapter VI, each component of the interaction potential V_{int} must be appropriately averaged. For the Hartree and XC potential, we saw that the appropriate average is simply

$$V_{\text{Hxc}} = \text{Tr}[\hat{V}_{\text{Hxc}}\hat{P}]/\text{Tr}[\hat{P}], \quad (\text{VII.2})$$

where the operator $\hat{V}_{\text{Hxc}}$ may approximately scale with N^σ but the averaging scheme does not. However, unlike $\hat{V}_{\text{Hxc}} \equiv \hat{V}_{\text{Hxc}}[n^\uparrow, n^\downarrow]$, which acts on one state but is generated by all occupied states, the DFT+ U potential, given by

$$\hat{V}_{U_{\text{in}}}^\sigma = \frac{U_{\text{in}}}{2}(\hat{1} - 2\hat{n}^\sigma) \quad (\text{VII.3})$$

is intrinsically both specific and due to each subspace occupancy matrix eigenvector individually. Thus, we find that the simple trace

$$V_{U_{\text{in}}}^\sigma = \text{Tr}[\hat{V}_{U_{\text{in}}}^\sigma] = \frac{U_{\text{in}}}{2}(\text{Tr}[\hat{P}] - 2N^\sigma) \quad (\text{VII.4})$$

is that which scales appropriately with N^σ (or equivalently N). Put another way, $V_{U_{\text{in}}}^\sigma$ is the average DFT+ U potential acting on a subspace eigenvector, since there are $\text{Tr}[\hat{P}]$ copies of that eigenvector, and is therefore scalable along with V_{Hxc} .

To first treat the test case of a one-electron system, it naturally follows that the interacting and Hubbard potentials depend on one spin channel only, such that $N = N^\sigma$ and $V_{U_{\text{in}}} = U_{\text{in}}(\text{Tr}[\hat{P}] - 2N)/2$. Then, starting from Eq. (VI.21), the single-site variational LR Hubbard U_{out} , in the presence of a non-zero U_{in} , may be written as

$$U_{\text{out}} = \frac{dV_{\text{int}}}{dN} = \frac{dV_{\text{Hxc}} + dV_{U_{\text{in}}}}{dN} = \frac{dV_{\text{Hxc}}}{dN} - U_{\text{in}} = F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}}) - U_{\text{in}},$$

where $F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}}) \equiv \frac{dV_{\text{Hxc}}}{dN}.$ (VII.5)

Here, the subspace-bare, bath-screened and subspace-averaged Hxc interaction $F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}}) \equiv F_{\text{int}}^{\sigma\sigma}$ is calculated at the fully-relaxed DFT+ U_{in} ground-state and specifically due, in this example, to like-spin interactions only.

From Eq. VII.5 we may now readily identify three unique self-consistency criteria. The first is a very plausible self-consistency criterion, first proposed in Ref. [441] and later utilised in Refs. [354, 410], which requires that

$$U_{\text{out}} = U_{\text{in}} \quad \text{giving} \quad U^{(1)} \equiv F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}})/2. \quad (\text{VII.6})$$

This U_{in} , denoted here as $U^{(1)}$, appears to account for, or cancel away, precisely one-half of the subspace SIE that remains at that DFT+ U_{in} and is represented by the triangle in Fig. VII.1. The second criterion, denoted by $U^{(2)}$, dictates that

$$U_{\text{out}} = 0 \quad \text{giving} \quad U^{(2)} \equiv F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}}), \quad (\text{VII.7})$$

and implies that U_{in} fully cancels the subspace-related SIE computed at the same DFT+ $_{\text{in}}$ ground-state. This is indicated by the diamond in Fig. VII.1.

Finally, the third condition, denoted by $U^{(3)} \equiv U_{\text{out}}(0)$ is one that matches the original self-consistency scheme [396] where it is denoted U_{scf} , albeit with a different underlying linear-response procedure. Here, the linear-extrapolation of $U_{\text{out}}(U_{\text{in}})$ (for sufficiently large U_{in} to obtain a good fit) is taken back to $U_{\text{in}} = 0$ eV, as shown in Fig. VII.1 by the circle.

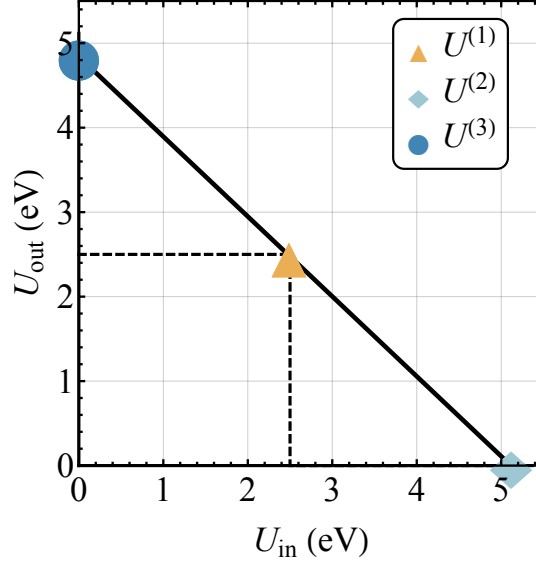


Figure VII.1: An illustration of a typical U_{in} vs U_{out} profile for H_2^+ , indicating each of the self-consistent criteria: $U^{(1)}$ (triangle), $U^{(2)}$ (diamond), and $U^{(1)}$ (circle). We find a highly-linear profile across all bond-lengths for this system and LR methodology.

For our present purposes, it is reasonable to assume that a DFT+ U corrected electronic structure has been well-obtained at $U^{(2)}$, and thus performing the linear extrapolation for $U^{(3)}$ around $U^{(2)}$, we find that

$$U^{(3)} \equiv U^{(2)} \left(1 - \left. \frac{dF_{\text{Hxc}}^{\hat{P}}}{dU_{\text{in}}} \right|_{U^{(2)}} \right). \quad (\text{VII.8})$$

From this, a clear interpretation of $U^{(3)}$ as screened version of $U^{(2)}$ emerges, in the sense that, instead of an externally applied potential being attenuated by relaxation of the electronic structure, it is the externally applied *interaction correction* which is attenuated.

A normal dielectric screening operator measures the rate of change of the potential with respect to an external perturbation, taking the form

$$\hat{\epsilon}^{-1} = \frac{d\hat{v}_{\text{KS}}}{d\hat{v}_{\text{ext}}} = \hat{1} + \hat{f}_{\text{Hxc}}\hat{\chi}. \quad (\text{VII.9})$$

A generalised screening function here instead measures the rate of reduction in the subspace-averaged SIE with respect to U_{in} , and is given by

$$\epsilon_U^{-1} = -\frac{dU_{\text{out}}}{dU_{\text{in}}} = 1 - \frac{dF_{\text{Hxc}}^{\hat{P}}}{dU_{\text{in}}} \quad (\text{VII.10})$$

Therefore, while we might expect a DFT+ U correction with parameter $U^{(2)}$ to cancel the subspace-averaged SIE, including all self-consistent response effects in the electronic structure, when we have done so we have in fact removed an SIE (with respect to DFT) of magnitude $U^{(3)} = \epsilon_U^{-1}U^{(2)}$, which is typically smaller in magnitude than $U^{(2)}$. In other words, there is a numerically relevant distinction between the external ‘bare’ U_{in} that we apply using DFT+ U , and the ‘screened’ SIE quantifier U_{out} that we then measure.

Moreover, we find the SIE measure $U^{(3)}$, calculated around the $U^{(2)}$ ground-state, of particular interest. For example, it may find use in quantifying the change in SIE in a subspace in response to an external parameter such as atomic position, or in comparing the SIE of an atom in two different charge states. We also expect $U^{(3)}$ to be suitable as an input Hubbard U parameter for non-self-consistent protocols such as in a post-processing DFT+ U_1+U_2 procedure, or DFT+ U band-structure correction based on the DFT density, or a DFT + dynamical mean-field theory (DMFT) calculation with no density self-consistency. The central message is that $U^{(3)}$ linearly accounts for the resistance to SIE reduction that *would* be met were density self-consistency in response to U allowed.

On the basis of the above analysis, however, we surmise that the criterion presented by $U^{(2)}$ represents the appropriate self-consistency scheme for the variational linear-response method, wherever the standard self-consistent response of the density occurs upon application of DFT+ U . Furthermore, the value of $U^{(2)}$ may be efficiently obtained, for example via the bisection method. The three self-consistency conditions discussed heretofore are summarised graphically in Fig. VII.1 above, and Table VII.1.

2.1 WHICH SELF-CONSISTENCY SCHEME?: REVISITING H_2^+

In order to assess each of the self-consistency conditions outlined in Table VII.1, and select the appropriate scheme we applied them to dissociating H_2^+ . For each bond-

Notation	Condition	Formula derived from Eq. VII.5
$U^{(1)}$	$U_{\text{out}} = U_{\text{in}}$	$U_{\text{in}} = F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}})/2$
$U^{(2)}$	$U_{\text{out}} = 0$	$U_{\text{in}} = F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}})$
$U^{(3)}$	$U_{\text{out}}(0)$	$U_{\text{out}}(0) = U^{(2)}(1 - dF_{\text{Hxc}}^{\hat{P}}/dU_{\text{in}} _{U^{(2)}})$

Table VII.1: Summary of three first-principles Hubbard U self-consistency criteria derived from Eq. VII.5.

length, a U_{in} versus U_{out} profile was calculated according to Eq. VII.5, an example of which is illustrated by Fig VII.1, with due care to error accumulation. These profiles were found to remain highly linear across all bond-lengths for this particular system and LR methodology, and we note that the slope remained greater than -1 throughout, signifying $dF_{\text{Hxc}}^{\hat{P}}/dU_{\text{in}} > 0$ and a ‘resistance’ to SIE reduction, for all but the shortest bond-lengths ($\lesssim 1.3 a_0$) strongly affected by subspace double-counting.

The linear fit to $U_{\text{out}}(U_{\text{in}})$ was then used to evaluate $U^{(1)}$, $U^{(2)}$, $U^{(3)}$, according to Table VII.1, and their values are depicted by dashed, dotted and dot-dashed lines, respectively, in Fig. VII.2. For each bond-length, we also estimated, by interpolation, the U_{int} (solid line) required to recover the exact total-energy.

The $U^{(2)}$ and $U^{(3)}$ schemes, and particularly the former, closely approximate the U_{int} required to correct the SIE in the total-energy in the dissociated limit, whereas $U^{(1)}$ clearly represents an underestimation by a factor of 2, as suggested by Table VII.1. The numerical situation is reversed within the equilibrium bond-length of approximately $2 a_0$, where $U^{(1)}$ appears to perform better than the alternatives. We emphasise that the latter result is misleading, however, since $U^{(1)}$ performs better at short bond-lengths only due to the serendipitous cancellation of its reduced magnitude with the double-counting effects of spatially overlapping DFT+ U subspaces. Notwithstanding, the breakdown of the subspace-bath separation underpinning DFT+ U takes place in the strong-bonding regime. This finding highlights a risk when assessing the relative merits of correction formulae of this kind solely on the basis of numerical results gathered under equilibrium conditions, where bonding or overlap effects complicate the analysis.

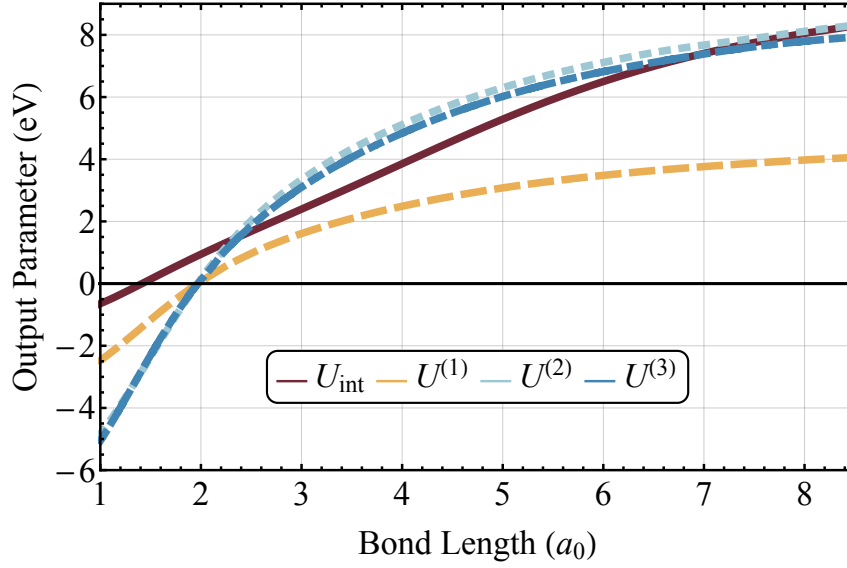


Figure VII.2: The estimated best U value, U_{int} (solid), for correcting the total-energy SIE in H_2^+ , shown with the $U^{(1)}$ (dashed), $U^{(2)}$ (dotted), and $U^{(3)}$ (dot-dashed) values. $U^{(2)}$ and $U^{(3)}$ approximately equal U_{int} in the dissociation limit, while $U^{(1)}$ is serendipitously more successful at equilibrium and below due to subspace overlap and double-counting.

PBE+ U_{out} total-energies

The total-energy based binding curves of H_2^+ were recalculated using the bond-length dependent $U^{(1)}$ (dashed), $U^{(2)}$ (dotted), and $U^{(3)}$ (dot-dashed), for comparison with the exact total-energy (solid) in Fig. VII.3.

As already suggested by Fig. VII.2, $U^{(1)}$ fails to correct the SIE in the total-energy at bond-lengths further from equilibrium, whereas $U^{(2)}$ and $U^{(3)}$ provide a more universal correction of the total-energy, becoming acceptable in the dissociation limit. The inset of Fig. VII.3 illustrates, however, that the PBE+ $U^{(3)}$ scheme, which is numerically equivalent to no Hubbard U self-consistency in this particular system, begins to under-perform with respect to PBE+ $U^{(2)}$ in the dissociated limit. The PBE+ $U^{(2)}$ total-energy, meanwhile, seems to converge upon the exact total-energy asymptotically. Our results confirm that DFT+ U is capable of precisely correcting the total-energy SIE of a one-electron system under ideal population-analysis conditions but especially, it seems, when using the appropriate self-consistency scheme, $U^{(2)}$. It is

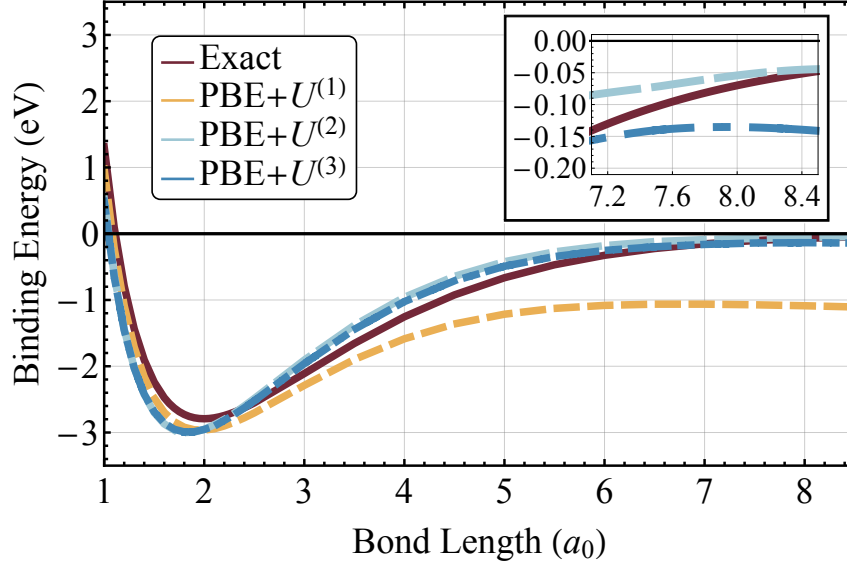


Figure VII.3: The H_2^+ binding curves of the exact functional (solid), $\text{PBE}+U^{(1)}$ (dashed), $\text{PBE}+U^{(2)}$ (dotted), and $\text{PBE}+U^{(3)}$ (dot-dashed). The reference energy for each curve is that of the isolated H atom calculated with the corresponding XC functional. In the dissociated limit (inset), the $U^{(2)}$ result tends asymptotically to the exact one, and the $U^{(3)}$ scheme begins to deviate from it non-negligibly.

clear then, that DFT+ U is an efficient and effective corrector for the SIE manifested in the total-energy, as discussed in detail in Refs. [395, 396, 440].

Binding Curve Parameters

In order to further quantify the results of the various Hubbard U self-consistency schemes tested, and draw attention to the importance of population analysis in the dissociation limit, we determined the equilibrium bond-length R_e , dissociation energy E_D , harmonic frequency ω_e and anharmonicity $\omega_e\chi_e$, corresponding to each, as shown in Table. VII.2, by fitting a polynomial about the energy minima. Compared to the experimental data of Ref. [420], the exact calculations perform very well in determining the bond-length and harmonicity in particular with errors that reflect the inaccuracies due to our fitting scheme, finite computational basis set size, core pseudisation, and absent physical effects, as well as experimental factors.

The PBE functional, meanwhile, overestimates the equilibrium bond-length and dissociation energy, and underestimates the harmonic frequency and anharmonicity.

	R_e	E_D	ω_e	$\omega_e\chi_e$
Experiment [420]	1.988	2.6508	2321.7	66.2
Exact	1.997	2.7922	2323.6	59.9
PBE	2.138	2.9893	1912.0	37.9
PBE+ $U^{(1)}$	1.963	2.957(3)	2346(6)	57.7(3)
PBE+ $U^{(2)}$	1.827	2.990(3)	2799(5)	81.2(4)
PBE+ $U^{(3)}$	1.845	2.985(9)	2721(9)	76.9(7)
PBE+ $U_1 + U_2$	1.829	2.990(2)	2810(3)	81.8(6)

Table VII.2: Equilibrium bond-lengths R_e (bohr), dissociation energy E_D (eV), harmonic frequencies ω_e (cm^{-1}), and anharmonicities $\omega_e\chi_e$ (cm^{-1}) for each calculation scheme tested, for comparison with experimental values [420].

In order to ensure a complete comparison between all methods explored in this dissertation we have also included the generalised DFT+ U_1+U_2 functional¹ which is defined in Chapter VIII.

The various DFT+ U schemes tested generally preserve the PBE dissociation energy but they underestimate the equilibrium bond-length and overestimate the frequency and anharmonicity. The DFT+ $U^{(2)}$, DFT+ $U^{(3)}$ and DFT+ U_1+U_2 schemes, in particular are found to over-correct the latter three quantities and predict the experimental data as poorly as the uncorrected PBE, albeit in the opposite direction. We attribute this to imperfect DFT+ U population analysis at shorter bond-lengths, featuring both double-counting across the two subspaces and spillage, as well as the breakdown of the subspace-bath separation. The double-counting, in particular is not properly compensated by the self-consistently calculated U parameters, since the formula for U_{out} does not take orbital overlap into account. Conversely, the $U^{(1)}$ scheme performs well around equilibrium, as reflected also in Fig. VII.2, and approximately recovers the exact bond-length, harmonic frequency and anharmonicity. We again emphasise that this fortuitous outcome is due entirely to the $U^{(1)}$ parameter simply being smaller by a factor of two by definition, so that the over-correction due to double-counting is approximately halved. It therefore coincides with the exact

¹Here we have determined U_1 and U_2 by setting $U = U^{(2)}$ in Eq. (VIII.35)

regime serendipitously, rather than by deliberate design.

It is therefore clear that while the $U^{(2)}$ scheme is the one that correctly eliminates SIE in the one-electron system, for our variational linear-response definition of the Hubbard U , this choice hinges on the correct population analysis of the subspace at hand, as well as the assumption of a weak subspace-bath interaction, neither of which are met at the equilibrium bond-length of H_2^+ .

3 COUPLED SELF-CONSISTENT PARAMETERS IN MULTI-ELECTRONIC SYSTEMS

In spite of the simplicity of the self-consistent Hubbard U formulation for a one-electron system, this particular formula is not expected to apply in general. We are therefore obliged to derive the self-consistency formula again for multi-electronic systems, including those that are open-shell. Nonetheless, the correct self-consistency condition that we previously identified, i.e., that which completely removes the SIE subject to the standard self-consistent response of the density $U^{(2)}$, remains valid since the $+U$ correction still applies to one electron at a time. However, we must now consider a potential constructed from both spins.

To begin constructing this generalisation, let us revisit the spin-resolved expression for U in Eq (VI.22), including the spin-dependent Hubbard potentials $V_{U_{\text{in}}}^\sigma$. Thus, by performing the same procedure as before, we may compute the self-consistent Hubbard U for a multi-electronic system as follows

$$\begin{aligned}
 U_{\text{out}} &= \frac{1}{2} \left(\frac{dV_{\text{int}}^\uparrow}{dN} + \frac{dV_{\text{int}}^\downarrow}{dN} + \frac{dV_{U_{\text{in}}}^\uparrow}{dN} + \frac{dV_{U_{\text{in}}}^\downarrow}{dN} \right) \\
 &= \frac{1}{2} \left(\frac{dV_{\text{int}}^\uparrow}{dN} + \frac{dV_{\text{int}}^\downarrow}{dN} \right) - \frac{U_{\text{in}}}{2} \left(\frac{dN^\uparrow}{dN} + \frac{dN^\downarrow}{dN} \right) \\
 &= F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}}) - \frac{U_{\text{in}}}{2}.
 \end{aligned} \tag{VII.11}$$

In this expression, the subspace-averaged Hxc interaction $F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}})$, as defined in Eq. (VI.22), is now an implicit function of U_{in} . However, according to this self-consistency formula, the condition needed to completely remove the total subspace

SIE, i.e. that for which $U_{\text{out}} = 0$, now double-counts the total average interactions

$$U_{\text{in}} = 2F_{\text{Hxc}}^{\hat{P}} = \frac{1}{2} \left(F_{\text{int}}^{\uparrow\uparrow} + F_{\text{int}}^{\uparrow\downarrow} + F_{\text{int}}^{\downarrow\downarrow} + F_{\text{int}}^{\downarrow\uparrow} \right). \quad (\text{VII.12})$$

This result seems to suggest that the self-consistency scheme that completely removes the SIE for a multi-electronic system is therefore $U^{(1)} \equiv U_{\text{in}} = U_{\text{out}}$, which would introduce the required factor of one-half in order to re-scale the interaction. Indeed, this choice seems entirely reasonable and seems to have been the basis for the self-consistent criteria used in multiple studies [354, 410, 415, 441, 443, 539]. We argue, however, that this choice is incorrect, not only because it directly contradicts the more physically intuitive result derived in the previous section, but also because the expression for U_{out} now contains a mix of like and unlike-spin interactions (that were naturally absent from the one-electron case). Hence, in a multi-electronic system, the unlike-spin interactions are likely to be of a similar magnitude as the like-spin interactions and thus have an equal, but unwanted, effect. Moreover, the former do not feature at all in standard DFT+ U .

Moreover, as outlined in discussing around Eq. (VI.42), a more natural formulation of U , that is to say, consistent with its implementation in the DFT+ U functional, is one comprised of like-spin interactions only, i.e., $U_{\text{eff}} \sim F^{\sigma\sigma}$. It is therefore clear that we will need to consider interactions derived from the exchange parameter J in the context of a full, generalised DFT + U + J formulation [149, 337, 354, 391, 458, 467, 468], in order to fully account for the multi-electronic self-consistent calculation of U , and vice versa. In other words, the missing ingredient to reconnect the one-electron self-consistent condition with the multi-electronic one, is the explicit consideration of a J_{in} term.

3.1 GENERALISED, SELF-CONSISTENT U AND J FORMULAE

If we wish to construct a generalised self-consistency formula for U we must also consider potentials coupling unlike-spin density matrices $\langle \hat{n}^{\sigma} \hat{n}^{\bar{\sigma}} \rangle$, according to the

following, reduced DFT+ U + J correction functional

$$E_{U+J}[\{n^{I\sigma}\}] = \sum_{I\sigma} \left\{ \frac{U^I}{2} \text{Tr}[\hat{n}^{I\sigma} - \hat{n}^{I\sigma} \hat{n}^{I\sigma}] + \frac{J^I}{2} \text{Tr}[\hat{n}^{I\sigma} \hat{n}^{I\bar{\sigma}}] \right\}$$

where $\hat{V}_J^\sigma = \frac{\delta E_J}{\delta \hat{n}^{I\sigma}} = J^I \hat{n}^{I\bar{\sigma}}.$ (VII.13)

We have arranged this functional intentionally so that U only corresponds to interactions between density matrices of the same spin, i.e., U_{eff} , and J corresponds to interactions of opposite spin².

Now, returning to Eq. (VII.11), we may re-derive the self-consistency formula for a single-site model including contributions from $V_{J_{\text{in}}}^\sigma$

$$\begin{aligned} U_{\text{out}} &= \frac{1}{2} \left(\frac{dV_{\text{int}}^\uparrow}{dN} + \frac{dV_{\text{int}}^\downarrow}{dN} + \frac{dV_{U_{\text{in}}}^\uparrow}{dN} + \frac{dV_{U_{\text{in}}}^\downarrow}{dN} + \frac{dV_{J_{\text{in}}}^\uparrow}{dN} + \frac{dV_{J_{\text{in}}}^\downarrow}{dN} \right) \\ &= \frac{1}{2} \left(\frac{dV_{\text{int}}^\uparrow}{dN} + \frac{dV_{\text{int}}^\downarrow}{dN} \right) - \frac{U_{\text{in}}}{2} \left(\frac{dN^\uparrow}{dN} + \frac{dN^\downarrow}{dN} \right) + \frac{J_{\text{in}}}{2} \left(\frac{dN^\uparrow}{dN} + \frac{dN^\downarrow}{dN} \right) \\ &= F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}}, J_{\text{in}}) - \frac{U_{\text{in}}}{2} + \frac{J_{\text{in}}}{2}. \end{aligned} \quad (\text{VII.14})$$

It is then clear that the calculation of U_{out} depends non-trivially on the applied J_{in} , and naturally reduces to Eq. (VII.11) when the latter is set to zero. However, the interaction kernel F_{Hxc} is still the subspace average of *all* Coulomb and XC interactions, as it was in Eq. (VI.22), and so we are no closer to acquiring like-spin only interactions with this formulation alone. To proceed, we must calculate the corresponding self-consistency equation for J_{out} , while considering an applied U_{in} , which will comprise the interaction kernel F_J , defined in Eq. (VI.40). We therefore proceed as follows

$$\begin{aligned} J_{\text{out}} &= -\frac{1}{2} \left(\frac{dV_{\text{int}}^\uparrow}{dM} - \frac{dV_{\text{int}}^\downarrow}{dM} + \frac{dV_{U_{\text{in}}}^\uparrow}{dM} - \frac{dV_{U_{\text{in}}}^\downarrow}{dM} + \frac{dV_{J_{\text{in}}}^\uparrow}{dM} - \frac{dV_{J_{\text{in}}}^\downarrow}{dM} \right) \\ &= -\frac{1}{2} \left(\frac{dV_{\text{int}}^\uparrow}{dM} - \frac{dV_{\text{int}}^\downarrow}{dM} \right) + \frac{U_{\text{in}}}{2} \left(\frac{dN^\uparrow}{dM} - \frac{dN^\downarrow}{dM} \right) + \frac{J_{\text{in}}}{2} \left(\frac{dN^\uparrow}{dM} - \frac{dN^\downarrow}{dM} \right) \\ &= F_J^{\hat{P}}(U_{\text{in}}, J_{\text{in}}) + \frac{U_{\text{in}}}{2} + \frac{J_{\text{in}}}{2}. \end{aligned} \quad (\text{VII.15})$$

²An alternative derivation of the following using the original DFT+ U + J functional in Eq. (V.24) is presented in Appendix C.

We have now constructed a pair of coupled equations expressing U_{out} and J_{out} in terms of the applied parameters U_{in} and J_{in} , and the intrinsic interaction kernels F_{Hxc} and F_J . Computing the linear combinations of Eqs. (VII.14) & (VII.15) thus decouples the expressions and yields a set the effective Coulomb parameters in terms of the respective input parameters

$$\begin{aligned} U_{\text{eff}} &= U_{\text{out}} - J_{\text{out}} = (F_{\text{Hxc}} - F_J) - U_{\text{in}} \\ J_{\text{eff}} &= U_{\text{out}} + J_{\text{out}} = (F_{\text{Hxc}} + F_J) + J_{\text{in}}. \end{aligned} \quad (\text{VII.16})$$

We may now invoke the self-consistency condition previously identified to completely remove the one-site interaction error, i.e., $U_{\text{eff}} = 0$, such that the input parameters corresponding to this condition pertains to like-spin interactions only, as desired,

$$U_{\text{in}} = (F_{\text{Hxc}} - F_J) = \frac{1}{2} (F^{\uparrow\uparrow} + F^{\downarrow\downarrow}) \quad (\text{VII.17})$$

. If we operate under the assumption that the same self-consistency condition will apply to J then we arrive at a similar formula related to the correction of interactions between un-like spins

$$J_{\text{in}} = -(F_{\text{Hxc}} + F_J) = -\frac{1}{2} (F^{\uparrow\downarrow} + F^{\downarrow\uparrow}). \quad (\text{VII.18})$$

Hence, in the multi-electronic formulation, subject to the correction functional presented in Eq. (VII.13), we predict that a combined self-consistency condition applied to both U_{in} and J_{in} may become satisfied

$$U_{\text{eff}}(U_{\text{in}}, J_{\text{in}}) = J_{\text{eff}}(U_{\text{in}}, J_{\text{in}}) = 0 \quad (\text{VII.19})$$

and are precisely those that relate to the interactions we wish to address.

We have now resolved the question we posed at the close of Chapter VI. The application of U_{in} serves, as we have already seen, to decrease the computed U_{out} by mitigating the delocalisation and reducing the spurious electronic curvature. This leads to a convenient linear relationship between the two that forms the basis and motivation for the self-consistency regime. Incidentally, U_{in} has the opposite effect on J_{out} and increases the resulting magnetic responses. This makes sense if we recall

that U_{in} enforces localisation of both spin-channels, such that the energy cost of perturbing either increases as the electron response stiffens and, thus, the curvature with respect to magnetisation increases.

Meanwhile, J_{in} increases both the computed U_{out} and J_{out} for similar reasons. The J term encourages polarisation, thereby promoting same-spin charge to occupy the same region, which increases the self-interaction error and hence the magnitude of U_{out} . Similarly, J is related to the negative of the energy with respect to magnetisation (c.f. Eq. (VI.33)) and so a positive J will only exacerbate that curvature and increase the calculated J_{out} .

Finally, we can speculate why the self-consistency condition of $U_{\text{in}} = U_{\text{out}}$, chosen in Refs. [354, 410, 415, 441, 443, 539], produces a U_{out} of the correct magnitude but for the wrong reason. In these multi-electronic systems there is no self-consistent treatment of the exchange term. As such, the calculated U_{out} , or the average on-site interaction, is likely over-estimated by an approximate factor of two [410, 415], which explains $U_{\text{out}} = U_{\text{in}}$ as the suggested self-consistency condition.

The method presented here, on the other hand, provides a complete picture of the underlying interactions by explicitly incorporating the J -term. Moreover, the interaction terms, to which the U and J parameters correspond, are revealed to be consistent with their intended application in the DFT+ U + J functional. We shall now describe extensive numerical calculations on NiO, which showcase all plausible combinations of self-consistent U and J , to illustrate that our derived scheme is indeed correct.

3.2 APPLICATION TO NiO

Presented in Fig. VII.4 are the calculated profiles of U_{in} vs U_{out} (solid), U_{in} vs J_{out} (dashed), and corresponding U_{in} vs U_{eff} (dotted), where each exhibits a strongly linear behaviour. For U_{out} we calculate a slope = $-0.64(2)$, and for J_{out} we get a slope = $0.486(4)$, for which the resulting profile for $U_{\text{eff}} = U_{\text{out}} - J_{\text{out}}$ has a slope of $-1.12(2)$.

The derived values for U for each self-consistency condition, along with the associated J_{out} and interaction kernel F_J at the corresponding U_{in} , are presented in the

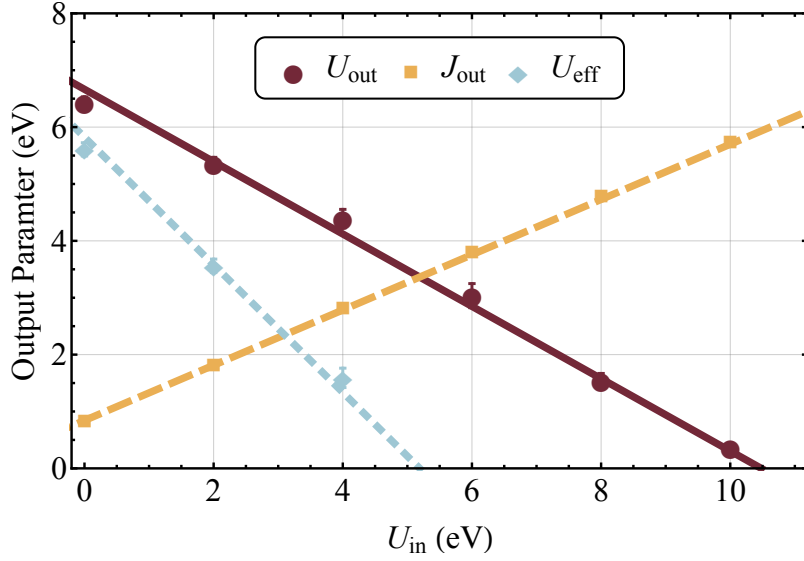


Figure VII.4: Curves, with accompanied error bars, for U_{out} (solid), J_{out} (dashed), and U_{eff} (dot-dashed), with respect to the applied U_{in} for NiO. From the linear fits we compute $U^{(1)} = 4.1(1)$ eV, $U^{(2)} = 10.5(5)$ eV, $U^{(3)} = 6.7(1)$ eV, with $J_{\text{out}} = 5.93(7)$ eV at $U_{\text{in}} = 10.5$ eV.

left hand side of Table VII.3. In the right hand side of Table VII.3, we present the same values for the self-consistency conditions applied to U_{eff} curve.

Condition	U (eV)	J_{out} (eV)	F_J (eV)	U_{eff} (eV)	J_{out} (eV)	F_J (eV)
$U^{(1)}$	4.1(1)	2.82(4)	0.78(4)	2.7(1)	2.17(4)	0.80(4)
$U^{(2)}$	10.5(5)	5.93(7)	0.69(7)	5.2(2)	3.36(6)	0.77(7)
$U^{(3)}$	6.7(1)	0.84(3)	0.84(3)	5.8(1)	0.84(3)	0.84(3)

Table VII.3: The values determined from U_{out} (left) for each self-consistency scheme applied to NiO with the corresponding J_{out} and interaction kernel F_J . On the right hand side are the same conditions applied to the U_{eff} curve.

The calculated values for $U^{(1)}$ and $U^{(3)}$ here seem quite reasonable and fall in range of the values calculated in other studies [337, 342, 458, 467, 468]. This lends credence to the selection of one of these values as a self-consistency scheme in absence of the arguments made in the previous section. In comparison, the value of $U^{(2)}$ is much larger than the necessary correction, which, in isolation, over-corrects the SIE by double-counting the average subspace interaction.

Meanwhile, the corresponding J_{out} values span a relatively large range for the U_{in} . For instance, the J_{out} related to $U^{(1)}$ and $U^{(3)}$ seem quite plausible, and are very similar to previous values [337, 458, 467, 468], but the J_{out} for $U^{(2)}$ is certainly much too large. Since J_{out} scales linearly with the applied U_{in} (c.f. Eq. (VII.15)) it may be more appropriate to pair the U_{out} values with the corresponding interaction terms F_J , plotted in Fig. VII.5, which are all < 1 eV. Moreover, we will also consider the effective $U - J$ curve acquired from the pairs of U, J that arise from each self-consistency point on the U_{out} curve.

We emphasise, however, that these are not necessarily the same values that arise from the self-consistency conditions applied to the U_{eff} curve itself. Applying the self-consistency schemes to the U_{eff} curve yields different values, which also all seem very plausible. However, in this analysis, we will restrict our investigation to $U_{\text{eff}}^{(2)}$. Finally, we shall pair $U_{\text{eff}}^{(2)}$ with the corresponding J_{out} and F_J , where these parameters will be applied explicitly to unlike spin interactions.

From the data in Fig. VII.4, we may also derive the corresponding interaction kernels F_{Hxc} (circles) and F_J (squares), and the average of the like-spin and unlike-spin interactions $F^{\sigma\sigma}$ (up triangles) and $F^{\sigma\bar{\sigma}}$ (down triangles), which are presented in Fig. VII.5. We see here that the largest interactions occur between un-like spins $F^{\sigma\bar{\sigma}}$, which diminish from 7.5 eV to 6 eV over the range of U_{in} . This is similar in magnitude to $F^{\sigma\sigma}$, as we earlier predicted, which takes values between 6 eV to 4.5 eV over the same range. The average of the two returns the interaction kernel F_{Hxc} , which then varies from 6.5 eV to 5 eV and corresponds to the U values in Table VII.4 that give the best agreement with experiment according to Fig. VII.6.

Consequently, half the difference between $F^{\sigma\bar{\sigma}}$ and $F^{\sigma\sigma}$ yields F_J , which is much smaller by comparison (≈ 0.7 eV), but compares well to J determined in other works (see Table VII.4) but particularly with cRPA [504, 540–544]. It changes very little with respect to U_{in} , between 0.8-0.6 eV, and is of the correct order of exchange parameters typically used in spin-exchange correction (see Table VII.4).

Finally, we observe that the slopes for F_{Hxc} , $F^{\sigma\sigma}$ and $F^{\sigma\bar{\sigma}}$ are approximately equal and are calculated to be ≈ -0.14 . This corresponds to very little variation in these interactions, no more than ≈ 1.5 eV, over a range of 10 eV for U_{in} and indicates a

high resistance to SIE correction.

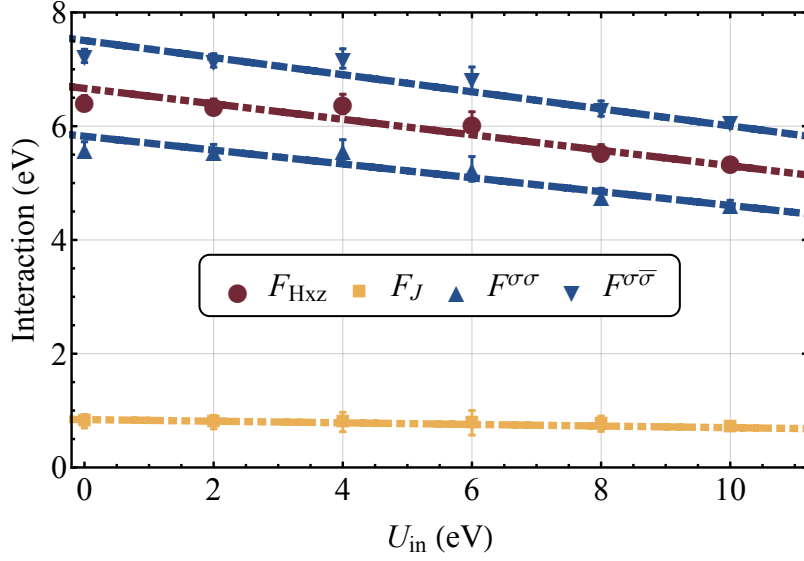


Figure VII.5: Curves, with accompanied error bars, for the interaction kernels F_{Hxz} (circles) and F_J (squares), as well as the average like and unlike-spin interactions $F^{\sigma\sigma}$ (up triangles) and $F^{\sigma\bar{\sigma}}$ (down triangles), with respect to the applied U_{in} for NiO.

We performed each calculation from the selection presented above, in which the applied U and J parameters are those that feature in the original DFT+ U + J functional in Eq. (V.24). Values from the U_{eff} curve, however, along with the accompanying J or F_J , are used instead in the modified DFT+ U + J functional in Eq. (VII.13) since the $U - J$ scaling has already taken place³.

