

Corrective First-Principles Approaches for the Theoretical Spectroscopy of Transition-Metal Systems

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Summary

Density-functional theory within its practical, widespread Kohn-Sham formalism (KS-DFT), is an effective approach for providing the starting point for advanced first-principles spectroscopy simulations of molecules and solids in the linear-response regime. Within available approximations for the electronic exchange-correlation energy, however, KS-DFT exhibits certain systematic errors such as self-interaction error (SIE), which dominates the error in insulating and optical gaps. Particularly, transition-metal systems in general have large SIE that manifest as large delocalisation error of $3d$ states of such systems. Consequently, spectroscopy simulations of these systems starting from KS-DFT are unreliable. Here, we introduce computationally feasible and quantitatively accurate corrective approaches to encounter such errors in first-principles spectroscopy simulations, particularly with a view to enabling future high-throughput spectroscopy for transition-metal systems.

Accurate spectra of selected noble-metal solids and their alloys were obtained using the random-phase approximation (RPA) on top of G_0W_0 quasiparticle-corrected band-structures using the first-principle stretching operators, which modify the electronic bands around the Fermi level to imitate the non-local many-body effects. Quantitative accuracy is achieved while preserving minimal additional costs. A number of promising candidate alloys are predicted for plasmonic applications.

The time-domain extension of $DFT+U$, namely $TDDFT+U$, was developed and implemented with a linear-scaling framework. This corrects SIE of particle-hole pairs built from localised orbitals in the context of linear-response time-dependent DFT (TDDFT) within adiabatic semi-local approximations for transition-metal systems. It is demonstrated using representative three coordination complexes that $TDDFT+U$ can significantly improve the descriptions of low-lying excitations accurately from first-principles.

Despite its great success, conventional DFT+ U fails to predict the insulating gap of TiO₂ as its valance edge states are dominated by $2p$ states of O atoms. Hence, a $+U$ correction is required for both the $3d$ states of Ti and the $2p$ states of O, giving DFT+ U^d+U^p . The insulating gaps of TiO₂-rutile and TiO₂-anatase were calculated accurately within DFT+ U^d+U^p with Hubbard U and Hund's J parameters calculated from first-principles. Furthermore, the defect states of neutral O vacancies in TiO₂-rutile and TiO₂-anatase were investigated within the same approach. Our calculations provide a first-principles assessment of the vacancy states in these important materials, and show that DFT+ U can behave well for closed-shell transition-metal systems if used with appropriate care.

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List of abbreviations, acronyms and symbols

Eq.	Equation
Fig.	Figure
Chap.	Chapter
Sec.	Section
Subsec.	Subsection
Ref(s).	Reference(s)
EM	Electro-magnetic
LRT	Linear-response theory
FGR	Fermi's golden rule
EES	Electron excitation spectra
ABS	Absorption spectra
EELS	Electron energy-loss spectroscopy
TDPT	Time-dependent perturbation theory
DFT	Density-functional theory
KS	Kohn-Sham
KS-DFT	Kohn-Sham DFT
SCF	Self-consistent field
NSCF	Non-self-consistent field
SCFP	Self-consistent field potential
LS-KS-DFT	Linear-scaling KS-DFT
NGWFs	Non-orthogonal generalized Wannier functions
TDDFT	Time-dependent DFT
LR-TDDFT	Linear-response TDDFT
LR-LS-TDDFT	Linear-scaling LR-TDDFT
$+U$	The Hubbard U correction
$\mathbb{E}$	Electric field
$\mathbb{B}$	Magnetic induction
Ψ	Many-body electronic wave-function
ψ_i	Single-particle electronic wave-function

φ_m	The localised orbitals representing the correlated sub-space
ϕ_α	Occupied NGWFs
ϕ_β	Unoccupied NGWFs
ϵ_i	Single-particle eigenenergy
ε	Microscopic dielectric function

Reduced Planck constant: $\hbar$	1 (in atomic units)
Elementary charge: e	1 (in atomic units)
Electron mass: m_e	1 (in atomic units)
Vacuum permittivity: $4\pi\varepsilon_0$	1 (in atomic units)
Vacuum permeability: $4\pi\mu_0$	1 (in atomic units)

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Motivation and Outline

Transition-metal systems from small molecules to nano-clusters and solids are the class of condensed matter systems widely used in opto-electronic applications such as solar energy harvesting, photo-assisted catalysis and water decontamination processes, photo-controlled drug delivery nano-particles *etc.* because of their strong optical responses throughout the infrared-visible-ultraviolet (IR-vis-UV) spectral ranges as well as their chemical and thermal stabilities. Due to continuously growing demand for more efficient and cost effective materials in such technologies, first-principles simulations of such materials are crucial.

Theoretical spectroscopy combines quantum theories of condensed matter, the classical description of electro-magnetism and computational methods to study the response of matters exposed to external electro-magnetic (EM) radiations. For low-energy EM radiations and low temperatures, the light-matter interaction can be formulated as a purely electronic problem that is perturbed from its ground-state by an external time-dependent potential within the Born-Oppenheimer approximation and linear-response theory. Hence, a well-described electronic ground-state is required as the starting point for practical theoretical spectroscopy simulations.

Undoubtedly, density-functional theory (DFT) within its applicable Kohn-Sham DFT (KS-DFT) scheme, is the most widely used tool to study ground-state properties of quantum many-body system by means of reducing the order of the problem as well as its suitability for efficient computational implementation. However, KS-DFT has inevitable limitations and systematic errors caused by (semi-)local density approximation (LDA) to the electronic exchange-correlation (xc-) functional responsible for quantum many-body interaction. Naturally, theoretical spectroscopy simulations using approximate KS-DFT as starting points inherit these drawbacks. Furthermore, the time-domain extension of DFT, namely time-dependent density-functional theory (TDDFT), relies on analogous approximations for the excitonic exchange-correlation interactions.

KS-DFT maps the interacting system of N electrons on an auxiliary non-interacting system with the identical density, to reduce the problem into N coupled single-particle equations. KS-DFT within local density approximation ignores any effects due to non-local quantum many-body interactions. Such effects can be crucial particularly for systems, where large numbers of electronic states are packed at narrow energy windows, such the noble metal solids, which have fully-filled d -bands close to the Fermi level contributing strongly to the vis-UV spectral range. A more non-local perspective can be partially achieved by mapping the interacting system on a weakly interacting system of virtual composite particles of electrons and positively charged

duals namely holes within so called the quasiparticle (QP) formalism. The QP formalism improves the description of the under-lying KS band-structures used as starting points for linear-response approaches such as Fermi's golden rule (FGR) and random phase approximation (RPA) to obtain optical spectra of solids.

KS-DFT within local density approximations for the electronic xc-interaction lead to inevitable systematic errors in the ground-state electronic structure. One such error is called self-interaction error (SIE), which dominates the error in the insulating gap. SIE is particularly large for electronic densities associating with highly localised states such as $3d$ and $4f$ character electronic states. Thereupon, SIE leads to the delocalisation error as localised features of such electronic states are underestimated with KS-DFT. The linear-response formalism of TDDFT suffers such errors. Furthermore, approximate xc-kernels, which include quantum many-body interactions of excitons, are limited to adiabatic local density approximations (ALDA) derived from LDA at the adiabatic limit. The Hubbard U correction to KS-DFT known as DFT+ U provides a computationally feasible tool to encounter SIE. Inevitably, the time-domain extension of DFT+ U , namely TDDFT+ U , offers a systematic approach to correct SIE of excitons. Moreover, the Hubbard parameters can be determined within first-principles methods providing a fully self-consistent scheme.

This dissertation aims to treat these problems in theoretical spectroscopy simulations of transition-metal systems in the linear-response regime within feasible approaches. For these reasons, this dissertation has two principle motivations. The first motivation is to determine appropriate methods to include quantum-many body interactions beyond local density approximations within high-throughput simulations starting from KS-DFT for extended systems. The second motivation is to develop an approach to correct SIE of excitons within linear-response TDDFT level self-consistently with KS-DFT for spatially more complex systems.

Outline

Part I covers the general theoretical background for this work within the first four chapters. In Chap. 1, the concepts of theoretical spectroscopy within the linear-response regime are introduced by imposing experimental laboratory conditions of this study, the non-interacting description of electronic transitions via Fermi's golden rule, and its connections to commonly used spectra in molecular spectroscopy and the macroscopic optical functions of solids. In

Chap. 2, the fundamental basis of DFT, its widely-used KS-DFT formalism are constructed as well as the most commonly used algorithms for the computational implementation using plane-wave bases. The density-matrix formalism is introduced for linear-scaling implementation of KS-DFT, particularly within the Order-N Electronic Total Energy Package (ONETEP) in Chap. 3. Lastly, the conceptual limitations of DFT in the excited-state regime, the systematic errors due to LDA and related approximations in KS-DFT, and the errors due to practical implementations, as well as corrective approaches to these drawbacks, are discussed in Chap. 4.

Part II focuses on developing feasible yet accurate approaches suitable for high-throughput simulations of optical spectroscopy of alloys of the form $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ for engineered plasmonic response. In Chap. 5, two main phenomena contributing to spectra of metallic solids, the inter-band and the intra-band transitions, are introduced within the random phase approximation (RPA) and the classical Drude-Lorentz model, respectively. Theoretical tools to obtain quasiparticle energies are discussed within the context of the non-self-consistent, one-shot GW approximation, namely G_0W_0 . In Chap. 6, the optical spectra of pure bulk Au, Ag, and Cu are presented at various levels of theory as benchmark simulations to determine the general work-flow for obtaining spectra of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ accurately with minimum computational effort. Stretching parameters for approximate KS band-structures are calculated via quasiparticle eigen-energies, which are evaluated for chosen bands at chosen Brillouin zone points. The inter-band contributions to spectra are determined with RPA on top of stretched KS band-structures, giving $G_0W_0+\text{RPA}$. The intra-band contributions are added with the Drude free electron model. While the Drude plasmon energies (ω_p) are calculated fully from first-principles by approximating the electronic effective masses via the average Fermi velocities, the phenomenological inverse life-times (η) and the electric permittivities at the infinite frequency limit (ϵ_∞) are obtained via semi-empirical methods. The spectra of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ for chosen stoichiometric ratios are calculated through a standardised work-flow. Three quality factors are used to discuss the strengths of the plasmonic responses with respect to the stoichiometric ratios for the chosen solid-state lasers. Final spectra for chosen stoichiometric ratios are used to predict the efficient plasmonic response under various conditions.

Part III incorporates applications of TDDFT and beyond on coordination complexes and nano-clusters of TiO_2 . In Chap. 7, the fundamental theoretical background of the linear-response TDDFT within the Casida formalism and Tamm-Dancoff approximation (TDA), as well as linear-scaling implementations within ONETEP, are discussed in detail.