In the following section, we discuss a subset of these calculations in detail and present the associated DOS plots⁴. In particular we compare the $p - s$ band gap E_{p-s} , the $p - d$ transition energy E_{p-d} (quantified by the position of the peak in the conduction band), and the magnetic moment m to the experimental measurements. The remaining DOS plots are available in Appendix C.

We also compute the total normalised root-mean-square (NRMS) error of these results compared to the experimental values, and rank the schemes based on this overall metric in Fig. VII.6. Here, the shaded regions denote approximate margins of error, which for E_{p-s} and E_{p-d} is taken to be ± 0.5 eV, and for the magnetic mo-

³Equivalently, one could use Eq. (V.24) with parameters $(U_{\text{eff}} + J)$ and J .

⁴There are some redundancies, however, e.g., $U^{(3)} + J^{(3)} = U^{(3)} + F_J^{(3)}$, and $(U - J)^{(3)} = U_{\text{eff}}^{(3)}$.

ment the boundary is represented by the two experimental values. A comprehensive summary of the results is presented (not in order of performance) in Table VII.4, in which we have highlighted the five schemes with the best overall agreement in bold font.

Calculation	U (eV)	J (eV)	E_{p-s} (eV)	E_{p-d} (eV)	m (μB)
Experiments [456, 457, 459–461, 465]	-	-	3.1	4.3	1.64-1.9
Refs. [337, 467, 468]	8.0	0.95	3.1-3.4	-	1.56-1.74
Ref. [458]	5.0	0.95	2.8	-	1.73
Ref. [342]	4.6	0.0	2.7	-	1.7
PBE	0.0	0.0	1.66	2.27	1.37
PBE + $U^{(1)}$	4.1	0.0	2.96	3.65	1.53
PBE+ $U^{(2)}$	10.5	0.0	3.06	5.84	1.73
PBE + $U^{(3)}$	6.7	0.0	3.05	4.44	1.62
PBE+ $U^{(1)}+J^{(1)}$	4.1	2.82	1.52	3.67	1.68
PBE+ $U^{(2)}+J^{(2)}$	10.5	5.9	0.63	6.87	1.86
PBE+ $U^{(3)}+J^{(3)}$	6.7	0.84	2.95	4.87	1.66
PBE + $U^{(1)}+F_J^{(1)}$	4.1	0.78	2.86	3.97	1.58
PBE+ $U^{(2)}+F_J^{(2)}$	10.5	0.69	3.01	6.22	1.75
PBE+ $(U-J)^{(1)}$	1.3	0	2.17	2.78	1.43
PBE+ $(U-J)^{(2)}$	4.6	0	2.99	3.80	1.54
PBE + $(U-J)^{(3)}$	5.9	0	3.01	4.19	1.59
PBE + $U_{\text{eff}}^{(2)}$	5.2	0	3.01	3.97	1.57
PBE+ $U_{\text{eff}}^{(2)}+J_{\text{eff}}^{(2)}$	5.2	3.48	2.55	6.66	1.80
PBE+ $U_{\text{eff}}^{(2)}+f_{J,\text{eff}}^{(2)}$	5.2	0.84	2.94	4.63	1.64

Table VII.4: Summary of DFT+ $U+J$ parameters for NiO, from this work and similar studies, such as the U (eV), J (eV), $p-s$ band gap E_{p-s} (eV), $p-d$ transition energy E_{p-d} (eV), and magnetic moment m (μB) compared to experimental data. The five schemes with the best overall agreement with experiment are given in bold.

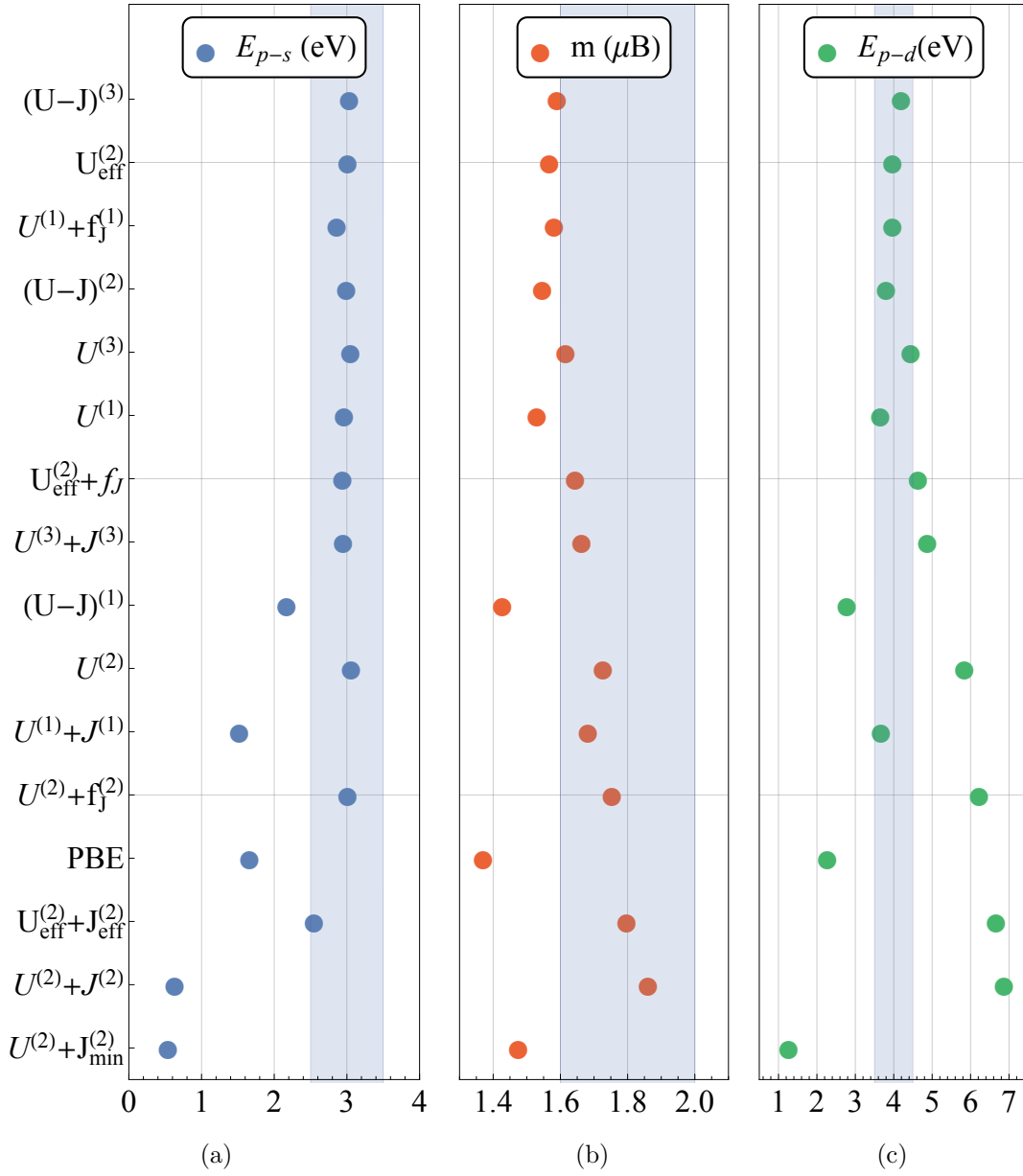


Figure VII.6: Ranking of all self-consistency schemes according to the total normalised root-mean-square error with respect to the experimental measurements for E_{p-s} (eV), m (μB), and E_{p-d} (eV). Shaded regions denote approximate margins of error, which is given by ± 0.5 eV for E_{p-s} and E_{p-d} , and by the experimental values for m .

3.3 COMPARISON OF SELF-CONSISTENCY SCHEMES

Before delving into the calculation details, let us examine the broader performance of the schemes against each other, as depicted in Fig. VII.6, with regards to replicating the experimental results. Here, the shaded regions illustrate heuristic (and ultimately arbitrary) margins of error for the experimental values, which are 3 ± 0.5 eV for the $p-s$ band gap and 4 ± 0.5 eV for the $p-d$ transition energy. The shaded region for the magnetic moment, meanwhile, is bounded by the experimental values 1.64 [456] μB and 1.9 [457] μB , respectively⁵. We find that the band gap is the easiest to reproduce since it is the result of a dispersive s state, which is unperturbed (ignoring screening effects) by DFT+ U + J potentials. In contrast, the magnetic moment is the most difficult and requires large U or J to attain at the expense of the other two properties, which is most often E_{p-d} . In general, we can produce two of the three properties within the error bars⁶.

We find the best eight calculations provide very good agreement with experiment. In fact, all of these calculations invoke U values in the range 4.1 eV to 6.7 eV (which, as we have seen, is the approximate range spanned by $F^{\sigma\sigma}$) and only a small J , if any.

The next four calculations, between $(U - J)^{(1)}$ and $U^{(2)} + F_J^{(2)}$, quickly deteriorate in accuracy. In these instances, the results are poor because a U is applied that is either too small, as is the case for $(U - J)^{(1)}$ and $U^{(1)} + J^{(1)}$, which underestimates the band gap, or too large, i.e., $U^{(2)}$, which pushes the conduction band peak too high in energy.

The next best is the PBE calculation, which underestimates all three quantities significantly yet, surprisingly, is not at the bottom of the list. Indeed, the worst calculations are those that invoke the largest J values, which have a detrimental effect on the calculation results regardless of the U .

Let us now inspect some calculations and DOS plots in detail.

⁵However, based on the relative scatter of these results, and assuming a consistent level of accuracy between all three properties, one would be lead to believe the magnetic moment for NiO is ≈ 1.6 eV. If this were the case, $U_{\text{eff}}^{(2)}$ would give the best overall agreement.

⁶ $U^{(3)}$ is the exception, however it does not provide the best overall performance.

PBE and PBE+ $U^{(3)}$

To compare the following results to the PBE DOS, we refer the reader to Fig. VI.6. Since the conventional U is computed without any applied U_{in} , as in the previous Chapter, it is very similar to $U^{(3)}$ such that it is sufficient to regard Fig. VI.7 as that pertaining to PBE+ $U^{(1)} = 6.7$ eV. Let us now look toward examining some of the remaining schemes, including $U^{(1)}$ and $U^{(2)}$.

PBE+ $U^{(1)}$

The DOS computed from $U^{(1)} = 4.1$ eV is plotted in Fig. VII.7, and shows reasonable agreement with experiment in terms of the results for the band gap, transition energy and magnetic moment. It is not surprising then that this encouraging result would lead users to choose this condition. However, we argue that this selection is founded on more of an empirical, rather than mathematical, footing and in light of the evidence presented in preceding sections, we may discard this scheme in favour of better alternatives.

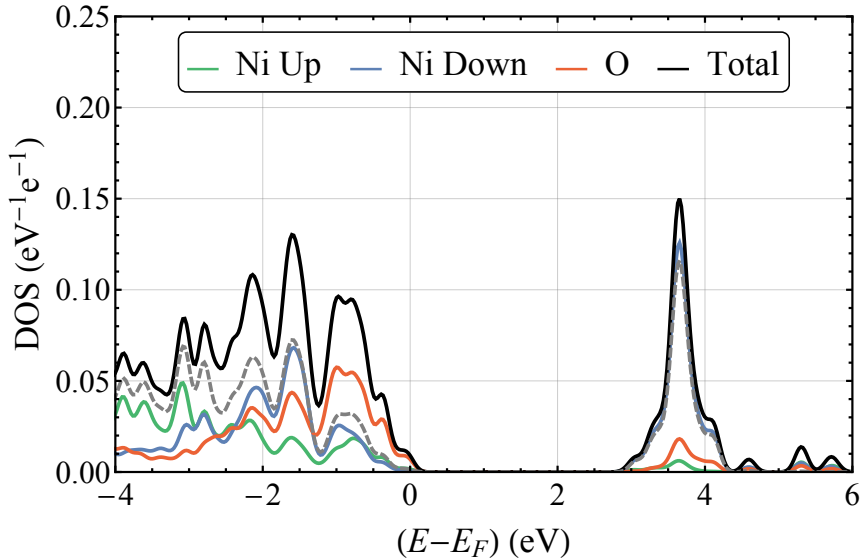


Figure VII.7: The species-resolved density-of-states of NiO with half-width Gaussian smearing of 0.1 eV and the zero-energy set to the Fermi level (eV) for PBE+ $U^{(1)} = 4.1$ eV. The lines depict Ni majority-spin (green), Ni minority-spin (blue), O (red), total (black), and Hubbard total (dashed grey)

PBE+ $U^{(2)}$

If we instead opt to use the self-consistency condition proven to be the best for a one-electron system, i.e., $U^{(2)} = 10.5$ eV, and neglect the double-counting of the interaction when extended to multiple electrons, the resulting DOS is that presented in Fig. VII.8. Here, the large U parameter clearly exceeds the necessary correction and causes the conduction band peak to migrate to 6 eV above the Fermi level. If we attempt to mitigate the correction with a J , the corresponding DFT+ U + J calculation, shown in Fig. C.2, now pulls the conduction peak below the Fermi level and leaves behind sparse conduction states that are not observed in experiments at all. Finally, if we include the supplementary term relating to orbital exchange in Eq. 7 of Ref. [354], (PBE+ $U^{(2)} + J_{\min}^{(2)}$) it makes matters worse still by breaking the spin-symmetry of the DOS and rendering it ferromagnetic. This is shown in Fig. C.10, and the comprehensive failure by all three approaches leaves us no choice but to abandon this scheme entirely.

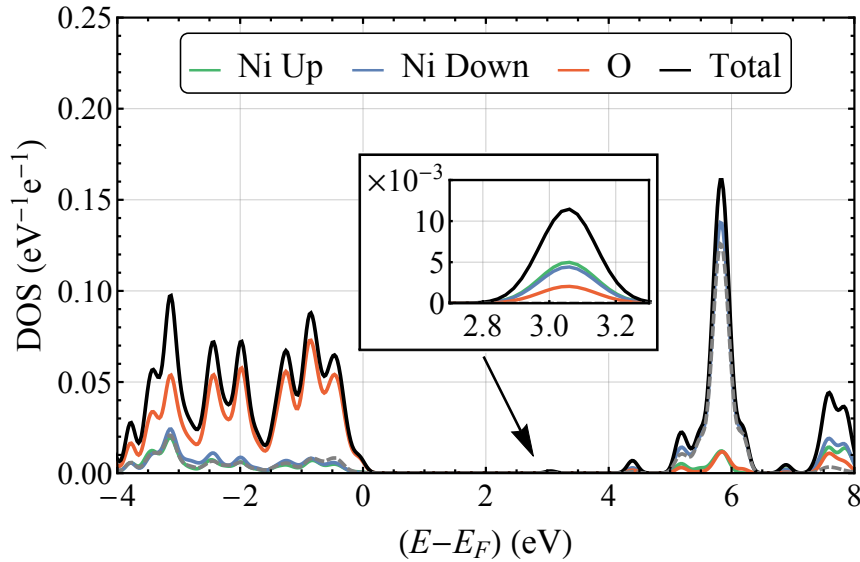


Figure VII.8: The species-resolved density-of-states of NiO with half-width Gaussian smearing of 0.1 eV and the zero-energy set to the Fermi level (eV) for PBE+ $U^{(2)} = 10.5$ eV.

$\text{PBE}+U^{(3)}+J^{(3)}$

Let us now consider augmenting the original $\text{PBE}+U^{(3)}$ calculation presented in Fig VI.7, with the corresponding $J = 0.84$ eV. Depicted in Fig. VII.9 is the resulting DOS, in which there is qualitatively little change in comparison to its predecessor. Some minor change of character in the valence states is observed between -4 eV and -2 eV, however, this is unlikely to affect the overall chemical behaviour significantly. We therefore conclude that $J < 1$ eV will not induce any significant changes in calculation results.

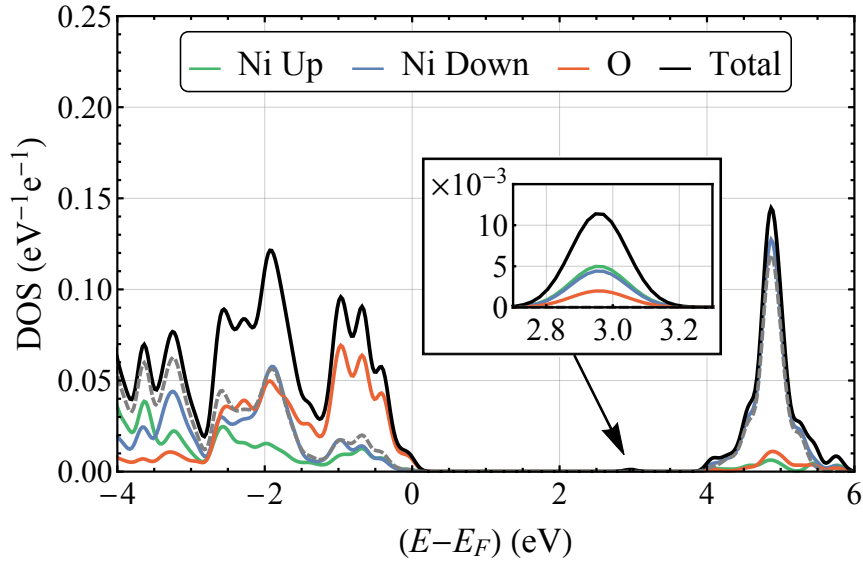


Figure VII.9: As in Fig VII.7. The DOS for $\text{PBE}+U = 6.7^{(3)}$ eV + $J^{(3)} = 0.84$ eV.

$\text{PBE}+U_{\text{eff}}^{(2)}$

Finally, the DOS for $U_{\text{eff}} = 5.2$ eV is shown in Fig. VII.10, and returns a qualitatively accurate profile based on current experimental measurements. The band gap is found to be 3 eV while the d -peak correctly occurs at 4 eV, and the magnetic moment is $1.57 \mu_B$, which are all in excellent agreement with experimental values.

Moreover, the constituent states of the valence band from -1.5 eV up to the Fermi level are 32% Ni and 68% O, in comparison to the conduction band whose makeup as far as 5 eV is 88% Ni and 12% O, which correctly categorise NiO as a charge transfer type semi-conductor. This self-consistency scheme therefore repro-

duces both qualitative and quantitative experiment results and shares this status with the $\text{PBE}+(U-J)^{(3)}$ calculation (shown in Fig. C.7). Given that the two U values implemented differ only by 0.7 eV, and give qualitatively similar results, we consider their treatments equivalent for our current purposes.

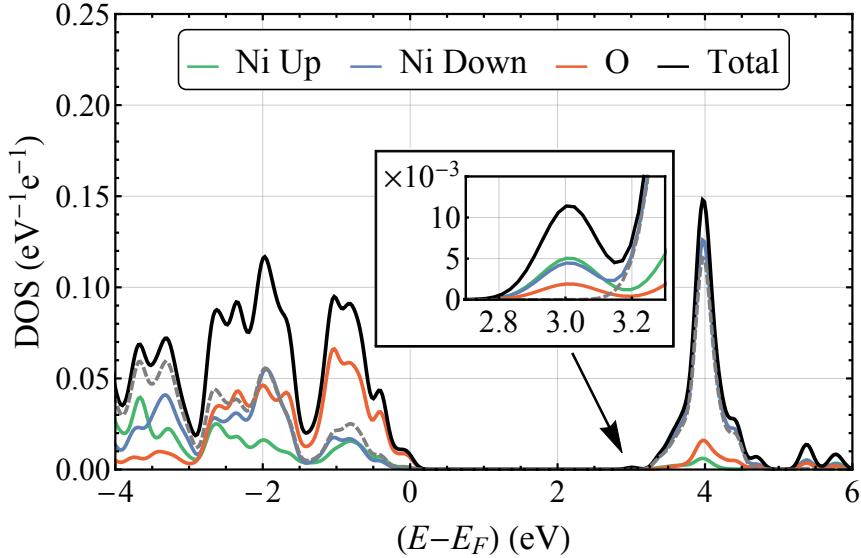


Figure VII.10: As in Fig VII.7. The DOS for $\text{PBE}+U_{\text{eff}} = 5.2$ eV.

We have by now demonstrated that our motivations for selecting $U_{\text{eff}}^{(2)}$ as the appropriate correction scheme are not only well founded on comprehensive mathematical analysis, but now strongly supported by numerical calculations that prove the same. We have also shown that the conventional U parameter may also be sufficient in some circumstances, and may perform even better when replaced by $U - J$. We expect however, that self-consistency schemes will become essential when removing the SIE in systems that transition from a metallic to an insulating state when treated with $\text{DFT}+U$. This kind of electronic behaviour may increase the differences between $U^{(1)}$, $U^{(2)}$ and $U^{(3)}$, as featured in Fig. VII.5.

Finally, we direct the reader to the remaining DOS figures presented in Appendix C, which describe the other schemes in Table VII.4 not discussed here.

4 A SELF-CONSISTENT J APPLIED TO H_2

Now that we have a firm handle on the self-consistent calculation of U parameters, let us apply these lessons to calculate J in the dissociation limit of H_2 . For every internuclear distance considered over the binding curve, we performed a J_{in} vs J_{out} according to Eq. (VII.15), for which $U_{\text{in}} = 0$ and negative J_{in} values were applied in the modified DFT+ U + J functional in Eq. (VII.13). The negative J_{in} ensures that the system does not spontaneously polarise when a magnetic perturbation is applied. Across the binding curve, we found that the absolute magnitude of J_{in} required to ensure this stable equilibrium increased with the bond-length.

In Fig. VII.11 we present two sample J_{in} vs J_{out} profiles corresponding to the limits of the binding curve at bond-lengths of 1 a_0 and 6 a_0 , respectively. For 1 a_0 , the profile has an enormous slope of $-14.0 \pm 0.1 \text{ eV}^{-1}$ which renders an extremely large $J^{(3)} = 154.0 \pm 0.2 \text{ eV}$, as well as more reasonable, but still over calculated, $J^{(1)} = 10.3 \pm 0.1 \text{ eV}$, $J^{(2)} = 11.0 \pm 0.1 \text{ eV}$. These values are, without question, much too big for this bonding regime. It is evident that the large subspace overlap near the equilibrium bond-length, coupled with the breakdown of a weakly interacting subspace with its bath, contributes to the calculation of excessively large linear-response parameters.

Similarly at 6 a_0 bond-length we also get highly accurate⁷ (and negative) $J^{(1)} = -1.9 \text{ eV}$, $J^{(2)} = -3.0 \text{ eV}$, $J^{(3)} = -5.2 \text{ eV}$, with a slope of -1.72 which are much more reasonable indeed and shows that the calculated J_{out} values change sign over the binding curve. Moreover, we see the Coulson-Fischer point at $\approx 3.5 \text{ a}_0$ where the measured J_{out} passes through zero. This serves as a graphical illustration for the necessity of a J_{in} , especially after this point. A negative J_{out} suggests that the system prefers an open-shell configuration but it is held in an unstable equilibrium by the spin-symmetry. The energy difference between the two states is exactly the SCE (c.f. Fig. V.8).

⁷Here, the errors are $\sim 10^{-4} \text{ eV}$.

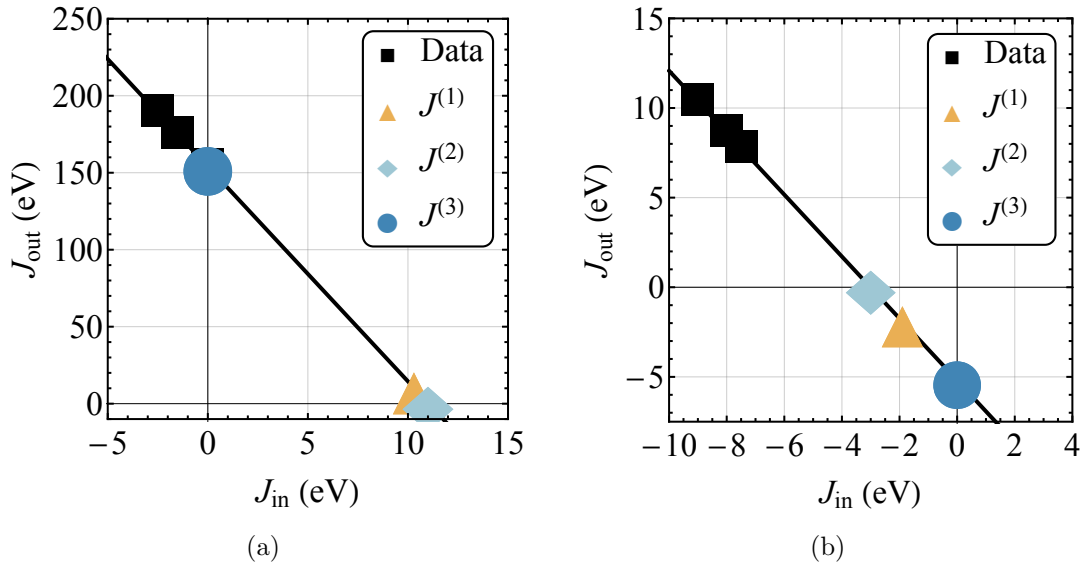


Figure VII.11: J_{in} vs J_{out} calculations for H_2 , with error bars, at (a) $1 a_0$ (b) $6 a_0$ bond-length illustrating each of the self-consistency schemes $J^{(1)}$ (triangle), $J^{(2)}$ (diamond), and $J^{(3)}$ (circle). We find a highly-linear profile across all bond-lengths for this system with very small errors despite only three data points. Between these bond-lengths we see that the J_{out} changes sign.

4.1 CORRECTING SCE WITH J

If we proceed to plot the various J schemes against the estimated J_{int} required to correct the total-energy (which is incidentally negative for all bond-lengths), some very interesting behaviour emerges, as shown in Fig. VII.12. Unsurprisingly, all three schemes substantially overestimate the required J for short bond-lengths, in which $J^{(1)}$ attains a maximum of 154 eV. This is reminiscent of a similar issue that occurred with H_2^+ , albeit much worse, and is also due to imperfect population analysis caused by occupancy double-counting and charge spillage, as well as the breakdown of the subspace-bath separation.

Beyond the Coulson-Fischer point, however, and toward the dissociation limit, the J values quickly decrease and attain much more reasonable values. While $J^{(3)}$ is now underestimated, and $J^{(1)}$ is still slightly too large, it is $J^{(2)}$ that converges to the correct values and gives remarkable agreement with J_{int} toward dissociation.

In Fig. VII.13 we plot the $\text{PBE}+J^{(2)}$ total-energy resulting from this scheme

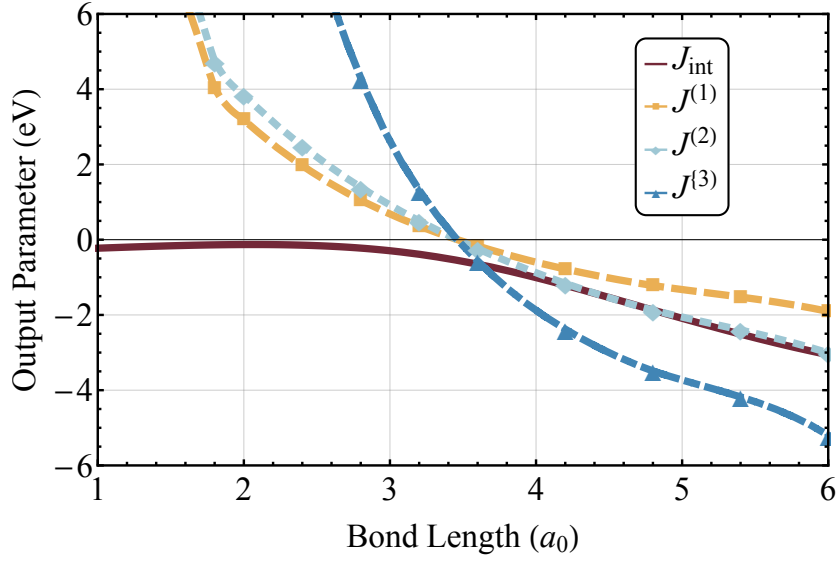


Figure VII.12: The estimated best J value, J_{int} (solid), for correcting the total-energy SCE in H_2 , shown with the $J^{(1)}$ (dashed), $J^{(2)}$ (dotted), and $J^{(3)}$ (dot-dashed) values with error bars. All schemes give values that are much too large at short bond-lengths. Beyond the Coulson-Fischer point $J^{(2)}$ converges on J_{int} with excellent agreement.

in comparison to the full configuration interaction (FCI) total-energy presented earlier. We see that around equilibrium the total-energy has been considerably over-estimated, as expected from the large J values computed at these bond-lengths. After the Coulson-Fischer point, however, the $\text{PBE}+J^{(2)}$ total-energy quickly converges on the FCI total-energy. The inset figure further illustrates that this remarkable agreement is within 0.05 eV.

This result seems to suggest that J_{out} alone is sufficient to correct the SCE, that is

$$J_{\text{out}} = 0 \quad \Rightarrow \quad J_{\text{in}} = 2F_J^{\hat{P}} = \frac{1}{2} (F^{\uparrow\uparrow} - F^{\uparrow\downarrow} + F^{\downarrow\downarrow} - F^{\downarrow\uparrow}), \quad (\text{VII.20})$$

and that our earlier concern for the presence of a factor of two in this equation is therefore unsubstantiated.

Indeed, this result seems to indicate that there is no need to consider U_{out} , and that the $J_{\text{eff}} = 0$ condition leads to the wrong result. It is, as of yet, unclear why the self-consistency conditions we require to cancel the spurious curvatures differ between U and J , but it presents a possible avenue for future work. Nonetheless, we have provided an encouraging, preliminary demonstration that $\text{DFT}+J$, when

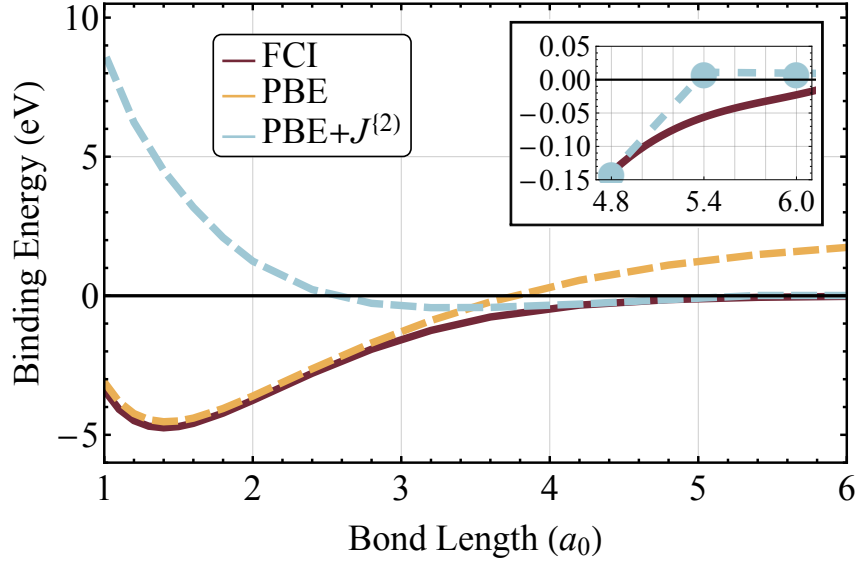


Figure VII.13: The H_2 binding curve calculated with FCI (red), PBE (orange), and $\text{PBE}+J^{(2)}$ (blue). The reference energy for each curve is that of two isolated H atoms calculated with the corresponding XC functional. In the dissociated limit (inset), the $J^{(2)}$ result tends asymptotically to the exact one, which suggests that J_{out} alone is sufficient to correct the SCE.

provided with suitably calculated J , particularly at self-consistency, may be a remedy for SCE, albeit only for large enough bond-lengths and the appropriate population analysis. Acquiring the same correction for short bond-lengths is a feature intended for future development.

4.2 WILL U_{EFF} AND J_{EFF} IMPROVE H_2 ?

As a final proposition, we consider if the results presented above may be improved by instead considering U_{eff} and J_{eff} , especially in the near-bonding regime where the J values are too large. Given this observation, one may argue that we are encountering a similar problem to that discussed around Eq VII.11, where the absence of considering J_{out} resulted in a U_{out} that over-corrected the interaction. Indeed, in this instance, our self-consistency condition $J_{\text{out}} = 0$ alludes to a similar scenario

$$J_{\text{out}} = 0 \quad \Rightarrow \quad J_{\text{in}} = 2F_J^{\hat{P}} = \frac{1}{2} (F^{\uparrow\uparrow} - F^{\uparrow\downarrow} + F^{\downarrow\downarrow} - F^{\downarrow\uparrow}), \quad (\text{VII.21})$$

where the factor of two here raises concern.

We might then suggest adding to this term the computed U_{out} from the same calculations, in a similar manner to how we calculated U_{eff} for NiO (c.f. Fig. VII.4). For a closed-shell system, however, computing U from magnetic perturbations is very challenging, if not impossible since the resulting potentials in the $1s$ subspace will conserve the net charge, such that U cannot be reliably computed⁸.

We instead calculated the U values for dissociating H_2 from the usual uniform perturbation $\alpha = \pm 0.05$ eV applied to the subspace of one of the H atoms (as we previously showed in Fig. VI.3). We determined the U value self-consistently at $2.8 a_0$ in the near bond-length regime, to illustrate that a non-self-consistent U provides an adequate approximation to the fully self-consistent $U^{(2)}$. Indeed, the U_{in} vs U_{out} curve depicted in Fig. VII.14, gives $U^{(2)} = 4.68 \pm 0.05$ eV and $U^{(3)} = 4.38 \pm 0.02$ eV. We therefore refrain from calculating the U self-consistently at all bond-lengths, for

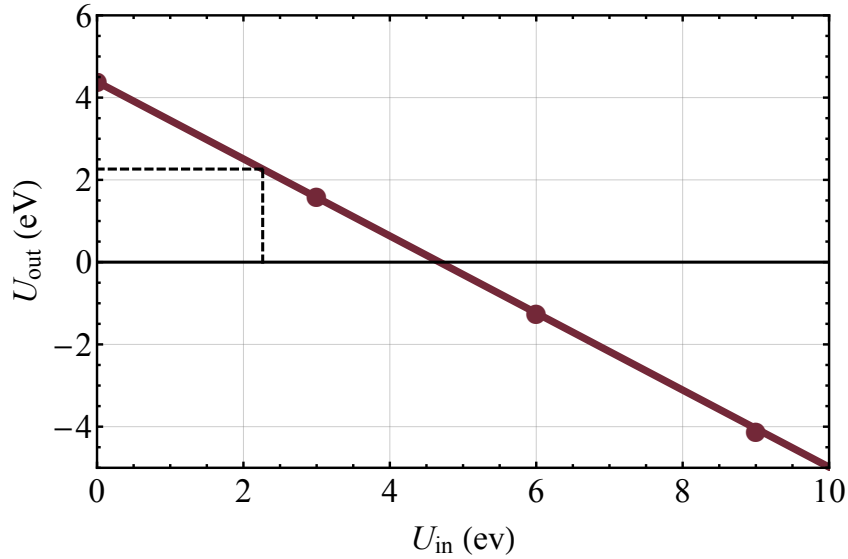


Figure VII.14: The self-consistency calculation for the U parameter at $2.8 a_0$ along the binding curve of H_2 . From this we compute $U^{(1)} = 2.26 \pm 0.02$ eV, $U^{(2)} = 4.68 \pm 0.05$ eV, and $U^{(3)} = 4.38 \pm 0.02$ eV, which are very accurately determined and show that $U^{(3)} \approx U^{(2)}$.

convenience, and proceed with the non-self-consistent U values.

The effective Hubbard parameters resulting from this procedure, approximated

⁸In fact, we tried this approach with the J calculations but we found enormous error bars on the U values

by $U_{\text{eff}} = U^{(2)} - J^{(2)} \approx U^{(3)} - J^{(2)}$ and $J_{\text{eff}} = U^{(2)} + J^{(2)} \approx U^{(3)} + J^{(2)}$ are shown in Fig. VII.15. Here we observe that these effective parameters do not compare at all

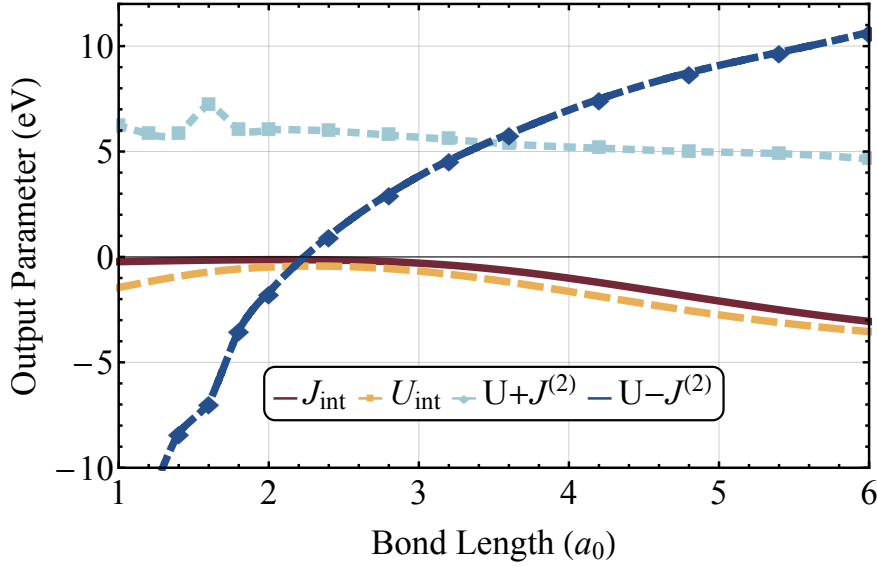


Figure VII.15: The approximated J_{eff} (dotted) and U_{eff} (dot-dashed) compared to the required J_{int} (solid) and U_{int} (dashed), separately estimated to correct the total-energy in dissociating H_2 . These effective quantities do not compare to those required and so provide no additional advantage over $J^{(2)}$.

to the U or J values required to correct the total-energy (with either DFT+ U or DFT+ J), and therefore suggest no reason to use them in place of $J^{(2)}$. It is therefore not necessary, or advised, it seems, to consider U_{eff} and J_{eff} when treating SCE in H_2 , wherein J_{out} provides the best possible correction. The precise reasons for this outcome are not yet clear and a more thorough investigation of this result remains an open prospect for the future.

5 CHOICE OF SUBSPACE PROJECTORS

The choice of subspace projectors $\{\varphi_m\}$ plays a crucial role in the both the calculation and application of the U and J parameters. Throughout this dissertation we utilise static pseudoatomic orbitals (PAO) that are generated from the occupied KS state of the neutral atom with the underlying XC functional. Other projectors that may be chosen include hydrogenic wave functions [342, 440], maximally-localised Wannier

functions [414, 434], and linear-muffin tin orbitals [149, 337, 338, 455] (LMTO), which may also be optimised self-consistently [389].

The DFT+ U method operates under the assumption that the localised charged encapsulated by the projectors is only weakly interacting with the charge in the surrounding electron bath. Furthermore, we require that projectors are sufficiently well separated such that the overlap matrix between adjacent sites $O_{mm'}^{IJ} = \langle \varphi_m^I | \hat{\rho} | \varphi_{m'}^J \rangle$ is minimal. However, when the on-site projectors do not sufficiently capture all of the localised charge, or where the overlap between adjacent sites $O_{mm'}^{IJ}$ is large, the inappropriate population analysis can result in incorrect calculations of U and J .

These effects are clearly evident in the calculation of U in Fig. VII.2 and J in Fig. VII.12. For short bond-lengths there is significant spatial overlap between the 1s projectors on both H atoms where the charge contained in $O_{mm'}^{IJ}$ represents a large fraction of $\text{Tr}[\hat{n}_{mm'}^I]$. Therefore, any perturbation applied to the targeted subspace, e.g., uniform or magnetic, will also inadvertently affect the charge contained in the other subspace, i.e., the bath, and the interaction cannot be considered weak. Thus, calculating U (or J) in this regime also takes into account the interactions present in the adjacent subspace and exaggerates the corresponding response functions.

Indeed, we see that the negative U values calculated in Fig. VII.2 at short bond lengths are lower than what is required by as much as 4 eV. On the other hand, those calculated between 3 a_0 and 6 a_0 are too large, but the error is relatively smaller since the overlap is less extreme. In Fig. VII.12 the $J^{(2)}$ values calculated before the Coulson-Fischer point are also much too large. In the dissociation limit in both examples, however, where the projector overlap is minimal, the calculated U and J values are in very reasonable agreement with what is required.