The time-domain extension of DFT+ U , so called TDDFT+ U , is developed and its effects on the electron-excitation spectra (EES) are demonstrated with a four-level toy model. In the next chapter, the newly-developed TDDFT+ U approach is applied to two small closed-shell Ni-centred coordination complexes, namely the planar tetracyanonickelate anion $\text{Ni}(\text{CN})_4^{2-}$ and the tetrahedral nickel tetracarbonyl $\text{Ni}(\text{CO})_4$, with a variable Hubbard U parameter. Then, the first-principles Hubbard parameters for these systems, in addition to that the open-shell Co-centred coordination complex CoL_2Cl_2 ($\text{L} = 2\text{-aminopyrimidine: C}_4\text{H}_5\text{N}_3$), are calculated and the self-consistent EES and the dipole-dipole absorption spectra of these systems are presented using various combinations of DFT+ U and TDDFT+ U alongside previous experimental and first-principles results. Lastly, in Chap. 9, efficient self-consistent strategies to obtain the band gaps of bulk TiO_2 -rutile and TiO_2 -anatase, by extending DFT+ U to both $3d$ -states of Ti and $2p$ -states of O, symbolically DFT+ U^d+U^p , are discussed with various approaches calculating the Hubbard parameters. Comprehensive approaches for bulk TiO_2 -rutile and TiO_2 -anatase are deployed to study the lowest excitations of such previously-studied small nano-clusters as $(\text{TiO}_2)_{12}$ and $(\text{TiO}_2)_{48}$. Furthermore, the same methods are used to investigate single O vacancies in TiO_2 -rutile and TiO_2 -anatase.

The dissertation concluded with a the synopsis and some prospects for further research aligned with this work in Part. IV.

Part I

Theoretical Background

Chapter 1

A brief introduction to theoretical spectroscopy

Theoretical spectroscopy combines quantum theories and computational methods to investigate the dynamics of quantum many-body systems interacting with external radiation. In more strict terms, it refers to the study of the response of condensed matter to external electro-magnetic (EM) radiation. Theoretically, it is a quantum mechanical problem for the system of coupled equations of light and matter expressed through the total Hamiltonian

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{M}} + \hat{\mathcal{H}}_{\text{L}} + \hat{\mathcal{H}}_{\text{LM}}, \quad (1.1)$$

where $\hat{\mathcal{H}}_{\text{M}}$, $\hat{\mathcal{H}}_{\text{L}}$, and $\hat{\mathcal{H}}_{\text{LM}}$ are the many-body Hamiltonian, the quantum field Hamiltonian of light and the light-matter interaction Hamiltonian. There does not exist any analytical or numerical solution for such a complex problem except in some very simple cases. Since theoretical spectroscopy aims to produce observable spectra of realistic systems, this problem can be reduced to a more feasible problem by imposing certain laboratory conditions on experimental measurements.

In this chapter, the general framework of this work is constructed by imposing the set of approximations deduced from the experimental laboratory conditions. First, the initial problem is reduced to a purely electronic problem interacting with a time-dependent external potential within the semi-classical definition of the light-matter interaction in the linear-response regime. In the following section, the fundamental physical phenomena in matter and the perturbative approaches to describe them within the linear-response regime are introduced. Then, some typical spectra in molecular spectroscopy namely the electronic excitation spectra (EES) and the dipole-dipole absorption spectra are represented conceptually. Finally, the macroscopic complex dielectric function and its connections to other optical functions in the study of solid-state spectroscopy are described within Maxwell's equations in the linear-response regime.

1.1 The semi-classical definition of the light-matter interaction

Spectroscopic measurements in the IR-vis-UV spectral range are commonly performed with high-intensity, monochromatic light sources. The average energy-loss of single EM radiation

is negligible except in cases of annihilation and creation corresponding to absorption and emission respectively. Hence, EM radiation can be assumed to be unaffected except in these cases, which can be enforced by hand through quantisation of particles. Furthermore, EM radiation can be described as classical waves at the large wavelength limit, where the wavelengths are far larger than most molecular systems, nano-clusters, or unit-cells of solids. Using a classical definition of EM radiation is also advantageous for natural connections to experimental observations. On the other hand, such an approach is not capable of including any field-spin coupling effect through the Bohr-van Leeuwen theorem^[1-3]. Justifying this, however, is the fact that the coupling of the spins and the magnetic field is expected to be negligible for non-magnetic materials for such EM radiations^[4]. As the total light-matter complex is reduced to an interacting quantum many-body system with some classical EM waves, this picture is referred to as the semi-classical definition of the light-matter interaction.

1.1.1 The adiabatic approximation

In the semi-classical definition, dynamical evolution of photons are negligible except in the cases of *annihilation* and *creation*, which correspond to *absorption* and *emission*, respectively. These cases can be imposed explicitly through quantisation of matter. Hence, the original coupled light-matter complex is reduced to the time-dependent many-body problem with the non-relativistic Hamiltonian

$$\hat{\mathcal{H}} = \left[\hat{\mathcal{T}}_n + \hat{\mathcal{V}}_{nn} + \hat{\mathcal{V}}_{\text{field}-n} \right] + \left[\hat{\mathcal{T}}_e + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{\text{field}-e} \right] + \hat{\mathcal{V}}_{ne}, \quad (1.2)$$

where the first set of terms comprise the nuclear Hamiltonian including the nuclear kinetic energy, the nucleus-nucleus interaction and the nuclei-field interaction operators, whereas the second parenthesis is the electronic Hamiltonian. The last term $\hat{\mathcal{V}}_{ne}$ includes the nuclear-electron interaction.

At the low temperature limit, the nuclear motion is slow in closely packed matter. Additionally, EM radiation in relevant spectral ranges is low-energy compared to bonds between nuclei, so it is not strong enough to stimulate nuclear motions. Under these conditions, the nuclear Hamiltonian and the electronic Hamiltonian can be partially uncoupled by the well-known Born-Oppenheimer approximation^[5]. The key idea is that electrons move several orders of magnitude faster compared to nuclei, as they have much smaller masses and

they re-configure themselves for a given nucleic configuration instantaneously. Correspondingly, nuclei experience a time-averaged potential due to the electronic configuration. Mathematically, the total wave-function is expressed as the product of the nuclear and the electronic wave-functions as

$$\Phi(\mathbf{R}_1, \dots, \mathbf{R}_{N_n}; \mathbf{r}_1, \dots, \mathbf{r}_{N_e}, t) = \Psi_n(\mathbf{R}_1, \dots, \mathbf{R}_{N_n}) \Psi_e(\mathbf{R}_1, \dots, \mathbf{R}_{N_n}; \mathbf{r}_1, \dots, \mathbf{r}_{N_e}, t), \quad (1.3)$$

where N_n and N_e are the numbers of nuclei and electrons, respectively. It is assumed that EM radiation in question are not able to stimulate any nuclear motion, the nuclear part of the problem becomes time-independent and can be solved classically thanks to the Hellmann-Feynman theorem^[6-9]. Consequently, the problem becomes just an electronic problem for a given nuclear configuration expressed as¹

$$\hat{\mathcal{H}}_{\text{field-e}} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t) = i \frac{\partial}{\partial t} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t), \quad (1.4)$$

where the field-electron Hamiltonian is given by

$$\begin{aligned} \hat{\mathcal{H}}_{\text{field-e}} &= \left[\hat{\mathcal{T}}_e + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{\text{ext}} + \hat{\mathcal{V}}_{\text{field-e}} \right] \\ &= \left[\frac{1}{2} \sum_i^N \hat{\mathbf{p}}_i^2 + \frac{1}{2} \sum_{i,j}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} + \sum_i^N \hat{v}_{\text{ext}}(\mathbf{r}_i) \right] + \hat{\mathcal{V}}_{\text{field-e}}, \end{aligned} \quad (1.5)$$

where the first term and the second term are called *the kinetic energy operator* $\hat{\mathcal{T}}_e$ and *the electron-electron interaction operator* $\hat{\mathcal{V}}_{ee}$. The third term $\hat{\mathcal{V}}_{\text{ext}}$ is *the external potential operator* due to positive ionic background. Finally, the last term $\hat{\mathcal{V}}_{\text{field-e}}$ is *the field-electron interaction operator*.

1.1.2 The field-electron interaction operator

In classical electromagnetic theory, EM radiation is defined as classical transverse waves with the electric field $\mathbb{E}(\mathbf{r}, t)$ and the magnetic field $\mathbb{B}(\mathbf{r}, t)$ components satisfying a set of equations, namely Maxwell's equations^[10,11]. Alternatively, they are represented via the

¹The sub-index of the many-body electronic wave-function is dropped for simplicity also for further parts by setting $\Psi_e = \Psi$.

vector potential $\mathbf{A}(\mathbf{r}, t)$ and the scalar potential $\phi(\mathbf{r}, t)$. In the radiation gauge, the general solution for Maxwell's equations is given by

$$\begin{aligned}\mathbb{E}(\mathbf{r}, t) &= -\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t}, & \mathbb{B}(\mathbf{r}, t) &= \nabla \times \mathbf{A}(\mathbf{r}, t) \\ \mathbf{A}(\mathbf{r}, t) &= \frac{1}{2} \mathbf{A}_0 \left(e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \right), & \phi(\mathbf{r}, t) &= 0,\end{aligned}\tag{1.6}$$

where $\mathbf{k}$ is the wave vector perpendicular to $\mathbb{E}(\mathbf{r}, t)$ and $\mathbb{B}(\mathbf{r}, t)$, and ω is the angular frequency of the EM radiation. The connection to the quantum picture is constructed through the quantum energy of photons by using the correlation between the norm of the wave vector and the wave length as

$$E = \omega = |\mathbf{k}|c.\tag{1.7}$$

Due to particle nature of a photon, it also carries a momentum given by expression

$$\mathbf{p} = \mathbf{k}\tag{1.8}$$

recalling that $\hbar = 1$ in atomic units.

The field-electron interaction operator can be constructed by starting with the classical force experienced by electron, namely the Lorentz force

$$\mathbf{F}(\mathbf{r}, t) = q (\mathbb{E}(\mathbf{r}, t) + \mathbf{v}(t) \times \mathbb{B}(\mathbf{r}, t)).\tag{1.9}$$

In the Lagrangian mechanics, the associating classical potential of the Lorentz force for electrons can be expressed as

$$V_{field-e}(\mathbf{r}, t) = \dot{\mathbf{r}}(t) \cdot \mathbf{A}(\mathbf{r}, t) - \phi(\mathbf{r}, t),\tag{1.10}$$

where the generalized momentum becomes^[12]

$$\mathbf{p} = \dot{\mathbf{r}}(t) - \mathbf{A}(\mathbf{r}, t).\tag{1.11}$$

By using the canonical commutation relation, the generalised momentum operator for electron

in EM field can be expressed in the interacting picture as

$$\hat{\mathbf{p}}'(t) = \hat{\mathbf{p}}(t) - \hat{\mathbf{A}}(\mathbf{r}, t). \quad (1.12)$$

Inserting this generalized momentum into Eq. (1.4) for the single electron, we have

$$\hat{\mathcal{H}}_{\text{field-e}} = \frac{1}{2} \hat{\mathbf{p}}^2 + v_{\text{ext}}(\mathbf{r}, t) - \frac{1}{2} \left(\hat{\mathbf{p}} \cdot \hat{\mathbf{A}} + \hat{\mathbf{A}} \cdot \hat{\mathbf{p}} \right) + \left| \hat{\mathbf{A}} \right|^2. \quad (1.13)$$

The quadratic term in Eq. (1.14) can be neglected for low-energy EM fields. Moreover, $\hat{\mathbf{p}}$ and $\hat{\mathbf{A}}$ commute in the Coulomb gauge; hence the field-electron interaction operator in Eq. (1.9) for N electron system can be expressed as

$$\hat{\mathcal{V}}_{\text{field-e}}[t] = - \sum_i^N \hat{\mathbf{p}}_i(t) \cdot \hat{\mathbf{A}}(\mathbf{r}_i, t). \quad (1.14)$$

Having shown that the initial problem is reduced to a purely electronic many-body problem, which is interacting with an external field, we now go on to discuss its dynamics in the linear-response regime.

1.2 Linear-response regime

In principle, our goal is to determine the time-dependent many-body wave-function in Eq. (1.4), which contains complete information about the system of N electrons evolving under the influence of an external EM field at any given time. Despite the substantially reduced complexity, such a problem is far beyond any analytical or computational tool. Recalling the laboratory conditions once again, this problem can be reduced to a more feasible problem. Spectroscopic measurements are performed on the stationary state of systems, where the external field is turned on at a certain time. At low energies, the system is expected to return to its initial state if that external field is not strong enough to distort the system permanently. From a theoretical perspective, this translates to a process such that the system, which is initially at its ground-state, is exposed to a weak external field turned on adiabatically at a given time. The change in the system is described as some perturbation from its ground-state. For weak external fields, this perturbation can be introduced as the first-order correction to the ground-state within the linear-response theory (LRT). In general terms, the first-order correction to any ground-state observable of the system $\delta \langle \hat{O} \rangle$ due to a weak

external field $\mathbb{F}$ is defined through the linear-response function as

$$\delta\langle\hat{O}\rangle = \chi\mathbb{F}, \quad (1.15)$$

where χ is *the linear-response function*. In the particular case in this work, the weak external field is the time-dependent vector field in Eq. (1.6) perturbing a many-body electronic system from its electronic ground-state to another electronic state with a higher energy level.

1.2.1 The time-dependent perturbation

In the linear-response regime, the perturbation of a system from its ground-state due to some weak time-dependent external field is obtained using a first order correction with time-dependent perturbation theory (TDPT)^[12]. Within TDPT, the time-dependent many-body electronic Hamiltonian is re-expressed conveniently in the interaction picture as

$$\hat{\mathcal{H}}_{\text{field-e}}(t) = \hat{\mathcal{H}}_0 + \Theta(t)\hat{\mathcal{V}}_{\text{field-e}}(t), \quad (1.16)$$

where $\hat{\mathcal{H}}_0$ is the time-independent many-body electronic Hamiltonian, and $\Theta(t)$ is the Heaviside step function for the switch-on of the field-electron interaction at $t = 0$. For $t < 0$, the many-body electronic states are determined by solving the time-independent Schrödinger equation given by

$$\hat{\mathcal{H}}_0|\Psi_i\rangle = E_i|\Psi_i\rangle, \quad (1.17)$$

where $\Psi_i(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is the many-body electronic function representing the electronic state of the system with the energy level E_i . The time-evolution of any many-body electronic state without any external field is

$$|\bar{\Psi}\rangle = \sum_i c_i e^{-iE_i t} |\Psi_i\rangle \quad (1.18)$$

using the time-evolution operator. The time-dependent many-body electronic states of Eq. (1.16) can be written as

$$|\bar{\Psi}(t)\rangle = \sum_i c_i(t) e^{-iE_i t} |\Psi_i\rangle, \quad (1.19)$$

that is as expansions of the time-independent many-body electronic states with some time-dependent expansion coefficients. Inserting Eq. (1.19) into the time-dependent Schrödinger equation and multiplying with $\langle \Psi_f |$ from left-hand-side, the differential equations for the time-dependent expansion coefficients are obtained as

$$i \frac{dc_f(t)}{dt} = \sum_i c_i(t) e^{i\omega_{fi}t} \langle \Psi_f | \hat{V}_{field-e}(t) | \Psi_i \rangle, \quad (1.20)$$

where $\omega_{fi} = E_f - E_i$. Within TDPT, the time-dependent coefficients can be expanded in the case of some weak external field as

$$c_f(t) = c_f^{(0)}(t) + c_f^{(1)}(t) + c_f^{(2)}(t) + \dots, \quad (1.21)$$

where the 0th order correction is nothing but δ_{fi} , and the first-order correction becomes

$$c_f^{(1)}(t) = -i \int_{-\infty}^t dt' e^{i\omega_{fi}t'} \langle \Psi_f | \hat{V}_{field-e}(t') | \Psi_i \rangle. \quad (1.22)$$

The norm square of Eq. (1.22) is called *the transition probability*, which measures the probability of transition from the initial state Ψ_i to the final state Ψ_f . For the particular case of the field-electron operator in Eq. (1.14), the transition probability becomes

$$P_{f \leftarrow i}(t) = \left| \langle \Psi_f | \hat{\mathbf{p}} \cdot \mathbf{A}_0 e^{i\mathbf{k} \cdot \mathbf{r}} | \Psi_i \rangle \right|^2 \left| \int_{-\infty}^t dt' \left(e^{i(\omega_{fi}-\omega)t'} + e^{i(\omega_{fi}+\omega)t'} \right) \right|^2, \quad (1.23)$$

where the first and the second terms in the time-dependent integral are *resonant phase* and *anti-resonant phase*. For $t \gg \omega_{fi}^{-1}$, Eq. (1.23) becomes

$$P_{f \leftarrow i}(t) = 2\pi t \left| \langle \Psi_f | \hat{\mathbf{p}} \cdot \mathbf{A}_0 e^{i\mathbf{k} \cdot \mathbf{r}} | \Psi_i \rangle \right|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega)], \quad (1.24)$$

which obviously diverges as time tends to infinity. The transition probability per unit time, also so called *Fermi's golden rule* (FGR)^[13], is a more useful quantity expressed as

$$R_{f \leftarrow i} = \frac{P_{f \leftarrow i}(t)}{t} = 2\pi \left| \langle \Psi_f | \hat{\mathbf{p}} \cdot \mathbf{A}_0 e^{i\mathbf{k} \cdot \mathbf{r}} | \Psi_i \rangle \right|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega)]. \quad (1.25)$$

For large wavelengths, where $|\mathbf{k}| = 2\pi/\lambda \ll 1$, the higher terms of expansion

$$e^{i\mathbf{k} \cdot \mathbf{r}} = 1 + i\mathbf{k} \cdot \mathbf{r} - \frac{1}{2}(\mathbf{k} \cdot \mathbf{r})^2 + \dots, \quad (1.26)$$

becomes infinitely small; hence $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$, which is called *the electric dipole approximation* as it only includes the electric dipole term in multipole expansion of the EM radiation. Within this approximation, the FGR of the electronic transition from i to f for an isotropic vector field becomes

$$R_{f \leftarrow i} = 2\pi \frac{|\mathbb{E}_0|^2}{\omega^2} |\langle \Psi_f | \hat{\mathbf{p}} | \Psi_i \rangle|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega)], \quad (1.27)$$

where $\mathbb{E}_0 = \omega \mathbf{A}_0$ by Eq. (1.6). Eq. (1.27) can be re-expressed in position space using the canonical commutation relation of the time-independent electronic Hamiltonian and the position operator

$$[\hat{\mathcal{H}}_0, \hat{\mathbf{r}}] = -\hat{\mathbf{p}}, \quad (1.28)$$

which results in

$$R_{f \leftarrow i} = 2\pi |\mathbb{E}_0|^2 |\langle \Psi_f | \hat{\mathbf{r}} | \Psi_i \rangle|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega)], \quad (1.29)$$

where $\mu_{f \leftarrow i} = \langle \Psi_f | \hat{\mathbf{r}} | \Psi_i \rangle$ is *the transition dipole moment*.

1.2.2 The selection rules and the oscillator strength

For perfectly centro-symmetric environments, where electronic wave-functions are expected to have spatial parity with respect to the inversion center, the transition dipole moments follow a set of rules namely *selection rules*, or *Laporte's selection rules*^[14]. The transition dipole moment in the integral form is

$$\mu_{f \leftarrow i} = \int_{-\infty}^{\infty} d\mathbf{r} \Psi_f^*(\mathbf{r}) \mathbf{r} \Psi_i(\mathbf{r}), \quad (1.30)$$

where it becomes more clear that the product in the integral is required to have *gerade* (g)¹ parity for non-zero value, whereas it becomes zero for an *ungerade* (u)² parity. Since $\mathbf{r}$ itself has u-parity, it is expected that the final and initial states should have opposite parities for a non-zero transition dipole moment. These conditions can be summarized for atomic orbitals

¹The German word for 'even'.

²The German word for 'odd'.

as

$$\Delta l = \pm 1 \quad \text{and} \quad \Delta m = 0, \quad (1.31)$$

where l and m are *angular momentum quantum number* and *magnetic moment quantum number*, respectively. For instance, the selection rules forbids the transitions between $p \rightarrow p$, $d \rightarrow d$ and also spin-flipping transitions. The electronic transition with the zero transition dipole moments are called *forbidden transitions*, or *parity conserving transitions*, or *optically dark transitions*, whereas electronic transitions with the non-zero transitions dipole moments are called *optically allowed transitions*, or *parity changing transitions*. The relative strength of an electronic transition is *the oscillator strength* defined as

$$f_{f \leftarrow i} = \left(\frac{\mu_{f \leftarrow i}}{\mu_1} \right)^2, \quad (1.32)$$

where μ_1 is the transition dipole moment of a single electron under a 3-dimensional harmonic potential.