It is therefore clear that the degree of overlap between subspace projectors $O_{mm'}^{IJ}$ strongly influences the calculation of U and J and must be considered in systems where such overlapping is prevalent. However, rather than reconstructing the formulas for the Hubbard parameters to explicitly account for $O_{mm'}^{IJ}$, a more effective solution may be achieved by redefining the projectors themselves. We therefore propose to construct the projectors to span all the subspaces that belong to a specific group $\mathcal{G}$, characterised by a certain species, spin-orientation, location etc. In this scheme,

which we have dubbed the *unified sites* approach (US), the group projector is defined as follows

$$\hat{P}_{mm'}^{\mathcal{G}} = \sum_{I,J} |\varphi_m^I\rangle \langle \varphi_{m'}^J| \quad \text{with} \quad I, J \in \mathcal{G}, \quad (\text{VII.22})$$

and is a sparse matrix that spans the subspace combining all the atoms. Thus, uniform and magnetic perturbations, as well as the on-site interactions that determine U and J , are contained within the unified subspace and circumvent the introduction of explicit double-counting corrections. Hence, the overlap between adjacent sites may be implicitly taken into account both in the calculation and application of the Hubbard parameters. We will discuss this feature further in our conclusions in Chapter IX.

6 CONCLUSION

In this Chapter, we have extended our linear-response method developed in Chapter VI to incorporate the self-consistent calculation of U and J , in which only quantities calculated from ground-state densities are required. This formalism simplifies the analysis of parameter self-consistency schemes considerably and, at least for this specific method, a clear best choice of self-consistency criterion for one electron emerged, $U^{(2)}$, which has been explored relatively little in the literature to date. In stringent calculations of the dissociated limit of the system affected by SIE alone H_2^+ , in which DFT+ U operates under ideal conditions, we are able to directly observe that the method corrects the SIE in the total-energy very precisely, as foreseen in Ref. [396]. It does so entirely from first-principles when the $U^{(2)}$ scheme is used.

Moreover, this method readily extends to the exchange parameter J , which is required in the multi-electronic extension to NiO to facilitate the correct self-consistency condition $U_{\text{eff}} = 0$. For this condition, the computed values for the band gap, transition energy and magnetic moment were in excellent agreement with experimental data.

Our analysis also shows that the comparison of thermodynamically relevant DFT+ U quantities such as the total-energy between dissimilar systems demanding different first-principles U parameters is, at least, well defined. Indeed, this compar-

ison evidently becomes one between purely ground-state properties when applied with parameter self-consistency, but there may well be other circumstances in which this also holds true.

Furthermore, the self-consistency formalism can be used to enhance the results of other methods as we shall see in the next Chapter. The procedure then extends the DFT+ $U^{(2)}$ full SIE correction of the H_2^+ total-energy to the highest occupied eigenvalue, approximately enforcing Koopmans' condition. We also recommend the use of a more complicated criterion, the previously proposed $U^{(3)}$, particularly for density-non-self-consistent methods such as post-processing DFT+DMFT.

The self-consistent scheme was also extended to calculate the exchange parameter J in dissociating H_2 . For this system we found it not only advantageous, but necessary, to calculate J self-consistently in order to correctly ameliorate the SCE beyond the Coulson-Fischer point and into the dissociation limit. In this instance we found that the PBE+ $J^{(2)}$ total-energy gave remarkable agreement with the FCI total-energy in the dissociation limit, despite drastically over-estimating it near equilibrium. Surprisingly, U_{eff} and J_{eff} did not coincide with the necessary values, which warrants further analysis into the disparity between the self-consistency regimes for U and J .

To properly account for SIE or SCE in the total-energy, both across the bond-length range of H_2^+ and in general, we note that one would need to fully take into account the effects of subspace charge spillage, overlap and double-counting, possibly through the use of Wannier functions [434] generated self-consistently with the DFT+ U electronic structure [389]. At least as important for correcting SIE in the bonding regime, perhaps, is the necessity to overcome the breakdown of the single-site approximation. For this, the account of inter-subspace SIE offered by the multi-site method such as DFT+ $U+V$ [441], or our proposed US approach, is a promising avenue for investigation.

Finally, in Appendix C, we present self-consistent calculations of U for $\text{Ni}(\text{CO})_4$ and Cr_2O_3 , which were also investigated as part of this work.

VIII

THE INVESTIGATION OF NON-LINEAR CONSTRAINTS AND A GENERALISED DFT+ U FUNCTIONAL

WHILE THE CONSTRUCTION of viable, explicit density functionals free of pathologies such as SIE is extremely challenging [9], we discussed in Chapter V some of the significant progress made in the development of implicit functionals toward this goal. Furthermore, we demonstrated in Chapters VI & VII how the DFT+ U method [343] may be utilised as an effective and computationally efficient, even linear-scaling [101], treatment for many-body SIE. However, as we illustrated in Fig. V.6, it is patently unable to provide any sort of correction to the Kohn-Sham eigenvalue, which is the relevant quantity for, e.g., calculating first ionisation energies, heterogeneous catalysis [512], and charge transfer energies [545–558]. This non-compliance of Koopman’s condition [330, 331, 334, 335] corresponds to a short-coming in the linear term affecting the potential, which in turn exposes a significant limitation in the applicability of the DFT+ U .

As a solution to this problem, we propose the construction of a generalised DFT+ U functional comprising separate U parameters for the linear and quadratic density terms, thereby allowing for an adaptive double-counting correction. Our goal is that DFT+ U may be simultaneously applied to two important sources of error, namely the many-body SIE and non-compliance with Koopman’s condition, which have long hindered the reliability of electronic structure calculations. Moreover, the additional degree of freedom provided by two parameters raises the possibility of developing a self-contained, self-consistency scheme for calculating both parameters. Hence, the challenge central to this Chapter is the development of such a scheme

that is comparable in efficiency and accuracy to the self-consistent linear-response approach described in the previous Chapters.

We begin by first exploring the self-contained calculation of conventional Hubbard U parameters by means of an automated variational extremisation approach. Indeed, the automated correction of subspace SIE is a compelling possibility in itself, and one that warrants a rigorous investigation as such a mechanism would be extremely useful for many practitioners and expedient in the context of high-throughput materials informatics [506–510]. This procedure may be in fact possible if we can effectively define the state that is free of SIE in terms of relevant constraints on the ground-state density. We therefore propose to exploit the efficiency of the optimisation methods encapsulated by constrained density-functional theory (cDFT) [416–418], to directly and automatically enforce SIE correction with the constraint-like form of the DFT+ U functional, for which the U^I resemble the Lagrange multipliers of constraints on the eigenvalues of $\hat{n}^{I\sigma}$.

We shall demonstrate, however, that cDFT is fundamentally incompatible with constraints beyond linear order, and that this prohibits the satisfaction of exact constraints targeting SIE interactions. Fundamentally, we show that one cannot excite a system afflicted with SIE into a state that reliably exhibits less, without breaking a physical symmetry or introducing auxiliary parameters.

However, we show that a two-parameter method is sufficient to precisely cancel the SIE and attain the exact subspace occupancy or exact eigenvalue when the free energy is considered instead. This finding illustrates that a generalised DFT+ U functional is effective in treating both the total-energy and ionisation potential of a one-electron system, entirely from first principles. Moreover, we derive formulae for estimating these parameters which depend only on ground-state DFT quantities and the self-consistent Hubbard U calculated from linear-response in the previous Chapters.

1 CONSTRAINED-DFT

Constrained density-functional theory (cDFT) [418] is a generalisation of DFT, in which the total-energy functional is augmented by one or more constraints. These constraints operate on the expectation values of charge or spin-density (or their sums, differences or moments), which are enforced by a set of *Lagrange multipliers* $\{V_c\}$.

The total-energy of a constrained system W , in which the total charge density in some region (in our case the localised subspace) is constrained, is given as follows

$$W[n, V_c] = E_{\text{DFT}}[n] + V_c E_c[n]$$

$$\text{where } E_c[n] = \left(\sum_{\sigma} \int d\mathbf{r} w_c^{\sigma}(\mathbf{r}) n(\mathbf{r}) - N_c^{\sigma} \right). \quad (\text{VIII.1})$$

The *weight function* $w_c^{\sigma}(\mathbf{r})$ specifies the region in which the constraint enforces the target charge N_c^{σ} .

Although constraints have long played a significant role in the interpretation of physical processes, the constraint-approach originally gained traction in the DFT community with the work of Dederichs [416] and other contributors [559–565], whose combined efforts facilitated the calculation of states not directly accessed by the unconstrained exchange-correlation functional, such as charge transfer energies, defect states, and magnetic impurities. However these calculations were computationally intensive to perform as they required the manual scanning over the space of Lagrange multipliers until the desired state was achieved.

The seminal work of Van Voorhis *et al.* [502, 547, 548, 551, 566–568], on which the contemporary application of cDFT is now based, later formalised an optimisation approach toward the solution of constraints, in which they established that the constraint is satisfied at an extremum of the total-energy with respect to the Lagrange multipliers V_c

$$\frac{dW}{dV_c} = 0 \quad \Rightarrow \quad E_c[n] = 0 \quad (\text{VIII.2})$$

and that the extremum corresponds to a maximum, guaranteed by a negative-definite curvature,

$$\frac{d^2W}{dV_c^2} \leq 0 \quad \text{for all } V_c, N_c. \quad (\text{VIII.3})$$

However, it was recently remarked by O'Regan and Teobaldi [502], that the assumption of stationary orbitals, which contributes to the derivation of Eq. (VIII.3) is incomplete when extended to variational procedures¹. Under this generalisation, the constraint is still satisfied at the energy maximum as in Eq. (VIII.2), but with the introduction of the inverse dielectric response ϵ^{-1} in the expression for Eq. (VIII.3). This means that the curvature is no longer *guaranteed* to be negative-definite for multiple constraints (thereby precluding the existence of a unique maximum) but is proven to be so for single constraints, or those that are not ill-posed.

cDFT has proven extremely useful in many applications over the years, including charge transfer calculations [545–558], electronic coupling parameters [556, 557, 569], and in calculating of Hubbard U parameters in DFT+ U [337, 414, 425, 570]. cDFT is also practiced in the correction of static correlation error to construction efficient, minimal basis sets for configuration interaction calculations [567, 568, 571, 572]. For a comprehensive account of the cDFT method, we refer the reader to Refs. [416, 418, 502, 558, 566].

The broad application of cDFT to date has focused primarily on constraints linear in density-dependent quantities while there have been sparse references to non-linear constraints in the prevailing literature [573–575], particularly in the realm of nuclear physics [576–578]. To our knowledge, however, a formal solution to non-linear constraints on the electronic density was not proposed in any, hence motivating our interest in their application.

2 NON-LINEAR CONSTRAINTS

To investigate the efficiency of non-linear constraints for targeting SIE, let us reconsider the one-electron system H_2^+ , which we showed in the previous Chapters to be highly amenable to DFT+ U type corrections. The simplest conceivable constraint functional that targets SIE assumes a quadratic form

$$C_2 = \sum_{I\sigma} (N^{I\sigma} - N_c^{I\sigma})^2 \quad \text{with} \quad N^{I\sigma} = \text{Tr}[\hat{n}^{I\sigma}], \quad (\text{VIII.4})$$

¹See Eq. 6 in Ref. [566] vs Eq. 14 in Ref. [502].

where $N^{I\sigma}$ is the total occupancy of the error-prone subspace I , and $N_c^{I\sigma}$ is its targeted value, for spin σ . Although this constraint is a functional of subspace total occupancies, rather than the occupancy eigenvalues as in DFT+ U , it is an unimportant distinction for single-orbital sites. For M identical subspaces with $N_c^{I\sigma} = N_c$ for all I and σ , the total-energy of the system is given by

$$W[n, V_c] = E_{\text{DFT}}[n] + MV_c C_2[n] \quad (\text{VIII.5})$$

where V_c is the common cDFT Lagrange multiplier. This gives rise to a constraining potential of the form

$$\hat{v}_c^{I\sigma} = 2V_c \sum_I (N^{I\sigma} - N_c) \hat{P}^I \quad (\text{VIII.6})$$

which depends explicitly on the violation of the constraint, i.e., it is attractive for $N^{I\sigma} < N_c$ and repulsive for $N^{I\sigma} > N_c$. This, in turn, generates a corrective interaction-kernel given by

$$\hat{f}_c = \frac{\delta \hat{v}_c^{I\sigma}}{\delta \hat{n}} = 2V_c \sum_I \hat{P}^I \hat{P}^I \quad (\text{VIII.7})$$

which acts to modify the energy-density profile. In fact, the interaction-kernel $\hat{f}_c$ is identical to that generated by DFT+ U when $V_c = -U^I/2$, and thus motivates our initial choice of a quadratic constraint. Moreover, following the procedure prescribed in Ref. [502] for the self-consistent cDFT problem, the Hellmann-Feynman theorem provides that the first energy derivative with respect to the Lagrange multiplier is simply the constraint functional

$$\frac{dW}{dV_c} = C_2 = (N^{I\sigma} - N_c)^2, \quad (\text{VIII.8})$$

so that the total-energy $W(V_c)$ always finds a stationary point when the constraint is satisfied, i.e., $C_2 = 0$.

In order to assess the potency of this functional to correct SIE in a one-electron model, we investigate the H_2^+ molecule at an intermediate bond-length of 4 a_0 , using the same calculation parameters outlined in Chapter V. At this bond-length, the overlap of the two PBE $1s$ orbitals yields an intermediate double-counting in the subspace total occupancy of 24%. A physically intuitive target occupancy of

$N_c = 0.5$ e per atom is chosen², which requires a repulsive constraint and, therefore, a positive V_c . However, the same qualitative outcome can be composed from the selection of any $N_c \neq N_{\text{DFT}}$, where N_{DFT} is the unperturbed ground-state subspace density.

The total-energy of the system as a function of the Lagrange multiplier V_c is illustrated in Fig. VIII.1, in which it is clearly demonstrated that the C_2 constraint cannot be enforced, as was similarly remarked by Staszczak in Ref. [577], since $W(V_c)$ fails to attain a stationary point. This is further emphasised by the exponential decay of the total-energy derivatives, the first three of which are also depicted.

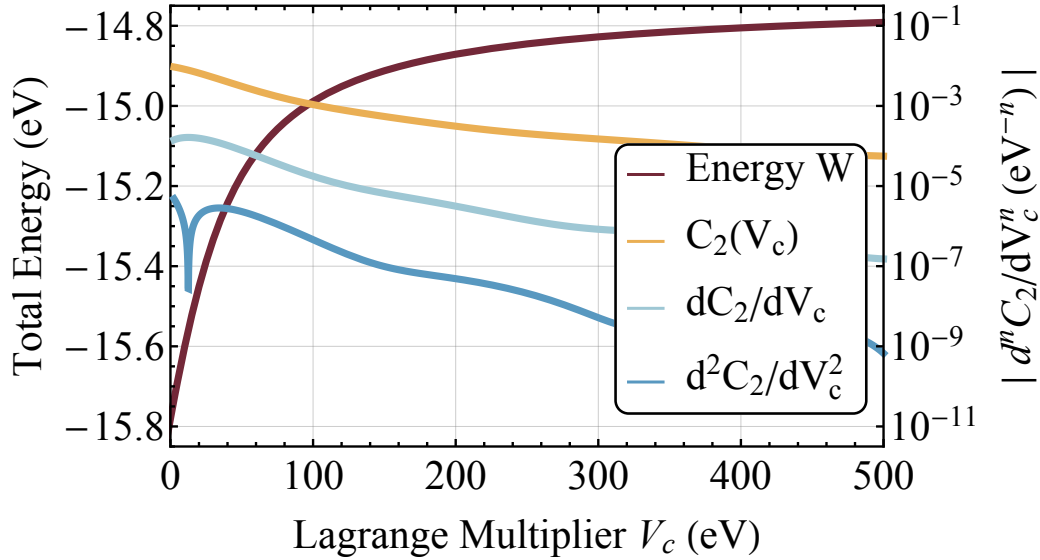


Figure VIII.1: The total-energy of constrained H_2^+ at $4 a_0$ bond-length, with a target occupancy of $N_c = 0.5$ e per atom against the cDFT Lagrange multiplier V_c . Also shown is the constraint functional $C_2 = (N - N_c)^2$, averaged over the two atoms, and its first and second derivatives, which all rapidly diminish with V_c .

Indeed, the key to understanding the failure of the C_2 constraint lies in the rapid decline in the self-consistent cDFT response functions [502] $d^m N / dV_c^m \sim d^{m+1} W / dV_c^{m+1}$, the first three of which are depicted in Fig. VIII.2. This results in diminishing returns in regard to the efficacy of the constraining potential as V_c is increased. In other words, as the constraint asymptotically approaches satisfaction with increasing V_c , the density becomes less and less responsive to the perturbation

²Henceforth in this analysis, we shall suppress the site and spin indices for brevity.

incurred by V_c , and so never attains the target value.

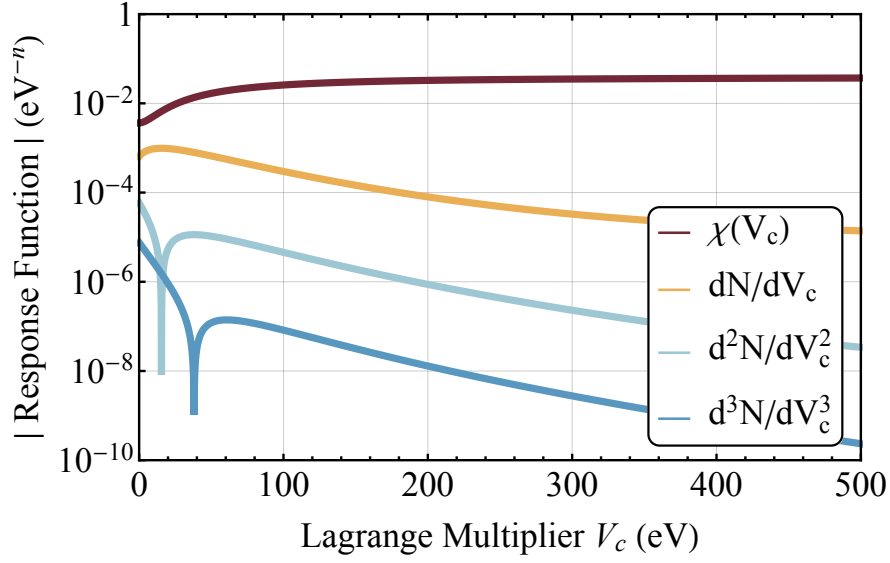


Figure VIII.2: The magnitudes of the interacting density response $\chi = \text{Tr} \left[\frac{dN}{d\hat{v}_{\text{ext}}} \hat{P} \right]$ and cDFT response functions $d^m N/dV_c^m$, calculated from a polynomial fit to the average subspace occupancy of H_2^+ at $4 a_0$. The responses diminish as we asymptotically approach constraint satisfaction, while the occupancy, and hence χ , tends to a constant value.

2.1 PROOF OF THE INAPPLICABILITY OF NON-LINEAR CONSTRAINTS

The incapability of the quadratic constraint to attain a stationary point for this simple system presents a surprising result. We are therefore motivated to investigate whether non-linear constraints of a general form

$$C_n = (N - N_c)^n \quad \text{with} \quad n \in \{\mathbb{N}; n \geq 2\}, \quad (\text{VIII.9})$$

are also unable to be satisfied for a target occupancy $N_c \neq N_{\text{DFT}}$, or if this outcome is specific to quadratic constraints only. To preface this inquiry, it is provided that the $n = 0$ case is trivial, and $n = 1$ returns a conventional linear constraint. Moreover, the constraint is ill-defined for $n < 0$ since the total-energy would diverge upon constraint satisfaction, and C_n becomes imaginary for non-integer n when $(N - N_c)$ is negative. We shall, therefore, limit our discussion to constraints of integer order $n \geq 2$.

To assess the ease of accessing the stationary points sought by non-linear constraints we must investigate the nature of the derivatives of the total-energy $W(V_c)$. We begin this analysis with the first derivative, which simply returns the constraint itself

$$\frac{dW}{dV_c} = C_n, \quad (\text{VIII.10})$$

as in Eq. (VIII.8). Hence, the first derivative is trivially equal to zero at the stationary point. We proceed then to the second derivative, which follows directly from the first and is

$$\frac{d^2W}{dV_c^2} = \frac{dC_n}{dV_c} = n(N - N_c)^{n-1} \frac{dN}{dV_c} = nC_{n-1} \frac{dN}{dV_c}. \quad (\text{VIII.11})$$

It is constructive from here on to express the total-energy derivatives in terms of the subspace-projected interacting response function

$$\chi = \text{Tr} \left[\frac{dN}{d\hat{v}_{\text{ext}}} \hat{P} \right], \quad (\text{VIII.12})$$

since this object - unlike the cDFT response functions - is independent of the form of the constraint, where the external potential is denoted by

$$\hat{v}_{\text{ext}} = \hat{v}_c = V_c \frac{\delta C_n}{\delta \hat{\rho}} = nV_c (N - N_c)^{n-1} \hat{P}. \quad (\text{VIII.13})$$

An expression for the cDFT response function dN/dV_c may then be derived by means of the chain rule via the external potential, as follows

$$\begin{aligned} \frac{dN}{dV_c} &= \text{Tr} \left[\frac{dN}{d\hat{v}_{\text{ext}}} \frac{d\hat{v}_{\text{ext}}}{dV_c} \right] = \text{Tr} \left[\frac{dN}{d\hat{v}_{\text{ext}}} \frac{d}{dV_c} \left(nV_c (N - N_c)^{n-1} \hat{P} \right) \right] \\ &= \text{Tr} \left[\frac{dN}{d\hat{v}_{\text{ext}}} \hat{P} \right] \frac{d}{dV_c} (nV_c C_{n-1}) = n\chi \left(C_{n-1} + V_c \frac{dC_{n-1}}{dV_c} \right) \\ &= n\chi \left(C_{n-1} + V_c (n-1)(N - N_c)^{n-2} \frac{dN}{dV_c} \right) \\ &= n\chi \left(C_{n-1} + V_c (n-1) C_{n-2} \frac{dN}{dV_c} \right). \end{aligned} \quad (\text{VIII.14})$$

Thus, simplifying the terms in the last step yields the first cDFT response function

$$\frac{dN}{dV_c} = \frac{n\chi C_{n-1}}{1 - n(n-1)\chi V_c C_{n-2}}. \quad (\text{VIII.15})$$

Substituting Eq. (VIII.15) into Eq. (VIII.11) then gives the second energy derivative in terms of the constraint and subspace interacting response

$$\frac{d^2 W}{dV_c^2} = \frac{\chi n^2 C_{n-1}^2}{1 - n(n-1)\chi V_c C_{n-2}}. \quad (\text{VIII.16})$$

For any valid stationary point, where $N = N_c$, the constraint is satisfied by construction: $C_n = 0$. Conversely, the Lagrange multiplier V_c , the interacting response χ , and the energy derivatives beyond first order must all remain finite to distinguish the unique inflection point. Inspecting Eqs. (VIII.15) & (VIII.16) again, we see that the numerators for the response dN/dV_c and energy curvature $d^2 W/dV_c^2$ vanish at the stationary point since

$$C_{n-1} = (N - N_c)^{n-1} = 0 \quad \text{for } n \geq 2. \quad (\text{VIII.17})$$

The latter is therefore not a stationary point discriminant, and we must inspect higher-order derivatives instead. Continuing from Eq. (VIII.11), the third derivative of the total-energy is³

$$\frac{d^3 W}{dV_c^3} = n(n-1)C_{n-2} \left(\frac{dN}{dV_c} \right)^2 + nC_{n-1} \frac{d^2 N}{dV_c^2}. \quad (\text{VIII.18})$$

which depends on the both the first and second-order responses. Since we have shown the former vanishes at the stationary point, it remains to be proven for the latter.

Beginning with the last line in Eq. (VIII.14), the second-order response may be derived thence. We begin by evaluating the first term in the derivative of the expansion:

$$\begin{aligned} T_1 &= \frac{d}{dV_c} [n\chi C_{n-1}] = n \frac{d\chi}{dV_c} C_{n-1} + n\chi \frac{C_{n-1}}{V_c} \\ &= n \frac{d\chi}{dV_c} C_{n-1} + n(n-1)\chi C_{n-2} \frac{dN}{dV_c}. \end{aligned} \quad (\text{VIII.19})$$

³In general, the energy derivative of order m involves cDFT response functions up to order $m-1$, and positive integer powers of $(N - N_c)$, which vanish for all $n \neq m-1$, but do not diverge.

The second term is then given by

$$\begin{aligned}
 T_2 &= n(n-1) \frac{d}{dV_c} \left[\chi V_c C_{n-2} \frac{dN}{dV_c} \right] \\
 &= n(n-1) \left[\frac{d\chi}{dV_c} V_c C_{n-2} \frac{dN}{dV_c} + \chi C_{n-2} \frac{dN}{dV_c} + \chi V_c \frac{dC_{n-2}}{dV_c} \frac{dN}{dV_c} + \chi V_c C_{n-2} \frac{d^2 N}{dV_c^2} \right] \\
 &= n(n-1) \frac{dN}{dV_c} \left[\frac{d\chi}{dV_c} V_c C_{n-2} + \chi C_{n-2} + \chi V_c (n-2) C_{n-3} \frac{dN}{dV_c} \right] \\
 &\quad + n(n-1) \chi V_c C_{n-2} \frac{d^2 N}{dV_c^2} \\
 &= T'_2 + n(n-1) \chi V_c C_{n-2} \frac{d^2 N}{dV_c^2}, \tag{VIII.20}
 \end{aligned}$$

where in the last step we have grouped terms depending on dN/dV_c into the term T'_2 . Gathering the terms from T_1 and T_2 , the second-order response function may be constructed as

$$\frac{d^2 N}{dV_c^2} = \frac{T_1 + T'_2}{1 - n(n-1) \chi V_c C_{n-2} \frac{d^2 N}{dV_c^2}}, \tag{VIII.21}$$

where the numerator is given by

$$\begin{aligned}
 T_1 + T'_2 &= n \frac{d\chi}{dV_c} C_{n-1} \\
 &\quad + n(n-1) \frac{dN}{dV_c} \left[\frac{d\chi}{dV_c} V_c C_{n-2} + 2\chi C_{n-2} + \chi V_c (n-2) C_{n-3} \frac{dN}{dV_c} \right], \tag{VIII.22}
 \end{aligned}$$

and depends explicitly on the terms C_{n-1} and dN/dV_c , which, as we have seen, vanish at the stationary point $N = N_c$ for $n \geq 2$. Furthermore, any potentially non-zero terms, such as C_{n-2} or C_{n-3} ⁴, are contained in the square brackets, which are pre-multiplied by the vanishing dN/dV_c . Therefore, the second-order response $d^2 N/dV_c^2$ and, by extension $d^3 W/dV_c^3$, both vanish at stationary points for all $n \geq 2$, due to the vanishing C_{n-1} in the first term in the numerator, and the vanishing dN/dV_c coupled to all remaining terms.

In general, the cDFT response function $d^m N/dV_c^m$ comprises terms proportional to response functions of lower order, in addition to mixed terms composed of the

⁴For $n = 3$, $C_{n-3} = C_0 = 1$ and the result is still valid.

interacting response function χ and its derivatives $d^{m-1}\chi/dV_c^{m-1}$, and constraint terms C_n , such that

$$\frac{d^m N}{dV_c^m} \equiv \frac{d^m N}{dV_c^m} \left[\left\{ \frac{d^{m-k} N}{dV_c^{m-k}} \right\}, \left\{ \frac{d^{m-1-k} \chi}{dV_c^{m-1-k}} \right\}, \{C_{n-k}\} \right] = 0, \\ \forall m \quad \text{with} \quad k = \{1, \dots, m-1\}. \quad (\text{VIII.23})$$

It is then always the case that potentially finite terms, such as χ and its derivatives, or non-divergent powers of $(N - N_c)$, are coupled to response functions, or the vanishing constraint C_{n-1} . It follows, that response functions of all orders vanish as we approach a stationary point, as illustrated in Fig. VIII.2, since each depends successively on vanishing lower-order response functions, beginning with the first: dN/dV_c .

Then, since each term in the m^{th} energy derivative is always proportional to non-divergent powers of $(N - N_c)$ and response functions of (at most) order $m - 1$, the same logic applies, and all energy derivatives tend to zero as well, as depicted in Fig. VIII.1, thereby proving the conjecture. This serves as an inductive proof that non-linear constraints targeting SIE, of the form C_n , cannot be enforced.

2.2 CONSTRUCTION OF SEPARABLE CONSTRAINTS

In light of the failure of non-linear constraints to attain a stationary point, one possible option remains: to re-cast the C_2 functional targeting SIE into a more viable form comprising separate linear and quadratic constraints. For a particular site, this new constraint functional is constructed by expanding the terms in C_2 as follows

$$\begin{aligned} C_2 &= (N - N_c)^2 \\ &= N^2 + N_c^2 - 2NN_c \\ &= N^2 + N_c^2 - 2NN_c + 2N_c^2 - 2N_c^2 \\ &= N^2 - N_c^2 + 2N_c(N_c - N) \\ &= -2N_c(N - N_c) - (N_c^2 - N^2). \end{aligned} \quad (\text{VIII.24})$$

Invoking separate Lagrange multipliers in this reformulation may then afford the system an additional degree of freedom to satisfy the individual constraints.

It is instructive to write this result in the notation of DFT+ U . By invoking a small change of variables, we arrive at the constraint energy for all sites (neglecting spin)

$$E_{C_2} = \sum_I \frac{U_1}{2} (N^I - N_c) + \sum_I \frac{U_2}{2} (N_c^2 - (N^I)^2)$$

where $U_1 = -2N_c V_c$ and $U_2 = -V_c$. (VIII.25)

The vanishing response problem can now be circumvented by decoupling the linear and quadratic Hubbard-like parameters U_1 and U_2 , and interpreting them as separate Lagrange multipliers. The corrective potential is then modified to

$$\hat{V}_{U_1, U_2} = \sum_{I\sigma} \sum_{mm'} |\varphi_m^I\rangle \left(\frac{U_1^I}{2} - U_2^I \hat{n}_{mm'}^{I\sigma} \right) \langle \varphi_{m'}^I|, \quad (\text{VIII.26})$$

so that the characteristic occupancy eigenvalue dividing an attractive from a repulsive potential is changed from $1/2$ to $U_1/2U_2$. Here, the U_2 parameters are responsible for correcting the interaction and for any modification to the gap. The U_1 parameters, meanwhile, may be used to adjust the linear dependence of the energy on the subspace occupancies, and thereby refine eigenvalue derived properties such as the ionisation potential (IP).

Fig. VIII.3 shows the total-energy W contour plot of the H_2^+ system as before against the U_1 and U_2 defined in Eq. (VIII.25). The subspace target occupancy is $N_c = N_{\text{exact}} = 0.602$ e, where the population of each of the two PBE $1s$ orbital subspaces was calculated using the exact functional. We see that the total-energy is maximised along the heavy white line at ~ 0.92 eV below the exact energy, for which the constraint is satisfied for non-unique pairs of (U_1, U_2) .

To understand why the total-energy stationary points are always degenerate, and hence why the occupancy condition fails to distinguish a unique (U_1, U_2) , we must conduct a second derivative test on the Hessian of the constraint functional⁵, given by

$$H_{ij} = \frac{d^2 W}{dU_i dU_j}. \quad (\text{VIII.27})$$

⁵Total-derivatives are used here to indicate that self-consistent density response effects are included. The Hubbard parameters remain independent variables.

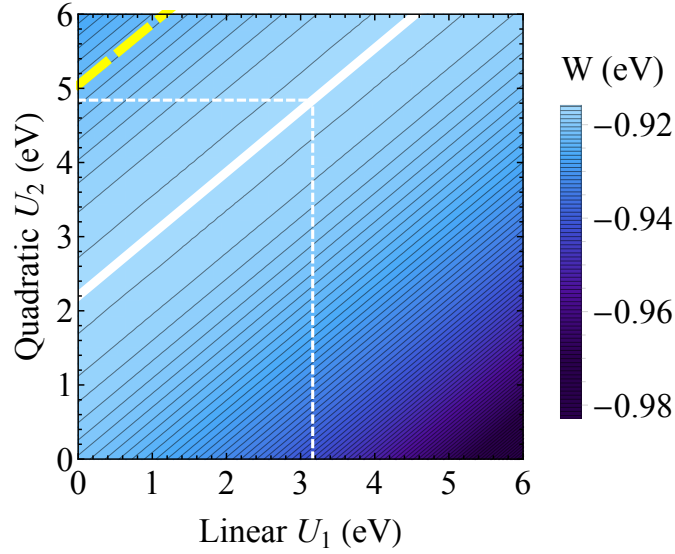


Figure VIII.3: The constrained energy of H_2^+ at $4 a_0$ relative to the exact total-energy, against U_1 and U_2 , with target occupancy $N_c = N_{\text{exact}}$. The constraint is satisfied at the total-energy maximum along the solid white line, which lies ~ 1 eV below the exact energy. The ionisation potential (IP) is exact along the thick yellow line. The linear-response Hubbard U_2 , together with the U_1 , needed to recover the exact subspace density and maximise the total-energy, are shown using thin dashed lines.

It directly follows that the determinant of $\mathbf{H}$ is conveniently calculated in terms of the response functions

$$\begin{aligned} |\mathbf{H}| &= \frac{1}{2} \begin{vmatrix} dN/dU_1 & -dN^2/dU_1 \\ dN/dU_2 & -dN^2/dU_2 \end{vmatrix} = \frac{1}{2} \begin{vmatrix} dN/dU_1 & -2NdN/dU_1 \\ dN/dU_2 & -2NdN/dU_2 \end{vmatrix} \\ &= N \left(\frac{dN}{dU_1} \frac{dN}{dU_2} - \frac{dN}{dU_1} \frac{dN}{dU_2} \right) = 0, \end{aligned} \quad (\text{VIII.28})$$

since

$$\frac{dW}{dU_1} = \frac{1}{2}(N - N_c) \quad \text{and} \quad \frac{dW}{dU_2} = \frac{1}{2}(N_c^2 - N^2). \quad (\text{VIII.29})$$

Given an inconclusive second derivative test, this implies a vanishing energy curvature along the lines which contain a constant corrective potential and, hence, no unique maximum, as shown by Fig. VIII.3.

Suppose we may identify a unique maximum by directly calculating the U_2 parameter first, and then optimising the total-energy along U_1 . The self-consistent

linear-response U calculated at this bond-length is 4.84 eV. If we intuitively set $U_2 = U$, based on the correspondence between the interaction corrections in both approaches, then an associate $U_1 = 3.16$ eV is required to recover the exact subspace density. These values are indicated by the intersecting white dashed lines in Fig. VIII.3. However, the maximum constrained total-energy is still bounded by the choice of target occupancy and remains ~ 1 eV below the exact energy unless supplemented with an additional energy correction.

Alternatively, if we select another plausible target occupancy $N_c = 0.511$ e the constrained energy can be tuned to reach a maximum at the exact energy, however it requires an unphysical $U_1 = U_2 \approx -444$ eV to do so.

Finally, the line on which the IP is exact intercepts $U_1 = 0$ eV at the linear-response $U_2 \approx U$, echoing the ‘SIC’ double-counting correction proposed in Ref. [579]. However, the IP is also irreconcilable with the exact total-energy, for any U_1 and U_2 , unless subsidised with an energy correction as well. We conclude, therefore, that a ground-state susceptible to SIE cannot be excited in a systematic way to a state that is free from SIE by means of exact constraints on the density, without breaking a physical symmetry. In other words, the total-energy cannot typically be corrected of SIE in this scheme by altering the density alone, and a non-zero energy correction term is typically required.

3 A GENERALISED DFT+ U FORMULA

We have heretofore shown that non-linear constraints targeting the SIE of a one-electron system cannot restore the exact total-energy by means of automated methods. Moreover, we have observed that attaining the exact total-energy or eigenvalue from a linear combination of occupancy-dependent constraints is not feasible without a supplemental energy term. Motivated by these findings, we return toward the development of a generalised DFT+ U functional - one that can simultaneously correct the SIE and restore Koopmans’ condition. The strategy we elect to explore in the remainder of this Chapter then is that of computing the U_1 and U_2 parameters from first-principles from linear-response methodology.

Returning again to Eq. (VIII.25), let us omit the target density dependence (by setting $N_c^I = 0$) and extract the free-energy [566] while adapting the treatment of the subspace occupancy to multi-orbital sites and neglecting inter-eigenvalue terms by resetting $N \rightarrow \text{Tr}[\hat{n}]$, in the spirit of DFT+ U . By the above modifications, we arrive at the generalised DFT+ U functional, given by

$$E_{U_1, U_2} = \sum_{I\sigma} \frac{U_1^I}{2} \text{Tr} [\hat{n}^{I\sigma}] - \sum_{I\sigma} \frac{U_2^I}{2} \text{Tr} [(\hat{n}^{I\sigma})^2], \quad (\text{VIII.30})$$

where the conventional DFT+ U functional of Eq. (V.25) is recovered by simply setting $U_1^I = U_2^I$ ⁶.

The supplemental energy correction we previously sought in order to reconcile the eigenvalue is hereby provided by the linear term in Eq. (VIII.30), the total-energy generated by which is shown in Fig. VIII.4 against U_1 and U_2 as before. The zero of energy is again set to the exact energy E_{exact} , the intercept of which with the PBE+ U_1+U_2 energy is indicated by the heavy dashed line. The thin dashed lines then indicate the previously calculated Hubbard $U_2 = 4.84$ eV, and the corresponding $U_1 = 4.44$ eV required to recover it. We note these are remarkably similar to the U value needed by a traditional DFT+ U calculation ($U_1 = U_2 = 3.85$ eV) to do the same.

The heavy white line, indicates where the exact subspace occupancy is acquired, as in Fig. VIII.3, which intersects with the exact total-energy (orange dashed line) at $U_1 = 5.73$ eV and $U_2 = 6.98$ eV, at which point E_{exact} and N_{exact} are simultaneously attained. At the same point, however, the KS eigenvalue ε_{DFT} lies ~ 2.8 eV above $\varepsilon_{\text{exact}}$. This highlights that an accurate total-energy at a particular occupancy may coincide with an inaccurate ionisation energy, and vice versa, as was recently shown in detailed analyses of the residual SIE in hybrid functionals [419] and in DFT+ U itself [395], at fractional total occupancies.

However, the generalised DFT+ U functional does in fact enable the simultaneous correction of the IP (yellow line in Fig. VIII.3) and the total-energy at $U_1 = 10.03$ eV and $U_2 = 14.18$ eV. This preliminary finding is very encouraging and in the following

⁶ We also note a resemblance between Eq. (VIII.30) and the three-parameter DFT+ $U\alpha\beta$ functional proposed in Ref. [580], however the functional forms are quite different.

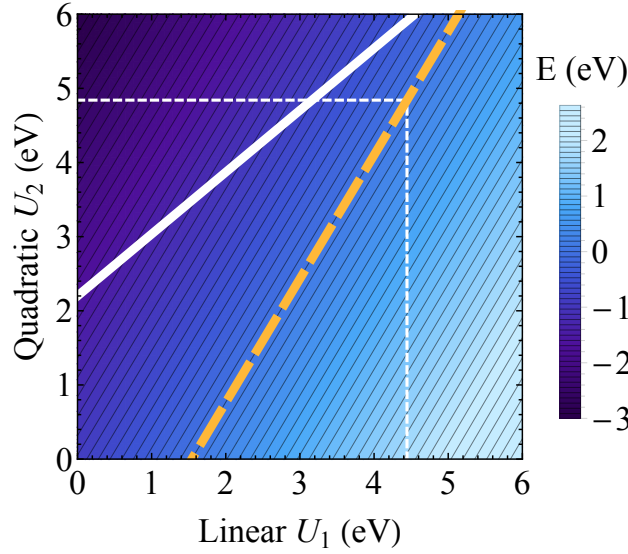


Figure VIII.4: The free energy of H_2^+ at $4 a_0$ relative to the exact total-energy, obtained from the generalised DFT+ U functional in Eq. (VIII.30) against U_1 and U_2 , with target occupancy $N_c = N_{\text{exact}}$. The thick orange line is the exact energy intercept, and the thin dashed lines show the linear-response U_2 together with the corresponding U_1 needed to recover the exact energy. The solid white line indicates where the exact subspace occupancy is recovered, as in Fig. VIII.3.

section, we will endeavour to invoke these exact conditions across the entire dissociation of H_2^+ . We have shown, however, that the generalised DFT+ U formula may provide the correction of any two of the exact energy, eigenvalue, or occupancy, but not all three simultaneously. This highlights the inherent limitation of this generalised functional going forward.