1.2.3 Life-time broadening of electronic excitations

Electronic excitations occur where the system at its ground-state gains certain energy transferred by EM radiation, and transitions to an excited-state with higher energy. In reality, the excited system has the tendency to return to its ground-state either releasing excess energy back as photons, dissipating thermally through nuclear motion, or utilising some other scattering processes. Hence, excited states have finite life-times and go thorough either radiative or non-radiative de-excitations. The finite life-time of the electronic transitions can be introduced with an exponential decaying function as

$$e^{-\frac{\Gamma t}{2}}, \quad (1.33)$$

with the phenomenological inverse life-time $\Gamma = 1/\tau$. The resonant phase in Eq. 1.23 becomes for $t \rightarrow \infty$ as

$$I(\omega) = \left| \int_{-\infty}^{\infty} dt' e^{-i\Gamma t'/2} e^{i(\omega_{fi} - \omega)t'} \right|^2 = \frac{\Gamma/2}{(\omega - \omega_{fi})^2 + (\Gamma/2)^2}, \quad (1.34)$$

where $I(\omega)$ is called *the line-shape function* with a full-width Γ .

1.2.4 Linear-response function

Within LRT, the simplest approach to determine the imaginary part of the response function of an electronic density to an external EM radiation is to sum over induced electric dipoles using FGR with the life-time broadening for the all accessible states as^[12],

$$\chi_2(\omega) = 2\pi\mathbb{E}_0 \sum_{f,i} |\langle \Psi_f | \hat{\mathbf{r}} | \Psi_i \rangle|^2 \frac{\Gamma_{fi}/2}{(\omega - \omega_{fi})^2 + (\Gamma_{fi}/2)^2}, \quad (1.35)$$

where $E_f > E_i$ to ensure that energy gained by the system. By the causality condition of the linear-response function, the real part of the response function can be constructed by means of the Kramers-Kronig relation^[15–17] as

$$\chi_1(\omega) = \frac{2}{\pi} \mathcal{P} \int_0^\infty d\omega' \frac{\chi_2(\omega')}{\omega' - \omega}, \quad \chi_2(\omega) = -\frac{2}{\pi} \mathcal{P} \int_0^\infty d\omega' \frac{\chi_1(\omega')}{\omega' - \omega}, \quad (1.36)$$

where $\mathcal{P}$ is the Cauchy principal value. The total response function becomes, for the excitation case,

$$\chi(\omega) = \chi_1(\omega) + i\chi_2(\omega) = 2\pi\mathbb{E}_0 \sum_{fi} \frac{|\langle \Psi_f | \hat{\mathbf{r}} | \Psi_i \rangle|^2}{\omega - \omega_{fi} + i\Gamma_{fi}}. \quad (1.37)$$

Eq. (1.37) is basically the superposition of the individual excitations within a non-interacting picture of excitations¹.

1.3 Molecular spectroscopy

Molecular spectroscopy refers to the measurement of spectra arising due to transitions between molecular states. At low temperature, molecular orbitals are almost purely electronic states, which are comprised of bonding, anti-bonding or non-bonding atomic orbitals. Bonding molecular orbitals are the result of constructive superposition of atomic orbitals commonly with lower energies than the constituting states, while anti-bonding molecular orbitals are the result of destructive superposition of atomic orbitals with higher energies than

¹It may be important to state prematurely the distinction between interacting and non-interacting pictures of electrons and excitations (de-excitations). The many-body electronic wave-functions in Eq. (1.37) are quantum states of fully interacting many-body systems. However, Eq. (1.37) is constructed using the transition probabilities of induced electric dipoles, which are not interacting.

the constituting states. Non-bonding molecular orbitals are formed when some atomic orbitals of parental atoms have mismatching symmetries and cannot form bonds. Bonding and anti-bonding molecular orbitals in centro-symmetric environments have spatial symmetries with respect to inversion center, similarly to atomic orbitals, namely $\sigma, \pi, \delta, \phi$, and $\sigma^*, \pi^*, \delta^*, \phi^*$ respectively. Hence, the electronic transitions among such molecular orbitals are subjected to selection rules similar to the atomic case discussed in Sec. 1.2.2 in centro-symmetric environments. In ground-state, N electrons occupy molecular states starting from the lowest energy one, consecutively by virtue of Pauli's exclusion principle^[18], up to the N^{th} lowest energy molecular orbital. Molecular orbitals highly localised on nuclei are called *bound states*, of which is strongly bounded occupied ones with lowest energies are particularly classified as *core states*. In the IR-vis-UV spectral range, electronic transitions occur commonly between higher-energy occupied and lower-energy unoccupied molecular orbitals.

Most spectroscopic measurements of molecules are performed in the gas phase, in solution, or on some substrate matrix with well-known electro-chemical properties. In this work, the first-principles simulations of molecular spectroscopy will be performed in the gas phase. In gas phase measurements, the absorption (emission) peaks are averaged and smeared due to molecular motions, introduced through life-time broadening in Subsec. 1.2.3. Two essential molecular spectroscopies are now introduced to investigate excited-state properties and optical responses of molecules.

1.3.1 Electronic excitation spectra

Electronic excitation spectra (EES) are constructed by including both optically allowed and forbidden excitations with the unit oscillator strength given by

$$\text{EES}(\omega) = \sum_{ij} \frac{\Gamma/2}{(\omega - \omega_{ji})^2 + (\Gamma/2)^2}, \quad (1.38)$$

where i and j denote occupied and the unoccupied molecular electronic states respectively. EES is useful to investigate excited-states of molecular systems. Moreover, realistic systems are not perfectly centro-symmetric due to distortions and some coupling with molecular motions such as rotation or vibrations, which lead to some weak signals for optically forbidden transitions mostly smeared out by optically allowed transitions. EES becomes important to characterise such transitions.

1.3.2 Dipole-dipole absorption spectra

Dipole-dipole absorption spectra are most common spectra to measure the optical response of molecules at the low energy spectral range. Unlike EES, the contributions of the individual excitations are weighted by the normalized oscillator strength, which is related to transition dipole moments of transitions. This results in

$$\text{ABS}(\omega) = \sum_{ij} f_{j \leftarrow i} \frac{\Gamma/2}{(\omega - \omega_{ji})^2 + (\Gamma/2)^2}, \quad (1.39)$$

and this spectra is main formula used for comparability with observations.

1.4 Solid-state spectroscopy

Solids are theoretically infinite objects of repeating cells of closely packed atoms. Electronic states here may be thought of as overlapping molecular orbitals forming continuous functions, namely *electronic bands*. Electronic bands with lower energy and strongly localised on nuclei are called *core states*, where occupied bands with higher energies at the ground-state are called *valence bands* and unoccupied bound states are called *conduction bands*. Also, valence bands crossing the Fermi level in metals, or semiconductors are sometimes called *metallic bands*. In the IR-vis-UV spectral range, two main mechanisms contribute to the spectra of solids. The first mechanism is common for all solids, namely *inter-band transitions*, which are electronic transitions between valence and conduction bands. The second mechanism is exclusive to solids with metallic bands, namely *intra-band transitions*, which can be described as collective oscillations of electrons in metallic bands in phase with the inducing EM radiation.

1.4.1 Macroscopic optical functions

As macroscopic objects, the spectra of solids can be described within classical EM theory. In classical EM theory, EM waves are described through Maxwell's equations^[10,19], in the

frequency domain in Gaussian units as

$$\nabla \cdot \mathbb{D}(\omega) = 4\pi\rho_{\text{ext}} \quad (1.40)$$

$$\nabla \times \mathbb{E}(\omega) = -\frac{i\omega}{c}\mathbb{B}(\omega) \quad (1.41)$$

$$\nabla \cdot \mathbb{B}(\omega) = 0 \quad (1.42)$$

$$\nabla \times \mathbb{H}(\omega) = \frac{4\pi}{c}\mathbf{j}_{\text{ext}} + \frac{i\omega}{c}\mathbb{D}(\omega), \quad (1.43)$$

where $\mathbb{D}$, $\mathbb{E}$, $\mathbb{H}$ and $\mathbb{B}$ are the *displacement field*, *electric field*, *magnetic field*, and *magnetic induction*, respectively; ρ_{ext} and $\mathbf{j}_{\text{ext}}$ are the external charge and current densities, respectively. The relations between displacement and magnetic fields and their driving fields are given as

$$\mathbb{D}(\omega) = \mathbb{E}(\omega) + 4\pi\mathbb{P}(\omega) \quad (1.44)$$

$$\mathbb{H}(\omega) = \mathbb{B}(\omega) - 4\pi\mathbb{M}(\omega), \quad (1.45)$$

where $\mathbb{P}$ and $\mathbb{M}$ are *polarisation* and *magnetisation*, respectively. Within LRT, $\mathbb{P}$ and $\mathbb{M}$ can be defined through the linear-response functions,

$$\mathbb{P}(\omega) = \chi_e(\omega)\mathbb{E}(\omega) \quad (1.46)$$

$$\mathbb{M}(\omega) = \chi_m(\omega)\mathbb{H}(\omega), \quad (1.47)$$

where χ_e and χ_m are called *electric susceptibility* and *magnetic permeability tensors*. Inserting Eq. (1.45) and Eq. (1.46) into Eq. (1.44) and Eq. (1.45) respectively, gives

$$\mathbb{D}(\omega) = (\mathbb{I} + 4\pi\chi_e(\omega))\mathbb{E}(\omega) = \mathcal{E}(\omega)\mathbb{E}(\omega) \quad (1.48)$$

$$\mathbb{B}(\omega) = (\mathbb{I} + 4\pi\chi_m(\omega))\mathbb{H}(\omega) = \mathcal{M}(\omega)\mathbb{H}(\omega), \quad (1.49)$$

where $\mathcal{E}(\omega)$ and $\mathcal{M}(\omega)$ are *macroscopic dielectric* and *macroscopic permeability* tensors. In the most general definition, they are tensors with rank-2. However, for isotropic environments and cubic crystal symmetries, they can be reduced to complex functions of frequency.