3.1 NON-SELF-CONSISTENT ESTIMATES FOR U_1 AND U_2

We have thus far been able to effectively estimate the U_1 and U_2 values required to attain the exact total-energy and IP by exploring the energy landscape and taking reasonable extrapolations. This procedure, however, is not practical to follow for all bond-lengths, and a more efficient means of computing U_1 and U_2 must be employed. Fortuitously, in a one-electron case such as H_2^+ , the degrees of freedom afforded by the two Hubbard parameters allow us to simultaneously resolve the exact total-energy and IP using simple linear algebra.

As demonstrated by the occupancy curves in Fig. V.3, there is a negligible charge and kinetic screening effect upon applying a $+U$ correction. We may therefore estimate the required U_1 and U_2 values non-self-consistently by simply supplementing the PBE total-energy (Fig. V.2) with the DFT+ U_1+U_2 functional, and the ionisation potential (Fig. V.4) with the corresponding correction potential given in Eq. (VIII.26). We may then fit these curves against the exact total-energy profile with respect to the U_1 and U_2 parameters, to acquire reliable estimates.

Here, we have also used the convenient feature of H_2^+ that the PBE $1s$ orbital subspace projectors closely match the KS orbitals in spatial profile, and almost exactly so at dissociation. Consequently, the red and blue open circles in Fig. VIII.5 illustrate the values of U_1 and U_2 required to perform this task, as a function of internuclear distance, which at first seem very large but, nonetheless, deliver the desired result.

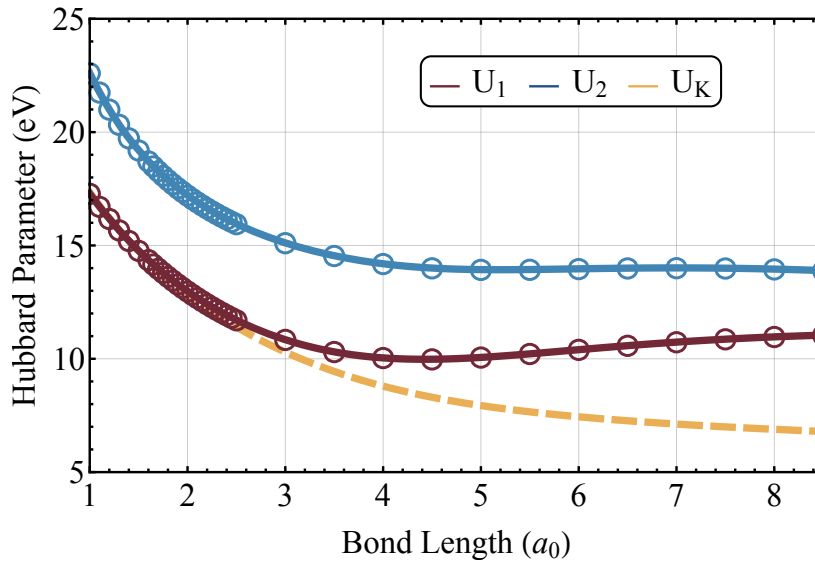


Figure VIII.5: Generalised Hubbard U_1 and U_2 parameters (red, blue) estimated to recover the exact total-energy and Koopmans' condition in dissociating H_2^+ using Eq. (VIII.35). Open circles show the corresponding quantities estimated from linear regression of the exact total-energy and the PBE+ U total-energy. The Koopmans U_K is also shown (orange), which dominates U_1 at short bond-lengths.

Let us now attempt to derive formulae to estimate U_1 and U_2 from ground-state DFT quantities. Upon the application of a conventional DFT+ U correction, stiffening

in the subspace response is typically observed [396, 415], as demonstrated by the comparable occupancies in Fig. V.3 for $U = 0$ eV and $U = 8$ eV. It is therefore reasonable to construct a charge non-self-consistent first-principles calculation scheme for U_1 and U_2 , e.g., for use in refining DFT+ U calculations in order to approximately enforce Koopmans' condition, and we may ask if we can conveniently estimate U_1 and U_2 using intrinsic quantities of a PBE calculation, without explicit access to the exact values. It would also be advantageous to establish a relationship between U_1 and U_2 and the linear-response U . In this section, we shall therefore outline a procedure to estimate the charge non-self-consistent U_1 and U_2 parameters for H_2^+ without relying on the fitting of curves with the exact energy profile post-process.

For M equivalent one-orbital subspaces contributing to the energy band responsible for the eigenvalue ε_{DFT} , the exact total-energy and eigenvalue may be approximated from their corresponding PBE quantities as follows

$$E_{\text{exact}} \approx E_{\text{DFT}} + M \left(\frac{U_1}{2} N_{\text{DFT}} - \frac{U_2}{2} N_{\text{DFT}}^2 \right) \quad (\text{VIII.31})$$

$$\varepsilon_{\text{exact}} \approx \varepsilon_{\text{DFT}} + \frac{U_1}{2} - U_2 N_{\text{DFT}} \quad (\text{VIII.32})$$

with density non-self-consistent U_1 and U_2 , where $N_{\text{DFT}} = \text{Tr} [\hat{n}_{\text{DFT}}]$, and neglecting overlap and spillage.

Let us now suppose that we have calculated a conventional U which reconciles the total-energy reasonably, so that

$$E_{\text{exact}} \approx E_{\text{DFT}} + M \frac{U}{2} (N_{\text{DFT}} - N_{\text{DFT}}^2). \quad (\text{VIII.33})$$

Finally, we wish to exactly satisfy Koopmans' condition:

$$\varepsilon_{\text{exact}} = E_{\text{DFT}}[N] - E_{\text{DFT}}[N - 1], \quad (\text{VIII.34})$$

where the term $E[N - 1]$ is the DFT-estimated total-energy of the ionised system, which in this case, is simply the ion-ion energy $E_{\text{ion-ion}}$.

Thus, combining Eqs. (VIII.31) - (VIII.34), where only convenient, approximate DFT quantities have been used, we arrive at

$$\begin{aligned} U_1 &\approx U (1 - N_{\text{DFT}}) (2 - M N_{\text{DFT}}) + U_K \\ \text{and } N_{\text{DFT}} U_2 &\approx U (1 - N_{\text{DFT}}) (1 - M N_{\text{DFT}}) + U_K, \end{aligned} \quad (\text{VIII.35})$$

where we have defined the ‘Koopmans U ’ as follows

$$U_K = 2 (\varepsilon_{\text{DFT}} - \{E_{\text{DFT}}[N] - E_{\text{DFT}}[N-1]\}). \quad (\text{VIII.36})$$

This term is the part of the correction that effectively imposes Koopmans’ condition, primarily affecting U_1 . These results correspond remarkably well with the exact values required, as shown by the solid lines in Fig. VIII.5, and confirms the validity of approximating a negligible density response.

The interdependence between the parameters for any value of M

$$U_1 - U_2 N_{\text{DFT}} \approx U (1 - N_{\text{DFT}}) \quad (\text{VIII.37})$$

also reveals the role of U in characterising the degree of splitting between U_1 and U_2 . Moreover, enforcing Koopmans’ condition in H_2^+ pushes both U_1 and U_2 up to considerably higher values than are commonplace [343] in conventional DFT+ U . In Fig. VIII.5, we see that U_1 is dominated by U_K at short bond-lengths, where $U_1 \approx N_{\text{DFT}} U_2$, before ultimately falling off to the average of U and U_2 in the fully dissociated limit. Over the same range, U_K composes 75% - 50% of U_2 .

3.2 APPLICATION TO H_2^+

Using the estimated U_1 and U_2 values in Eq. (VIII.35), we performed density non-self-consistent DFT+ U_1+U_2 calculations on H_2^+ using the non-self-consistent formulae for the PBE total-energy and occupied KS eigenvalue given in Eqs. (VIII.33) & (VIII.34). To put the method on a first-principles footing, we invoke the self-consistent $U^{(2)}$ value, (calculated using the methods described in Chapters VI & VII) to determine U_1 and U_2 . The resulting corrections to the total-energy E and eigenvalue ε take the form

$$\Delta E = U^{(2)}(N - N^2) \quad \text{and} \quad \Delta v_U = \frac{U^{(2)}}{2}(1 - 2N) - \frac{U_K}{2},$$

where $U_K/2 = \varepsilon_{\text{PBE}} - (E_{\text{PBE}} - E_{\text{ion-ion}}).$ (VIII.38)

Fig. VIII.6 illustrates the result of this simple technique, which simultaneously reconciles the total-energy and eigenvalue-derived binding curves with the exact result⁷ in Fig. V.2.

⁷ The total-energy here is that of PBE+ $U^{(2)}$ given in Fig. VII.3.

Although the correction is imprecise, since this is a non-self-consistent post-processing step, it nonetheless presents a compelling possibility toward extending DFT+ U to ameliorate the IP. Indeed, in the dissociating limit, where changes to the occupied Kohn-Sham orbital are negligible and $N \rightarrow 1/2$, we find that

$$\begin{aligned}\varepsilon_{\text{PBE}+U_1+U_2} &= \varepsilon_{\text{PBE}} - (E_{\text{ion-ion}} - E_{\text{PBE}} + \varepsilon_{\text{PBE}}) \\ &= -(E_{\text{ion-ion}} - E_{\text{PBE}+U_1+U_2}) \equiv -\text{IP},\end{aligned}\quad (\text{VIII.39})$$

which restores Koopmans compliance for a SIE correction strength U .

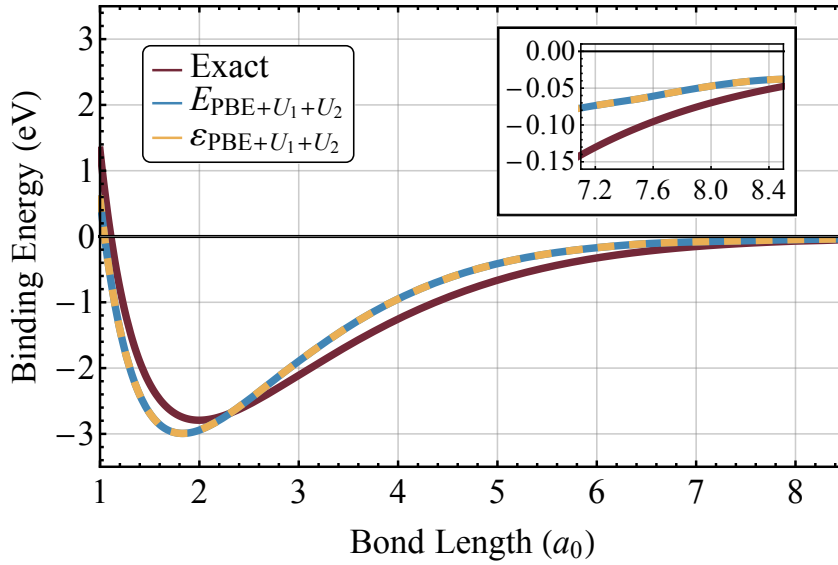


Figure VIII.6: Exact (red), total-energy based $E_{\text{PBE}+U_1+U_2}$ (blue), and eigenvalue based $\varepsilon_{\text{PBE}+U_1+U_2}$ (orange) binding curves for H_2^+ , calculated using DFT+ U_1+U_2 , which enables the simultaneous SIE correction of the total-energy and Kohn-Sham eigenvalue to precisely the same accuracy.

4 CONCLUSION

To conclude, we have proven analytically, and with stringent numerical tests, that non-linear constraints are incompatible with the correction of SIE with cDFT. It is not possible, therefore, to automate systematic SIE corrections of the type provided by DFT+ U by means of cDFT, notwithstanding the great utility of the latter.

We demonstrated that progress can be made, however, by constructing separate constraints for the linear and quadratic density terms and decoupling the corresponding Lagrange multipliers. As we have shown, the resultant non-uniqueness of stationary points of such a scheme requires the introduction of additional physics, such as linear-response theory for U_2 .

Our conclusion that a ground-state afflicted by SIE cannot be systematically excited to a state that is less so, by means of constraints, is reinforced by the fact that it is the target-independent free-energy, and not total-energy, that agrees with the exact energy. Indeed, the free-energy of this functional, equivalent to a generalised DFT+ U energy, allows both the exact occupancy and energy to be recovered for a reasonable pair of U parameters, which improves upon the performance of conventional DFT+ U . It also provides for the correction of the eigenvalue and the exact energy simultaneously, but at the forfeit of the exact density.

Nonetheless, we have found that the free-energy functional offers the capability of simultaneously correcting two central quantities in DFT, the total-energy and the highest occupied orbital energy. This provides further motivation for our so-called ‘generalised DFT+ U ’ functional, the results of which highlight the potential of the DFT+ $U_1 + U_2$ functional and its immediate compatibility with self-consistently calculated Hubbard U parameters.

The approximate formulae for the required parameters, which may differ greatly from the familiar Hubbard U (even in a one-electron system), offer a novel framework in which to further develop double-counting techniques and first-principles schemes for the promising class of methods correcting SIE based on DFT+ U [343, 395, 396, 440], as well as opening up possibilities for their diverse application. For example, we envisage that SIE correction schemes of two or more parameters may also be useful for generalising the exchange fraction of hybrid functionals [419], and for DFT+ U type corrections of perturbative many-body approximations such as GW [543], the deviation from linearity of which is somewhat analogous [581, 582]. More pragmatically, we expect the extra degree of freedom furnished by U_1 to be beneficial in cases where the quadratic approximation to the subspace-averaged self-interaction does not remain valid all the way down to the ionised state, which is particularly relevant

for H_2^+ , since that is where the state corresponds to the low-density limit.

Interesting avenues for the immediate development of this method include its extension to multi-electron, heterogeneous, and non-trivially spin-polarised systems, as well as to perform self-consistency over the density and to lift the fixed-occupancy approximation, as outlined in Ref. [413]. For compliance with Koopmans' condition, it seems unavoidable for now that data must be collected from both the approximate neutral and ionised systems (the total-energy of which may be sufficient), to calculate U_1 and U_2 . In the manner in which we have performed it here, non-self-consistent DFT+ $U_1 + U_2$ requires only one total-energy calculation at the ionised state, on top of the usual apparatus of a linear-response DFT+ U calculation, in order to simultaneously (albeit approximately) correct the total-energy and the HOMO eigenvalue for SIE. In principle, a further refinement of the method might entail the self-consistent linear-response calculation of U_1 and U_2 separately for the neutral and ionised states.

Nonetheless, what is revealed in this Chapter is a convenient scheme for correcting the exact energy and eigenvalue, in conjunction with a U calculated via self-consistent ground-state linear-response approach (or otherwise), for a system with negligible variance in average subspace occupancy under an applied U .

IX

CONCLUDING REMARKS

IT IS THE DESIRE OF every postgraduate student to contribute meaningfully and fruitfully, in a manner however small, to the body of work cultivated by their mentor, colleagues, and predecessors. In this dissertation, we have strived, as much as possible, to present a comprehensive and coherent account of our modest research, for both posterity and the hope that it may contribute to new paths forward. We now end with a brief summary on the central findings of each Chapter and a discussion on some potential avenues for further research based on our research.

1 SYNOPSIS

We began our discussion in Chapter II by outlining the chronology of significant developments that gave rise to Kohn-Sham DFT, which is now routinely applied in contemporary research in chemistry and materials science. We highlighted the important consequences of utilising approximate exchange-correlation functionals, which includes, but is not limited to, the qualitative mischaracterisation of strongly-correlated systems due to the onset of self-interaction (SIE) and static correlation (SCE) errors. Moreover, we placed a special emphasis on the exploitation of the near-sightedness of quantum mechanical interactions [26], which contributed to the development of linear-scaling methods.

In Chapters III & IV we presented the results of a comprehensive set of DFT calculations on the puckered phase of phosphorus, arsenic, antimony, and their few-layer counterparts. We discovered that the mechanical properties of these materials are well described by approximate DFT and corroborate experimental measurements. This enables further predictions regarding the mechanical properties of these novel 2D materials, such as their use in nano-composite materials [181, 583], to be made in confidence.

The electronic properties, on the other hand, were found to be largely underestimated with respect to the experimental values, a result that is characteristic of the SIE. Nonetheless, we expect general trends in electronic behaviour to be reliable and we made preliminary predictions of possible Weyl and Dirac states in many of these structures. Our preliminary results in this section showcase the possible exciting directions that developments in these materials may take the near future such as in high-mobility conductors [193, 203, 224, 224, 232, 292–294], battery materials [175, 176], transistors [190, 191], and catalysts [199, 584]. Indeed, from our results we have shown that reasonable strains, which are experimentally accessible, provide a convenient mechanism to attain exotic electronic behaviour in the group-V materials without the need for doping.

In Chapter V, we explored the nature of the SIE and SCE in greater detail. In particular, we discussed how they relate to violations of the physical conditions obeyed by the exact functional, namely piece-wise linearity and piece-wise constancy, which may be respectively understood from the perspectives of fractional occupancies and fractional spins. We also discussed some historically successful procedures to ameliorate these conditions and recognised the noteworthy contributions of Perdew and Zunger [20], and Dabo [330]. In particular, we note the efforts of the latter to restore Koopmans’ compliance, as well as the widely successful DFT+Hubbard U (DFT+ U) method [343], the marriage of which is a central focus of this thesis.

The calculation of Hubbard U parameters from first-principles in a code utilising direct minimisation motivated the work discussed in Chapter VI. We outlined the challenges we faced with the popular linear-response method of Cococcioni and co-workers [342, 354] and our approach for modifying it to surpass them.

The calculated parameters were accompanied by small statistical errors and generalised easily to multi-electronic systems. The DFT+ U calculations performed on various strongly-correlated systems, including bulk NiO and Cr₂O₃, yielded results that greatly improved upon the uncorrected DFT treatment without exception and were in line with qualitative and quantitative experimental data provided by colleagues. This showed that our method was highly robust, readily applicable to a broad range of systems, and capable of competing with other state-of-the-art methods.

A key advantage of our adapted method is that the response functions, and by extension the Hubbard U and J parameters, are computed as ground-state properties of the system, thereby elevating DFT+ U to the status of a self-contained, ground-state density-functional theory. This was not the case beforehand and precluded the direct comparison of DFT+ U total energies needed for computing thermodynamic quantities, which were inherently ill-defined as a result. The fact that the Hubbard U parameter can now be regarded as an implicit functional of the ground-state density represents an important first step toward enabling this functionality and will be a welcome upgrade for many researchers in this field [393, 444, 446, 447].

We also drew upon the observations we made in Chapter V to propose a similar procedure for calculating the exchange parameter J . The exchange parameters were also determined very accurately and were largely in line with values calculated in previous studies. These results were greatly encouraging and provided a firm framework as we progressed to establishing self-consistency schemes for both parameters.

Our desire for a framework enabling the direct comparison of DFT+ U total-energies to facilitate the calculation of thermodynamic quantities, was outlined in Chapter VII. We discussed how the comparability of total-energies depends on the condition that the applied U (or J) is a functional of the DFT+ U ground-state density to which it is applied. We therefore extended the variational linear-response method to allow the self-consistent calculation of U and J . Here, they became implicit functionals of both the ground-state density and input parameters and thereby provided a convenient mechanism to identify the self-consistency scheme that fully corrects the SIE. The resulting output parameters were also highly accurately resolved and extensive investigation of the different schemes applied to NiO allowed us to identify the self-consistency schemes that provided the best agreement with experiment, which were also in line with our model predictions.

This approach was then used to correct the SCE of H_2 in the dissociating limit with a self-consistently calculated J , which is the first instance that this parameter has been used in this manner. We showed that not only was a self-consistent J capable of quantifying and removing the SCE in H_2 beyond the Coulson-Fischer point, but a self-consistent scheme was actually required to do so. This confirmed

our earlier empirical observation that both J and the SCE relate to the total-energy curvature with respect to magnetisation and indicates that a combined correction of SIE and SCE may be possible. However, more research is required to render the scheme applicable for short bond-lengths.

Our findings in this section provide new and interesting insights toward the efficient first-principles correction of SIE and SCE. Our scheme is not only accurate and transferable, but it is also applicable in direct minimisation and SCF codes alike and, therefore, has far reaching potential to be useful across many platforms and for a large variety of systems.

We then motivated our development of a generalised DFT+ U functional that allowed for the simultaneous treatment of both SIE and non-compliance with Koopman’s theorem in Chapter VIII. We first demonstrated that the automatic removal of SIE in a system by means of enforcing non-linear constraints within constrained-DFT (cDFT) to be unfeasible, even for a one-electron system. This presented a surprising impasse through which we make progress by instead limiting the directions of methods based on this strategy.

Nevertheless, we showed that a two-parameter DFT+ U functional could correct both the total-energy and eigenvalue. We then derived an approximate scheme to calculate the U_1 and U_2 parameters required to restore Koopmans’ compliance and correct SIE in a one electron system with a generalised DFT+ U functional. We provided the formulae with the best self-consistent U values derived in Chapter VII, and proceeded to correct the total-energy and eigenvalue for dissociating H_2^+ to precisely the same accuracy.

This very promising result prompts the development of an application to multi-electronic systems where it would be useful for instance in heterogeneous catalysis and charge transfer calculations. Indeed, we expect that the novel developments made in this dissertation will contribute greatly towards the high-throughput calculation computation of thermodynamical quantities [399, 444–448], reaction barriers [508–510], charge-transfer energies [5, 59, 60, 324, 545], and formation enthalpies. These quantities are central to the development of solutions to many of the challenges we currently face in the 21st century in sustainable energy, transport, materials

science, and engineering. We have therefore shown that there still lies much scope in the development of DFT+ U and its utility in electronic structure methods has yet untapped potential to provide more valuable and exciting contributions toward these endeavours.

2 FUTURE WORK

Let us now briefly discuss some of the possible future directions of research based on the works presented in this dissertation.

It is clear that Koopmans' compliance remains a vexing challenge for the design of self-contained methods, even for very sophisticated exchange-correlation functionals and correction schemes. On the basis of our results in Chapter VIII, a generalised functional, such as our DFT+ U_1+U_2 , presents an intriguing and very promising avenue of exploration for future methods.

If the proposed scheme described earlier is applied to supplement an existing DFT+ U calculation that has already accurately recovered the total-energy, then it is sufficient to set $U = 0$ eV in our approximate formulae of Eq. (VIII.35). This is because the SIE interaction has already been treated by an appropriate + U_0 correction. An approximately Koopmans-compliant DFT+ U calculation may then be performed by a simple change of parameters

$$(U_1, N_{\text{DFT}}U_2) \rightarrow (U_K, U_K), \quad (\text{IX.1})$$

which only requires knowledge of the ionised state $E[N - 1]$.

The scheme may also be generalised to multi-orbital subspaces straightforwardly, by replacing N_{DFT} with a sum over the eigenvalues of $\hat{n}_{\text{DFT}}^I$, given as follows

$$N_{\text{DFT}} \rightarrow \sum_m [\hat{n}_{mm'}^I] \quad \text{and} \quad N_{\text{DFT}}^2 \rightarrow \sum_m [\hat{n}_{mm'}^I \hat{n}_{m'm}^I], \quad (\text{IX.2})$$

which ignores intra-subspace interactions in the spirit of DFT+ U .

Finally, the approximation of constant N_{DFT} may be replaced by a linear-response approximation, in terms of the response function χ ,

$$N_{\text{DFT}} \rightarrow \chi \text{Tr}[\hat{v}_{\text{ext}} \hat{P}] \quad (\text{IX.3})$$

or lifted entirely by means of a parametrisation of the occupancies in terms of $\text{Tr}[\hat{v}_{U_1 U_2}]$ and a numerical solution of the resulting equations. In this work, we have opened the door to the possibility of designing other generalised functionals, which may be motivated by the need for other specialised purposes that are beyond the scope of the traditional DFT+ U functional. The possibilities for such will only become apparent with time, and will hopefully illuminate new paths in future research.

On the basis of the modest success of our self-consistency schemes for U , we are obliged to investigate more thoroughly the extension to the self-consistent J . A puzzling outcome was the facile agreement of the PBE+ $J^{(2)}$ scheme with the H_2 total-energy at dissociation, where the expected J_{eff} scheme was clearly inappropriate. We are hence motivated to investigate the difference in the self-consistency calculation schemes presented for the U and J terms, in correcting the SIE and SCE, respectively.

Furthermore, the analysis of the U_{in} vs U_{out} and related procedures, raises many questions about the nature of the full 4-dimensional space described by U_{in} , U_{out} , J_{in} , and J_{out} . We may ask, what are the self-consistency schemes arising from the intersections of each curve with the axes, in particular the location of the point where $U_{\text{eff}} = J_{\text{eff}} = 0$.

The calculation of U heretofore, has only considered uniform perturbations to both spins in a subspace. An interesting generalisation of this, which is currently being pursued by our colleague, Edward Linscott, is the calculation of a Hubbard U matrix indexed by spin instead of site.

$$U^{\sigma\bar{\sigma}} = \begin{pmatrix} F^{\uparrow\uparrow} & F^{\uparrow\downarrow} \\ F^{\downarrow\uparrow} & F^{\downarrow\downarrow} \end{pmatrix} \quad (\text{IX.4})$$

The advantage here is one could compute each (screened) spin interaction precisely, and no longer have to rely on averages. An encouraging preliminary test shows that the method conveniently reduces to the average on-site U value, at least for closed-shell systems, when averaged over all interactions in the U matrix.

Another modification to DFT+ U that we discussed in section 5, pertains to the definition of the subspace projectors. Our proposal to circumvent the inaccurate population analysis that arises in cases of strong subspace overlap is to redefine the projectors to span the subspaces that belong to a specific group $\mathcal{G}$, characterised

by a certain properties in a so-called unified sites (US) approach. This proposed scheme is reminiscent of the DFT+ U + V functional in Ref. [441], which invokes an inter-site V term, and is expected to be advantageous under conditions of strong subspace hybridisation, for example, in the near-bonding regimes for dissociating dimers. Another possible application is in VO_2 where the U parameter applied to the individual subspaces of each V atom is known to erroneously cause them to dimerise, and ultimately fails to produce a gap [93]. In the US approach, we would compute and apply a U parameter that is bare to the *combined* V atom subspace with the intention to avoid the spurious dimerisation. Our colleague, Evan Sheridan, is currently working on this approach and initial testing on VO_2 has been very promising.

Finally, building upon our exercise in two-dimensional materials, we propose some candidates that may benefit from a DFT+ U treatment in conjunction with a self-consistent U . Some nascent materials in this class include transition metal diborides [585, 586] such as titanium diboride (TiB_2) [290, 587, 588], and magnesium diboride (MgB_2) [589–591], as well as vanadium oxide (V_2O_5) [592–595], for which current literature does not feature DFT+ U calculations on the few-layer structures.

A

SAMPLE INPUT FILES

1 SAMPLE QUANTUMESPRESSO INPUT FILE

```
&control
  title = 'p',
  calculation = 'relax',
  restart_mode='from_scratch',
  prefix='p',
  pseudo_dir = '~/pseudos'
  verbosity='normal',
  tprnfor=.true.,
  tstress=.true.
  etot_conv_thr = 1.0E-7,
/
&system
 ibrav=0
  celldm(1)=6.2618
  nat=8
  ntyp=1
  nspin=1
  nbnd=40
  vdW_corr='DFT-D'
  ecutwfc = 80
  ecutrho = 640
  occupations='smearing'
  smearing='marzari-vanderbilt'
  degauss=0.0001
/
&electrons
  mixing_mode = 'TF'
  conv_thr = 1.0e-10
/
&ions
  ion_dynamics = 'bfgs'
/
&cell
  cell_dynamics = 'bfgs'
/

ATOMIC_SPECIES
P      30.973761998 P.pbe-n-rrkjus_psl.0.1.UPF

ATOMIC_POSITIONS angstrom
<ATOMIC POSITIONS>

CELL_PARAMETERS alat
<CELL PARAMETERS>

K_POINTS automatic
15 15 15 0 0 0
```

2 SAMPLE ONETEP INPUT FILE

```
#####
#####
##          ONETEP TEMPLATE INPUT FILE          ##
##          Glenn M Moynihan 2015              ##
#####
#####

# =====
#          SETUP PARAMETERS                      #
# =====

# -----
# Task Type
# -----
task                : SINGLEPOINT

# -----
# How much detail?
# -----
output_detail       : NORMAL

# -----
# Specify Cutoff Energy ~ 1170 eV
# -----
psinc_spacing       : 0.420266667 0.420266667 0.420266667

# -----
# XC Functional Type and Options
# -----
xc_functional       : PBE

# -----
# Toggle Read/Write Restart Files
# -----
write_converged_dk_ngwfs : F
write_denskernel     : T
write_tightbox_ngwfs   : T
read_denskernel      : F
read_tightbox_ngwfs    : F

# =====
#          MULTITHREADING                      #
# =====

threads_max         : 2
threads_num_fftboxes : 2
threads_per_fftbox   : 1
threads_per_cellfft  : 1

# =====
#          TECHNICAL PARAMETERS                #
# =====

# -----
# Density Kernel Optimisation (Inner Loop)
# -----
lnv_cg_max_step      : 10.0
maxit_lnv             : 35
minit_lnv            : 5
```

```

lnv_check_trial_steps      : T
kernel_update              : T

# -----
# NGWF Optimisation (Outer Loop)
# -----
ngwf_threshold_orig        : 2.0e-6
ngwf_cg_max_step           : 4.0
maxit_ngwf_cg              : 100
elec_cg_max                : 5
delta_e_conv               : T
ELEC_ENERGY_TOL            : 1.0e-4 eV

# -----
# Better nursing parameters for solid oxides
# -----
maxit_pen                   : 0
maxit_palser_mano           : -1
maxit_kernel_fix           : 3
kerfix                     : 2
maxit_hotelling             : 0
pen_param                   : 20

charge                      : 0          # Set Background Charge
dos_smear                   : 0.10 eV    # Densities of states
occ_mix                     : 0.25       # Occupational Mixing
timings_level               : 1          # Set level of detail in timings

# =====
#                               TURN FEATURES ON/OFF                               #
# =====

# Toggle Spin
spin_polarized              : T
spin                        : 0

# Toggle Hartree Potential
#turn_off_hartree           : F

# Toggle Unify Sites
hubbard_unify_sites         : F

# Print potentials to calculate U
hubbard_calculating_U       : T

# Print calculation summary
print_qc                    : T

# Output formats:
cube_format                 : F
grd_format                  : F

# Plot densities, orbitals
write_density_plot          : T
lumo_dens_plot              : 1
homo_dens_plot              : 1
lumo_plot                   : 1
homo_plot                   : 1

# Check atomic positions
check_atoms                 : T

```

2. Sample ONETEP input file

```
# Plot NGWFs, see %block species_ngwf_plot
write_ngwf_plot          : F

# Do post-processing
do_properties            : T

# Compute dipole moment
polarisation_calculate   : F

# Spherical harmonic decomposition of NGWFs
ngwf_analysis            : F

# Forces
write_forces             : T

popn_calculate           : T
initial_dens_realspace    : T
write_params             : T
write_initial_radial_ngwfs : F

# =====
#                               ATOMIC SETUP                               #
# =====

# -----
# Species List
# -----
%block species_ngwf_plot
Ni1
Ni2
O1
O2
%endblock species_ngwf_plot

# -----
#! Block describing NGWFs of species
# -----
# Species, Label, Atomic number, #NGWF's, NGWF cutoff
%block species
bohr
Ni1 Ni 28 9 11.0
Ni2 Ni 28 9 11.0
O1  O  8 4 11.0
O2  O  8 4 11.0
%endblock species

# -----
# NGWF initial configuration guesses
# -----
%block species_atomic_set
Ni1 SOLVE conf=3s2 3p6 4s2 3d8 INIT SPIN=+2 CHARGE=+2
Ni2 SOLVE conf=3s2 3p6 4s2 3d8 INIT SPIN=-2 CHARGE=+2
O1  SOLVE ws=5.0 wp=5.0
O2  SOLVE ws=5.0 wp=5.0
%endblock species_atomic_set

# -----
# Pseudopotentials or PAW atomic data
# -----
%block species_pot
Ni1 "Ni_GGA_P2.recpot"
Ni2 "Ni_GGA_P2.recpot"
O1  "o-pbe.recpot"
```

```
02 "o-pbe.recpot"
%endblock species_pot

# -----
# Atomic decomposition of density of states
# -----

%block species_ldos_groups
Ni1
Ni2
O1
O2
%endblock species_ldos_groups

#-----
# Unit Cell Lattice Parameters
# -----

%block lattice_cart
31.5200 0.0000 0.0000
0.0000 31.5200 0.0000
0.0000 0.0000 31.5200
%endblock lattice_cart

# =====
#                               DFT+U Options                               #
# =====
# Species, L, Uin, Jin, Hub proj character, alpha, -2beta
%block hubbard
Nix 2 5.2 0.0 -1 0.0 0.0
%endblock hubbard

# -----
# Atomic Positions
# -----

%block positions_abs
# <ATOMIC POSITIONS>

%endblock positions_abs
```

B

SUPPLEMENTAL DATA FOR GROUP-V 2D MATERIALS

1 DERIVATION OF THE VOIGT-REUSS-HILL EQUATIONS

In this Appendix, we shall re-derive the formulae for the elastic properties of a planar material as a function of orientation of the in-plane stress as outlined in Ref. [268]. The general form of Hooke's law for a non-isotropic material is expressed as the linear mapping $\varepsilon_{ij} = C_{ijkl}\sigma_{kl}$ between the stress tensor $\boldsymbol{\sigma}$ and strain tensor $\boldsymbol{\varepsilon}$ by a fourth-order stiffness tensor $\mathbf{C}$. In cartesian coordinates the stress and strain tensors are 3×3 matrices, given by

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{21} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \quad \text{and} \quad \boldsymbol{\varepsilon} = \begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{21} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{bmatrix}. \quad (\text{B.1})$$

This relation may be transformed into a rotated reference frame via a rotational matrix $\mathbf{R}$ applied to each of the tensors. If we consider rotations about the z-axis, and ignore contributions to the stresses in that direction, the rotation matrix is

$$\mathbf{R}_z(\theta) = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (\text{B.2})$$

where the transformed stress-tensor as a function of θ is now

$$\boldsymbol{\sigma}'(\theta) = \mathbf{R}_z(\theta)\boldsymbol{\sigma}\mathbf{R}_z^T(\theta), \quad (\text{B.3})$$

and likewise for the strain-tensor. For orthotropic materials subject to in-plane stress, Hooke's law may be re-expressed in Voigt notation, where the stiffness tensor is a

symmetric 3×3 matrix given by

$$C_{2D} = \begin{bmatrix} c_{11} & c_{12} & 0 \\ c_{12} & c_{22} & 0 \\ 0 & 0 & c_{66} \end{bmatrix} \quad \text{with} \quad S_{2D} = C_{2D}^{-1}, \quad (\text{B.4})$$

where S is the compliance matrix. Here, the reduced stress and strain vectors are

$$\sigma^T = [\sigma_{11}, \sigma_{22}, \sigma_{12}] \quad \text{and} \quad \varepsilon^T = [\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{12}], \quad (\text{B.5})$$

arising from planar symmetries. The reduced stress-vector of a rotated stress-tensor relates the new coordinate system to the original via a matrix operation $\sigma' = \mathbf{M}\sigma$, with

$$\mathbf{M} = \begin{bmatrix} \cos^2 \theta & \sin^2 \theta & \cos \theta \sin \theta \\ \sin^2 \theta & \cos^2 \theta & -\cos \theta \sin \theta \\ -2 \cos \theta \sin \theta & 2 \cos \theta \sin \theta & \cos^2 \theta - \sin^2 \theta \end{bmatrix}, \quad (\text{B.6})$$

and similarly for the strain tensor ε . From this, Hooke's law in a rotated frame can be expressed in the original basis as

$$\varepsilon' = \mathbf{C}'\sigma' \Rightarrow \mathbf{M}\varepsilon = \mathbf{C}'\mathbf{M}\sigma \quad (\text{B.7})$$

$$\Rightarrow \varepsilon = \mathbf{M}^T \mathbf{C}' \mathbf{M} \sigma \Rightarrow \varepsilon = \mathbf{C} \sigma, \quad (\text{B.8})$$

with $\mathbf{C} = \mathbf{M}^T \mathbf{C}' \mathbf{M}$ and similarly $\mathbf{S} = \mathbf{M}^T \mathbf{S}' \mathbf{M}$. Shown below in Eq. B.9 are the elements of the rotated C_{2D} , where the Reuss equations $S_{ij}(\theta)$ are obtained by substituting the elements $c_{ij} \rightarrow s_{ij}$:

$$\begin{aligned} C_{11}(\theta) &= c_{11} \cos^4 \theta + c_{22} \sin^4 \theta + (2c_{12} + c_{66}) \cos^2 \theta \sin^2 \theta \\ C_{22}(\theta) &= c_{11} \sin^4 \theta + c_{22} \cos^4 \theta + (2c_{12} + c_{66}) \cos^2 \theta \sin^2 \theta \\ C_{66}(\theta) &= (4c_{11} + 4c_{22} - 8c_{12} - 2c_{66}) \cos^2 \theta \sin^2 \theta + c_{66}(\cos^4 \theta + \sin^4 \theta) \\ C_{12}(\theta) &= c_{12}(\cos^4 \theta + \sin^4 \theta) + (c_{11} + c_{22} - c_{66}) \cos^2 \theta \sin^2 \theta. \end{aligned} \quad (\text{B.9})$$

From these, one can resolve the in-plane elastic properties as a function of orientation and, by integrating over θ , the average in-plane properties can be extracted from the fully isotropic tensors.

Finally, the above derivation can be easily extended to three dimensions. A general rotation matrix $\mathbf{R} = \mathbf{R}_1(\alpha)\mathbf{R}_2(\beta)\mathbf{R}_3(\gamma)$ about the coordinate axes can be

constructed by compounding three rotation matrices, parameterised by three angles of rotation α , β , γ . The elastic matrices for any rotated reference frame may be constructed by applying this general transformation to the stress and strain tensors. One arrives exactly at the Voigt [245, 246] and Reuss [247] equations from the which the Hill-averages [248] are considered reliable estimates for physical values by integrating these matrices over each of the angles α , β , γ . Presented here are the equations for the Voigt estimate for the Young's Y_V and shear modulus G_V :

$$Y_V = \frac{(A - B + 3C)(A + 2B)}{2A + 3B + C} \quad \text{and} \quad G_V = \frac{A - B + 3C}{5}, \quad (\text{B.10})$$

where the parameters A , B and C are expressed in terms of the stiffness tensor elements

$$A = \frac{c_{11} + c_{22} + c_{33}}{3}, \quad B = \frac{c_{23} + c_{13} + c_{12}}{3}, \quad \text{and} \quad C = \frac{c_{44} + c_{55} + c_{66}}{3}. \quad (\text{B.11})$$

Similarly, the equations for the Reuss estimate for the Young's Y_R and shear modulus G_R are given by

$$Y_R = \frac{5}{3A' + 2B' + C'} \quad \text{and} \quad G_R = \frac{5}{4A' - 4B' + 3C'}, \quad (\text{B.12})$$

where the parameters A' , B' and C' are expressed in terms of the compliance tensor elements

$$A' = \frac{s_{11} + s_{22} + s_{33}}{3}, \quad B' = \frac{s_{23} + s_{13} + s_{12}}{3}, \quad \text{and} \quad C' = \frac{s_{44} + s_{55} + s_{66}}{3}. \quad (\text{B.13})$$

2 CALCULATED ELASTIC TENSOR ELEMENTS

Presented in Table B.1 are the calculated stiffness tensor elements for each of the phases of P, As and Sb with available experimental data from Refs. [264, 265] given in parentheses.

	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{23}	c_{13}	c_{12}
P _{mono}	79.48	25.33	-	-	-	20.86	-	-	16.50
P _{bi}	95.16	30.44	-	-	-	28.71	-	-	20.95
P _{bulk}	187.92	55.06	67.64	4.55	22.04	64.85	1.52	10.37	42.15
Ref. [265]	178	55.1	53.6	5.5	11.1-21.3	14.5-15.6			
Ref. [264]	284	80	74	10.8	7.2	59.4			
As _{mono}	40.35	8.04	-	-	-	11.31	-	-	11.68
As _{bi}	71.25	24.91	-	-	-	23.58	-	-	23.70
As _{bulk}	134.24	41.34	93.24	11.18	20.13	49.26	15.27	23.37	43.64
Sb _{mono}	31.23	12.93	-	-	-	13.60	-	-	14.53
Sb _{bi}	36.78	14.10	-	-	-	19.47	-	-	15.36
Sb _{bulk}	70.79	29.56	111.52	15.82	22.06	37.63	18.08	26.99	26.47

Table B.1: Elements of stiffness tensor in GPa of each structure. Experimental values for bulk P from Refs. [264, 265] are also presented. The stiffness in general increases with the number of layers and decreases as we move from P to As to Sb, whereas the anisotropy increases for both cases.

3 GROUP-V IN-PLANE ELASTIC EXTREMA

	$Y_{\min}$	θ	$Y_{\max}$	θ	$\langle Y \rangle$	$G_{\min}$	θ	$G_{\max}$	θ	$\langle G \rangle$	$\nu_{\min}$	θ	$\nu_{\max}$	θ	$\langle \nu \rangle$
P _{mono}	17.1	69°	72.4	0°	36.4	20.9	90°	42.2	45°	31.0	0.3	31°	0.5	63°	0.5
P _{bi}	20.5	75°	85.6	0°	44.4	28.1	90°	49.2	45°	37.8	0.31	34°	0.5	68°	0.4
P _{bulk}	34.2	87°	166.4	0°	85.7	64.9	87°	92.4	45°	74.5	0.2	36°	0.5	75°	0.3
As _{mono}	-2.1	90°	30.5	18°	12.7	10.4	77°	13.8	45°	11.2	0.2	39°	0.9	90°	0.4
As _{bi}	9.7	90°	56.0	0°	31.0	23.0	78°	28.6	45°	24.3	0.4	40°	0.6	90°	0.5
As _{bulk}	10.9	90°	105.1	20°	55.0	44.4	73°	51.1	45°	66.7	0.3	40°	0.7	90°	0.4
Sb _{mono}	1.4	90°	24.4	22°	12.6	8.9	45°	13.6	90°	9.4	0.3	43°	0.8	90°	0.6
Sb _{bi}	2.6	90°	31.6	33°	16.3	11.8	45°	19.5	90°	12.8	0.2	42°	0.8	90°	0.5
Sb _{bulk}	12.4	90°	58.9	30°	35.4	28.1	59°	28.2	45°	63.2	0.2	41°	0.6	90°	0.4

Table B.2: Summary of the minima and maxima of the Hill-averaged in-plane Young's modulus $Y(\theta)$ (GPa), shear modulus $G(\theta)$ (GPa), and Poisson's ratio $\nu(\theta)$ as well as the angle θ with respect to the $\vec{x}$ -direction (zigzag) at which they occur in degrees, and their in-plane averages.

4 BLACK PHOSPHORUS EXPERIMENTAL DATA

Volume fraction (%)	Young's Modulus (MPa)
0 ± 0	551 ± 118
0.037 ± 0.002	418 ± 152
0.055 ± 0.003	629 ± 123
0.073 ± 0.004	466 ± 78
0.110 ± 0.005	635 ± 53
0.037 ± 0.002	632 ± 217
0.055 ± 0.003	712 ± 85.2
0.073 ± 0.004	757 ± 120
0.11 ± 0.01	824 ± 194
0.183 ± 0.01	726 ± 139
0.294 ± 0.01	930 ± 135

Table B.3: Summary of the experimental data associated with the analysis in section 3.4. The Young's modulus (MPa) of the BP:PVC composite was measured while varying the volume fraction (%) of the BP nano-flakes. The data on top were acquired from the small nano-flakes with mean-length $L_s = 130 \pm 111$ nm, and the data on the bottom were from the large nano-flakes with mean-length $L_l = 2260 \pm 1000$ nm.

5 SUMMARY OF ELECTRONIC PROPERTIES

	E_g (eV)	$Me_{\Gamma-X}$	$Me_{\Gamma-Y}$	$Mh_{\Gamma-X}$	$Mh_{\Gamma-Y}$
P _{mono}	0.9	1.25(1)	0.16(1)	2.8(2)	0.14(1)
As _{mono}	0.15 [★]	1.16(1)	0.26(1)	1.09(1)	0.18(2)
Sb _{mono}	0.2 [★]	1.10(1)	0.28(1)	1.04(1)	0.19(2)
P _{bi}	0.4	1.41(1)	0.19(1)	1.21(3)	0.15(2)
As _{bi}	0.45	1.15(1)	0.24(1)	0.94(4)	0.17(2)
Sb _{bi}	0 [†]	1.16(1)	0.39(1)	0.99(4)	0.33(4)
P _{bulk}	0 [‡]	-	0.37(2)	-	0.21(2)
As _{bulk}	0 [‡]	-	0.36(1)	-	0.30(3)
Sb _{bulk}	0 [‡]	-	-	-	-

Table B.4: Kohn-Sham band gaps (eV), indicating the indirect semiconducting (★), semi-metallic (†) and metallic (‡) states, as well as the charge-carrier effective masses (m_0) for each phase of P, As, Sb.

6 SUMMARY OF ELECTRONIC TRANSITIONS

	Transition	Direction	Strain (%)
P_{bi}	D Gap $\rightarrow$ SM $^{\Delta}$	xx, yy	-5
	D Gap $\rightarrow$ ID Gap	xx, yy	+2
P_{bulk}	SM $\rightarrow$ D Gap $\rightarrow$ ID Gap	xx, yy	+1 $\rightarrow$ +3
	SM $\rightarrow$ SM $^{\nabla}$	xx, yy	+2
As_{mono}	ID $\rightarrow$ D Gap	xx	-3
	ID Gap $\rightarrow$ SM	xx	+2
	ID Gap $\rightarrow$ SM	xx	+2
	SM $\rightarrow$ SM $^{\Delta}$	xx	+5
As_{bi}	D Gap $\rightarrow$ ID Gap $\rightarrow$ D Gap	xx	+2 $\rightarrow$ +3
	D Gap $\rightarrow$ ID Gap	yy	-3,+2
As_{bulk}	SM $\rightarrow$ D Gap $\rightarrow$ ID Gap	xx	0 $\rightarrow$ +3
	SM $\rightarrow$ D Gap	yy	0 $\rightarrow$ +3
	SM $\rightarrow$ SM $^{\nabla}$	xx, yy	+1
Sb_{mono}	ID Gap $\rightarrow$ SM	xx	-2
	ID Gap $\rightarrow$ D Gap $\rightarrow$ SM $^{\Delta}$	xx	+2 $\rightarrow$ +4
	ID Gap $\rightarrow$ SM	yy	-2
Sb_{bi}	SM $\rightarrow$ SM $^{\Delta}$	xx	+4
	Structural Transition	yy	-3
	SM $\rightarrow$ ID Gap	yy	+3

Table B.5: Summary of the band gap transitions including direct (D); indirect (ID); metallic (M); and semi-metallic (SM), in particular those that indicate potential Dirac states (Δ), Weyl states (∇), and the structural phase-transition.

7 BAND STRUCTURES FIGURES

In this section we present the band structures of the relaxed P, As and Sb discussed in Chapter IV, which were calculated without spin-orbit coupling (SOC). Band structures of the strained phases may be found in the supplemental material of Ref. [297].

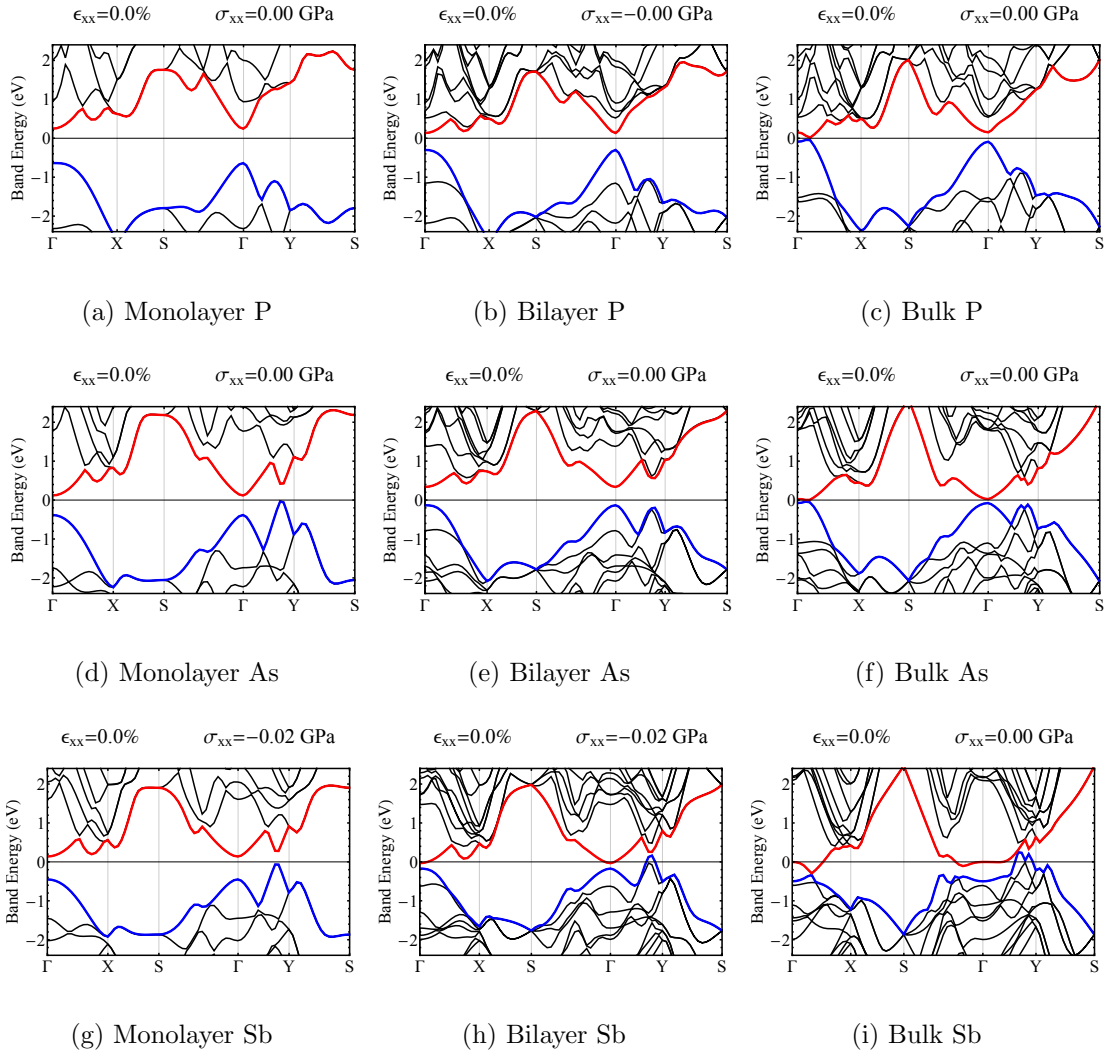


Figure B.1: Band structures of relaxed group-V materials in the monolayer, bilayer and bulk phases.

C

FURTHER DISCUSSION ON SELF-CONSISTENCY SCHEMES

1 ALTERNATIVE DERIVATION FOR U_{OUT} AND J_{OUT}

In this section we present an alternative derivation for J_{out} when used in the original DFT+ U + J functional, given by

$$E_{U+J} = \sum_{I\sigma} \left\{ \frac{(U^I - J^I)}{2} \text{Tr} [\hat{n}^{I\sigma} - \hat{n}^{I\sigma} \hat{n}^{I\sigma}] + \frac{J^I}{2} \text{Tr} [\hat{n}^{I\sigma} \hat{n}^{I\bar{\sigma}}] \right\}, \quad (\text{C.1})$$

in which the potential for U remains the same, but J now applies to both like and unlike-spins. The potential for J in this instance is then

$$\hat{V}_J^\sigma = \frac{\delta E_J}{\delta \hat{n}^{I\sigma}} = J^I \left(\hat{n}^{I\sigma} + \hat{n}^{I\bar{\sigma}} - \frac{1}{2} \right) \Rightarrow V_J^\sigma = J \left(N - \frac{1}{2} \right), \quad (\text{C.2})$$

which we see is symmetric for both spin up and spin down potentials. From this, we follow the same procedure as in Eqs. (VII.14) & (VII.15) and find that

$$\begin{aligned} U_{\text{out}} &= \frac{1}{2} \left(\frac{dV_{\text{int}}^\uparrow}{dN} + \frac{dV_{\text{int}}^\downarrow}{dN} + \frac{dV_{U_{\text{in}}}^\uparrow}{dN} + \frac{dV_{U_{\text{in}}}^\downarrow}{dN} + \frac{dV_{J_{\text{in}}}^\uparrow}{dN} + \frac{dV_{J_{\text{in}}}^\downarrow}{dN} \right) \\ &= \frac{1}{2} \left(\frac{dV_{\text{int}}^\uparrow}{dN} + \frac{dV_{\text{int}}^\downarrow}{dN} \right) - \frac{U_{\text{in}}}{2} \left(\frac{dN^\uparrow}{dN} + \frac{dN^\downarrow}{dN} \right) + \frac{J_{\text{in}}}{2} \left(\frac{dN}{dN} + \frac{dN}{dN} \right) \\ &= F_{\text{Hxc}}^{\hat{P}}(U_{\text{in}}, J_{\text{in}}) - \frac{U_{\text{in}}}{2} + J_{\text{in}}. \end{aligned} \quad (\text{C.3})$$

Where U_{out} now depends on J_{in} instead of $J_{\text{in}}/2$. Furthermore, we find with surprise that J_{out} does not depend on J_{in} at all since the contributions from the symmetric

J potentials now cancel:

$$\begin{aligned}
 J_{\text{out}} &= -\frac{1}{2} \left(\frac{dV_{\text{int}}^{\uparrow}}{dM} - \frac{dV_{\text{int}}^{\downarrow}}{dM} + \frac{dV_{U_{\text{in}}}^{\uparrow}}{dM} - \frac{dV_{U_{\text{in}}}^{\downarrow}}{dM} + \frac{dV_{J_{\text{in}}}^{\uparrow}}{dM} - \frac{dV_{J_{\text{in}}}^{\downarrow}}{dM} \right) \\
 &= -\frac{1}{2} \left(\frac{dV_{\text{int}}^{\uparrow}}{dM} - \frac{dV_{\text{int}}^{\downarrow}}{dM} \right) + \frac{U_{\text{in}}}{2} \left(\frac{dN^{\uparrow}}{dM} - \frac{dN^{\downarrow}}{dM} \right) + \frac{J_{\text{in}}}{2} \left(\frac{dN}{dM} - \frac{dN}{dM} \right) \\
 &= F_J^{\hat{P}}(U_{\text{in}}, J_{\text{in}}) + \frac{U_{\text{in}}}{2}. \tag{C.4}
 \end{aligned}$$

The linear combination of U_{out} and J_{out} results in the expression for U_{eff} now depending explicitly on J_{in} , such that

$$\begin{aligned}
 U_{\text{eff}} &= U_{\text{out}} - J_{\text{out}} = (F_{\text{Hxc}} - F_J) - U_{\text{in}} + J_{\text{in}} \\
 J_{\text{eff}} &= U_{\text{out}} + J_{\text{out}} = (F_{\text{Hxc}} + F_J) + J_{\text{in}}. \tag{C.5}
 \end{aligned}$$

However, invoking the self-consistency condition that completely removes the effective interactions, i.e., $U_{\text{eff}} = J_{\text{eff}} = 0$, gives

$$\begin{aligned}
 U_{\text{in}} - J_{\text{in}} &= (F_{\text{Hxc}} - F_J) = \frac{1}{2} (F^{\uparrow\uparrow} + F^{\downarrow\downarrow}) \\
 J_{\text{in}} &= -(F_{\text{Hxc}} + F_J) = -\frac{1}{2} (F^{\uparrow\downarrow} + F^{\downarrow\uparrow}). \tag{C.6}
 \end{aligned}$$

Here, the formula for J is unchanged, whereas U is now scaled by J , thereby producing an ‘effective’ U_{in} coupling same-spin interactions, which is exactly the formulation given in Eqs. (VII.17) & (VII.18). Thus, the two derivations are equivalent and produce the same effect with this condition when provided with the corresponding U and J parameters.

2 SUPPLEMENTAL DOS PLOTS FOR NiO

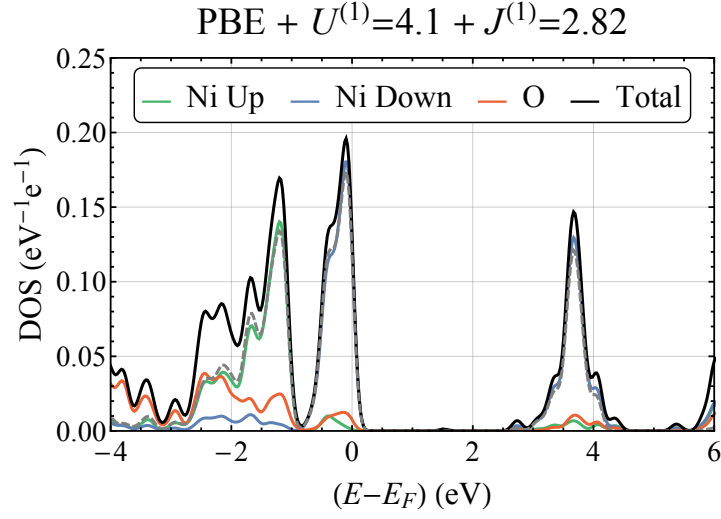


Figure C.1: Although the $\text{PBE}+U^{(1)}$ calculation performed well, the addition of a relatively large J here decreases the band gap. However, the magnetic moment is reasonable.

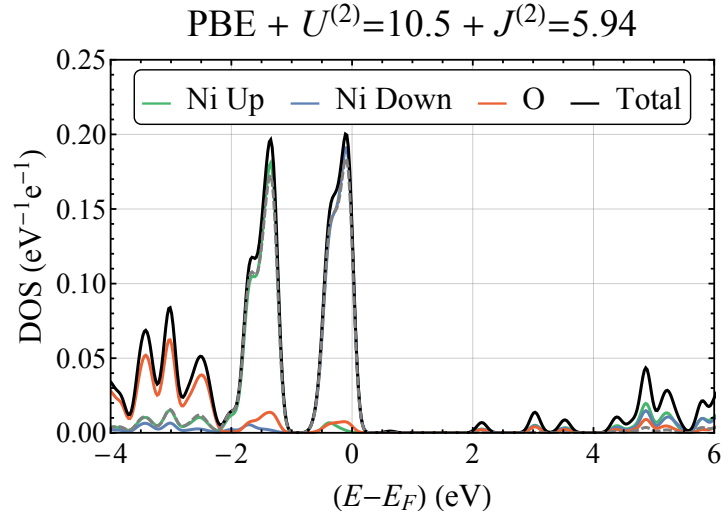


Figure C.2: This calculation produces terrible results as the large J pulls the conduction band peak below the Fermi energy and leaves behind depleted conduction states.

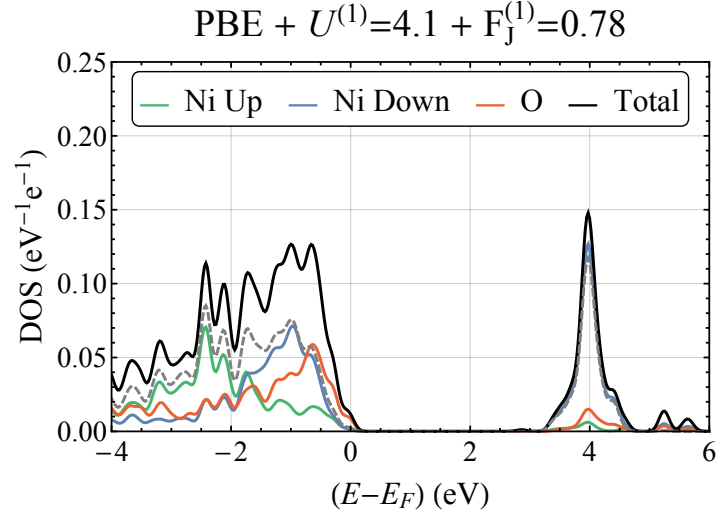


Figure C.3: This calculation produces excellent agreement with the experimental measurements in this case, but it is generally not the scheme that is mathematically proven to remove the SIE.

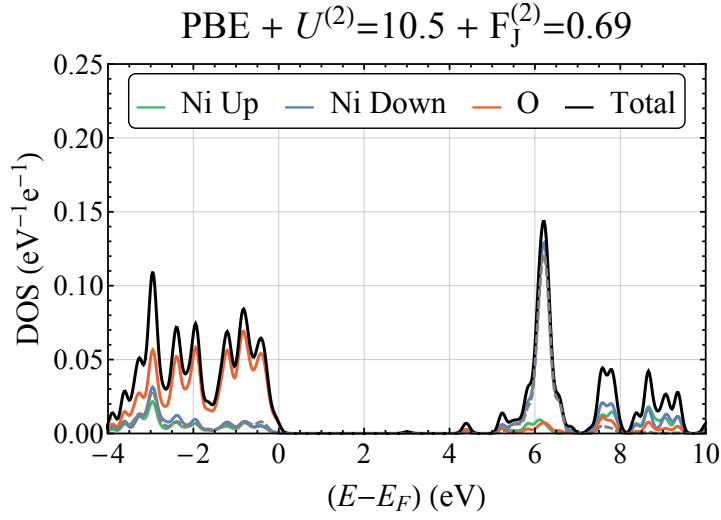


Figure C.4: This calculation, while producing the correct band gap and magnetic moment, has pushed the conduction band peak up too high to be in agreement with experiment.

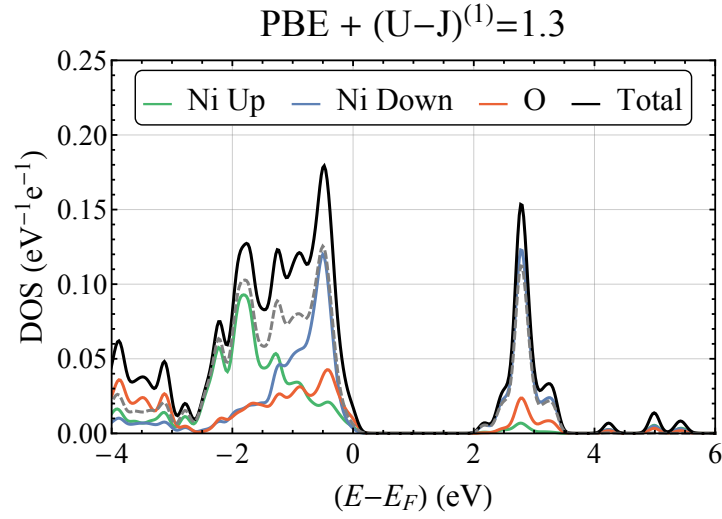


Figure C.5: This calculation under-estimates all three properties and does not offer much improvement over the PBE as the effective U value is much too small.

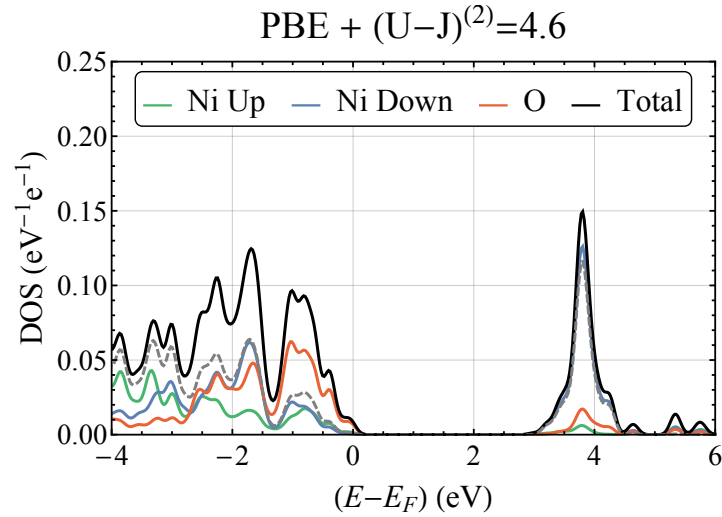


Figure C.6: Similar to the PBE+ $U^{(2)}$ calculation, the results produced here are in very good agreement with experiment as the U value is approximately the correct magnitude.

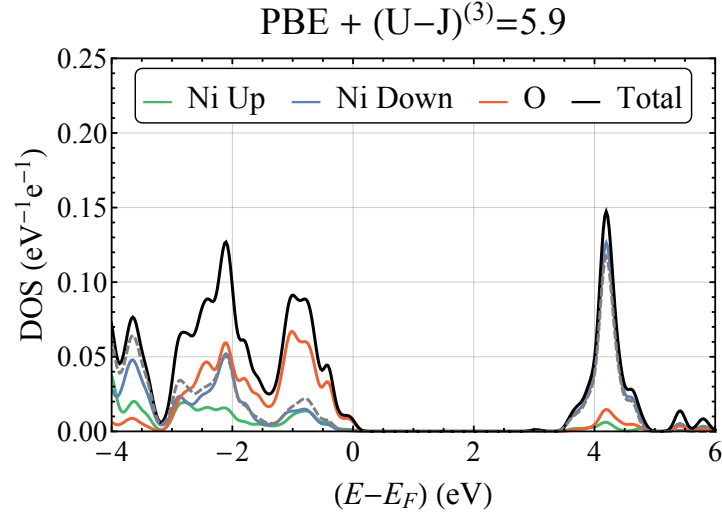


Figure C.7: This calculation produces the best overall agreement with the experimental data but is certainly within the margin of error achieved by the $\text{PBE}+U_{\text{eff}}^{(2)}$ calculation discussed earlier.

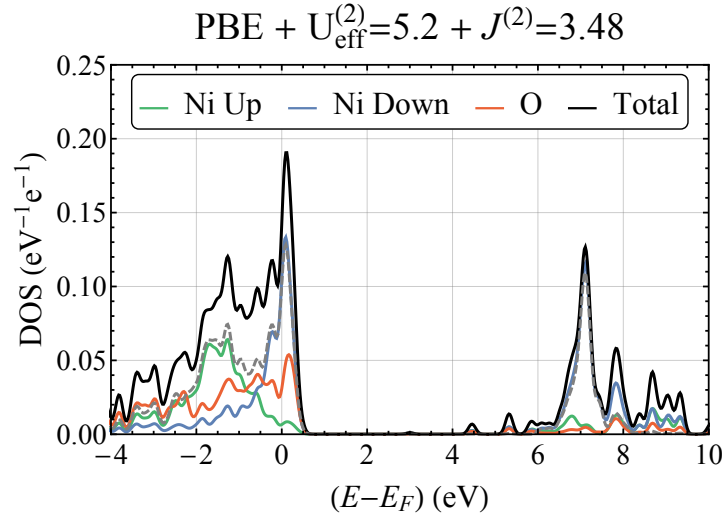


Figure C.8: While producing a magnetic moment exactly between the experimental measurements, the band gap and transition energy computed here are grossly incorrect.

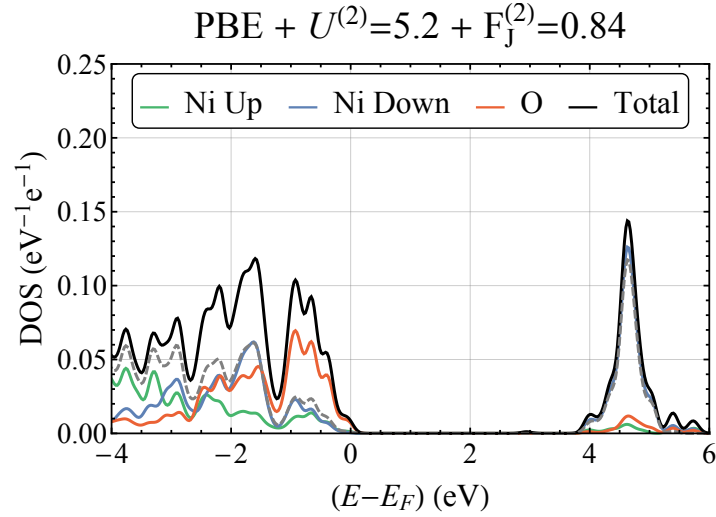


Figure C.9: This calculation produces reasonable agreement with experiment but it is not the most effective.

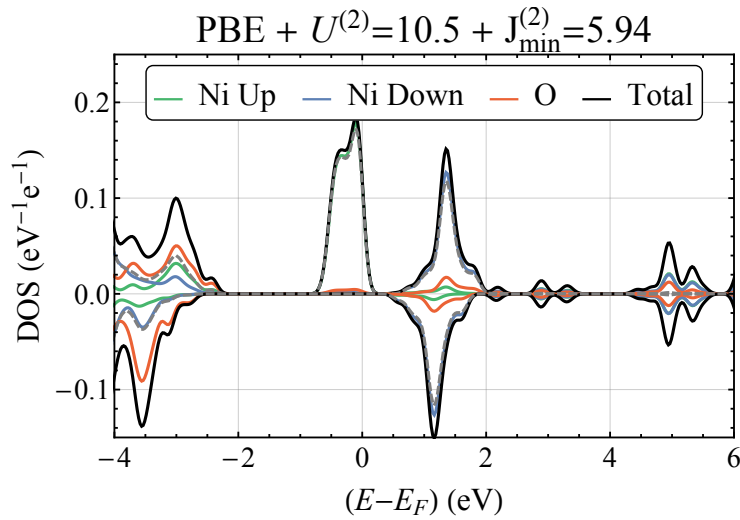


Figure C.10: This calculation produces the worst results by far, where the spin-symmetry of the system is broken rendering a ferromagnetic system. The large J here exacerbates the spin-minority term invoked from Ref. [354].

2.1 SELF-CONSISTENCY CALCULATIONS FOR $\text{Ni}(\text{CO})_4$

Here we present the U_{in} vs U_{out} curve computed for $\text{Ni}(\text{CO})_4$ with non-spin-polarised calculations, such that the corresponding J_{out} could not be determined. We observe that $U^{(2)} \approx U^{(3)} \approx 11$ eV, and in fact, the HOMO-LUMO gap computed with PBE+ $U^{(2)}$ is also 4.56 eV, while for PBE+ $U^{(1)}$ it is 4.22 eV. Hence there is little change in the frontier orbitals of $\text{Ni}(\text{CO})_4$ upon application of relatively large U corrections. Nonetheless, the gap is in better agreement with the experimental value [451] of 4.83 eV.

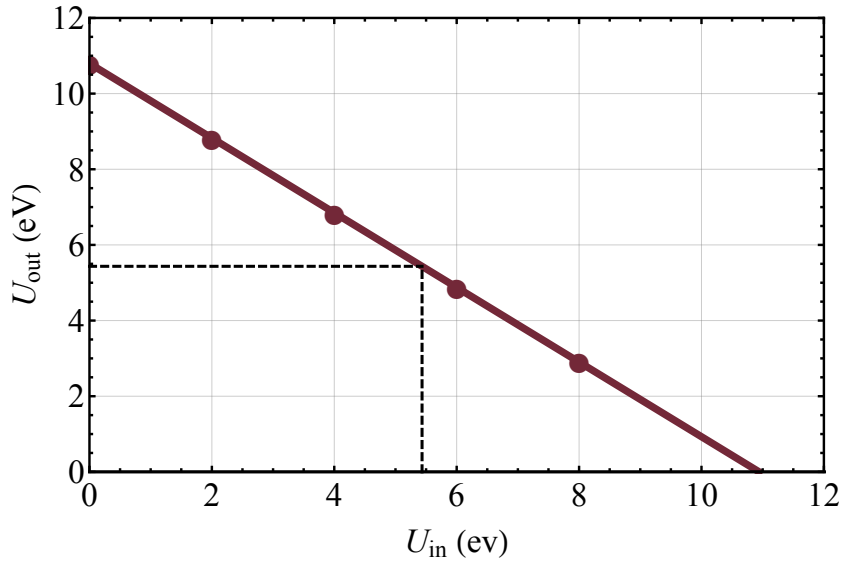


Figure C.11: Non-spin-polarised U_{in} vs U_{out} profile for $\text{Ni}(\text{CO})_4$ with error bars. From this we compute $U^{(1)} = 5.43 \pm 0.01$ eV, $U^{(2)} = 10.94 \pm 0.03$ eV, and $U^{(3)} = 10.80 \pm 0.01$ eV, for which we see $U^{(2)} \approx U^{(3)}$.

2.2 SELF-CONSISTENCY CALCULATIONS FOR Cr_2O_3

Here we present the computed curves, with accompanied error bars, for U_{out} (solid), J_{out} (dashed), and U_{eff} (dotted) with respect to applied U_{in} for Cr_2O_3 , which are again very accurately determined.

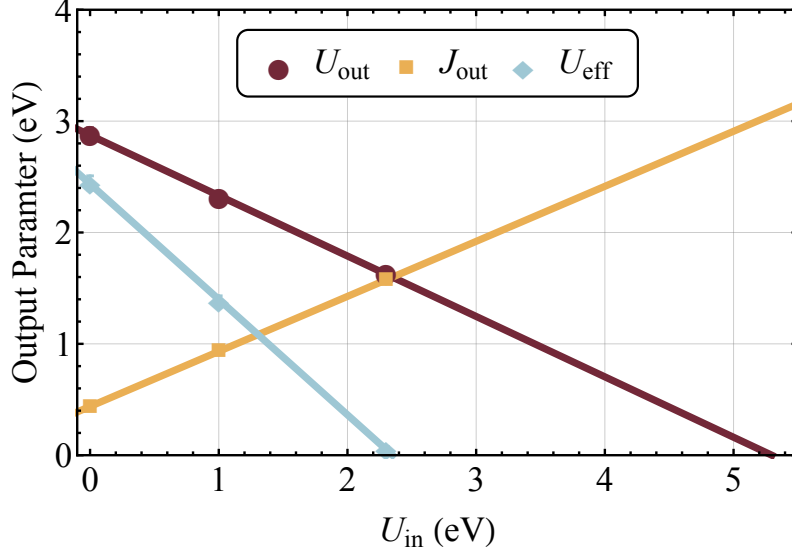


Figure C.12: Curves, with accompanied error bars, for U_{out} (solid), J_{out} (dashed), and U_{eff} (dot-dashed), with respect to the applied U_{in} for Cr_2O_3 . From the linear fits we compute $U^{(1)} = 1.86 \pm 0.02$ eV, $U^{(2)} = 5.3 \pm 0.1$ eV, and $U^{(3)} = 2.87 \pm 0.02$ eV.

Likewise, the evaluated interaction terms are presented in Fig. C.13. Here, $F^{\sigma\bar{\sigma}}$ varies between 3.5 eV to 2.5 eV, and $F^{\sigma\sigma}$ varies between 2.5 eV to 2.0 eV, which hints toward desired values of U . The average on-site interaction F_{Hxc} ranges from 3 eV to 2.5 eV, while F_J remains approximately 0.5 eV.

Since we discussed earlier that calculations are relatively unchanged when $J < 1$ eV, we assume here that there will be very little difference between the DFT calculation evaluated with $U_{\text{eff}}^{(2)} = 2.35 \pm 0.04$ eV, and that of a DFT+ U + J calculation using Eq. (V.24) with $U^{(3)} = 2.76$ eV and $J^{(3)} = 0.435 \pm 0.004$ eV, since $(U - J)^{(3)} = 2.32 \approx U_{\text{eff}}^{(2)}$. We therefore refrain from providing excessive plots and instead refer the reader to the DOS of the latter presented previously in in Fig. VI.16.

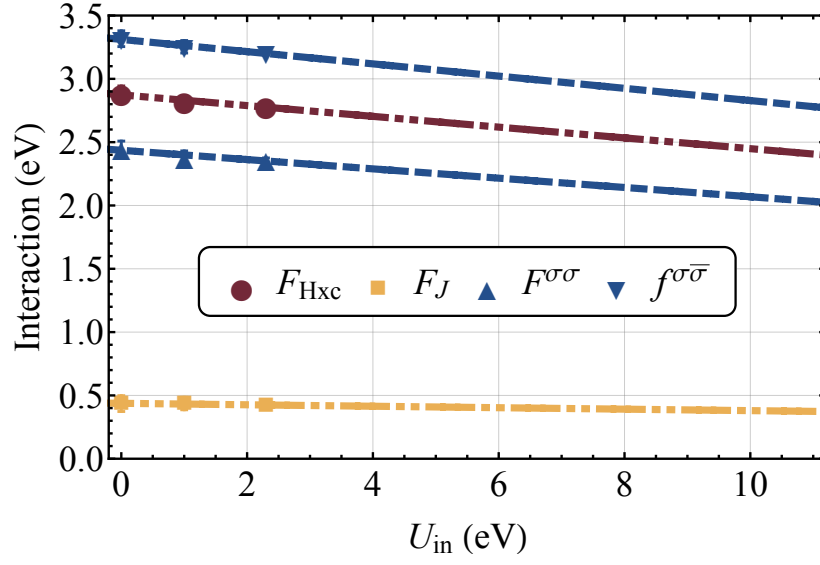


Figure C.13: Curves, with accompanied error bars, for the interaction kernels F_{Hxc} (circles) and F_J (squares), as well as the average like and unlike-spin interactions $F^{\sigma\sigma}$ (up triangles) and $F^{\sigma\bar{\sigma}}$ (down triangles), with respect to the applied U_{in} for Cr_2O_3 .

BIBLIOGRAPHY

- [1] G. E. P. Box, Journal of the American Statistical Association **71**, 791 (1976),
URL <http://www.tandfonline.com/doi/abs/10.1080/01621459.1976.10480949>.
- [2] C. A. Mack, IEEE Transactions on Semiconductor Manufacturing **24**, 202 (2011), ISSN 0894-6507.
- [3] S. L. Sass, *The Substance of Civilization: Materials and Human History from the Stone Age to the Age of Silicon* (Arcade Publishing, New York, 1998).
- [4] A. Trabesinger, Nature Physics **8**, 263 (2012), ISSN 1745-2473, URL <http://dx.doi.org/10.1038/nphys2258>.
- [5] R. M. Martin, *Electronic structure: basic theory and practical methods* (Cambridge University Press, 2004).
- [6] A. D. Becke, The Journal of Chemical Physics **140**, 18A301 (2014), URL <http://dx.doi.org/10.1063/1.4869598>.
- [7] W. Kohn, Reviews of Modern Physics **71**, 1253 (1999), URL <https://link.aps.org/doi/10.1103/RevModPhys.71.1253>.
- [8] J. A. Pople, Reviews of Modern Physics **71**, 1267 (1999), URL <https://link.aps.org/doi/10.1103/RevModPhys.71.1267>.
- [9] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Chemical Reviews **112**, 289 (2012),
URL <http://dx.doi.org/10.1021/cr200107z>.
- [10] R. O. Jones, Reviews of Modern Physics **87**, 897 (2015), URL <http://link.aps.org/doi/10.1103/RevModPhys.87.897>.
- [11] K. Burke, The Journal of Chemical Physics **136**, 150901 (2012), URL <http://dx.doi.org/10.1063/1.4704546>.