Substituting Eq. (1.44) and Eq. (1.45) into Eq. (1.43) without any external current density

($\mathbf{j}_{\text{ext}} = 0$),

$$\begin{aligned}\nabla \times \mathbb{B}(\omega) &= \frac{i\omega}{c} \mathbb{E}(\omega) + \frac{4\pi}{c} i\omega \mathbb{P}(\omega) + \frac{4\pi}{c} \nabla \times \mathbb{M}(\omega) \\ &= \frac{i\omega}{c} \mathbb{E}(\omega) + \frac{4\pi}{c} \mathbf{j}_{\text{ind}}(\omega),\end{aligned}\tag{1.50}$$

is obtained, where $\mathbf{j}_{\text{ind}}$ is *the induced current density*. Similarly, Eq. (1.40) becomes without any external charge density ($\rho_{\text{ext}} = 0$) by using Eq. (1.44)

$$\begin{aligned}\nabla \cdot (\mathbb{E}(\omega) + 4\pi \mathbb{P}(\omega)) &= 0 \\ \Rightarrow \nabla \cdot \mathbb{E}(\omega) &= -4\pi \nabla \cdot \mathbb{P}(\omega) = 4\pi \rho_{\text{ind}}(\omega),\end{aligned}\tag{1.51}$$

where ρ_{ind} is called *induced charge density*. Immediately, substituting these expressions into of Eq. (1.41), the charge conservation can be derived as

$$\frac{i4\pi\omega}{c} \rho_{\text{ind}}(\omega) + \frac{4\pi}{c} \nabla \cdot \mathbf{j}_{\text{ind}}(\omega) = 0.\tag{1.52}$$

The induced current density consists of two parts induced by the electric and magnetic fields. The magnetic field contributes to it due to spin of electrons; however, for non-magnetic systems, the contribution due the magnetic fields is negligible. Omitting this part, and recalling the definition in Eq. (1.51), we have

$$\mathbf{j}_{\text{ind}}(\omega) = i\omega \mathbb{P}(\omega) = i\omega \chi_e(\omega) \mathbb{E}(\omega) = \sigma(\omega) \mathbb{E}(\omega),\tag{1.53}$$

where σ is the electric conductivity, which can be related to the macroscopic dielectric function through Eq. (1.46) and Eq. (1.48) as,

$$\sigma(\omega) = \frac{i\omega}{4\pi} (\mathcal{E}(\omega) - 1).\tag{1.54}$$

Using Eq. (1.43) for $\mathbf{j}_{\text{ext}} = 0$ and $\rho_{\text{ext}} = 0$, the wave equation for the electric field is obtained via Eq. (1.41) as

$$\nabla^2 \mathbb{E}(\omega) = \frac{\omega^2}{c^2} \mathcal{E}(\omega) \mathbb{E}(\omega).\tag{1.55}$$

For the electric field described in Eq. (1.6), the following dispersion relation can be

obtained

$$|\mathbf{k}|^2 = \frac{\omega^2}{c^2} \mathcal{E}(\omega), \quad (1.56)$$

where $(c/\omega)|\mathbf{k}|$ is defined as *complex refractive index*

$$\tilde{n}(\omega) = n(\omega) + i\kappa(\omega) \quad (1.57)$$

where n and κ are called *refractive index* and *extinction coefficient* respectively, and they are connected to the microscopic complex dielectric function with

$$n(\omega) = \frac{\sqrt{\mathcal{E}_1(\omega) + |\mathcal{E}(\omega)|}}{\sqrt{2}}, \quad \kappa(\omega) = \frac{\sqrt{-\mathcal{E}_1(\omega) + |\mathcal{E}(\omega)|}}{\sqrt{2}}. \quad (1.58)$$

Introducing the definition of complex refractive index, the electric field of a linearly polarized wave propagating in $\hat{\mathbf{z}}$ -direction with the amplitude E_0 is given by

$$\mathbb{E}(z, \omega) = E_0 e^{-\frac{\omega}{c}\kappa(\omega)z} e^{i(\frac{\omega}{c}n(\omega)z - \omega t)}, \quad (1.59)$$

where the first part describes attenuation and the second part describes propagations. We may now state Lambert's law, for the depth z dependence of the wave intensity $I = |\mathbb{E}|^2$, namely

$$I = I_0 e^{-\alpha(\omega)z} = E_0^2 e^{-2\frac{\omega}{c}\kappa(\omega)z}, \quad (1.60)$$

where $\alpha(\omega)$ is *absorption coefficient* expressed as

$$\alpha(\omega) = 2\frac{\omega}{c}\kappa(\omega) = 2\frac{\omega}{c} \frac{\sqrt{-\mathcal{E}_1(\omega) + |\mathcal{E}(\omega)|}}{\sqrt{2}}. \quad (1.61)$$

When an electromagnetic wave strikes the surface of a medium with the complex refraction index, $\tilde{n}$, some portion will be transmitted into the medium, while the remaining part will be reflected. By using the boundary condition on the surface for the tangential components of the electric and magnetic fields, the following relations can be established:

$$\begin{aligned} E_i + E_r &= E_t, \\ \frac{\omega}{c}(E_i - E_r) &= \tilde{n}(\omega)E_t, \end{aligned} \quad (1.62)$$

where E_i , E_r , and E_t are the amplitudes of the incident, the reflected and the transmitted waves normal to surface. *Normal incident reflectivity* R , and *normal incident transmission* T are defined as

$$R(\omega) = \left| \frac{E_r}{E_i} \right|^2 = \frac{(n(\omega) - 1)^2 + k(\omega)^2}{(n(\omega) + 1)^2 + k(\omega)^2}, \quad \text{and} \quad T(\omega) = 1 - R(\omega). \quad (1.63)$$

These optical functions are used to describe various conditions for optical response of solids. Above all, the cardinal quantity is the macroscopic dielectric function as all other optical functions are defined in terms of it.

1.4.2 Optical absorption spectra

Optical absorption spectra (ABS) of metallic solids in the IR-vis-UV spectral range are the result of inter-band transitions with significant oscillator strengths and collective oscillations of nearly free electrons. In solid-state spectra, it is directly related to the macroscopic dielectric function by the expression

$$\text{ABS}(\omega) = \Im[\mathcal{E}(\omega)] = \frac{4\pi}{\omega} \Re[\sigma(\omega)]. \quad (1.64)$$

1.4.3 Electron energy-loss spectroscopy

EELS^[20–26] is constructed by examining the changes in kinetic energies and momenta of accelerated electrons after interacting with solids. The de Broglie wavelength of the accelerated electrons are approximately $\sim 10^3$ larger than photons with the same energies. Hence, plasmons, which are screened collective oscillations of free electrons resulting from inter-band transitions, can be observed in EELS. EELS is also related to the macroscopic dielectric function by^[27]

$$\text{EELS}(\omega) = -\Im[\mathcal{E}^{-1}(\omega)]. \quad (1.65)$$

1.5 Conclusion

In this chapter, some basic concepts of theoretical spectroscopy were introduced. The laboratory conditions for the IR-vis-UV spectral range at low temperatures were invoked to reduce the initial coupled quantum problem of light-matter to a purely electronic problem perturbed by a weak external field from its ground-state. Moreover, the first-order perturbation from the ground-state was derived for a time-dependent external field within TDPT. Some constraints on spectra arising due to symmetry properties of underlying electronic states were discussed for centro-symmetric environments. The most widely used spectra were conceptually described for molecular spectroscopy, and the most common macroscopic optical functions within the classical EM theory were defined for solid-state spectroscopy. For these to be used, however, a well-defined ground-state electronic structure is required to predict spectra of condensed matter system in the linear-response regime. In the following three chapters, the theoretical and computational tools used to determine ground-state of a quantum many-body system will be discussed as well as their limitations and systematic errors.

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Chapter 2

Ground-state theory

Perturbative approaches for first-principles simulation of spectra arising from electronic transitions require well-defined ground-state electronic states, which are determined by solving the time-independent Schrödinger equation with the electronic Hamiltonian

$$\begin{aligned}\hat{\mathcal{H}} &= \hat{\mathcal{T}} + \hat{\mathcal{V}}_{\text{ee}} + \hat{\mathcal{V}}_{\text{ext}} \\ &= \frac{1}{2} \sum_i^N \hat{\mathbf{p}}_i^2 + \frac{1}{2} \sum_{i,j}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} + \sum_i^N \hat{v}_{\text{ext}}(\mathbf{r}_i)\end{aligned}\tag{2.1}$$

for a system of N electrons. Needless to say, tackling such a problem is implausible by any analytical or numerical methods due to the $3N$ -variable dependence of the electronic wave-function that are only plausible to be solved using Quantum Monte Carlo^[1] or configuration interaction methods^[2,3] for relatively small systems.

In this chapter, an alternative formulation of ground-state many-body electronic problem, namely density-functional theory (DFT), and its most common practical implementations will be introduced. Two ground-breaking theorems, namely the Hohenberg-Kohn theorems, which lay the theoretical foundations of DFT, will be proved. Then, the applicable scheme of DFT, namely Kohn-Sham DFT (KS-DFT), and its computational implementation using plane-waves will be introduced with some crucial additional approximations that are advantageous for using efficient algorithms. Lastly, the extension of KS-DFT to the conduction band manifold within a non-self-consistent scheme will be briefly mentioned.

2.1 Density-functional theory

Density-functional theory is an ingenious theory that formulates the ground-state many-body problem in terms of the particle density, equivalently to the wave-function formalism. Besides its well-established theoretical framework, DFT provides a suitable laboratory for simulating many realistic many-body quantum systems within a self-consistent, parameter-free approach. Particularly with rapidly progressing numerical techniques and computer hardware, DFT has become one of the most commonly used methods both in academic and industrial scientific communities.

The preliminary idea of describing the electronic configuration of a many-body system solely in terms of the electronic density goes back to the works of Thomas and Fermi, in *the*

Thomas-Fermi model^[4,5]. The total interaction energy is there expressed as a functional of the electronic density via semi-classical approximations. The kinetic energy is approximated via the non-interacting electronic cloud around the nuclei, while the electron-electron interaction is approximated as the classical Coulombic interaction energy of electron densities, namely *Hartree energy*. The resulting universal Thomas-Fermi functional, which depends on only the intrinsic properties of the system becomes

$$F[n] = \frac{3}{10} (3\pi^2)^{2/3} \int d\mathbf{r} |n(\mathbf{r})|^{5/3} + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.2)$$

Despite its significance as the precursor of DFT, it fails to include the exchange-correlation (xc) interaction of electrons; hence, it fails to describe the electronic systems with any complex density distribution quantitatively.

Similarly, the cardinal idea of DFT is to describe the many-body electronic problem through a single-variable electronic density $n(\mathbf{r})$ instead of the multi-variable electronic wave-function $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$. Via the density operator, the relation of the density to the wave-function is established as

$$n(\mathbf{r}_i) = \int \prod_{j \neq i}^N d\mathbf{r}_j |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2. \quad (2.3)$$

Recalling Eq. (2.1), for any given state Ψ with the corresponding density $\rho(\mathbf{r})$, the eigenenergy is expressed as

$$\begin{aligned} E &= \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle = \langle \Psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \Psi \rangle + \sum_i^N \int v_{\text{ext}}(\mathbf{r}_i) \prod_{j \neq i}^N d\mathbf{r}_j |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 \\ &= \langle \Psi | \hat{\mathcal{T}} | \Psi \rangle + \sum_i^N v_{\text{ext}}(\mathbf{r}_i) n(\mathbf{r}_i). \end{aligned} \quad (2.4)$$

Rewriting the expression above for the continuous density by replacing the sum with the integral over the electronic density leads to

$$E[n] = F[n] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}). \quad (2.5)$$

Assuming that the relation in Eq. (2.3) can be inverted, Ψ can be constructed from n , which means in principle that n carries all information carried by the wave-function. As a result, any

ground-state observable of a system can be expressed as the functional of n .

2.1.1 The Hohenberg-Kohn theorems

The formal basis of DFT has been established by the ground-breaking work of Kohn and Hohenberg^[6] in 1964 by proving two pivotal theorems, namely the Hohenberg-Kohn (HK) theorems, which enable us to reformulate the quantum many-body electronic problem in terms of the electronic density only.