- [12] M. Casida and M. Huix-Rotllant, Annual Review of Physical Chemistry **63**, 287 (2012), pMID: 22242728, URL <https://doi.org/10.1146/annurev-physchem-032511-143803>.
- [13] G. Goldbeck, Goldbeck Consulting Limited (2012), URL <http://gerhardgoldbeck.wordpress.com/2012/07/10/the-economic-impact-ofmolecular-modelling-of-chemicals-and-materials>.
- [14] P. Hohenberg and W. Kohn, Physical Review **136**, B864 (1964), URL <http://link.aps.org/doi/10.1103/PhysRev.136.B864>.
- [15] W. Kohn and L. J. Sham, Physical Review **140**, A1133 (1965), URL <http://dx.doi.org/10.1103/PhysRev.140.A1133>.
- [16] D. M. Ceperley and B. J. Alder, Physical Review Letters **45**, 566 (1980), URL <https://link.aps.org/doi/10.1103/PhysRevLett.45.566>.
- [17] U. von Barth and L. Hedin, Journal of Physics C: Solid State Physics **5**, 1629 (1972), URL <http://stacks.iop.org/0022-3719/5/i=13/a=012>.
- [18] A. K. Rajagopal and J. Callaway, Physical Review B **7**, 1912 (1973), URL <https://link.aps.org/doi/10.1103/PhysRevB.7.1912>.
- [19] J. P. Perdew and Y. Wang, Physical Review B **45**, 13244 (1992), URL <https://link.aps.org/doi/10.1103/PhysRevB.45.13244>.
- [20] J. P. Perdew and A. Zunger, Physical Review B **23**, 5048 (1981), URL <http://link.aps.org/doi/10.1103/PhysRevB.23.5048>.
- [21] J. P. Perdew, K. Burke, and Y. Wang, Physical Review B **54**, 16533 (1996), URL <https://link.aps.org/doi/10.1103/PhysRevB.54.16533>.
- [22] J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters **77**, 3865 (1996), URL <http://link.aps.org/doi/10.1103/PhysRevLett.77.3865>.
- [23] R. O. Jones and O. Gunnarsson, Reviews of Modern Physics **61**, 689 (1989), URL <https://link.aps.org/doi/10.1103/RevModPhys.61.689>.

- [24] C. Fonseca Guerra, J. G. Snijders, G. te Velde, and E. J. Baerends, Theoretical Chemistry Accounts **99**, 391 (1998), ISSN 1432-2234, URL <https://doi.org/10.1007/s002140050353>.
- [25] W. Yang, Physical Review Letters **66**, 1438 (1991), URL <https://link.aps.org/doi/10.1103/PhysRevLett.66.1438>.
- [26] W. Kohn, Physical Review Letters **76**, 3168 (1996), URL <https://link.aps.org/doi/10.1103/PhysRevLett.76.3168>.
- [27] D. R. Bowler and T. Miyazaki, Journal of Physics: Condensed Matter **22**, 074207 (2010), URL <http://stacks.iop.org/0953-8984/22/i=7/a=074207>.
- [28] S. Goedecker, Reviews of Modern Physics **71**, 1085 (1999), URL <https://link.aps.org/doi/10.1103/RevModPhys.71.1085>.
- [29] C.-K. Skylaris, P. D. Haynes, A. A. Mostofi, and M. C. Payne, Journal of Chemical Physics **122**, 084119 (2005), URL <http://dx.doi.org/10.1063/1.1839852>.
- [30] N. D. Hine, P. D. Haynes, A. A. Mostofi, C.-K. Skylaris, and M. C. Payne, Comput. Phys. Communications **180**, 1041 (2009), URL <http://www.sciencedirect.com/science/article/pii/S0010465508004414>.
- [31] N. Hine, P. Haynes, A. Mostofi, and M. Payne, Journal of Chemical Physics **133**, 114111 (2010), URL <http://scitation.aip.org/content/aip/journal/jcp/133/11/10.1063/1.3492379>.
- [32] M. Gillan, D. Bowler, A. Torralba, and T. Miyazaki, Computer Physics Communications **177**, 14 (2007), ISSN 0010-4655, Proceedings of the Conference on Computational Physics 2006, URL <http://www.sciencedirect.com/science/article/pii/S0010465507001658>.
- [33] D. R. Bowler, T. Miyazaki, and M. J. Gillan, Journal of Physics: Condensed Matter **14**, 2781 (2002), URL <http://stacks.iop.org/0953-8984/14/i=11/a=303>.

- [34] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, *Journal of Physics: Condensed Matter* **14**, 2745 (2002), URL <http://stacks.iop.org/0953-8984/14/i=11/a=302>.
- [35] E. Artacho, E. Anglada, O. Diéguez, J. D. Gale, A. García, J. Junquera, R. M. Martin, P. Ordejón, J. M. Pruneda, D. Sánchez-Portal, et al., *Journal of Physics: Condensed Matter* **20**, 064208 (2008), URL <http://stacks.iop.org/0953-8984/20/i=6/a=064208>.
- [36] L. Genovese, B. Videau, M. Ospici, T. Deutsch, S. Goedecker, and J.-F. Méhaut, *CR Mecanique* **339**, 149 (2011), ISSN 1631-0721, URL <http://www.sciencedirect.com/science/article/pii/S1631072110002135>.
- [37] T. Ozaki, *Physical Review B* **67**, 155108 (2003), URL <https://link.aps.org/doi/10.1103/PhysRevB.67.155108>.
- [38] T. Ozaki and H. Kino, *Physical Review B* **72**, 045121 (2005), URL <http://link.aps.org/doi/10.1103/PhysRevB.72.045121>.
- [39] V. Weber, J. VandeVondele, J. Hutter, and A. M. N. Niklasson, *Journal of Chemical Physics* **128**, 084113 (2008), URL <http://dx.doi.org/10.1063/1.2841077>.
- [40] E. Schrödinger, *Physical Review* **28**, 1049 (1926), URL <https://link.aps.org/doi/10.1103/PhysRev.28.1049>.
- [41] M. Born and R. Oppenheimer, *Annalen der Physik* **389** (1927), ISSN 1521-3889, URL <http://dx.doi.org/10.1002/andp.19273892002>.
- [42] A. Scherrer, F. Agostini, D. Sebastiani, E. K. U. Gross, and R. Vuilleumier, *Physical Review X* **7**, 031035 (2017), URL <https://link.aps.org/doi/10.1103/PhysRevX.7.031035>.
- [43] A. P. Horsfield, D. R. Bowler, and A. J. Fisher, *Journal of Physics: Condensed Matter* **16**, L65 (2004), URL <http://stacks.iop.org/0953-8984/16/i=7/a=L03>.

- [44] A. P. Horsfield, D. R. Bowler, A. J. Fisher, T. N. Todorov, and C. G. Sánchez, *Journal of Physics: Condensed Matter* **16**, 8251 (2004), URL <http://stacks.iop.org/0953-8984/16/i=46/a=012>.
- [45] T. A. Arias, M. C. Payne, and J. D. Joannopoulos, *Physical Review Letters* **69**, 1077 (1992), URL <https://link.aps.org/doi/10.1103/PhysRevLett.69.1077>.
- [46] R. Car and M. Parrinello, *Physical Review Letters* **55**, 2471 (1985), URL <https://link.aps.org/doi/10.1103/PhysRevLett.55.2471>.
- [47] K. Capelle, *Brazilian Journal of Physics* **36**, 1318 (2006), ISSN 0103-9733, URL http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0103-97332006000700035&nrm=iso.
- [48] W. Pauli, *Physical Review* **58**, 716 (1940), URL <https://link.aps.org/doi/10.1103/PhysRev.58.716>.
- [49] D. R. Hartree, *Mathematical Proceedings of the Cambridge Philosophical Society* **24**, 89–110 (1928).
- [50] V. Fock, *Zeitschrift für Physik* **61**, 126 (1930), ISSN 0044-3328, URL <https://doi.org/10.1007/BF01340294>.
- [51] J. C. Slater, *Physical Review* **35**, 210 (1930), URL <https://link.aps.org/doi/10.1103/PhysRev.35.210.2>.
- [52] A. J. Cohen and P. Mori-Sánchez, *Physical Review A* **93**, 042511 (2016), URL <https://link.aps.org/doi/10.1103/PhysRevA.93.042511>.
- [53] A. Makmal, S. Kümmel, and L. Kronik, *Physical Review A* **83**, 062512 (2011), URL <https://link.aps.org/doi/10.1103/PhysRevA.83.062512>.
- [54] E. Matito, D. Casanova, X. Lopez, and J. M. Ugalde, *Theoretical Chemistry Accounts* **135**, 226 (2016), ISSN 1432-2234, URL <https://doi.org/10.1007/s00214-016-1982-x>.

- [55] J. D. Ramsden and R. W. Godby, Physical Review Letters **109**, 036402 (2012), URL <https://link.aps.org/doi/10.1103/PhysRevLett.109.036402>.
- [56] M. Rahm and R. Hoffmann, Journal of the American Chemical Society **138**, 3731 (2016), pMID: 26910496, URL <http://dx.doi.org/10.1021/jacs.5b12434>.
- [57] A. Droghetti, I. Rungger, C. Das Pemmaraju, and S. Sanvito, Physical Review B **93**, 195208 (2016), URL <http://link.aps.org/doi/10.1103/PhysRevB.93.195208>.
- [58] M.-C. Kim, E. Sim, and K. Burke, Physical Review Letters **111**, 073003 (2013), URL <http://link.aps.org/doi/10.1103/PhysRevLett.111.073003>.
- [59] C. Toher, A. Filippetti, S. Sanvito, and K. Burke, Physical Review Letters **95**, 146402 (2005), URL <http://link.aps.org/doi/10.1103/PhysRevLett.95.146402>.
- [60] S.-H. Ke, H. U. Baranger, and W. Yang, Journal of Chemical Physics **126**, 201102 (2007), URL <http://scitation.aip.org/content/aip/journal/jcp/126/20/10.1063/1.2743004>.
- [61] Y. Zhao, B. J. Lynch, and D. G. Truhlar, Journal of Physical Chemistry A **108**, 2715 (2004), URL <http://dx.doi.org/10.1021/jp049908s>.
- [62] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Physical Review Letters **91**, 146401 (2003), URL <https://link.aps.org/doi/10.1103/PhysRevLett.91.146401>.
- [63] A. D. Becke, The Journal of Chemical Physics **98**, 1372 (1993), URL <http://dx.doi.org/10.1063/1.464304>.
- [64] T. Schwabe and S. Grimme, Physical Chemistry Chemical Physics **8**, 4398 (2006), URL <http://dx.doi.org/10.1039/B608478H>.
- [65] S. Kozuch and J. M. L. Martin, Journal of Computational Chemistry **34**, 2327 (2013), ISSN 1096-987X, URL <http://dx.doi.org/10.1002/jcc.23391>.

- [66] V. A. Rassolov, J. A. Pople, P. C. Redfern, and L. A. Curtiss, Chemical Physics Letters **350**, 573 (2001), ISSN 0009-2614, URL <http://www.sciencedirect.com/science/article/pii/S0009261401013458>.
- [67] V. Heine, Solid State Physics **24**, 1 (1970), ISSN 0081-1947, URL <http://www.sciencedirect.com/science/article/pii/S0081194708600697>.
- [68] J. C. Phillips, Physical Review **112**, 685 (1958), URL <https://link.aps.org/doi/10.1103/PhysRev.112.685>.
- [69] J. C. Phillips and L. Kleinman, Physical Review **116**, 287 (1959), URL <https://link.aps.org/doi/10.1103/PhysRev.116.287>.
- [70] P. E. Blöchl, Physical Review B **50**, 17953 (1994), URL <https://link.aps.org/doi/10.1103/PhysRevB.50.17953>.
- [71] G. Kresse and D. Joubert, Physical Review B **59**, 1758 (1999), URL <https://link.aps.org/doi/10.1103/PhysRevB.59.1758>.
- [72] C. Herring, Physical Review **57**, 1169 (1940), URL <https://link.aps.org/doi/10.1103/PhysRev.57.1169>.
- [73] D. R. Hamann, M. Schlüter, and C. Chiang, Physical Review Letters **43**, 1494 (1979), URL <https://link.aps.org/doi/10.1103/PhysRevLett.43.1494>.
- [74] G. P. Kerker, Journal of Physics C: Solid State Physics **13**, L189 (1980), URL <http://stacks.iop.org/0022-3719/13/i=9/a=004>.
- [75] D. R. Hamann, Physical Review B **40**, 2980 (1989), URL <https://link.aps.org/doi/10.1103/PhysRevB.40.2980>.
- [76] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Physical Review B **41**, 1227 (1990), URL <http://link.aps.org/doi/10.1103/PhysRevB.41.1227>.
- [77] S. G. Louie, S. Froyen, and M. L. Cohen, Physical Review B **26**, 1738 (1982), URL <https://link.aps.org/doi/10.1103/PhysRevB.26.1738>.

- [78] D. D. Koelling and G. O. Arbman, *Journal of Physics F: Metal Physics* **5**, 2041 (1975), URL <http://stacks.iop.org/0305-4608/5/i=11/a=016>.
- [79] O. K. Andersen, *Physical Review B* **12**, 3060 (1975), URL <https://link.aps.org/doi/10.1103/PhysRevB.12.3060>.
- [80] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, *Physical Review B* **71**, 035109 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevB.71.035109>.
- [81] D. J. Cole, D. D. O'Regan, and M. C. Payne, *Journal of Physical Chemistry Letters* **3**, 1448 (2012), pMID: 26285620, URL <http://dx.doi.org/10.1021/jz3004188>.
- [82] C. Weber, D. J. Cole, D. D. O'Regan, and M. C. Payne, *Proceedings of the National Academy of Sciences* **111**, 5790 (2014), URL <http://www.pnas.org/content/111/16/5790.abstract>.
- [83] G. Lever, D. J. Cole, R. Lonsdale, K. E. Ranaghan, D. J. Wales, A. J. Mulholland, C.-K. Skylaris, and M. C. Payne, *The Journal of Physical Chemistry Letters* **5**, 3614 (2014), pMID: 26278727, URL <http://dx.doi.org/10.1021/jz5018703>.
- [84] S. J. Fox, J. Dziedzic, T. Fox, C. S. Tautermann, and C.-K. Skylaris, *Proteins: Structure, Function, and Bioinformatics* **82**, 3335 (2014), ISSN 1097-0134, URL <http://dx.doi.org/10.1002/prot.24686>.
- [85] N. D. M. Hine, K. Frensch, W. M. C. Foulkes, and M. W. Finnis, *Physical Review B* **79**, 024112 (2009), URL <https://link.aps.org/doi/10.1103/PhysRevB.79.024112>.
- [86] F. Corsetti and A. A. Mostofi, *Physical Review B* **84**, 035209 (2011), URL <https://link.aps.org/doi/10.1103/PhysRevB.84.035209>.
- [87] L. E. Ratcliff, N. D. M. Hine, and P. D. Haynes, *Physical Review B* **84**, 165131 (2011), URL <https://link.aps.org/doi/10.1103/PhysRevB.84.165131>.

- [88] L. E. Ratcliff and P. D. Haynes, *Physical Chemistry Chemical Physics* **15**, 13024 (2013), URL <http://dx.doi.org/10.1039/C3CP52043A>.
- [89] V. Vitale, J. Dziedzic, A. Albaugh, A. M. N. Niklasson, T. Head-Gordon, and C.-K. Skylaris, *The Journal of Chemical Physics* **146**, 124115 (2017), URL <http://dx.doi.org/10.1063/1.4978684>.
- [90] N. D. M. Hine, M. Robinson, P. D. Haynes, C.-K. Skylaris, M. C. Payne, and A. A. Mostofi, *Physical Review B* **83**, 195102 (2011), URL <http://link.aps.org/doi/10.1103/PhysRevB.83.195102>.
- [91] V. Vitale, J. Dziedzic, S. M.-M. Dubois, H. Fangohr, and C.-K. Skylaris, *Journal of Chemical Theory and Computation* **11**, 3321 (2015), pMID: 26575766, URL <http://dx.doi.org/10.1021/acs.jctc.5b00391>.
- [92] J. Dziedzic, H. H. Helal, C.-K. Skylaris, A. A. Mostofi, and M. C. Payne, *EPL (Europhysics Letters)* **95**, 43001 (2011), URL <http://stacks.iop.org/0295-5075/95/i=4/a=43001>.
- [93] C. Weber, D. D. O'Regan, N. D. M. Hine, M. C. Payne, G. Kotliar, and P. B. Littlewood, *Physical Review Letters* **108**, 256402 (2012), URL <https://link.aps.org/doi/10.1103/PhysRevLett.108.256402>.
- [94] N. Hine, P. Haynes, A. Mostofi, C.-K. Skylaris, and M. Payne, *Computer Physics Communications* **180**, 1041 (2009), ISSN 0010-4655, URL <http://www.sciencedirect.com/science/article/pii/S0010465508004414>.
- [95] Álvaro Ruiz-Serrano and C.-K. Skylaris, *The Journal of Chemical Physics* **139**, 054107 (2013), URL <http://dx.doi.org/10.1063/1.4817001>.
- [96] E. Poli, J. D. Elliott, L. E. Ratcliff, L. Andrinopoulos, J. Dziedzic, N. D. M. Hine, A. A. Mostofi, C.-K. Skylaris, P. D. Haynes, and G. Teobaldi, *Journal of Physics: Condensed Matter* **28**, 074003 (2016), URL <http://stacks.iop.org/0953-8984/28/i=7/a=074003>.

- [97] C.-K. Skylaris, P. D. Haynes, A. A. Mostofi, and M. C. Payne, *Journal of Physics: Condensed Matter* **17**, 5757 (2005), URL <http://stacks.iop.org/0953-8984/17/i=37/a=012>.
- [98] P. D. Haynes, C.-K. Skylaris, A. A. Mostofi, and M. C. Payne, *Physica Status Solidi B* **243**, 2489 (2006), ISSN 1521-3951, URL <http://dx.doi.org/10.1002/pssb.200541457>.
- [99] P. D. Haynes, C.-K. Skylaris, A. A. Mostofi, and M. C. Payne, *Journal of Physics: Condensed Matter* **20**, 294207 (2008), URL <http://stacks.iop.org/0953-8984/20/i=29/a=294207>.
- [100] C.-K. Skylaris, P. D. Haynes, A. A. Mostofi, and M. C. Payne, *Journal of Physics: Condensed Matter* **20**, 064209 (2008), URL <http://stacks.iop.org/0953-8984/20/i=6/a=064209>.
- [101] D. D. O'Regan, N. D. M. Hine, M. C. Payne, and A. A. Mostofi, *Physical Review B* **85**, 085107 (2012), URL <http://link.aps.org/doi/10.1103/PhysRevB.85.085107>.
- [102] E. Hernández and M. J. Gillan, *Physical Review B* **51**, 10157 (1995), URL <https://link.aps.org/doi/10.1103/PhysRevB.51.10157>.
- [103] G. Galli and M. Parrinello, *Physical Review Letters* **69**, 3547 (1992), URL <https://link.aps.org/doi/10.1103/PhysRevLett.69.3547>.
- [104] A. Einstein, *Annalen der Physik* **354**, 769 (1916), ISSN 1521-3889, URL <http://dx.doi.org/10.1002/andp.19163540702>.
- [105] W. Yang and T.-S. Lee, *The Journal of Chemical Physics* **103**, 5674 (1995), URL <http://dx.doi.org/10.1063/1.470549>.
- [106] W. Kohn, *Chemical Physics Letters* **208**, 167 (1993), ISSN 0009-2614, URL <http://www.sciencedirect.com/science/article/pii/000926149389056N>.

- [107] P. Ordejón, D. A. Drabold, R. M. Martin, and M. P. Grumbach, *Physical Review B* **51**, 1456 (1995), URL <https://link.aps.org/doi/10.1103/PhysRevB.51.1456>.
- [108] F. Mauri, G. Galli, and R. Car, *Physical Review B* **47**, 9973 (1993), URL <https://link.aps.org/doi/10.1103/PhysRevB.47.9973>.
- [109] X.-P. Li, R. W. Nunes, and D. Vanderbilt, *Physical Review B* **47**, 10891 (1993), URL <https://link.aps.org/doi/10.1103/PhysRevB.47.10891>.
- [110] R. McWeeny, *Reviews of Modern Physics* **32**, 335 (1960), URL <https://link.aps.org/doi/10.1103/RevModPhys.32.335>.
- [111] R. W. Nunes and D. Vanderbilt, *Physical Review B* **50**, 17611 (1994), URL <https://link.aps.org/doi/10.1103/PhysRevB.50.17611>.
- [112] M. S. Daw, *Physical Review B* **47**, 10895 (1993), URL <https://link.aps.org/doi/10.1103/PhysRevB.47.10895>.
- [113] J. F. Janak, *Physical Review B* **18**, 7165 (1978), URL <http://link.aps.org/doi/10.1103/PhysRevB.18.7165>.
- [114] F. Jensen, *Wiley Interdisciplinary Reviews: Computational Molecular Science* **3**, 273 (2013), ISSN 1759-0884, URL <http://dx.doi.org/10.1002/wcms.1123>.
- [115] J. VandeVondele and J. Hutter, *The Journal of Chemical Physics* **127**, 114105 (2007), URL <http://dx.doi.org/10.1063/1.2770708>.
- [116] P. Haynes, C.-K. Skylaris, A. Mostofi, and M. Payne, *Chemical Physics Letters* **422**, 345 (2006), ISSN 0009-2614, URL <http://www.sciencedirect.com/science/article/pii/S0009261406002843>.
- [117] J. Ihm, A. Zunger, and M. L. Cohen, *Journal of Physics C: Solid State Physics* **12**, 4409 (1979), URL <http://stacks.iop.org/0022-3719/12/i=21/a=009>.
- [118] P. J. H. Denteneer and W. van Haeringen, *Journal of Physics C: Solid State Physics* **18**, 4127 (1985), URL <http://stacks.iop.org/0022-3719/18/i=21/a=010>.

- [119] G. Kresse and J. Furthmüller, Computational Materials Science **6**, 15 (1996), ISSN 0927-0256, URL <http://www.sciencedirect.com/science/article/pii/0927025696000080>.
- [120] G. Kresse and J. Furthmüller, Physical Review B **54**, 11169 (1996), URL <https://link.aps.org/doi/10.1103/PhysRevB.54.11169>.
- [121] C. V. Loan, *Back Matter* (Society for Industrial and Applied Mathematics, 1992), pp. 259–273, URL <http://epubs.siam.org/doi/abs/10.1137/1.9781611970999.bm>.
- [122] A. A. Mostofi, P. D. Haynes, C.-K. Skylaris, and M. C. Payne, The Journal of Chemical Physics **119**, 8842 (2003), URL <http://dx.doi.org/10.1063/1.1613633>.
- [123] D. Baye and P. H. Heenen, Journal of Physics A: Mathematical and General **19**, 2041 (1986), URL <http://stacks.iop.org/0305-4470/19/i=11/a=013>.
- [124] G. H. Wannier, Physical Review **52**, 191 (1937), URL <https://link.aps.org/doi/10.1103/PhysRev.52.191>.
- [125] J. D. Cloizeaux, Physical Review **135**, A685 (1964), URL <https://link.aps.org/doi/10.1103/PhysRev.135.A685>.
- [126] L. He and D. Vanderbilt, Physical Review Letters **86**, 5341 (2001), URL <https://link.aps.org/doi/10.1103/PhysRevLett.86.5341>.
- [127] C. Brouder, G. Panati, M. Calandra, C. Mourougane, and N. Marzari, Physical Review Letters **98**, 046402 (2007), URL <https://link.aps.org/doi/10.1103/PhysRevLett.98.046402>.
- [128] I.-M. Høyvik, J. Olsen, and P. Jørgensen, Molecular Physics **115**, 16 (2017), URL <https://doi.org/10.1080/00268976.2016.1173733>.
- [129] E. Artacho and L. Miláns del Bosch, Physical Review A **43**, 5770 (1991), URL <https://link.aps.org/doi/10.1103/PhysRevA.43.5770>.

- [130] M. R. Hestenes and E. Stiefel, *Methods of conjugate gradients for solving linear systems*, vol. 49-1 (NBS, 1952).
- [131] D. D. O'Regan, *Optimised projections for the ab initio simulation of large and strongly correlated systems* (Springer, Berlin, Heidelberg, 2011).
- [132] N. W. Ashcroft and N. D. Mermin, *Solid State Physics (Holt, Rinehart and Winston, New York, 1976)* (Brooks Cole, 2005).
- [133] F. Bloch, *Zeitschrift für Physik* **52**, 555 (1929), ISSN 0044-3328, URL <https://doi.org/10.1007/BF01339455>.
- [134] L. P. Bouckaert, R. Smoluchowski, and E. Wigner, *Physical Review* **50**, 58 (1936), URL <https://link.aps.org/doi/10.1103/PhysRev.50.58>.
- [135] D. J. Chadi and M. L. Cohen, *Physical Review B* **8**, 5747 (1973), URL <https://link.aps.org/doi/10.1103/PhysRevB.8.5747>.
- [136] H. J. Monkhorst and J. D. Pack, *Physical Review B* **13**, 5188 (1976), URL <https://link.aps.org/doi/10.1103/PhysRevB.13.5188>.
- [137] G. Makov and M. C. Payne, *Physical Review B* **51**, 4014 (1995), URL <https://link.aps.org/doi/10.1103/PhysRevB.51.4014>.
- [138] J. E. Saal, S. Kirklin, M. Aykol, B. Meredig, and C. Wolverton, *JOM* **65**, 1501 (2013), ISSN 1543-1851, URL <https://doi.org/10.1007/s11837-013-0755-4>.
- [139] D. Gunceler, K. Letchworth-Weaver, R. Sundararaman, K. A. Schwarz, and T. A. Arias, *Modelling and Simulation in Materials Science and Engineering* **21**, 074005 (2013), URL <http://stacks.iop.org/0965-0393/21/i=7/a=074005>.
- [140] M. Lüders, M. A. L. Marques, N. N. Lathiotakis, A. Floris, G. Profeta, L. Fast, A. Continenza, S. Massidda, and E. K. U. Gross, *Physical Review B* **72**, 024545 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevB.72.024545>.

- [141] A. Floris, G. Profeta, N. N. Lathiotakis, M. Lüders, M. A. L. Marques, C. Franchini, E. K. U. Gross, A. Continenza, and S. Massidda, Physical Review Letters **94**, 037004 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevLett.94.037004>.
- [142] D. Xiao, Y. Yao, W. Feng, J. Wen, W. Zhu, X.-Q. Chen, G. M. Stocks, and Z. Zhang, Physical Review Letters **105**, 096404 (2010), URL <https://link.aps.org/doi/10.1103/PhysRevLett.105.096404>.
- [143] W. Feng, D. Xiao, J. Ding, and Y. Yao, Physical Review Letters **106**, 016402 (2011), URL <https://link.aps.org/doi/10.1103/PhysRevLett.106.016402>.
- [144] W. Feng, D. Xiao, Y. Zhang, and Y. Yao, Physical Review B **82**, 235121 (2010), URL <https://link.aps.org/doi/10.1103/PhysRevB.82.235121>.
- [145] J. Paier, R. Asahi, A. Nagoya, and G. Kresse, Physical Review B **79**, 115126 (2009), URL <https://link.aps.org/doi/10.1103/PhysRevB.79.115126>.
- [146] Y. Kanai and J. C. Grossman, Nano Letters **8**, 908 (2008), pMID: 18290634, URL <http://dx.doi.org/10.1021/nl0732777>.
- [147] J. P. Holdren et al., National Science and Technology Council OSTP. Washington, USA (2011).
- [148] S. Kirklin, J. E. Saal, B. Meredig, A. Thompson, J. W. Doak, M. Aykol, S. Rühl, and C. Wolverton, Computational Materials **1**, 15010 EP (2015), URL <http://dx.doi.org/10.1038/npjcompumats.2015.10>.
- [149] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Physical Review B **57**, 1505 (1998), URL <http://link.aps.org/doi/10.1103/PhysRevB.57.1505>.
- [150] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Science **321**, 792 (2008), URL <http://science.sciencemag.org/content/321/5890/792.short>.

- [151] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666 (2004), ISSN 0036-8075, URL <http://science.sciencemag.org/content/306/5696/666>.
- [152] A. K. Geim, *Science* **324**, 1530 (2009), ISSN 0036-8075, URL <http://science.sciencemag.org/content/324/5934/1530>.
- [153] K. Novoselov, *Physics World* **22**, 27 (2009), URL <http://stacks.iop.org/2058-7058/22/i=08/a=33>.
- [154] A. K. Geim and K. S. Novoselov, *Nature Materials* **6**, 183 (2007), ISSN 1476-1122, URL <http://dx.doi.org/10.1038/nmat1849>.
- [155] D. Larousserie, *The Guardian* (2013), URL <https://www.theguardian.com/science/2013/nov/26/graphene-molecule-potential-wonder-material>.
- [156] M. J. Allen, V. C. Tung, and R. B. Kaner, *Chemical Reviews* **110**, 132 (2010), PMID: 19610631, URL <http://dx.doi.org/10.1021/cr900070d>.
- [157] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, *Reviews of Modern Physics* **81**, 109 (2009), URL <https://link.aps.org/doi/10.1103/RevModPhys.81.109>.
- [158] A. K. Mishra and S. Ramaprabhu, *Desalination* **282**, 39 (2011), ISSN 0011-9164, Current Development of Wastewater Treatment in India, URL <http://www.sciencedirect.com/science/article/pii/S001191641100049X>.
- [159] F. Liu, P. Ming, and J. Li, *Physical Review B* **76**, 064120 (2007), URL <https://link.aps.org/doi/10.1103/PhysRevB.76.064120>.
- [160] F. Jamieson, *Translational Materials Research* **1**, 020204 (2014), URL <http://stacks.iop.org/2053-1613/1/i=2/a=020204>.
- [161] M. Yi and Z. Shen, *Journal of Materials Chemistry A* **3**, 11700 (2015), URL <http://dx.doi.org/10.1039/C5TA00252D>.

- [162] G. Giovannetti, P. A. Khomyakov, G. Brocks, P. J. Kelly, and J. van den Brink, *Physical Review B* **76**, 073103 (2007), URL <https://link.aps.org/doi/10.1103/PhysRevB.76.073103>.
- [163] C. R. Dean, F. A. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, et al., *Nature Nanotechnology* **5**, 722 (2010), ISSN 1748-3387, URL <http://dx.doi.org/10.1038/nnano.2010.172>.
- [164] Q. Peng, W. Ji, and S. De, *Computational Materials Science* **56**, 11 (2012), ISSN 0927-0256, URL <http://www.sciencedirect.com/science/article/pii/S0927025611006902>.
- [165] L. Song, L. Ci, H. Lu, P. B. Sorokin, C. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson, et al., *Nano Letters* **10**, 3209 (2010), pMID: 20698639, URL <http://dx.doi.org/10.1021/nl1022139>.
- [166] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, *Nano Letters* **10**, 1271 (2010), pMID: 20229981, URL <http://dx.doi.org/10.1021/nl903868w>.
- [167] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, *Nature Nanotechnology* **6**, 147 (2011), ISSN 1748-3387, URL <http://dx.doi.org/10.1038/nnano.2010.279>.
- [168] H. S. S. Ramakrishna Matte, A. Gomathi, A. Manna, D. Late, R. Datta, S. Pati, and C. Rao, *Angewandte Chemie International Edition* **49**, 4059 (2010), ISSN 1521-3773, URL <http://dx.doi.org/10.1002/anie.201000009>.
- [169] M. Xie, S. Zhang, B. Cai, Y. Huang, Y. Zou, B. Guo, Y. Gu, and H. Zeng, *Nano Energy* **28**, 433 (2016), ISSN 2211-2855, URL <http://www.sciencedirect.com/science/article/pii/S221128551630355X>.
- [170] M. Bernardi, M. Palummo, and J. C. Grossman, *Nano Letters* **13**, 3664 (2013), pMID: 23750910, URL <http://dx.doi.org/10.1021/nl401544y>.

- [171] Z. Liu, Q. Liu, Y. Huang, Y. Ma, S. Yin, X. Zhang, W. Sun, and Y. Chen, *Advanced Materials* **20**, 3924 (2008), ISSN 1521-4095, URL <http://dx.doi.org/10.1002/adma.200800366>.
- [172] Y. Wang, X. Chen, Y. Zhong, F. Zhu, and K. P. Loh, *Applied Physics Letters* **95**, 063302 (2009), URL <http://dx.doi.org/10.1063/1.3204698>.
- [173] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, *Nature Nanotechnology* **7**, 699 (2012), ISSN 1748-3387, URL <http://dx.doi.org/10.1038/nnano.2012.193>.
- [174] C.-M. Park and H.-J. Sohn, *Advanced Materials* **19**, 2465 (2007), ISSN 1521-4095, URL <http://dx.doi.org/10.1002/adma.200602592>.
- [175] L.-Q. Sun, M.-J. Li, K. Sun, S.-H. Yu, R.-S. Wang, and H.-M. Xie, *Journal of Physical Chemistry C* **116**, 14772 (2012), URL <http://dx.doi.org/10.1021/jp302265n>.
- [176] J. Sun, H.-W. Lee, M. Pasta, H. Yuan, G. Zheng, Y. Sun, Y. Li, and Y. Cui, *Nature Nanotechnology* **10**, 980 (2015), ISSN 1748-3387, URL <http://dx.doi.org/10.1038/nnano.2015.194>.
- [177] F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff, and V. Pellegrini, *Science* **347** (2015), ISSN 0036-8075, URL <http://science.sciencemag.org/content/347/6217/1246501>.
- [178] E. Yoo, J. Kim, E. Hosono, H.-s. Zhou, T. Kudo, and I. Honma, *Nano Letters* **8**, 2277 (2008), pMID: 18651781, URL <http://dx.doi.org/10.1021/nl1800957b>.
- [179] C. Liu, F. Li, L.-P. Ma, and H.-M. Cheng, *Advanced Materials* **22**, E28 (2010), ISSN 1521-4095, URL <http://dx.doi.org/10.1002/adma.200903328>.
- [180] S.-M. Paek, E. Yoo, and I. Honma, *Nano Letters* **9**, 72 (2009), pMID: 19090687, URL <http://dx.doi.org/10.1021/nl802484w>.

- [181] D. Hanlon, C. Backes, E. Doherty, C. S. Cucinotta, N. C. Berner, C. Boland, K. Lee, A. Harvey, P. Lynch, Z. Gholamvand, et al., *Nature Communications* **6**, 8563 (2015), ISSN 2041-1723, URL <http://europepmc.org/articles/PMC4634220>.
- [182] J. Sun, G. Zheng, H.-W. Lee, N. Liu, H. Wang, H. Yao, W. Yang, and Y. Cui, *Nano Letters* **14**, 4573 (2014), pMID: 25019417, URL <http://dx.doi.org/10.1021/nl501617j>.
- [183] S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang, and P. M. Ajayan, *Advanced Materials* **25**, 2452 (2013), ISSN 1521-4095, URL <http://dx.doi.org/10.1002/adma.201204453>.
- [184] G. Zhan and H. C. Zeng, *Advanced Functional Materials* **26**, 3268 (2016), ISSN 1616-3028, URL <http://dx.doi.org/10.1002/adfm.201505380>.
- [185] J. Yang, D. Voiry, S. J. Ahn, D. Kang, A. Y. Kim, M. Chhowalla, and H. S. Shin, *Angewandte Chemie International Edition* **52**, 13751 (2013), ISSN 1521-3773, URL <http://dx.doi.org/10.1002/anie.201307475>.
- [186] M. Wu, H. Fu, L. Zhou, K. Yao, and X. C. Zeng, *Nano Letters* **15**, 3557 (2015), pMID: 25844524, URL <http://dx.doi.org/10.1021/acs.nanolett.5b01041>.
- [187] J. Guan, Z. Zhu, and D. Tománek, *Physical Review Letters* **113**, 046804 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevLett.113.046804>.
- [188] Z. Zhu and D. Tománek, *Physical Review Letters* **112**, 176802 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevLett.112.176802>.
- [189] J. Guan, Z. Zhu, and D. Tománek, *ACS Nano* **8**, 12763 (2014), pMID: 25418761, URL <http://dx.doi.org/10.1021/nn5059248>.
- [190] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, and Y. Zhang, *Nature Nanotechnology* **9**, 372 (2014), ISSN 1748-3387, URL <http://dx.doi.org/10.1038/nnano.2014.35>.

- [191] F. Xia, H. Wang, and Y. Jia, *Nature Communications* **5**, 4458 EP (2014), ISSN 1748-3387, URL <http://dx.doi.org/10.1038/ncomms5458>.
- [192] S. P. Koenig, R. A. Doganov, H. Schmidt, A. H. C. Neto, and B. Ozyilmaz, *Applied Physics Letters* **104**, 103106 (2014), URL <http://dx.doi.org/10.1063/1.4868132>.
- [193] H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, and P. D. Ye, *ACS Nano* **8**, 4033 (2014), pMID: 24655084, URL <http://dx.doi.org/10.1021/nn501226z>.
- [194] X. Ling, H. Wang, S. Huang, F. Xia, and M. S. Dresselhaus, *Proceedings of the National Academy of Sciences of the United States of America* **112**, 4523 (2015).
- [195] J. R. Brent, N. Savjani, E. A. Lewis, S. J. Haigh, D. J. Lewis, and P. O'Brien, *Chemical Communications* **50**, 13338 (2014), URL <http://dx.doi.org/10.1039/C4CC05752J>.
- [196] A. S. Rodin, A. Carvalho, and A. H. Castro Neto, *Physical Review Letters* **112**, 176801 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevLett.112.176801>.
- [197] X. Peng, Q. Wei, and A. Copple, *Physical Review B* **90**, 085402 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevB.90.085402>.
- [198] J.-W. Jiang and H. S. Park, *Physical Review B* **91**, 235118 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.91.235118>.
- [199] B. Sa, Y.-L. Li, J. Qi, R. Ahuja, and Z. Sun, *Journal of Physical Chemistry C* **118**, 26560 (2014), URL <http://dx.doi.org/10.1021/jp508618t>.
- [200] M. Elahi, K. Khaliji, S. M. Tabatabaei, M. Pourfath, and R. Asgari, *Physical Review B* **91**, 115412 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.91.115412>.

- [201] T. Hu, Y. Han, and J. Dong, *Nanotechnology* **25**, 455703 (2014), URL <http://stacks.iop.org/0957-4484/25/i=45/a=455703>.
- [202] J.-W. Jiang and H. S. Park, *Nature Communications* **5**, 4727 EP (2014), URL <http://dx.doi.org/10.1038/ncomms5727>.
- [203] R. Fei and L. Yang, *Nano Letters* **14**, 2884 (2014), pMID: 24779386, URL <http://dx.doi.org/10.1021/nl500935z>.
- [204] H. Liu, Y. Du, Y. Deng, and P. D. Ye, *Chemical Society Reviews* **44**, 2732 (2015), URL <http://dx.doi.org/10.1039/C4CS00257A>.
- [205] J. Qiao, X. Kong, Z.-X. Hu, F. Yang, and W. Ji, *Nature Communications* **5**, 4475 EP (2014), URL <http://dx.doi.org/10.1038/ncomms5475>.
- [206] V. Tran, R. Soklaski, Y. Liang, and L. Yang, *Physical Review B* **89**, 235319 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevB.89.235319>.
- [207] R. W. Keyes, *Physical Review* **92**, 580 (1953), URL <https://link.aps.org/doi/10.1103/PhysRev.92.580>.
- [208] Q. Wei and X. Peng, *Applied Physics Letters* **104**, 251915 (2014), URL <http://aip.scitation.org/doi/abs/10.1063/1.4885215>.
- [209] C. Yongqing, Z. Gang, and Z. Yong-Wei, *Scientific Reports* pp. 1 – 6 (2014), ISSN 20452322, URL <http://elib.tcd.ie/login?url=http://search.ebscohost.com/login.aspx?direct=true&db=a9h&AN=99091207&site=eds-live&scope=site>.
- [210] A. C.-G. Zant, L. Vicarelli, E. Prada, J. O. Island, K. L. Narasimha-Acharya, S. I. Blanter, D. J. Groenendijk, M. Buscema, G. A. Steele, J. V. Alvarez, et al., *2D Materials* **1**, 025001 (2014), ISSN 2053-1583, URL <http://stacks.iop.org/2053-1583/1/i=2/a=025001>.
- [211] C. Kamal and M. Ezawa, *Physical Review B* **91**, 085423 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.91.085423>.

- [212] G. Wang, R. Pandey, and S. P. Karna, ACS Applied Materials and Interfaces **7**, 11490 (2015), pMID: 25955131, URL <http://dx.doi.org/10.1021/acsami.5b02441>.
- [213] I. Kokubo, Y. Yoshiike, K. Nakatsuji, and H. Hirayama, Physical Review B **91**, 075429 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.91.075429>.
- [214] Y. Lu, W. Xu, M. Zeng, G. Yao, L. Shen, M. Yang, Z. Luo, F. Pan, K. Wu, T. Das, et al., Nano Letters **15**, 80 (2015), pMID: 25495154, URL <http://dx.doi.org/10.1021/nl502997v>.
- [215] Z. Zhu, J. Guan, and D. Tománek, Nano Letters **15**, 6042 (2015), pMID: 26295748, URL <http://dx.doi.org/10.1021/acs.nanolett.5b02227>.
- [216] F. Shojaei and H. S. Kang, Journal of Physical Chemistry C **119**, 20210 (2015), URL <http://dx.doi.org/10.1021/acs.jpcc.5b07323>.
- [217] B. Liu, M. Köpf, A. N. Abbas, X. Wang, Q. Guo, Y. Jia, F. Xia, R. Weihrich, F. Bachhuber, F. Pielhofer, et al., Advanced Materials **27**, 4423 (2015), ISSN 1521-4095, URL <http://dx.doi.org/10.1002/adma.201501758>.
- [218] L. Kou, Y. Ma, X. Tan, T. Frauenheim, A. Du, and S. Smith, Journal of Physical Chemistry C **119**, 6918 (2015), URL <http://dx.doi.org/10.1021/acs.jpcc.5b02096>.
- [219] S. Zhang, Z. Yan, Y. Li, Z. Chen, and H. Zeng, Angewandte Chemie International Edition **54**, 3112 (2015), ISSN 1521-3773, URL <http://dx.doi.org/10.1002/anie.201411246>.
- [220] A. Manjanath, A. Samanta, T. Pandey, and A. K. Singh, Nanotechnology **26**, 075701 (2015), URL <http://stacks.iop.org/0957-4484/26/i=7/a=075701>.
- [221] J. Han, J. Xie, Z. Zhang, D. Yang, M. Si, and D. Xue, Applied Physics Express **8**, 041801 (2015), URL <http://stacks.iop.org/1882-0786/8/i=4/a=041801>.

- [222] Z. Zhu, J. Guan, and D. Tománek, *Physical Review B* **91**, 161404 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.91.161404>.
- [223] T. Hu and J. Dong, *Physical Review B* **92**, 064114 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.92.064114>.
- [224] Y. Lu, D. Zhou, G. Chang, S. Guan, W. Chen, Y. Jiang, J. Jiang, X.-s. Wang, S. A. Yang, Y. P. Feng, et al., *NPJ Computational Materials* **2**, 16011 EP (2016), URL <http://dx.doi.org/10.1038/npjcompumats.2016.11>.
- [225] Z. J. Xiang, G. J. Ye, C. Shang, B. Lei, N. Z. Wang, K. S. Yang, D. Y. Liu, F. B. Meng, X. G. Luo, L. J. Zou, et al., *Physical Review Letters* **115**, 186403 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevLett.115.186403>.
- [226] P.-L. Gong, D.-Y. Liu, K.-S. Yang, Z.-J. Xiang, X.-H. Chen, Z. Zeng, S.-Q. Shen, and L.-J. Zou, *Physical Review B* **93**, 195434 (2016), URL <https://link.aps.org/doi/10.1103/PhysRevB.93.195434>.
- [227] R. Fei, V. Tran, and L. Yang, *Physical Review B* **91**, 195319 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.91.195319>.
- [228] A. N. Abbas, B. Liu, L. Chen, Y. Ma, S. Cong, N. Aroonyadet, M. Köpf, T. Nilges, and C. Zhou, *ACS Nano* **9**, 5618 (2015), pMID: 25945545, URL <http://dx.doi.org/10.1021/acsnano.5b01961>.
- [229] L. Kou, T. Frauenheim, and C. Chen, *Journal of Physical Chemistry Letters* **5**, 2675 (2014), pMID: 26277962, URL <http://dx.doi.org/10.1021/jz501188k>.
- [230] T. Low, A. S. Rodin, A. Carvalho, Y. Jiang, H. Wang, F. Xia, and A. H. Castro Neto, *Physical Review B* **90**, 075434 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevB.90.075434>.
- [231] M. Baba, Y. Takeda, K. Shibata, T. Ikeda, and A. Morita, *Japanese Journal of Applied Physics* **28**, L2104 (1989), URL <http://stacks.iop.org/1347-4065/28/i=11A/a=2104>.

- [232] G. Yao, Z. Luo, F. Pan, W. Xu, Y. P. Feng, and X.-s. Wang, *Scientific Reports* **3**, 2010 EP (2013), URL <http://dx.doi.org/10.1038/srep02010>.
- [233] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, et al., *Journal of Physics: Condensed Matter* **21**, 395502 (2009), URL <http://stacks.iop.org/0953-8984/21/i=39/a=395502>.
- [234] D. Vanderbilt, *Physical Review B* **41**, 7892 (1990), URL <https://link.aps.org/doi/10.1103/PhysRevB.41.7892>.
- [235] E. Kucukbenli, M. Monni, B. Adetunji, X. Ge, G. Adebayo, N. Marzari, S. De Gironcoli, and A. D. Corso, arXiv preprint arXiv:1404.3015 (2014), URL <https://arxiv.org/abs/1404.3015>.
- [236] S. Grimme, *Journal of Computational Chemistry* **27**, 1787 (2006), ISSN 1096-987X, URL <http://dx.doi.org/10.1002/jcc.20495>.
- [237] N. Marzari, D. Vanderbilt, A. De Vita, and M. C. Payne, *Physical Review Letters* **82**, 3296 (1999), URL <https://link.aps.org/doi/10.1103/PhysRevLett.82.3296>.
- [238] V. Iyer, P. Ye, and X. Xu, *2D Materials* **4**, 021032 (2017), URL <http://stacks.iop.org/2053-1583/4/i=2/a=021032>.
- [239] D. R. Askeland, P. P. Fulay, and W. J. Wright, *The Science and Engineering of Materials* (Cengage Learning, 2011).
- [240] J. Halpin, *Journal of Composite Materials* **3**, 732 (1969), URL <http://dx.doi.org/10.1177/002199836900300419>.
- [241] J. C. H. Affdl and J. L. Kardos, *Polymer Engineering & Science* **16**, 344 (1976), ISSN 1548-2634, URL <http://dx.doi.org/10.1002/pen.760160512>.
- [242] R. Mullen, R. Ballarini, Y. Yin, and A. Heuer, *Acta Materialia* **45**, 2247 (1997), ISSN 1359-6454, URL <http://www.sciencedirect.com/science/article/pii/S1359645496003667>.

- [243] R. Hearmon, S. Balakrishne, M. Krishnamurthi, and B. Rao, *The elastic constants of polycrystalline aggregates*, vol. 1 (Academic Press, 1969).
- [244] J. M. J. den Toonder, J. A. W. van Dommelen, and F. P. T. Baaijens, Modelling and Simulation in Materials Science and Engineering **7**, 909 (1999), URL <http://stacks.iop.org/0965-0393/7/i=6/a=301>.
- [245] A. Reuss, Journal of Applied Mathematics and Mechanics **9**, 49 (1929), ISSN 1521-4001, URL <http://dx.doi.org/10.1002/zamm.19290090104>.
- [246] R. D. Cook and W. C. Young, *Advanced Mechanics of Materials*, vol. 2 (Pearson College Division, New York, 1998).
- [247] W. Voigt, Annals of Physics **274**, 573 (1889), ISSN 1521-3889, URL <http://dx.doi.org/10.1002/andp.18892741206>.
- [248] R. Hill, Proceedings of the Physical Society **65**, 349 (1952), URL <http://iopscience.iop.org/article/10.1088/0370-1298/65/5/307/meta>.
- [249] U. Khan, P. May, A. O'Neill, A. P. Bell, E. Boussac, A. Martin, J. Semple, and J. N. Coleman, Nanoscale **5**, 581—587 (2013), ISSN 2040-3364, URL <https://doi.org/10.1039/c2nr33049k>.
- [250] W. E. Mahmoud, European Polymer Journal **47**, 1534 (2011), ISSN 0014-3057, URL <http://www.sciencedirect.com/science/article/pii/S0014305711002023>.
- [251] J. Liang, Y. Huang, L. Zhang, Y. Wang, Y. Ma, T. Guo, and Y. Chen, Advanced Functional Materials **19**, 2297 (2009), ISSN 1616-3028, URL <http://dx.doi.org/10.1002/adfm.200801776>.
- [252] J. A. King, D. R. Klimek, I. Miskioglu, and G. M. Odegard, Journal of Applied Polymer Science **128**, 4217 (2013), ISSN 1097-4628, URL <http://dx.doi.org/10.1002/app.38645>.

- [253] R. J. Young, I. A. Kinloch, L. Gong, and K. S. Novoselov, *Composites Science and Technology* **72**, 1459 (2012), ISSN 0266-3538, URL <http://www.sciencedirect.com/science/article/pii/S0266353812001789>.
- [254] Y. Yang, W. Rigdon, X. Huang, and X. Li, *Scientific Reports* **3**, 2086 EP (2013), URL <http://dx.doi.org/10.1038/srep02086>.
- [255] S.-K. Kim, J. J. Wie, Q. Mahmood, and H. S. Park, *Nanoscale* **6**, 7430 (2014), URL <http://dx.doi.org/10.1039/C4NR01208A>.
- [256] J. Hermans, *Proceedings, Series B* **70**, 1 (1967).
- [257] S. Appalakondaiah, G. Vaitheeswaran, S. Lebègue, N. E. Christensen, and A. Svane, *Physical Review B* **86**, 035105 (2012), URL <https://link.aps.org/doi/10.1103/PhysRevB.86.035105>.
- [258] D. Kekik, E. Durgun, and S. Ciraci, *Physical Review B* **94**, 205410 (2016), URL <https://link.aps.org/doi/10.1103/PhysRevB.94.205410>.
- [259] Z. Zhang, J. Xie, D. Yang, Y. Wang, M. Si, and D. Xue, *Applied Physics Express* **8**, 055201 (2015), URL <http://stacks.iop.org/1882-0786/8/i=5/a=055201>.
- [260] Y. Xu, B. Peng, H. Zhang, H. Shao, R. Zhang, and H. Zhu, *Annals of Physics* **529**, 1600152 (2017), ISSN 1521-3889, 1600152, URL <http://dx.doi.org/10.1002/andp.201600152>.
- [261] L. Cartz, S. R. Srinivasa, R. J. Riedner, J. D. Jorgensen, and T. G. Worlton, *Journal of Chemical Physics* **71**, 1718 (1979), URL <http://dx.doi.org/10.1063/1.438523>.
- [262] P. M. Smith, A. J. Leadbetter, and A. J. Apling, *Philosophical Magazine* **31**, 57 (1975), URL <http://dx.doi.org/10.1080/14786437508229285>.
- [263] C. S. Barrett, P. Cucka, and K. Haefner, *Acta Crystallography* **16**, 451 (1963), URL <https://doi.org/10.1107/S0365110X63001262>.

- [264] M. Yoshizawa, I. Shirotani, and T. Fujimura, Journal of the Physical Society of Japan **55**, 1196 (1986), URL <http://dx.doi.org/10.1143/JPSJ.55.1196>.
- [265] Y. Kôzuki, Y. Hanayama, M. Kimura, T. Nishitake, and S. Endo, Journal of the Physical Society of Japan **60**, 1612 (1991), URL <http://dx.doi.org/10.1143/JPSJ.60.1612>.
- [266] Y. Wang and Y. Ding, Nanoscale Research Letters **10**, 254 (2015), ISSN 1556-276X, URL <http://dx.doi.org/10.1186/s11671-015-0955-7>.
- [267] T. Akai, S. Endo, Y. Akahama, K. Koto, and Y. Marljyama, High Pressure Research **1**, 115 (1989), URL <http://dx.doi.org/10.1080/08957958908201013>.
- [268] R. M. Jones, *Mechanics of Composite Materials*, vol. 193 (Scripta Book Company Washington, DC, 1975).
- [269] V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, and J. N. Coleman, Science **340** (2013), ISSN 0036-8075, URL <http://science.sciencemag.org/content/340/6139/1226419>.
- [270] J. D. Wood, S. A. Wells, D. Jariwala, K.-S. Chen, E. Cho, V. K. Sangwan, X. Liu, L. J. Lauhon, T. J. Marks, and M. C. Hersam, Nano Letters **14**, 6964 (2014), pMID: 25380142, URL <http://dx.doi.org/10.1021/nl5032293>.
- [271] D. Music, R. W. Geyer, and J. M. Schneider, Surface and Coatings Technology **286**, 178 (2016), ISSN 0257-8972, URL <http://www.sciencedirect.com/science/article/pii/S0257897215304515>.
- [272] S.-Y. Xu, I. Belopolski, N. Alidoust, M. Neupane, G. Bian, C. Zhang, R. Sankar, G. Chang, Z. Yuan, C.-C. Lee, et al., Science (2015), ISSN 0036-8075, URL <http://science.sciencemag.org/content/early/2015/07/15/science.aaa9297>.
- [273] V. Pardo and W. E. Pickett, Physical Review Letters **102**, 166803 (2009), URL <https://link.aps.org/doi/10.1103/PhysRevLett.102.166803>.

- [274] C. Shekhar, A. K. Nayak, Y. Sun, M. Schmidt, M. Nicklas, I. Leermakers, U. Zeitler, Y. Skourski, J. Wosnitza, Z. Liu, et al., *Nature Physics* **11**, 645 (2015), ISSN 1745-2473, URL <http://dx.doi.org/10.1038/nphys3372>.
- [275] X. Wan, A. M. Turner, A. Vishwanath, and S. Y. Savrasov, *Physical Review B* **83**, 205101 (2011), URL <https://link.aps.org/doi/10.1103/PhysRevB.83.205101>.
- [276] H. Nielsen and M. Ninomiya, *Physics Letters B* **130**, 389 (1983), ISSN 0370-2693, URL <http://www.sciencedirect.com/science/article/pii/0370269383915290>.
- [277] A. M. Turner, A. Vishwanath, and C. O. Head, *Topological Insulators 6*, vol. 1 (Elsevier, 2013).
- [278] S. A. Parameswaran, T. Grover, D. A. Abanin, D. A. Pesin, and A. Vishwanath, *Physical Review X* **4**, 031035 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevX.4.031035>.
- [279] S. M. Young, S. Zaheer, J. C. Y. Teo, C. L. Kane, E. J. Mele, and A. M. Rappe, *Physical Review Letters* **108**, 140405 (2012), URL <https://link.aps.org/doi/10.1103/PhysRevLett.108.140405>.
- [280] Z. Wang, Y. Sun, X.-Q. Chen, C. Franchini, G. Xu, H. Weng, X. Dai, and Z. Fang, *Physical Review B* **85**, 195320 (2012), URL <https://link.aps.org/doi/10.1103/PhysRevB.85.195320>.
- [281] Z. Wang, H. Weng, Q. Wu, X. Dai, and Z. Fang, *Physical Review B* **88**, 125427 (2013), URL <https://link.aps.org/doi/10.1103/PhysRevB.88.125427>.
- [282] Z. Liu, J. Wang, and J. Li, *Physical Chemistry Chemical Physics* **15**, 18855 (2013), URL <http://dx.doi.org/10.1039/C3CP53257G>.
- [283] J. Wang, S. Deng, Z. Liu, and Z. Liu, *National Science Review* **2**, 22 (2015), /oup/backfile/content_public/journal/nsr/2/1/10.1093/nsr_nwu080/2/nwu080.pdf, URL <http://dx.doi.org/10.1093/nsr/nwu080>.

- [284] H. Weyl, *Zeitschrift für Physik* **56**, 330 (1929), ISSN 0044-3328, URL <https://doi.org/10.1007/BF01339504>.
- [285] B. Yan and C. Felser, *Annual Review of Condensed Matter Physics* **8**, 337 (2017), URL <https://doi.org/10.1146/annurev-conmatphys-031016-025458>.
- [286] U. von Barth, *Physica Scripta* **2004**, 9 (2004), URL <http://stacks.iop.org/1402-4896/2004/i=T109/a=001>.
- [287] P. A. Dirac, in *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* (The Royal Society, 1928), vol. 117:778, pp. 610–624.
- [288] G. Xu, H. Weng, Z. Wang, X. Dai, and Z. Fang, *Physical Review Letters* **107**, 186806 (2011), URL <https://link.aps.org/doi/10.1103/PhysRevLett.107.186806>.
- [289] D. Bulmash, C.-X. Liu, and X.-L. Qi, *Physical Review B* **89**, 081106 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevB.89.081106>.
- [290] G. van Miert and C. M. Smith, *Physical Review B* **93**, 035401 (2016), URL <https://link.aps.org/doi/10.1103/PhysRevB.93.035401>.
- [291] S. M. Young and C. L. Kane, *Physical Review Letters* **115**, 126803 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevLett.115.126803>.
- [292] J. Kim, S. S. Baik, S. H. Ryu, Y. Sohn, S. Park, B.-G. Park, J. Denlinger, Y. Yi, H. J. Choi, and K. S. Kim, *Science* **349**, 723 (2015), ISSN 0036-8075, URL <http://science.sciencemag.org/content/349/6249/723>.
- [293] C. Wang, Q. Xia, Y. Nie, M. Rahman, and G. Guo, *AIP Advances* **6**, 035204 (2016), URL <http://dx.doi.org/10.1063/1.4943548>.
- [294] M. Zhao, X. Zhang, and L. Li, *Scientific Reports* **5**, 16108 (2015), ISSN 2045-2322, PMID: 26537994, URL <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC4633587/>.

- [295] A. D. Corso and A. M. Conte, Phys. Rev. B **71**, 115106 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevB.71.115106>.
- [296] S. S. Baik, K. S. Kim, Y. Yi, and H. J. Choi, Nano Letters **15**, 7788 (2015), pMID: 26572058, URL <http://dx.doi.org/10.1021/acs.nanolett.5b04106>.
- [297] G. Moynihan, S. Sanvito, and D. D. O'Regan, 2D Materials **4**, 045018 (2017), URL <http://stacks.iop.org/2053-1583/4/i=4/a=045018>.
- [298] D. Çakır, H. Sahin, and F. m. c. M. Peeters, Physical Review B **90**, 205421 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevB.90.205421>.
- [299] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Physical Review B **77**, 115123 (2008), URL <http://link.aps.org/doi/10.1103/PhysRevB.77.115123>.
- [300] Y. Hinuma, A. Grüneis, G. Kresse, and F. Oba, Physical Review B **90**, 155405 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevB.90.155405>.
- [301] H. Doh and H. J. Choi, 2D Materials **4**, 025071 (2017), URL <http://stacks.iop.org/2053-1583/4/i=2/a=025071>.
- [302] A. Morita, Applied Physics A **39**, 227 (1986), ISSN 1432-0630, URL <http://dx.doi.org/10.1007/BF00617267>.
- [303] D. Warschauer, Journal of Applied Physics **34**, 1853 (1963), URL <http://dx.doi.org/10.1063/1.1729699>.
- [304] S. Narita, Y. Akahama, Y. Tsukiyama, K. Muro, S. Mori, S. Endo, M. Taniguchi, M. Seki, S. Suga, A. Mikuni, et al., Physica B&C **117**, 422 (1983), ISSN 0378-4363, URL <http://www.sciencedirect.com/science/article/pii/0378436383905478>.
- [305] Y. Maruyama, S. Suzuki, K. Kobayashi, and S. Tanuma, Physica B&C **105**, 99 (1981), ISSN 0378-4363, URL <http://www.sciencedirect.com/science/article/pii/0378436381902230>.

- [306] G. Greaves, S. Elliott, and E. Davis, *Advances in Physics* **28**, 49 (1979), URL <http://dx.doi.org/10.1080/00018737900101355>.
- [307] O. U. Aktürk, V. O. Özçelik, and S. Ciraci, *Physical Review B* **91**, 235446 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.91.235446>.
- [308] G. Bihlmayer, O. Rader, and R. Winkler, *New Journal of Physics* **17**, 050202 (2015), URL <http://stacks.iop.org/1367-2630/17/i=5/a=050202>.
- [309] Z. S. Popović, J. M. Kurdestany, and S. Satpathy, *Physical Review B* **92**, 035135 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.92.035135>.
- [310] L. Yang, Y. Song, W. Mi, and X. Wang, *RSC Advances* **6**, 66140 (2016), URL <http://dx.doi.org/10.1039/C6RA13101H>.
- [311] A. Rohrbach, J. Hafner, and G. Kresse, *Physical Review B* **70**, 125426 (2004), URL <https://link.aps.org/doi/10.1103/PhysRevB.70.125426>.
- [312] Y. Zhang and W. Yang, *The Journal of Chemical Physics* **109**, 2604 (1998), URL <http://dx.doi.org/10.1063/1.476859>.
- [313] R. Merkle, A. Savin, and H. Preuss, *The Journal of Chemical Physics* **97**, 9216 (1992), URL <http://dx.doi.org/10.1063/1.463297>.
- [314] J. M. Seminario, *Recent developments and applications of modern density functional theory*, vol. 4 (Elsevier, 1996).
- [315] J. P. Perdew and M. Levy, *Physical Review B* **56**, 16021 (1997), URL <https://link.aps.org/doi/10.1103/PhysRevB.56.16021>.
- [316] P. Mori-Sánchez, A. J. Cohen, and W. Yang, *Physical Review Letters* **100**, 146401 (2008), URL <https://link.aps.org/doi/10.1103/PhysRevLett.100.146401>.
- [317] E. J. Baerends, *Physical Review Letters* **87**, 133004 (2001), URL <https://link.aps.org/doi/10.1103/PhysRevLett.87.133004>.

- [318] A. D. Becke, The Journal of Chemical Physics **119**, 2972 (2003), URL <http://dx.doi.org/10.1063/1.1589733>.
- [319] A. J. Cohen, P. Mori-Sánchez, and W. Yang, The Journal of Chemical Physics **129**, 121104 (2008), URL <http://dx.doi.org/10.1063/1.2987202>.
- [320] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Journal of Chemical Theory and Computation **5**, 786 (2009), pMID: 26609584, URL <http://dx.doi.org/10.1021/ct8005419>.
- [321] H. van Aggelen, Y. Yang, and W. Yang, Physical Review A **88**, 030501 (2013), URL <https://link.aps.org/doi/10.1103/PhysRevA.88.030501>.
- [322] P. Mori-Sánchez, A. J. Cohen, and W. Yang, Physical Review A **85**, 042507 (2012), URL <https://link.aps.org/doi/10.1103/PhysRevA.85.042507>.
- [323] J. P. Perdew, International Journal of Quantum Chemistry **28**, 497 (1985), ISSN 1097-461X, URL <http://dx.doi.org/10.1002/qua.560280846>.
- [324] E. Ruiz, D. R. Salahub, and A. Vela, The Journal of Physical Chemistry **100**, 12265 (1996), URL <http://dx.doi.org/10.1021/jp9533077>.
- [325] B. G. Johnson, C. A. Gonzales, P. M. Gill, and J. A. Pople, Chemical Physics Letters **221**, 100 (1994), ISSN 0009-2614, URL <http://www.sciencedirect.com/science/article/pii/0009261494870241>.
- [326] B. S. Jursic, Chemical Physics Letters **256**, 603 (1996), ISSN 0009-2614, URL <http://www.sciencedirect.com/science/article/pii/0009261496004800>.
- [327] J. Baker, J. Andzelm, M. Muir, and P. R. Taylor, Chemical Physics Letters **237**, 53 (1995), ISSN 0009-2614, URL <http://www.sciencedirect.com/science/article/pii/000926149500299J>.
- [328] T. Bally and G. N. Sastry, The Journal of Physical Chemistry A **101**, 7923 (1997), URL <http://dx.doi.org/10.1021/jp972378y>.

- [329] P. Mori-Sánchez, Q. Wu, and W. Yang, *Journal of Chemical Physics* **119**, 11001 (2003), URL <http://scitation.aip.org/content/aip/journal/jcp/119/21/10.1063/1.1630011>.
- [330] I. Dabo, A. Ferretti, N. Poilvert, Y. Li, N. Marzari, and M. Cococcioni, *Physical Review B* **82**, 115121 (2010), URL <http://link.aps.org/doi/10.1103/PhysRevB.82.115121>.
- [331] G. Borghi, A. Ferretti, N. L. Nguyen, I. Dabo, and N. Marzari, *Physical Review B* **90**, 075135 (2014), URL <http://link.aps.org/doi/10.1103/PhysRevB.90.075135>.
- [332] N. L. Nguyen, G. Borghi, A. Ferretti, I. Dabo, and N. Marzari, *Physical Review Letters* **114**, 166405 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevLett.114.166405>.
- [333] N. L. Nguyen, N. Colonna, A. Ferretti, and N. Marzari, arXiv preprint arXiv:1708.08518 (2017), URL <https://arxiv.org/abs/1708.08518>.
- [334] T. Koopmans, *Physica* **1**, 104 (1934), ISSN 0031-8914, URL <http://www.sciencedirect.com/science/article/pii/S0031891434900112>.
- [335] J. C. Phillips, *Phys. Rev.* **123**, 420 (1961), URL <https://link.aps.org/doi/10.1103/PhysRev.123.420>.
- [336] V. I. Anisimov and O. Gunnarsson, *Physical Review B* **43**, 7570 (1991), URL <http://link.aps.org/doi/10.1103/PhysRevB.43.7570>.
- [337] V. I. Anisimov, J. Zaanen, and O. K. Andersen, *Physical Review B* **44**, 943 (1991), URL <http://link.aps.org/doi/10.1103/PhysRevB.44.943>.
- [338] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyżyk, and G. A. Sawatzky, *Physical Review B* **48**, 16929 (1993), URL <http://link.aps.org/doi/10.1103/PhysRevB.48.16929>.
- [339] I. V. Solovyev, P. H. Dederichs, and V. I. Anisimov, *Physical Review B* **50**, 16861 (1994), URL <https://link.aps.org/doi/10.1103/PhysRevB.50.16861>.

- [340] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, *Physical Review B* **52**, R5467 (1995), URL <https://link.aps.org/doi/10.1103/PhysRevB.52.R5467>.
- [341] W. E. Pickett, S. C. Erwin, and E. C. Ethridge, *Physical Review B* **58**, 1201 (1998), URL <http://link.aps.org/doi/10.1103/PhysRevB.58.1201>.
- [342] M. Cococcioni and S. de Gironcoli, *Physical Review B* **71**, 035105 (2005), URL <http://link.aps.org/doi/10.1103/PhysRevB.71.035105>.
- [343] B. Himmetoglu, A. Floris, S. de Gironcoli, and M. Cococcioni, *International Journal of Quantum Chemistry* **114**, 14 (2014), ISSN 1097-461X, URL <http://dx.doi.org/10.1002/qua.24521>.
- [344] O. Gunnarsson, *Physical Review B* **41**, 514 (1990), URL <https://link.aps.org/doi/10.1103/PhysRevB.41.514>.
- [345] I. V. Solovyev and P. H. Dederichs, *Physical Review B* **49**, 6736 (1994), URL <http://link.aps.org/doi/10.1103/PhysRevB.49.6736>.
- [346] O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, *Physical Review B* **39**, 1708 (1989), URL <https://link.aps.org/doi/10.1103/PhysRevB.39.1708>.
- [347] A. Svane and O. Gunnarsson, *Physical Review B* **37**, 9919 (1988), URL <https://link.aps.org/doi/10.1103/PhysRevB.37.9919>.
- [348] A. Svane and O. Gunnarsson, *EPL (Europhysics Letters)* **7**, 171 (1988), URL <http://stacks.iop.org/0295-5075/7/i=2/a=013>.
- [349] A. Svane and O. Gunnarsson, *Physical Review Letters* **65**, 1148 (1990), URL <https://link.aps.org/doi/10.1103/PhysRevLett.65.1148>.
- [350] A. Svane, *Physical Review Letters* **68**, 1900 (1992), URL <https://link.aps.org/doi/10.1103/PhysRevLett.68.1900>.
- [351] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, *Journal of Physics Condensed Matter* **9**, 767 (1997), URL <http://stacks.iop.org/0953-8984/9/i=4/a=002>.

- [352] S. L. Dudarev, A. I. Liechtenstein, M. R. Castell, G. A. D. Briggs, and A. P. Sutton, *Physical Review B* **56**, 4900 (1997), URL <https://link.aps.org/doi/10.1103/PhysRevB.56.4900>.
- [353] V. I. Anisimov, A. I. Poteryaev, M. A. Korotin, A. O. Anokhin, and G. Kotliar, *Journal of Physics: Condensed Matter* **9**, 7359 (1997), URL <http://stacks.iop.org/0953-8984/9/i=35/a=010>.
- [354] B. Himmetoglu, R. M. Wentzcovitch, and M. Cococcioni, *Physical Review B* **84**, 115108 (2011), URL <http://link.aps.org/doi/10.1103/PhysRevB.84.115108>.
- [355] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, *Physical Review Letters* **49**, 1691 (1982), URL <http://link.aps.org/doi/10.1103/PhysRevLett.49.1691>.
- [356] P. W. Ayers, *Journal of Mathematical Chemistry* **43**, 285 (2008), ISSN 1572-8897, URL <https://doi.org/10.1007/s10910-006-9195-5>.
- [357] E. Fermi and E. Amaldi, *Mem. classe sci. fis. mat. nat. accad* (1934).
- [358] G. J. Martyna and M. E. Tuckerman, *Journal of Chemical Physics* **110**, 2810 (1999), URL <http://scitation.aip.org/content/aip/journal/jcp/110/6/10.1063/1.477923>.
- [359] T. Stein, L. Kronik, and R. Baer, *Journal of the American Chemical Society* **131**, 2818 (2009), pMID: 19239266, URL <http://dx.doi.org/10.1021/ja8087482>.
- [360] U. Salzner and R. Baer, *The Journal of Chemical Physics* **131**, 231101 (2009), URL <http://dx.doi.org/10.1063/1.3269030>.
- [361] T. Stein, L. Kronik, and R. Baer, *The Journal of Chemical Physics* **131**, 244119 (2009), URL <http://dx.doi.org/10.1063/1.3269029>.
- [362] S. Kümmel and L. Kronik, *Reviews of Modern Physics* **80**, 3 (2008), URL <https://link.aps.org/doi/10.1103/RevModPhys.80.3>.

- [363] A. Filippetti and N. A. Spaldin, Physical Review B **67**, 125109 (2003), URL <https://link.aps.org/doi/10.1103/PhysRevB.67.125109>.
- [364] M. d’Avezac, M. Calandra, and F. Mauri, Physical Review B **71**, 205210 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevB.71.205210>.
- [365] A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, and G. E. Scuseria, The Journal of Chemical Physics **125**, 194112 (2006), URL <http://dx.doi.org/10.1063/1.2387954>.
- [366] V. I. Anisimov, A. V. Kozhevnikov, M. A. Korotin, A. V. Lukoyanov, and D. A. Khafizullin, Journal of Physics: Condensed Matter **19**, 106206 (2007), URL <http://stacks.iop.org/0953-8984/19/i=10/a=106206>.
- [367] L. G. Ferreira, M. Marques, and L. K. Teles, Physical Review B **78**, 125116 (2008), URL <https://link.aps.org/doi/10.1103/PhysRevB.78.125116>.
- [368] M. Stengel and N. A. Spaldin, Physical Review B **77**, 155106 (2008), URL <https://link.aps.org/doi/10.1103/PhysRevB.77.155106>.
- [369] R. A. Heaton, M. R. Pederson, and C. C. Lin, The Journal of Chemical Physics **86**, 258 (1987), URL <http://dx.doi.org/10.1063/1.452616>.
- [370] O. A. Vydrov and G. E. Scuseria, The Journal of Chemical Physics **124**, 191101 (2006), URL <http://dx.doi.org/10.1063/1.2204599>.
- [371] O. A. Vydrov, G. E. Scuseria, J. P. Perdew, A. Ruzsinszky, and G. I. Csonka, The Journal of Chemical Physics **124**, 094108 (2006), URL <http://dx.doi.org/10.1063/1.2176608>.
- [372] S. Goedecker and C. J. Umrigar, Physical Review A **55**, 1765 (1997), URL <https://link.aps.org/doi/10.1103/PhysRevA.55.1765>.
- [373] A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, and G. E. Scuseria, The Journal of Chemical Physics **126**, 104102 (2007), URL <http://dx.doi.org/10.1063/1.2566637>.

- [374] Z. Szotek, W. M. Temmerman, and H. Winter, *Physical Review B* **47**, 4029 (1993), URL <https://link.aps.org/doi/10.1103/PhysRevB.47.4029>.
- [375] Z. Szotek, W. Temmerman, and H. Winter, *Physica B: Condensed Matter* **172**, 19 (1991), ISSN 0921-4526, URL <http://www.sciencedirect.com/science/article/pii/0921452691904117>.
- [376] W. M. Temmerman, Z. Szotek, and H. Winter, *Physical Review B* **47**, 11533 (1993), URL <https://link.aps.org/doi/10.1103/PhysRevB.47.11533>.
- [377] D. Vogel, P. Krüger, and J. Pollmann, *Physical Review B* **52**, R14316 (1995), URL <https://link.aps.org/doi/10.1103/PhysRevB.52.R14316>.
- [378] S. V. Beiden, W. M. Temmerman, Z. Szotek, and G. A. Gehring, *Physical Review Letters* **79**, 3970 (1997), URL <https://link.aps.org/doi/10.1103/PhysRevLett.79.3970>.
- [379] M. Lüders, A. Ernst, M. Däne, Z. Szotek, A. Svane, D. Ködderitzsch, W. Hergert, B. L. Györffy, and W. M. Temmerman, *Physical Review B* **71**, 205109 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevB.71.205109>.
- [380] R. G. Parr and R. G. Pearson, *Journal of the American Chemical Society* **105**, 7512 (1983), URL <http://pubs.acs.org/doi/abs/10.1021/ja00364a005?journalCode=jacsat>.
- [381] S. Lany and A. Zunger, *Physical Review B* **81**, 205209 (2010), URL <https://link.aps.org/doi/10.1103/PhysRevB.81.205209>.
- [382] T. S. Kasirga, D. Sun, J. H. Park, J. M. Coy, Z. Fei, X. Xu, and D. H. Cobden, *Nature Nanotechnology* **7**, 723 (2012), ISSN 1748-3387, URL <http://dx.doi.org/10.1038/nnano.2012.176>.
- [383] J. E. Coulter, E. Manousakis, and A. Gali, *Physical Review B* **90**, 165142 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevB.90.165142>.
- [384] E. Dagotto, *Science* **309**, 257 (2005), ISSN 0036-8075, URL <http://science.sciencemag.org/content/309/5732/257>.

- [385] Y. Zhou, X. Guan, H. Zhou, K. Ramadoss, S. Adam, H. Liu, S. Lee, J. Shi, M. Tsuchiya, D. D. Fong, et al., *Nature* **534**, 231 (2016), ISSN 0028-0836, URL <http://dx.doi.org/10.1038/nature17653>.
- [386] M. E. Alberto, T. Marino, N. Russo, E. Sicilia, and M. Toscano, *Physical Chemistry Chemical Physics* **14**, 14943 (2012), URL <http://dx.doi.org/10.1039/C2CP41836C>.
- [387] M. Däne, M. Lüders, A. Ernst, D. Ködderitzsch, W. M. Temmerman, Z. Szotek, and W. Hergert, *Journal of Physics: Condensed Matter* **21**, 045604 (2009), URL <http://stacks.iop.org/0953-8984/21/i=4/a=045604>.
- [388] P. W. Anderson, *Physical Review* **124**, 41 (1961), URL <https://link.aps.org/doi/10.1103/PhysRev.124.41>.
- [389] D. D. O'Regan, N. D. M. Hine, M. C. Payne, and A. A. Mostofi, *Physical Review B* **82**, 081102 (2010), URL <http://link.aps.org/doi/10.1103/PhysRevB.82.081102>.
- [390] J. C. Slater, *Quantum Theory of Atomic Structure* (McGaw-Hill, New York, 1960).
- [391] E. R. Ylvisaker, W. E. Pickett, and K. Koepernik, *Physical Review B* **79**, 035103 (2009), URL <https://link.aps.org/doi/10.1103/PhysRevB.79.035103>.
- [392] S. Fabris, S. de Gironcoli, S. Baroni, G. Vicario, and G. Balducci, *Physical Review B* **71**, 041102 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevB.71.041102>.
- [393] L. Wang, T. Maxisch, and G. Ceder, *Physical Review B* **73**, 195107 (2006), URL <https://link.aps.org/doi/10.1103/PhysRevB.73.195107>.
- [394] C. Loschen, J. Carrasco, K. M. Neyman, and F. Illas, *Physical Review B* **75**, 035115 (2007), URL <https://link.aps.org/doi/10.1103/PhysRevB.75.035115>.

- [395] Q. Zhao, E. I. Ioannidis, and H. J. Kulik, Journal of Chemical Physics **145**, 054109 (2016), URL <http://scitation.aip.org/content/aip/journal/jcp/145/5/10.1063/1.4959882>.
- [396] H. J. Kulik, M. Cococcioni, D. A. Scherlis, and N. Marzari, Physical Review Letters **97**, 103001 (2006), URL <http://link.aps.org/doi/10.1103/PhysRevLett.97.103001>.
- [397] H. J. Kulik and N. Marzari, Journal of Chemical Physics **135**, 194105 (2011), URL <http://dx.doi.org/10.1063/1.3660353>.
- [398] D. Lu and P. Liu, Journal of Chemical Physics **140**, 084101 (2014), URL <http://dx.doi.org/10.1063/1.4865831>.
- [399] M. Aykol and C. Wolverton, Physical Review B **90**, 115105 (2014), URL <http://link.aps.org/doi/10.1103/PhysRevB.90.115105>.
- [400] M. Fuchs, Y.-M. Niquet, X. Gonze, and K. Burke, The Journal of Chemical Physics **122**, 094116 (2005), URL <http://dx.doi.org/10.1063/1.1858371>.
- [401] M. J. G. Peach, A. M. Teale, and D. J. Tozer, The Journal of Chemical Physics **126**, 244104 (2007), URL <http://dx.doi.org/10.1063/1.2747248>.
- [402] J. S. Sims and S. A. Hagstrom, Journal of Chemical Physics **124**, 94101 (2006), URL <http://dx.doi.org/10.1063/1.2173250>.
- [403] J. S. Sims and S. Hagstrom, Physical Review A **4**, 908 (1971), URL <https://link.aps.org/doi/10.1103/PhysRevA.4.908>.
- [404] J. Frank, *Introduction to Computational Chemistry* (John Wiley & Sons, Inc., 1999).
- [405] J. J. Shepherd, G. Booth, A. Grüneis, and A. Alavi, Phys. Rev. B **85**, 081103 (2012), URL <https://link.aps.org/doi/10.1103/PhysRevB.85.081103>.
- [406] G. H. Booth, A. Grüneis, G. Kresse, and A. Alavi, Nature **493**, 365 EP (2012), URL <http://dx.doi.org/10.1038/nature11770>.