First Hohenberg-Kohn theorem: The ground-state density of an N electron system $n_0(\mathbf{r})$ and the external potential $v_{\text{ext}}(\mathbf{r})$, within an additive constant, determine each other uniquely. This theorem can be proved by proof via contradiction. Let us assume that there are two external potentials, $v_{\text{ext}}(\mathbf{r})$ and $v'_{\text{ext}}(\mathbf{r})$, differing by more than an additive constant with the corresponding Hamiltonians $\hat{\mathcal{H}}$ and $\hat{\mathcal{H}}'$ and the ground-state wave-functions $|\Psi_0\rangle$ and $|\Psi'_0\rangle$, respectively, produce the same ground-state density of N electron system $n_0(\mathbf{r})$. By the variational principle, one can write

$$\begin{aligned}
 E_0 &< \langle \Psi'_0 | \hat{\mathcal{H}} | \Psi'_0 \rangle = \langle \Psi'_0 | \hat{\mathcal{H}}' | \Psi'_0 \rangle + \langle \Psi'_0 | \hat{\mathcal{H}} - \hat{\mathcal{H}}' | \Psi'_0 \rangle \\
 &= E'_0 + \int d\mathbf{r} (v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})) n_0(\mathbf{r}) \\
 E'_0 &< \langle \Psi_0 | \hat{\mathcal{H}}' | \Psi_0 \rangle = \langle \Psi_0 | \hat{\mathcal{H}} | \Psi_0 \rangle + \langle \Psi_0 | \hat{\mathcal{H}}' - \hat{\mathcal{H}} | \Psi_0 \rangle \\
 &= E_0 + \int d\mathbf{r} (v'_{\text{ext}}(\mathbf{r}) - v_{\text{ext}}(\mathbf{r})) n_0(\mathbf{r}). \tag{2.6}
 \end{aligned}$$

By summing the inequalities side by side, the contradictory inequality is achieved as

$$E_0 + E'_0 < E'_0 + E_0, \tag{2.7}$$

which shows that two different external potential cannot result in the same ground-state of the system. The first theorem ensures a one-to-one mapping between an *v-representable density*, which arise from some potential $v[n]$ ^[7], and the corresponding external potentials.

Second Hohenberg-Kohn theorem: The total energy functional of the system, $E[n]$, takes its global minimum at the ground density, $n_0(\mathbf{r})$. It can be summarised as

$$E[n] = F[n] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \geq E[n_0], \quad (2.8)$$

where F is the universal functional of density consisting of all internal interactions and kinetic energy, and $n(\mathbf{r})$ is the any density.

The original HK theorems were stated for any ground-state density; however, it was discovered by Levy^[8] and Lieb^[9] that they can be applied only to a certain class of densities namely *the non-degenerate v -representable densities*. They have been modified to include also the degenerate ground-state case by Kohn later in 1985^[10]. The v -representable densities are constructed from the ground-state wave-functions, which are the formal solutions of the Schrödinger equation with a non-zero external potential and given electron number N . Levy and Lieb's work showed that some other anti-symmetric wave-functions, which are not necessarily the ground-state wave-functions, can produce the ground-state density. These types of density are called *N -representable densities*. The second HK theorem ensures that in principle the ground-state wave-function can be constructed through the ground-state density and offers a search scheme for the ground-state density. In N -representable densities, the second HK theorem becomes invalid, since wave-functions other than the ground-state wave-function producing the ground-state density will not minimize the total energy. Fortunately, it was shown that an energy functional variational principle can be formulated for the N -representable densities and deployed as a practical method by enforcing some constraints^[8,9,11,12]. In the Levy constrained search approach, the ground-state wave-function can be determined among all anti-symmetric wave-functions producing the ground-state density by checking the minimization of the internal energy function

$$F[n_0] = \min_{\psi \rightarrow n_0} \langle \psi | \hat{T} + \hat{V}_{\text{ee}} | \psi \rangle, \quad (2.9)$$

instead of the minimization scheme for $E[n]$. Trivially, the v -representable densities already include this condition.

2.1.2 The Kohn-Sham equations

Even though the HK theorems construct a completely abstract foundation, they do not provide an applicable scheme. Fortunately, an approximate and applicable scheme has been introduced by Kohn and Sham in 1965^[13], namely the Kohn-Sham DFT (KS-DFT). The inspiration for the development of KS-DFT can be seen in the most commonly used quantum chemistry method, namely the Hartree-Fock method^[14–16]. Hartree proposed to express the ground-state wave-function in terms of the single-electron wave-function constructed by solving and updating the effective potential in iterative steps. However, this method cannot satisfy the anti-symmetry condition of the fermionic wave-function; it lacks the electron exchange interaction. Fock expanded the idea by expressing the multi-variable wave-function as the Slater determinant of the single-particle wave-functions to include the exact exchange interaction. Due to absence of electron correlations in such approach, such wave-function is just an approximation rather than the exact wave-function.

The approach taken in KS-DFT is to map the N -electrons interacting system to an N -electrons non-interacting auxiliary system with the same density, thus the density is expressed the sum over the norm square of the single-particle functions,

$$n(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2, \quad (2.10)$$

where ψ_i are called *KS wave-functions* with the normalization condition

$$\int d\mathbf{r} n(\mathbf{r}) = N$$

to ensure the conservation of the particle number. By using KS wave-functions, the kinetic energy functional in Eq. (2.5) can be expressed as

$$T[n] = \left(-\frac{1}{2m} \sum_i^N \int d\mathbf{r} \psi_i(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) + \Delta T[n] \right) = T_{\text{KS}}[n] + \Delta T[n], \quad (2.11)$$

where $T_{\text{KS}}[n]$ is the single particle kinetic energy functional and $\Delta T[n]$ is the correction to it to achieve the kinetic energy functional of the interacting system. The next step is to determine the electron-electron interaction energy functional. This term can be approximated with the

Hartree energy as in the Thomas-Fermi model in Eq. (2.2) with an additive correction as

$$V_{ee}[n] = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \Delta V_{ee}[n]. \quad (2.12)$$

Combining the functional terms, the energy functional can be written as

$$\begin{aligned} E[n] = & -\frac{1}{2} \sum_i^N \int d\mathbf{r} \psi_i(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ & + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\text{xc}}[n], \end{aligned} \quad (2.13)$$

where $E_{\text{xc}}[n] = \Delta T[n] + \Delta V_{ee}[n]$ is called *the xc-functional* and includes all many-body quantum interactions of the system.

The second HK theorem imposes a stationary principle to the ground-state energy functional, with the constraint that the integrated density should be equal the number particle, as

$$\delta \left[E[n] - \mu \left(\int d\mathbf{r} n(\mathbf{r}) - N \right) \right] = 0, \quad (2.14)$$

gives the following Euler-Lagrange equation

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta F[n]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) = \mu, \quad (2.15)$$

where μ is referred to as the chemical potential.

Taking the functional derivative of the total-energy functional in Eq. (2.13) with respect to $\psi_i^*(\mathbf{r})$, a set of equations, namely the KS equation, is obtained as

$$\left[-\frac{1}{2} \nabla_i^2 + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{ext}}(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.16)$$

where the second term is called *the Hartree potential*. The compact form is expressed in the atomic units as

$$\left[-\frac{1}{2} \nabla_i^2 + v_{\text{KS}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.17)$$

where $v_{\text{KS}}(\mathbf{r}) = v_H(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$ is called *the KS potential*, and

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}$$

.

Within the KS scheme, the original electronic eigenvalue problem of N -variable wave-function is reduced to N eigenvalue problems with single variables. However, a practical DFT application is still not possible due to fact that the xc-energy functional is yet unknown.

2.1.3 Exchange-correlation functional

The exchange-correlation energy functional $E_{\text{xc}}[n]$ includes all omitted many-body effects in Eq. (2.11) in the kinetic energy functional and Eq. (2.12) the electron-electron interaction energy functional. The very-first and most commonly used approximation for $E_{\text{xc}}[n]$ is the so called local density approximation (LDA), which was suggested by Kohn and Sham^[13]. LDA approximates $E_{\text{xc}}[n]$ by means of a homogeneous electron gas, with the density n in unit volume dV , as

$$E_{\text{xc}}^{\text{LDA}}[n] = \int_{dV} d\mathbf{r} n(\mathbf{r}) \epsilon_{\text{xc}}^{\text{heg}}[n(\mathbf{r})], \quad (2.18)$$

where $\epsilon_{\text{xc}}^{\text{heg}}[n(\mathbf{r})]$ can be determined exactly for any homogeneous electron gas with any given density using Quantum Monte Carlo simulation at the high density limit^[17–19]. Since LDA is modelled based on the homogeneous electron gas, it is expected to work mostly for systems with spatially slowly varying densities. In modern practical DFT applications, the most commonly used $E_{\text{xc}}^{\text{LDA}}[n]$ is the Perdew-Zunger parametrization^[20].

Even though LDA is based on the homogeneous electronic gas, it is also quantitatively effective for many other systems with inhomogeneous densities as well. The reasoning behind its good performance can be explained by examining the general form of $E_{\text{xc}}[n]$ as

$$E_{\text{xc}}[n] = \frac{1}{2} \int d\mathbf{r} n(\mathbf{r}) \int d\mathbf{r}' \frac{n_{\text{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.19)$$

where $n_{\text{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$ is called *the exchange-correlation hole*, normalized to -1 since the depletion of the charge in the exchange process leads to unit charge. Considering the isotropic

character of the Coulomb interaction, it was shown that $E_{xc}[n]$ depends on the spherical averaging of $n_{xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$ ^[21]. Hence, despite the failure of LDA to describe the exchange-correlation holes for the inhomogeneous densities, it succeeds in determining the spherical average of the exchange-correlation holes of equivalent homogeneous densities.

Some technical improvements to LDA are suggested by a more accurate description of the exchange-correlation holes such as the local spin-density approximation (LSDA)^[22]. Furthermore, introducing various degrees of gradients of the density additional to the density, to fulfil the normalization of the exchange-correlation hole to the unit charge namely in the generalized gradient approximation (GGA)^[23–25], shows improvements over LDA. Alternatively, a mixing scheme of the HF exact exchange energy and LDA-based functional are developed, namely the hybrid functionals^[26,27]

$$E_{xc}[n] = \alpha E_x^{HF}[n] + (1 - \alpha) E_{xc}^{LDA}[n], \quad (2.20)$$

where α is a mixing parameter either tuned to experimental results or determined by schemes such as in optimally-tuned hybrid functionals^[28].