- [407] T. M. Henderson and G. E. Scuseria, *Molecular Physics* **108**, 2511 (2010), URL <http://dx.doi.org/10.1080/00268976.2010.507227>.
- [408] M. Setvin, C. Franchini, X. Hao, M. Schmid, A. Janotti, M. Kaltak, C. G. Van de Walle, G. Kresse, and U. Diebold, *Physical Review Letters* **113**, 086402 (2014), URL <http://link.aps.org/doi/10.1103/PhysRevLett.113.086402>.
- [409] J. M. Garcia-Lastra, J. S. G. Myrdal, R. Christensen, K. S. Thygesen, and T. Vegge, *Journal of Physical Chemistry C* **117**, 5568 (2013), URL <http://dx.doi.org/10.1021/jp3107809>.
- [410] M. Shishkin and H. Sato, *Physical Review B* **93**, 085135 (2016), URL <http://link.aps.org/doi/10.1103/PhysRevB.93.085135>.
- [411] D. D. O'Regan, M. C. Payne, and A. A. Mostofi, *Physical Review B* **83**, 245124 (2011), URL <http://link.aps.org/doi/10.1103/PhysRevB.83.245124>.
- [412] D. D. O'Regan, M. C. Payne, and A. A. Mostofi, *Phys. Rev. B* **85**, 193101 (2012), URL <https://link.aps.org/doi/10.1103/PhysRevB.85.193101>.
- [413] G. Moynihan, G. Teobaldi, and D. D. O'Regan, *Physical Review B* **94**, 220104 (2016), URL <http://link.aps.org/doi/10.1103/PhysRevB.94.220104>.
- [414] K. Nakamura, R. Arita, Y. Yoshimoto, and S. Tsuneyuki, *Physical Review B* **74**, 235113 (2006), URL <http://link.aps.org/doi/10.1103/PhysRevB.74.235113>.
- [415] D. A. Scherlis, M. Cococcioni, P. Sit, and N. Marzari, *Journal of Physical Chemistry B* **111**, 7384 (2007), pMID: 17547444, URL <http://dx.doi.org/10.1021/jp0705491>.
- [416] P. H. Dederichs, S. Blügel, R. Zeller, and H. Akai, *Physical Review Letters* **53**, 2512 (1984), URL <http://link.aps.org/doi/10.1103/PhysRevLett.53.2512>.

- [417] P.-L. Sit, M. Cococcioni, and N. Marzari, *Journal of Electroanalytical Chemistry* **607**, 107 (2007), URL <http://www.sciencedirect.com/science/article/pii/S0022072807000393>.
- [418] B. Kaduk, T. Kowalczyk, and T. Van Voorhis, *Chemical Reviews* **112**, 321 (2012), URL <http://dx.doi.org/10.1021/cr200148b>.
- [419] V. Atalla, I. Y. Zhang, O. T. Hofmann, X. Ren, P. Rinke, and M. Scheffler, *Physical Review B* **94**, 035140 (2016), URL <https://link.aps.org/doi/10.1103/PhysRevB.94.035140>.
- [420] G. Herzberg and C. Jungen, *Journal of Molecular Spectroscopy* **41**, 425 (1972), ISSN 0022-2852, URL <http://www.sciencedirect.com/science/article/pii/0022285272900641>.
- [421] C. W. M. Castleton, J. Kullgren, and K. Hermansson, *Journal of Chemical Physics* **127**, 244704 (2007), URL <http://scitation.aip.org/content/aip/journal/jcp/127/24/10.1063/1.2800015>.
- [422] B. J. Morgan and G. W. Watson, *Surface Science* **601**, 5034 (2007), ISSN 0039-6028, URL <http://www.sciencedirect.com/science/article/pii/S0039602807008758>.
- [423] S. P. Ong, V. L. Chevrier, G. Hautier, A. Jain, C. Moore, S. Kim, X. Ma, and G. Ceder, *Energy and Environmental Science* **4**, 3680 (2011), URL <http://dx.doi.org/10.1039/C1EE01782A>.
- [424] A. K. McMahan, R. M. Martin, and S. Satpathy, *Physical Review B* **38**, 6650 (1988), URL <https://link.aps.org/doi/10.1103/PhysRevB.38.6650>.
- [425] M. S. Hybertsen, M. Schlüter, and N. E. Christensen, *Physical Review B* **39**, 9028 (1989), URL <http://link.aps.org/doi/10.1103/PhysRevB.39.9028>.
- [426] I. V. Solovyev and M. Imada, *Physical Review B* **71**, 045103 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevB.71.045103>.

- [427] M. Springer and F. Aryasetiawan, Physical Review B **57**, 4364 (1998), URL <https://link.aps.org/doi/10.1103/PhysRevB.57.4364>.
- [428] F. Aryasetiawan, M. Imada, A. Georges, G. Kotliar, S. Biermann, and A. I. Lichtenstein, Physical Review B **70**, 195104 (2004), URL <https://link.aps.org/doi/10.1103/PhysRevB.70.195104>.
- [429] D. Pines and D. Bohm, Physical Review **85**, 338 (1952), URL <https://link.aps.org/doi/10.1103/PhysRev.85.338>.
- [430] D. Pines, Physical Review **92**, 626 (1953), URL <https://link.aps.org/doi/10.1103/PhysRev.92.626>.
- [431] T. Kotani, Journal of Physics: Condensed Matter **12**, 2413 (2000), URL <http://stacks.iop.org/0953-8984/12/i=11/a=307>.
- [432] C. E. Patrick and K. S. Thygesen, Physical Review B **93**, 035133 (2016), URL <https://link.aps.org/doi/10.1103/PhysRevB.93.035133>.
- [433] F. Aryasetiawan, K. Karlsson, O. Jepsen, and U. Schönberger, Physical Review B **74**, 125106 (2006), URL <http://link.aps.org/doi/10.1103/PhysRevB.74.125106>.
- [434] T. Miyake and F. Aryasetiawan, Physical Review B **77**, 085122 (2008), URL <http://link.aps.org/doi/10.1103/PhysRevB.77.085122>.
- [435] T. Miyake, F. Aryasetiawan, and M. Imada, Physical Review B **80**, 155134 (2009), URL <http://link.aps.org/doi/10.1103/PhysRevB.80.155134>.
- [436] E. Şaşıoğlu, C. Friedrich, and S. Blügel, Physical Review B **83**, 121101 (2011), URL <https://link.aps.org/doi/10.1103/PhysRevB.83.121101>.
- [437] M. R. Norman and A. J. Freeman, Physical Review B **33**, 8896 (1986), URL <https://link.aps.org/doi/10.1103/PhysRevB.33.8896>.
- [438] N. Marzari and D. Vanderbilt, Physical Review B **56**, 12847 (1997), URL <https://link.aps.org/doi/10.1103/PhysRevB.56.12847>.

- [439] I. Schnell, G. Czycholl, and R. C. Albers, *Physical Review B* **65**, 075103 (2002), URL <http://link.aps.org/doi/10.1103/PhysRevB.65.075103>.
- [440] H. J. Kulik and N. Marzari, *Journal of Chemical Physics* **133**, 114103 (2010), URL <http://scitation.aip.org/content/aip/journal/jcp/133/11/10.1063/1.3489110>.
- [441] V. L. C. Jr and M. Cococcioni, *Journal of Physics: Condensed Matter* **22**, 055602 (2010), URL <http://stacks.iop.org/0953-8984/22/i=5/a=055602>.
- [442] W.-J. Lee and Y.-S. Kim, *Journal of the Korean Physical Society* **60**, 781 (2012), ISSN 1976-8524, URL <https://doi.org/10.3938/jkps.60.781>.
- [443] H. Hsu, P. Blaha, M. Cococcioni, and R. M. Wentzcovitch, *Physical Review Letters* **106**, 118501 (2011), URL <http://link.aps.org/doi/10.1103/PhysRevLett.106.118501>.
- [444] S. Ping Ong, L. Wang, B. Kang, and G. Ceder, *Chemistry of Materials* **20**, 1798 (2008), URL <http://dx.doi.org/10.1021/cm702327g>.
- [445] M. Capdevila-Cortada, M. García-Melchor, and N. López, *Journal of Catalysis* **327**, 58 (2015), ISSN 0021-9517, URL <http://www.sciencedirect.com/science/article/pii/S0021951715001104>.
- [446] G. Hautier, S. P. Ong, A. Jain, C. J. Moore, and G. Ceder, *Physical Review B* **85**, 155208 (2012), URL <http://link.aps.org/doi/10.1103/PhysRevB.85.155208>.
- [447] A. Jain, G. Hautier, S. P. Ong, C. J. Moore, C. C. Fischer, K. A. Persson, and G. Ceder, *Physical Review B* **84**, 045115 (2011), URL <http://link.aps.org/doi/10.1103/PhysRevB.84.045115>.
- [448] V. Stevanović, S. Lany, X. Zhang, and A. Zunger, *Physical Review B* **85**, 115104 (2012), URL <http://link.aps.org/doi/10.1103/PhysRevB.85.115104>.
- [449] O. K. Orhan and D. D. O'Regan, *arXiv preprint arXiv:1703.05056* (2017), URL <https://arxiv.org/abs/1703.05056>.

- [450] L. Hedberg, T. Iijima, and K. Hedberg, *The Journal of Chemical Physics* **70**, 3224 (1979), URL <http://dx.doi.org/10.1063/1.437911>.
- [451] N. Roesch, M. Kotzian, H. Joerg, H. Schroeder, B. Rager, and S. Metev, *Journal of the American Chemical Society* **108**, 4238 (1986), URL <http://dx.doi.org/10.1021/ja00274a073>.
- [452] M. D. Towler, N. L. Allan, N. M. Harrison, V. R. Saunders, W. C. Mackrodt, and E. Aprà, *Physical Review B* **50**, 5041 (1994), URL <https://link.aps.org/doi/10.1103/PhysRevB.50.5041>.
- [453] F. Aryasetiawan and O. Gunnarsson, *Physical Review Letters* **74**, 3221 (1995), URL <https://link.aps.org/doi/10.1103/PhysRevLett.74.3221>.
- [454] X. Ren, I. Leonov, G. Keller, M. Kollar, I. Nekrasov, and D. Vollhardt, *Physical Review B* **74**, 195114 (2006), URL <https://link.aps.org/doi/10.1103/PhysRevB.74.195114>.
- [455] K. Terakura, T. Oguchi, A. R. Williams, and J. Kübler, *Physical Review B* **30**, 4734 (1984), URL <http://link.aps.org/doi/10.1103/PhysRevB.30.4734>.
- [456] H. Alperin, *Journal of Physical Society of Japan Supplemental B (3)* **17**, 12 (1962).
- [457] A. K. Cheetham and D. A. O. Hope, *Physical Review B* **27**, 6964 (1983), URL <https://link.aps.org/doi/10.1103/PhysRevB.27.6964>.
- [458] O. Bengone, M. Alouani, P. Blöchl, and J. Hugel, *Physical Review B* **62**, 16392 (2000), URL <https://link.aps.org/doi/10.1103/PhysRevB.62.16392>.
- [459] G. Lee and S.-J. Oh, *Physical Review B* **43**, 14674 (1991), URL <https://link.aps.org/doi/10.1103/PhysRevB.43.14674>.
- [460] G. A. Sawatzky and J. W. Allen, *Physical Review Letters* **53**, 2339 (1984), URL <https://link.aps.org/doi/10.1103/PhysRevLett.53.2339>.

- [461] R. Zimmermann, P. Steiner, R. Claessen, F. Reinert, S. Hübner, P. Blaha, and P. Dufek, *Journal of Physics: Condensed Matter* **11**, 1657 (1999), URL <http://stacks.iop.org/0953-8984/11/i=7/a=002>.
- [462] J.-L. Li, G.-M. Rignanese, and S. G. Louie, *Physical Review B* **71**, 193102 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevB.71.193102>.
- [463] S. Hübner, *Advances in Physics* **43**, 183 (1994), URL <http://dx.doi.org/10.1080/00018739400101495>.
- [464] R. Gillen and J. Robertson, *Journal of Physics: Condensed Matter* **25**, 165502 (2013), URL <http://stacks.iop.org/0953-8984/25/i=16/a=165502>.
- [465] S. Hübner, P. Steiner, I. Sander, F. Reinert, and H. Schmitt, *Zeitschrift für Physik B Condensed Matter* **86**, 207 (1992), ISSN 1431-584X, URL <http://dx.doi.org/10.1007/BF01313827>.
- [466] C. Gougoussis, M. Calandra, A. Seitsonen, C. Brouder, A. Shukla, and F. Mauri, *Physical Review B* **79**, 045118 (2009), URL <https://link.aps.org/doi/10.1103/PhysRevB.79.045118>.
- [467] A. B. Shick, A. I. Liechtenstein, and W. E. Pickett, *Physical Review B* **60**, 10763 (1999), URL <https://link.aps.org/doi/10.1103/PhysRevB.60.10763>.
- [468] F. Tran and P. Blaha, *Physical Review Letters* **102**, 226401 (2009), URL <https://link.aps.org/doi/10.1103/PhysRevLett.102.226401>.
- [469] E. Arca, K. Fleischer, and I. V. Shvets, *Applied Physics Letters* **99**, 111910 (2011), URL <http://dx.doi.org/10.1063/1.3638461>.
- [470] A. B. Kehoe, E. Arca, D. O. Scanlon, I. V. Shvets, and G. W. Watson, *Journal of Physics: Condensed Matter* **28**, 125501 (2016), URL <http://stacks.iop.org/0953-8984/28/i=12/a=125501>.
- [471] L. Farrell, K. Fleischer, D. Caffrey, D. Mullarkey, E. Norton, and I. V. Shvets, *Physical Review B* **91**, 125202 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.91.125202>.

- [472] E. Norton, L. Farrell, S. D. Callaghan, C. McGuinness, I. V. Shvets, and K. Fleischer, *Physical Review B* **93**, 115302 (2016), URL <https://link.aps.org/doi/10.1103/PhysRevB.93.115302>.
- [473] T. Gloege, H. Meyerheim, W. Moritz, and D. Wolf, *Surface Science* **441**, L917 (1999), ISSN 0039-6028, URL <http://www.sciencedirect.com/science/article/pii/S0039602899008705>.
- [474] R. H. Bruce and D. S. Cannell, *Physical Review B* **15**, 4451 (1977), URL <https://link.aps.org/doi/10.1103/PhysRevB.15.4451>.
- [475] R. Yacovitch and Y. Shapira, *Physica B&C* **86**, 1126 (1977), ISSN 0378-4363, URL <http://www.sciencedirect.com/science/article/pii/0378436377908166>.
- [476] L. M. Corliss, J. M. Hastings, R. Nathans, and G. Shirane, *Journal of Applied Physics* **36**, 1099 (1965), URL <http://dx.doi.org/10.1063/1.1714118>.
- [477] M. Catti, G. Sandrone, G. Valerio, and R. Dovesi, *Journal of Physics and Chemistry of Solids* **57**, 1735 (1996), ISSN 0022-3697, URL <http://www.sciencedirect.com/science/article/pii/0022369796000340>.
- [478] D. Fischer, *Journal of Physics and Chemistry of Solids* **32**, 2455 (1971), ISSN 0022-3697, URL <http://www.sciencedirect.com/science/article/pii/S0022369771800938>.
- [479] J. A. Crawford and R. W. Vest, *Journal of Applied Physics* **35**, 2413 (1964), URL <http://dx.doi.org/10.1063/1.1702871>.
- [480] A. Holt and P. Kofstad, *Solid State Ionics* **100**, 201 (1997), ISSN 0167-2738, URL <http://www.sciencedirect.com/science/article/pii/S0167273897003524>.
- [481] W.-Y. Hwang and R. Thorn, *Journal of Physics and Chemistry of Solids* **41**, 75 (1980), ISSN 0022-3697, URL <http://www.sciencedirect.com/science/article/pii/0022369780901237>.

- [482] E. Arca, K. Fleischer, S. A. Krasnikov, and I. Shvets, The Journal of Physical Chemistry C **117**, 21901 (2013), URL <http://dx.doi.org/10.1021/jp404230k>.
- [483] M. Muto, Y. Tanabe, T. Iizuka-Sakano, and E. Hanamura, Physical Review B **57**, 9586 (1998), URL <https://link.aps.org/doi/10.1103/PhysRevB.57.9586>.
- [484] A. Y. Dobin, W. Duan, and R. M. Wentzcovitch, Physical Review B **62**, 11997 (2000), URL <https://link.aps.org/doi/10.1103/PhysRevB.62.11997>.
- [485] D. O. Scanlon and G. W. Watson, Journal of Materials Chemistry **21**, 3655 (2011), URL <http://dx.doi.org/10.1039/C0JM03852K>.
- [486] F. Lebreau, M. M. Islam, B. Diawara, and P. Marcus, Journal of Physical Chemistry C **118**, 18133 (2014), URL <http://dx.doi.org/10.1021/jp5039943>.
- [487] N. J. Mosey and E. A. Carter, Journal of the Mechanics and Physics of Solids **57**, 287 (2009), ISSN 0022-5096, URL <http://www.sciencedirect.com/science/article/pii/S0022509608001816>.
- [488] N. J. Mosey and E. A. Carter, Physical Review B **76**, 155123 (2007), URL <https://link.aps.org/doi/10.1103/PhysRevB.76.155123>.
- [489] Y. Kota, H. Imamura, and M. Sasaki, Journal of Applied Physics **115**, 17D719 (2014), URL <http://dx.doi.org/10.1063/1.4865780>.
- [490] N. J. Mosey, P. Liao, and E. A. Carter, Journal of Chemical Physics **129**, 014103 (2008), URL <http://dx.doi.org/10.1063/1.2943142>.
- [491] S. Shi, A. L. Wysocki, and K. D. Belashchenko, Physical Review B **79**, 104404 (2009), URL <https://link.aps.org/doi/10.1103/PhysRevB.79.104404>.
- [492] S. Blügel and G. Bihlmayer, Forschungszentrum Jülich GmbH pp. 85–129 (2006), URL http://www.psi-k.org/workshops/workshops_2006/psik-NIC-WSCN.pdf.

- [493] Y. Wang, H. Fang, C. L. Zacherl, Z. Mei, S. Shang, L.-Q. Chen, P. D. Jablonski, and Z.-K. Liu, *Surface Science* **606**, 1422 (2012), ISSN 0039-6028, URL <http://www.sciencedirect.com/science/article/pii/S0039602812001677>.
- [494] C. Gray, Y. Lei, and G. Wang, *Journal of Applied Physics* **120**, 215101 (2016), URL <http://dx.doi.org/10.1063/1.4970882>.
- [495] J. J. Carey, M. Legesse, and M. Nolan, *Journal of Physical Chemistry C* **120**, 19160 (2016), URL <http://dx.doi.org/10.1021/acs.jpcc.6b05575>.
- [496] T. Yokobori, M. Okawa, K. Konishi, R. Takei, K. Katayama, S. Oozono, T. Shinmura, T. Okuda, H. Wadati, E. Sakai, et al., *Physical Review B* **87**, 195124 (2013), URL <https://link.aps.org/doi/10.1103/PhysRevB.87.195124>.
- [497] T. Cai, H. Han, Y. Yu, T. Gao, J. Du, and L. Hao, *Physica B: Condensed Matter* **404**, 89 (2009), ISSN 0921-4526, URL <http://www.sciencedirect.com/science/article/pii/S092145260800447X>.
- [498] G. K. H. Madsen and P. Novák, *EPL (Europhysics Letters)* **69**, 777 (2005), URL <http://stacks.iop.org/0295-5075/69/i=5/a=777>.
- [499] J. Hugel and M. Kamal, *Journal of Physics: Condensed Matter* **9**, 647 (1997), URL <http://stacks.iop.org/0953-8984/9/i=3/a=005>.
- [500] C. J. Calzado and J.-P. Malrieu, *Physical Review B* **63**, 214520 (2001), URL <https://link.aps.org/doi/10.1103/PhysRevB.63.214520>.
- [501] C. Calzado and J.-P. Malrieu, *The European Physical Journal B - Condensed Matter and Complex Systems* **21**, 375 (2001), ISSN 1434-6036, URL <https://doi.org/10.1007/s100510170181>.
- [502] D. D. O'Regan and G. Teobaldi, *Physical Review B* **94**, 035159 (2016), URL <http://link.aps.org/doi/10.1103/PhysRevB.94.035159>.
- [503] P. C. Coulson and M. I. Fischer, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **40**, 386 (1949), URL <http://dx.doi.org/10.1080/14786444908521726>.

- [504] K. Karlsson, F. Aryasetiawan, and O. Jepsen, *Physical Review B* **81**, 245113 (2010), URL <http://link.aps.org/doi/10.1103/PhysRevB.81.245113>.
- [505] M. Cococcioni, *Lecture Notes* (2012), URL <http://www.cond-mat.de/events/correl12/manuscripts/cococcioni.pdf>.
- [506] A. Jain, G. Hautier, C. J. Moore, S. P. Ong, C. C. Fischer, T. Mueller, K. A. Persson, and G. Ceder, *Computational Materials Science* **50**, 2295 (2011), URL <https://doi.org/10.1016/j.commatsci.2011.02.023>.
- [507] W. Setyawan and S. Curtarolo, *Computational Materials Science* **49**, 299 (2010), URL <https://doi.org/10.1016/j.commatsci.2010.05.010>.
- [508] S. Curtarolo, G. L. W. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, and O. Levy, *Nature Materials* **12**, 191 (2013), URL <http://dx.doi.org/10.1038/nmat3568>.
- [509] S. Curtarolo, W. Setyawan, G. L. Hart, M. Jahnatek, R. V. Chepulsii, R. H. Taylor, S. Wang, J. Xue, K. Yang, O. Levy, et al., *Computational Materials Science* **58**, 218 (2012), ISSN 0927-0256, URL <http://www.sciencedirect.com/science/article/pii/S0927025612000717>.
- [510] L. A. Agapito, S. Curtarolo, and M. Buongiorno Nardelli, *Physical Review X* **5**, 011006 (2015), URL <http://link.aps.org/doi/10.1103/PhysRevX.5.011006>.
- [511] M. Heinemann, B. Eifert, and C. Heiliger, *Physical Review B* **87**, 115111 (2013), URL <https://link.aps.org/doi/10.1103/PhysRevB.87.115111>.
- [512] R. Bliem, E. McDermott, P. Ferstl, M. Setvin, O. Gamba, J. Pavelec, M. A. Schneider, M. Schmid, U. Diebold, P. Blaha, et al., *Science* **346**, 1215 (2014), ISSN 0036-8075, URL <http://science.sciencemag.org/content/346/6214/1215>.
- [513] D. A. Andersson, S. I. Simak, B. Johansson, I. A. Abrikosov, and N. V. Skorodumova, *Physical Review B* **75**, 035109 (2007), URL <https://link.aps.org/doi/10.1103/PhysRevB.75.035109>.

- [514] G. Jomard, B. Amadon, F. m. c. Bottin, and M. Torrent, *Physical Review B* **78**, 075125 (2008), URL <https://link.aps.org/doi/10.1103/PhysRevB.78.075125>.
- [515] S. Bo and Z. Ping, *Chinese Physics B* **17**, 1364 (2008), URL <http://stacks.iop.org/1674-1056/17/i=4/a=035>.
- [516] M. Korshunov, A. Gavrichkov, S. G. Ovchinnikov, Z. V. Pchelkina, I. A. Nekrasov, M. A. Korotin, and V. I. Anisimov, *Journal of Experimental and Theoretical Physics* **99**, 559 (2004), ISSN 1090-6509, URL <https://doi.org/10.1134/1.1809685>.
- [517] V. I. Anisimov, S. Y. Ezhov, and T. M. Rice, *Physical Review B* **55**, 12829 (1997), URL <https://link.aps.org/doi/10.1103/PhysRevB.55.12829>.
- [518] C. J. Calzado, N. C. Hernández, and J. F. Sanz, *Physical Review B* **77**, 045118 (2008), URL <https://link.aps.org/doi/10.1103/PhysRevB.77.045118>.
- [519] M. C. Toroker, D. K. Kanan, N. Alidoust, L. Y. Isseroff, P. Liao, and E. A. Carter, *Physical Chemistry Chemical Physics* **13**, 16644 (2011), URL <http://dx.doi.org/10.1039/C1CP22128K>.
- [520] C. O'Rourke and D. R. Bowler, *Journal of Physical Chemistry C* **118**, 7261 (2014), URL <http://dx.doi.org/10.1021/jp407736f>.
- [521] M. Capdevila-Cortada, Z. Łodziana, and N. López, *ACS Catalysis* **6**, 8370 (2016), URL <http://dx.doi.org/10.1021/acscatal.6b01907>.
- [522] J. Yan and J. K. Nørskov, *Physical Review B* **88**, 245204 (2013), URL <http://link.aps.org/doi/10.1103/PhysRevB.88.245204>.
- [523] F. Zhou, M. Cococcioni, C. A. Marianetti, D. Morgan, and G. Ceder, *Physical Review B* **70**, 235121 (2004), URL <http://link.aps.org/doi/10.1103/PhysRevB.70.235121>.
- [524] S. P. Ong, V. L. Chevrier, and G. Ceder, *Physical Review B* **83**, 075112 (2011), URL <http://link.aps.org/doi/10.1103/PhysRevB.83.075112>.

- [525] M. Baldoni, L. Craco, G. Seifert, and S. Leoni, *Journal of Materials Chemistry A* **1**, 1778 (2013), URL <http://dx.doi.org/10.1039/C2TA00839D>.
- [526] F. Zhou, K. Kang, T. Maxisch, G. Ceder, and D. Morgan, *Solid State Communications* **132**, 181 (2004), ISSN 0038-1098, URL <http://www.sciencedirect.com/science/article/pii/S003810980400626X>.
- [527] S. Huang, B. E. Wilson, B. Wang, Y. Fang, K. Buffington, A. Stein, and D. G. Truhlar, *Journal of the American Chemical Society* **137**, 10992 (2015), pMID: 26264394, URL <http://dx.doi.org/10.1021/jacs.5b04690>.
- [528] S. Huang, B. E. Wilson, W. H. Smyrl, D. G. Truhlar, and A. Stein, *Chemistry of Materials* **28**, 746 (2016), URL <http://dx.doi.org/10.1021/acs.chemmater.5b03554>.
- [529] H. J. Kulik and N. Marzari, *Journal of Chemical Physics* **129**, 134314 (2008), URL <http://scitation.aip.org/content/aip/journal/jcp/129/13/10.1063/1.2987444>.
- [530] H. J. Kulik and N. Marzari, *Journal of Chemical Physics* **134**, 094103 (2011), URL <http://scitation.aip.org/content/aip/journal/jcp/134/9/10.1063/1.3559452>.
- [531] B. S. Youmbi and F. Calvayrac, *Surface Science* **621**, 1 (2014), ISSN 0039-6028, URL <http://www.sciencedirect.com/science/article/pii/S0039602813003087>.
- [532] Y. Aharbil, H. Labrim, S. Benmokhtar, M. A. Haddouch, L. Bahmad, and L. Laanab, *Materials Research Express* **3**, 086104 (2016), URL <http://stacks.iop.org/2053-1591/3/i=8/a=086104>.
- [533] T. Z. H. Gani and H. J. Kulik, *Journal of Chemical Theory and Computation* **12**, 5931 (2016), pMID: 27951665, URL <http://dx.doi.org/10.1021/acs.jctc.6b00937>.

- [534] H. Hsu, K. Umemoto, P. Blaha, and R. M. Wentzcovitch, *Earth and Planetary Science Letters* **294**, 19 (2010), ISSN 0012-821X, URL <http://www.sciencedirect.com/science/article/pii/S0012821X10001330>.
- [535] G. Mattioli, F. Filippone, P. Alippi, and A. Amore Bonapasta, *Physical Review B* **78**, 241201 (2008), URL <http://link.aps.org/doi/10.1103/PhysRevB.78.241201>.
- [536] P. M. Kowalski, M. F. Camellone, N. N. Nair, B. Meyer, and D. Marx, *Physical Review Letters* **105**, 146405 (2010), URL <http://link.aps.org/doi/10.1103/PhysRevLett.105.146405>.
- [537] G. Mattioli, P. Alippi, F. Filippone, R. Caminiti, and A. Amore Bonapasta, *Journal of Physical Chemistry C* **114**, 21694 (2010), URL <http://dx.doi.org/10.1021/jp1041316>.
- [538] C. Gougoussis, M. Calandra, A. P. Seitsonen, and F. Mauri, *Physical Review B* **80**, 075102 (2009), URL <http://link.aps.org/doi/10.1103/PhysRevB.80.075102>.
- [539] G. W. Mann, K. Lee, M. Cococcioni, B. Smit, and J. B. Neaton, *Journal of Chemical Physics* **144**, 174104 (2016), URL <http://dx.doi.org/10.1063/1.4947240>.
- [540] B.-C. Shih, Y. Zhang, W. Zhang, and P. Zhang, *Physical Review B* **85**, 045132 (2012), URL <https://link.aps.org/doi/10.1103/PhysRevB.85.045132>.
- [541] R. Sakuma and F. Aryasetiawan, *Physical Review B* **87**, 165118 (2013), URL <https://link.aps.org/doi/10.1103/PhysRevB.87.165118>.
- [542] L. Zhang, P. Staar, A. Kozhevnikov, Y.-P. Wang, J. Trinastic, T. Schulthess, and H.-P. Cheng, *arXiv preprint arXiv:1705.02387* (2017), URL <https://arxiv.org/abs/1705.02387>.
- [543] H. Jiang, R. I. Gomez-Abal, P. Rinke, and M. Scheffler, *Physical Review B* **82**, 045108 (2010), URL <https://link.aps.org/doi/10.1103/PhysRevB.82.045108>.

- [544] S. K. Panda, H. Jiang, and S. Biermann, *Physical Review B* **96**, 045137 (2017), URL <https://link.aps.org/doi/10.1103/PhysRevB.96.045137>.
- [545] A. M. Souza, I. Rungger, C. D. Pemmaraju, U. Schwingenschloegl, and S. Sanvito, *Phys. Rev. B* **88**, 165112 (2013), URL <https://link.aps.org/doi/10.1103/PhysRevB.88.165112>.
- [546] D. H. P. Turban, G. Teobaldi, D. D. O'Regan, and N. D. M. Hine, *Phys. Rev. B* **93**, 165102 (2016), URL <https://link.aps.org/doi/10.1103/PhysRevB.93.165102>.
- [547] Q. Wu and T. Van Voorhis, *Journal of Chemical Theory and Computation* **2**, 765 (2006), URL <http://dx.doi.org/10.1021/ct0503163>.
- [548] Q. Wu and T. Van Voorhis, *Journal of Physical Chemistry A* **110**, 9212 (2006), URL <http://dx.doi.org/10.1021/jp061848y>.
- [549] T. Tim Kowalczyk, L.-P. Wang, and T. Van Voorhis, *Journal of Physical Chemistry B* **115**, 12135 (2011), URL <http://dx.doi.org/10.1021/jp204962k>.
- [550] T. Kowalczyk, Z. Lin, and T. V. Voorhis, *Journal of Physical Chemistry A* **114**, 10427 (2010), URL <http://dx.doi.org/10.1021/jp103153a>.
- [551] Q. Wu and T. Van Voorhis, *Journal of Chemical Physics* **125**, 164105 (2006), URL <http://dx.doi.org/10.1063/1.2360263>.
- [552] F. Ding, H. Wang, Q. Wu, T. Van Voorhis, S. Chen, and J. P. Konopelski, *Journal of Physical Chemistry A* **114**, 6039 (2010), URL <http://dx.doi.org/10.1021/jp912049p>.
- [553] S. Yeganeh and T. Van Voorhis, *Journal of Physical Chemistry C* **114**, 20756 (2010), URL <http://dx.doi.org/10.1021/jp106989t>.
- [554] H. Oberhofer and J. Blumberger, *The Journal of Chemical Physics* **131**, 064101 (2009), URL <http://aip.scitation.org/doi/abs/10.1063/1.3190169>.
- [555] J. Behler, K. Reuter, and M. Scheffler, *Physical Review B* **77**, 115421 (2008), URL <http://link.aps.org/doi/10.1103/PhysRevB.77.115421>.

- [556] A. Kubas, F. Hoffmann, A. Heck, H. Oberhofer, M. Elstner, and J. Blumberger, *Journal of Chemical Physics* **140**, 104105 (2014), URL <http://dx.doi.org/10.1063/1.4867077>.
- [557] A. Kubas, F. Gajdos, A. Heck, H. Oberhofer, M. Elstner, and J. Blumberger, *Physical Chemistry Chemical Physics* **17**, 14342 (2015), URL <http://dx.doi.org/10.1039/C4CP04749D>.
- [558] H. Oberhofer, K. Reuter, and J. Blumberger, *Chemical Reviews* **117**, 10319 (2017), pMID: 28644623, URL <http://dx.doi.org/10.1021/acs.chemrev.7b00086>.
- [559] Z. Zhang and S. Satpathy, *Physical Review B* **44**, 13319 (1991), URL <https://link.aps.org/doi/10.1103/PhysRevB.44.13319>.
- [560] H. Akai, S. Blügel, R. Zeller, and P. H. Dederichs, *Physical Review Letters* **56**, 2407 (1986), URL <https://link.aps.org/doi/10.1103/PhysRevLett.56.2407>.
- [561] T. A. Wesolowski and A. Warshel, *The Journal of Physical Chemistry* **97**, 8050 (1993), URL <http://dx.doi.org/10.1021/j100132a040>.
- [562] G. Hong, M. Strajbl, T. A. Wesolowski, and A. Warshel, *Journal of Computational Chemistry* **21**, 1554 (2000), ISSN 1096-987X, URL [http://dx.doi.org/10.1002/1096-987X\(200012\)21:16<1554::AID-JCC12>3.0.CO;2-I](http://dx.doi.org/10.1002/1096-987X(200012)21:16<1554::AID-JCC12>3.0.CO;2-I).
- [563] J. Behler, B. Delley, S. Lorenz, K. Reuter, and M. Scheffler, *Physical Review Letters* **94**, 036104 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevLett.94.036104>.
- [564] J. Behler, B. Delley, K. Reuter, and M. Scheffler, *Physical Review B* **75**, 115409 (2007), URL <https://link.aps.org/doi/10.1103/PhysRevB.75.115409>.
- [565] J. Behler, B. Delley, K. Reuter, and M. Scheffler, Tech. Rep. cond-mat/0605292, CERN (2006), URL <http://cds.cern.ch/record/947885>.

- [566] Q. Wu and T. Van Voorhis, *Physical Review A* **72**, 024502 (2005), URL <http://link.aps.org/doi/10.1103/PhysRevA.72.024502>.
- [567] B. Kaduk, T. Tsuchimochi, and T. Van Voorhis, *Journal of Chemical Physics* **140**, 18A503 (2014), URL <http://scitation.aip.org/content/aip/journal/jcp/140/18/10.1063/1.4862497>.
- [568] Q. Wu, C.-L. Cheng, and T. Van Voorhis, *Journal of Chemical Physics* **127**, 164119 (2007), URL <http://scitation.aip.org/content/aip/journal/jcp/127/16/10.1063/1.2800022>.
- [569] H. Oberhofer and J. Blumberger, *The Journal of Chemical Physics* **133**, 244105 (2010), URL <http://dx.doi.org/10.1063/1.3507878>.
- [570] A. G. Petukhov, I. I. Mazin, L. Chioncel, and A. I. Lichtenstein, *Physical Review B* **67**, 153106 (2003), URL <http://link.aps.org/doi/10.1103/PhysRevB.67.153106>.
- [571] Q. Wu, B. Kaduk, and T. Van Voorhis, *Journal of Chemical Physics* **130**, 034109 (2009), URL <http://dx.doi.org/10.1063/1.3059784>.
- [572] B. Kaduk and T. Van Voorhis, *Journal of Chemical Physics* **133**, 061102 (2010), URL <http://dx.doi.org/10.1063/1.3470106>.
- [573] N. Marzari, D. Vanderbilt, and M. C. Payne, *Physical Review Letters* **79**, 1337 (1997), URL <https://link.aps.org/doi/10.1103/PhysRevLett.79.1337>.
- [574] P. D. Haynes and M. C. Payne, *Physical Review B* **59**, 12173 (1999), URL <https://link.aps.org/doi/10.1103/PhysRevB.59.12173>.
- [575] B. Giraud, J. L. Tourneux, and S. Wong, *Physics Letters B* **32**, 23 (1970), ISSN 0370-2693, URL <http://www.sciencedirect.com/science/article/pii/0370269370903254>.
- [576] H. Flocard, P. Quentin, A. Kerman, and D. Vautherin, *Nuclear Physics A* **203**, 433 (1973), ISSN 0375-9474, URL <http://www.sciencedirect.com/science/article/pii/0375947473903576>.

- [577] A. Staszczak, M. Stoitsov, A. Baran, and W. Nazarewicz, The European Physical Journal A **46**, 85 (2010), ISSN 1434-601X, URL <https://doi.org/10.1140/epja/i2010-11018-9>.
- [578] J. Peng, J. Meng, P. Ring, and S. Q. Zhang, Physical Review C **78**, 024313 (2008), URL <https://link.aps.org/doi/10.1103/PhysRevC.78.024313>.
- [579] D.-K. Seo, Physical Review B **76**, 033102 (2007), URL <https://link.aps.org/doi/10.1103/PhysRevB.76.033102>.
- [580] I. Dabo, Ph.D. thesis, Massachusetts Institute of Technology (2008), URL <https://dspace.mit.edu/handle/1721.1/44320>.
- [581] W. Nelson, P. Bokes, P. Rinke, and R. W. Godby, Physical Review A **75**, 032505 (2007), URL <https://link.aps.org/doi/10.1103/PhysRevA.75.032505>.
- [582] M. Dauth, F. Caruso, S. Kümmel, and P. Rinke, Physical Review B **93**, 121115 (2016), URL <https://link.aps.org/doi/10.1103/PhysRevB.93.121115>.
- [583] D. Li, A. E. D. R. Castillo, H. Jussila, G. Ye, Z. Ren, J. Bai, X. Chen, H. Lipsanen, Z. Sun, and F. Bonaccorso, Applied Materials Today **4**, 17 (2016), ISSN 2352-9407, URL <http://www.sciencedirect.com/science/article/pii/S2352940716300117>.
- [584] L. Kou, C. Chen, and S. C. Smith, Journal of Physical Chemistry Letters **6**, 2794 (2015), pMID: 26266865, URL <http://dx.doi.org/10.1021/acs.jpcLetters5b01094>.
- [585] Y. Liu, E. S. Penev, and B. I. Yakobson, Angewandte Chemie International Edition **52**, 3156 (2013), ISSN 1521-3773, URL <http://dx.doi.org/10.1002/anie.201207972>.
- [586] X.-B. Li, S.-Y. Xie, H. Zheng, W. Q. Tian, and H.-B. Sun, Nanoscale **7**, 18863 (2015), URL <http://dx.doi.org/10.1039/C5NR04359J>.

- [587] L. Z. Zhang, Z. F. Wang, S. X. Du, H.-J. Gao, and F. Liu, Physical Review B **90**, 161402 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevB.90.161402>.
- [588] J. Wang, M. Khazaei, M. Arai, N. Umezawa, T. Tada, and H. Hosono, Chemistry of Materials **29**, 5922 (2017), URL <http://dx.doi.org/10.1021/acs.chemmater.7b01433>.
- [589] H. Tang and S. Ismail-Beigi, Physical Review B **80**, 134113 (2009), URL <https://link.aps.org/doi/10.1103/PhysRevB.80.134113>.
- [590] S. A. Cybart, T. J. Wong, E. Y. Cho, J. W. Beeman, C. S. Yung, B. H. Moeckly, and R. C. Dynes, Applied Physics Letters **104**, 182604 (2014), URL <http://dx.doi.org/10.1063/1.4876129>.
- [591] S. Ma, K. Bao, Q. Tao, C. Xu, X. Feng, P. Zhu, and T. Cui, Inorganic Chemistry **55**, 11140 (2016), pMID: 27786444, URL <http://dx.doi.org/10.1021/acs.inorgchem.6b01685>.
- [592] C. Bhandari, W. R. L. Lambrecht, and M. van Schilfgaarde, Physical Review B **91**, 125116 (2015), URL <https://link.aps.org/doi/10.1103/PhysRevB.91.125116>.
- [593] T. Machej, J. Haber, A. M. Turek, and I. E. Wachs, Applied catalysis **70**, 115 (1991), URL [https://doi.org/10.1016/S0166-9834\(00\)84158-5](https://doi.org/10.1016/S0166-9834(00)84158-5).
- [594] J. Schoiswohl, S. Surnev, M. Sock, S. Eck, M. G. Ramsey, F. P. Netzer, and G. Kresse, Physical Review B **71**, 165437 (2005), URL <https://link.aps.org/doi/10.1103/PhysRevB.71.165437>.
- [595] C. Bhandari and W. R. L. Lambrecht, Physical Review B **89**, 045109 (2014), URL <https://link.aps.org/doi/10.1103/PhysRevB.89.045109>.