2.2 The plane-wave implementation of KS-DFT

The KS-DFT scheme provides an applicable approach for the first-principles simulation of ground-state properties of realistic systems. Fundamentally, the problem is an eigenvalue problem to be solved, with the Hamiltonian matrix

$$H_{ij} = \langle \psi_i | \hat{h}_{KS} | \psi_j \rangle, \quad (2.21)$$

which is constructed by multiplying Eq/ (2.17) by ψ_j from left-hand side. In the spin-polarized case¹, the Hamiltonian matrix is $N \times N$. In spin degenerate cases, each spin-up-down electron pair is represented by a single KS wave-function; hence the dimension of the problem becomes

¹The KS equation in Eq. (2.17) can re-written including the spin number as

$$\hat{h}_{KS}^\sigma \psi_{i,\sigma}(\mathbf{r}) = \left[-\frac{1}{2} \nabla_{i,\sigma}^2 + v_{KS}^\sigma(\mathbf{r}) \right] \psi_{i,\sigma}(\mathbf{r}) = \epsilon_{i,\sigma} \psi_{i,\sigma}(\mathbf{r}),$$

where v_{KS}^σ carries the spin-polarization through the exchange-correlation function approximated with the spin-polarized extension of LDA, namely *the local spin density approximation* (LSDA)^[29].

$N/2 \times N/2$. Such a self-consistent eigenvalue problem cannot be solved directly for most cases. However, the ground-state density can be determined by *the self-consistent field* (SCF) procedure by the virtue of the variational principle. The problem can be solved iteratively by improving the accuracy in KS wave-functions leading to the minimisation of the total KS energy of a system. However, such an iterative approach requires many operations, which are computationally expensive in each iteration. Thus, the problem is mapped to more practical methods through many well-studied algorithms and numerical approximations.

2.2.1 KS-DFT for periodic systems

Idealised solids can be described as repeating identical units, namely *the unit cell*, for which the smallest possible unit cell is called *the primitive unit cell*. Any unit cell contains integer multiples of the primitive unit cell; hence, any conditions applying to the primitive unit cell can be easily expanded to any unit cell of the solid. Taking advantage of this translational invariance, the single-particle electronic wave-function can be written via Bloch's theorem^[30], as

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{i,\mathbf{k}}(\mathbf{r}), \quad (2.22)$$

where *the reciprocal wave-vector* $\mathbf{k}$ is *the crystal momentum vector* lying in the first Brillouin zone, which is the unit cell in the reciprocal space corresponding to the real-space unit cell. The so called Bloch function $\psi_{i,\mathbf{k}}(\mathbf{r})$ has the same periodicity of the crystal periodicity defined by the unit cell vectors $\mathbf{R} = \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$ as

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{i,\mathbf{k}}(\mathbf{r} + \mathbf{R}). \quad (2.23)$$

For a periodic system with N_i cells in $i = 1, 2, 3$ directions, the Born-van Kármán boundary conditions becomes

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \psi_{i,\mathbf{k}}\left(\mathbf{r} + \sum_i^3 N_i \mathbf{a}_i\right), \quad (2.24)$$

where $n_i < N_i$ is an integer. By this boundary condition, the following relation arises to satisfy Bloch's theorem:

$$e^{i\mathbf{k}\cdot\sum_i^3 N_i \mathbf{a}_i} = 1 \implies \mathbf{k} \cdot \mathbf{a}_i = 2\pi l, \quad (2.25)$$

for some integer l . Hence, the $\mathbf{k}$ -wave vector $\mathbf{k}$ can be written as

$$\mathbf{k} = \sum_i^3 \frac{n_i}{N_i} \mathbf{b}_i, \quad (2.26)$$

where $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ and $\mathbf{b}_j$ are called *the reciprocal space unit vectors*. For $n_i = N_i$, this region spanned by wave-vector in Eq. (2.26) is called *the first Brillouin zone* containing all information about the system. Hence, KS wave-functions can be written as

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \psi_{i,\mathbf{k}+\mathbf{G}}(\mathbf{r}) \quad (2.27)$$

for any arbitrary vector $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$ of the reciprocal space, namely the first Brillouin zone. The first Brillouin zone is a continuous region for $N_i \rightarrow \infty$. In practical applications, a carefully chosen set of points in the Brillouin zone are used for discretisation of the problem in numerical simulations. This is called *Brillouin zone sampling*. The KS Hamiltonian is written in reciprocal space for a given point $\mathbf{k}$ as^[31]

$$\hat{h}_{\mathbf{k}} = -\frac{1}{2} (i\mathbf{k} + \nabla)^2 + v_{\text{KS}}(\mathbf{r}), \quad (2.28)$$

for the full local KS potential.

Mapping the problem onto the reciprocal space has certain advantages in terms of the computational efficiency by taking advantage of the fast Fourier transform (FFT)^[32] algorithms. The long-ranged terms like v_H and the ionic potential producing v_{ext} become local in reciprocal space, for example.

2.2.2 The pseudo-potential approximation

During the formation of molecules or crystals, the core states of parent atoms are expected to be modified only slightly, as they are tightly bound to nuclei, whereas the valence states are modified significantly as they are less strongly bounded to nuclei due to Coulombic screening by the core states. Hence, the KS equation may be solved for the *pseudo*-valence states with a

first-order correction to the KS potential

$$\begin{aligned} [h_{\text{KS}}(\mathbf{r}) + v_{\text{nl}}(\mathbf{r}, \mathbf{r}')] \psi_v^{\text{pseudo}}(\mathbf{r}) &= \epsilon_v \psi_v^{\text{pseudo}}(\mathbf{r}), \\ v_{\text{nl}}(\mathbf{r}, \mathbf{r}') &= \sum_j^{\text{core}} (\epsilon_v - \epsilon_j) \psi_v^{\text{pseudo}}(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_j(\mathbf{r}') \psi_v^{\text{pseudo}}(\mathbf{r}'), \end{aligned} \quad (2.29)$$

where ϵ_v is the KS energy of the valence state, φ_j and ϵ_j are the atomic core state and the corresponding eigenenergy. This method is known as *the pseudo-potential approximation*^[33–36], reduces the computational cost drastically by means of ignoring the explicit treatment of the core states. The accuracy in determining the true KS energy of the valence state depends on the construction of the potential in Eq. (2.23), namely *the pseudo-potential*. The pseudo-potentials used throughout this thesis are *the norm-conserving pseudo-potentials*^[37–39] produced by the pseudo-potential generator OPIUM^[40].

2.2.3 The plane-wave basis

Widely used KS-DFT-based software such as Quantum Espresso (QE)^[41,42], Abinit^[43–45] *etc.* use complex plane-waves as the basis functions, to express the KS wave-functions in Eq (2.21) as

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{i,\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (2.30)$$

where the $\mathbf{G}$ are the reciprocal vectors. A complete basis set of plane-waves is required to produce KS wave-functions exactly, though it is not possible in numerical simulations. Instead, a subset of plane-waves is chosen at suitably chosen grid points in reciprocal space, with a truncation scheme. There, *the kinetic energy cut-off energy* $E_{\text{cut-off}}$ is expressed as

$$\frac{1}{2}|\mathbf{k} + \mathbf{G}|^2 < E_{\text{cut-off}}. \quad (2.31)$$

The total KS energy converges monotonically with an increasing value of $E_{\text{cut-off}}$ as the variational principle holds.

Despite the restricted number of plane-waves, such an expansion is still a burden in terms of the computational cost for a system with a reasonable electron number. Hence, the pseudo-potential approximation is still essential to reduce of number of the KS wave-functions used in

routine simulations. With these two crucial approximations, the number of plane-waves going into numerical simulations is substantially reduced. The plane-wave basis is also a reasonable choice for working in reciprocal space; FFT algorithms are quite efficient due the appropriate forms of plane-waves.

2.2.4 Iterative solution of KS equations

Despite the substantial reduction of the size of problem using the pseudo-potential approximations and FFT algorithms with an appropriate basis set, the direct solution of the KS equations with the conventional linear algebra methods is both impractical and unnecessary due to fact that the number of basis functions $N_{basis} \gg N_{occ}$. Fortunately, computational methods for the eigenvalue problem with the large matrix sizes are well-studied and optimized. The most commonly applied methods in condensed matter are *the Davidson diagonalisation*^[46] and *the conjugate gradient diagonalisation*^[47] that are based on the inverse iteration of the generalised Rayleigh quotient^[48]. The generalised Rayleigh quotient for the KS Hamiltonian in the plane-wave basis $\{\phi\}$ for the trivial vector $\mathbf{x}_i$, given by

$$\psi_i(\mathbf{r}) = \min_{\mathbf{x}_i} \frac{\mathbf{x}_i^\dagger \mathbf{h}_{KS}^\phi \mathbf{x}_i}{\mathbf{x}_i^\dagger \mathbf{S}^\phi \mathbf{x}_i}, \quad (2.32)$$

is minimized iteratively until an accuracy threshold achieved under the constraint

$$\mathbf{x}_i^\dagger \mathbf{S}^\phi \mathbf{x}_j = \delta_{ij}. \quad (2.33)$$

While Davidson algorithms are faster, the conjugate gradient algorithm is generally more robust.

2.2.5 Assignments of occupancies and Fermi levels

In principle, the minimum number of KS states needed is $N/2$ for the non-spin-polarized case. However, the SCF cycle is not informed beforehand about the occupancies of KS states; hence, occupancies are assigned once the KS states are evaluated and Eq. (2.10) becomes

$$n(\mathbf{r}) = \sum_i^{N_b} f_i |\psi_i(\mathbf{r})|^2, \quad (2.34)$$

where N_b is the number of bands and the f_i are occupancies. In the ideal case, $N_b = N/2$ and $f_i = 2$; since spin-up-down pairs are degenerate in non-spin-polarized cases at zero temperature. By construction, DFT is an absolute zero temperature theory due to the second HK theorem, whereas real systems are at some finite temperature. For systems with insulating band-gaps, the finite temperature effects can be neglected as, at low temperatures, the highest occupied states and lowest unoccupied states are distinguishable in terms of their energies. The Fermi levels of such systems are generally aligned at the midpoint of their insulating band-gaps.

In metallic cases, occupancies are discontinuous at finite temperatures due to the discrete sampling of the Brillouin zone as the low-energy unoccupied states are close to the high energy occupied states. Commonly, this discontinuity is patched by introducing a smearing scheme for the states around the Fermi level; hence, one needs to include certain number of an additional KS states $N_b > N/2$ both to ensure KS states' orthogonality and to have sufficient number of KS states for the description of the occupancies around the Fermi level. The smearing scheme is a mathematical tool rather than a physical condition to mimic finite temperature effects in metals. Various smearing schemes in common usage are the Fermi-Dirac occupation function^[49], Methfessel-Paxton smearing^[50], Marzari-Vanderbilt cold smearing^[51]. Within these schemes, the Fermi level is commonly defined as the half-occupancy point.

2.2.6 The conduction states of KS-DFT

The self-consistent procedure to determine the single-particle KS orbitals can be applied only to the valence states as DFT relies on the variational principle by construction. Moreover, any property of the system beyond the ground-state requires a time-dependent theory such as time-dependent DFT (TDDFT) or many-body perturbation methods such as Green's function based approximations. However, a non-self-consistent field (NSCF) approach can be used to obtain approximate conduction electronic states by using the ground-state density from the self-consistent field calculations. Direct diagonalisation of the Hamiltonian constructed from the calculated valence KS states and some sufficient additional conduction KS states is required with the ground-state density. Such an approach relies on the orthogonality conditions of the KS states. However, the conduction states evaluated through the NSCF approach are representations of non-interacting excited states rather than exact excited states.

2.3 Conclusion

In this chapter, DFT and its applicable formulation KS-DFT were introduced starting from the foundations of the formalism, the HK theorems. Furthermore, some essential approximations for efficient computational implementations, particularly for solids, were discussed. Using the NSCF procedure, an approximate approach for the conduction manifold from the KS-DFT ground-state was briefly mentioned. The series of approximations deployed through this chapter will be important for us to understand the limitations and possible failures of conventional KS-DFT as a starting point in later parts of this work. Despite its success, KS-DFT within plane-wave implementations is still limited in terms of sizes of systems as it scales with $O(N^3)$. In the next chapter, an alternative formulation of KS-DFT suitable for linear-scaling, with appropriate approximations, will be introduced for future reference.

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Chapter 3

Linear-scaling density-functional theory

By construction, plane-wave based KS-DFT scales as $\mathcal{O}(N^3)$ in terms of the central processing unit (CPU) hours and as $\mathcal{O}(N^2)$ in terms of the random-access memory (RAM). Despite growing high performing computing technologies, plane-wave KS-DFT implementations are currently limited to the moderate system sizes as FFT algorithms are not suitable for the heavy parallelisation due to their requirements for instantaneous communication throughout all processors^[1] and the orthogonality conditions of the KS states. These technical constraints limit plane-wave KS-DFT implementations to small molecular systems, small nano-clusters, or ideal periodic systems with small number of atoms in their unit cells.

Linear-scaling KS-DFT (LS-KS-DFT)^[1–3] provides an approach to perform realistic first-principles simulations of spatially more complex large systems such as biological systems^[4–6], and systems with point defects^[7–9] with $\mathcal{O}(N)$ computational scaling with respect to electron number N and comparable accuracy to conventional KS-DFT implementations. Any LS-KS-DFT implementation is based on using a spatially localized basis set in real space to exploit *the near-sightedness*^[10,11] of quantum many-particle systems.

In this chapter, a brief overview of LS-KS-DFT will be given particularly in reference to the Order-N Electronic total-energy Package (ONETEP)^[12–18], as it is primary software used for a linear-scaling simulations and further implementations in this work. However, the core ideas are common for any LS-KS-DFT implementations. As the basis of any linear-scaling implementation, the density-matrix formalism and its spatial localisation will be introduced. The particular basis, support basis functions, and the general outline of the SCF algorithm adopted in ONETEP, will be discussed. Lastly, some methods used to construct unoccupied manifolds suitable for the linear-scaling formalism will be briefly mentioned.

3.1 The density-matrix formalism

The daunting constraint of orthogonality of the individual KS wave-functions representing each state can be replaced with an equivalent condition by formulating the problem in terms of *the*

density-matrix expressed as

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_i^N f_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}'), \quad (3.1)$$

with two conditions that ensure particle number conservation and Pauli's exclusion principle^[19]. The former condition is expressed as

$$\text{Tr}[\hat{\rho}] = N, \quad (3.2)$$

where the latter one known as *the idempotency* is

$$\hat{\rho}^2 = \hat{\rho} \implies \rho(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' \rho(\mathbf{r}, \mathbf{r}'') \rho(\mathbf{r}'', \mathbf{r}'). \quad (3.3)$$

The diagonal elements of density-matrix recovers the electronic density as

$$n(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r}). \quad (3.4)$$

Within these formulations, the mutual orthogonality conditions for each pair of KS wave-functions are bypassed by avoiding constructing KS wave-functions explicitly in each iteration of SCF. However, the idempotency and the particle number conservation conditions are still challenging in terms of efficient implementation. ONETEP employs advanced methods to maintain and improve the density-matrix throughout the energy minimisation process. We would like to refer the reader for more details to Refs. 15,20–23.

3.2 Localisation of the density-matrix

Wannier proposed that electronic wave-functions can be expressed as spatially localized functions on unit cells with the corresponding vector $\mathbf{R}^1$, namely as Wannier functions^[24]. The Wannier functions are the Fourier transform of the single-particle electronic wave-functions in Eq. (2.23) over the first Brillouin zone with

$$w_{i,\mathbf{R}}(\mathbf{r}) = \left(\frac{1}{V_{\text{FBZ}}} \right)^{1/2} \int d\mathbf{k} e^{-i\mathbf{k} \cdot \mathbf{R}} \psi_{i,\mathbf{k}}(\mathbf{r}), \quad (3.5)$$

¹In the case of finite systems, the simulation cell serves as the unit cell.

where V_{FBZ} is volume of the first Brillouin zone. The density-matrix for an insulating system¹ becomes in terms of Wannier functions,

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i, \mathbf{R}} f_i w_{i, \mathbf{R}}(\mathbf{r}) w_{i, \mathbf{R}}^*(\mathbf{r}'). \quad (3.6)$$

Wannier functions for insulating systems are exponentially decaying with distance $\tilde{r} = |\mathbf{r} - \mathbf{r}'|$ ^[25–27]. Hence, the elements of density-matrix in Eq. (3.6) becomes exponentially decreasing with increasing distance. Consequently, local potentials and local observables are negligibly dependent on spatially long-distance elements of density-matrix. By this corollary, a truncation scheme for the density-matrix can be suggested as

$$\rho(\mathbf{r}, \mathbf{r}') \approx 0 \quad \text{for} \quad |\mathbf{r} - \mathbf{r}'| > r_{\text{cut}}, \quad (3.7)$$

where r_{cut} is a cut-off radius. By making an appropriate choice of spatially highly localized basis set with this truncation scheme, the density-matrix and its corresponding Hamiltonian can be constructed as highly sparse matrices, which can be evaluated with linear-scaling effort using appropriate algorithms.

3.3 Support functions and basis functions

As discussed in Chap. 2, KS wave-functions are expressed in terms of a finite set of functions truncated with some conditions, in practical applications. For the sake of maintaining linear-scaling effort, non-orthogonal and spatially well localized basis sets are desired for an optimum localisation of the density-matrix. For such a basis set, the density-matrix can be written as^[28]²

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\alpha, \beta} \phi_{\alpha}(\mathbf{r}) K^{\alpha\beta} \phi_{\beta}^*(\mathbf{r}'), \quad (3.8)$$

¹Occupancies of KS wave-functions close to the Fermi level are $\mathbf{k}$ -dependent for non-insulating systems as briefly mentioned in Subsec. 2.2.5; hence, the Fourier transform in Eq. (2.23) is not well-defined.

²In the case of a non-orthogonal set of functions, a dual set of functions with contravariant and covariant tensorial properties are required to be able to define tensor products^[29,30] such as

$$\langle \psi_{\alpha} | \phi^{\beta} \rangle = \delta_{\alpha}^{\beta}, \quad |\phi^{\beta}\rangle = |\phi_{\alpha}\rangle S^{\alpha\beta}, \quad \text{where} \quad S^{\alpha\beta} = \langle \phi^{\alpha} | \phi^{\beta} \rangle \quad \text{and} \quad S^{\alpha\beta} = (S_{\alpha\beta})^{-1}.$$

Hence, Greek alphabet indices are for non-orthogonal function sets with the correct tensorial properties; while Latin alphabet indices are used for orthogonal function sets as before.

where $\{\phi_\alpha\}$ are called *the support functions*, and $K^{\alpha\beta}$ is *the density kernel*, which is given by

$$K^{\alpha\beta} = \sum_i \langle \phi^\alpha | \psi_i \rangle f_i \langle \psi_i | \phi^\beta \rangle = \sum_i M_i^\alpha f_i M_i^{\beta\dagger}. \quad (3.9)$$

The total energy of the independent particle system $E_{IP}[\hat{\rho}]$ and the particle number conservation in these dual function basis set can be re-expressed, respectively

$$E_{IP}[\hat{\rho}] = 2K^{\alpha\beta} H_{\beta\alpha} \quad \text{and} \quad N = 2K^{\alpha\beta} S_{\beta\alpha}, \quad (3.10)$$

where $H_{\alpha\beta}$ is

$$H_{\alpha\beta} = \langle \phi_\alpha | \hat{h}_{KS} | \phi_\beta \rangle. \quad (3.11)$$

ONETEP uses the non-orthogonal generalized Wannier functions (NGWFs) as the support functions. NGWFs are real valued functions spatially highly localized on the atomic centres; hence, they provide an appropriate function set for the linear-scaling implementation. Using an orthonormal variational function set namely *the psinc functions* to expand NGWFs also provides an efficient scheme to apply the density-matrix formalism to the extended periodic system, in an equivalent way to plane-wave implementations.

3.4 The psinc basis

ONETEP code uses the periodic cardinal sine (psinc) function set as the variational basis to expand the NGWFs. The psinc function is expressed for the grid point n as

$$D_{\{n\}}(\mathbf{r}) = D(\mathbf{r} - \mathbf{r}_{\{n\}}) = \prod_i \frac{1}{N_i} \sum_{p_i=-J_i}^{J_i} e^{ip_i \mathbf{b}_i \cdot (\mathbf{r} - \mathbf{r}_{\{n\}})}, \quad (3.12)$$

where $\{\mathbf{b}_i\}$ are the reciprocal unit vectors; N_i is the total number of the grid point in i^{th} direction, which satisfies $N_i = 2J_i + 1$, where $J_i \in \mathbb{N}$ to ensure maximisation at $\mathbf{r}_{\{n\}}$ and vanishing amplitude at finite size borders of simulation box. The delta-like center $\mathbf{r}_{\{n\}}$ of the

psinc functions defined as

$$\mathbf{r}_{\{n\}} = \sum_i^3 \frac{n_i}{N_i} \mathbf{a}_i. \quad (3.13)$$

NGWFs are expressed in the basis of the psinc functions for a given localisation center as

$$\phi_\alpha^D(\mathbf{r}) = \sum_{n_1}^{N_1-1} \sum_{n_2}^{N_2-1} \sum_{n_3}^{N_3-1} C_{\{n\},\alpha} D_{\{n\}}(\mathbf{r}), \quad (3.14)$$

where $C_{\{n\},\alpha}$ are expansion coefficients, which are nothing but the overlap integrals of the psinc functions and NGWFs

$$C_{\{n\},\alpha} = \int d\mathbf{r} D_{\{n\}}(\mathbf{r}) \phi_\alpha(\mathbf{r}) = \frac{V_{\text{cell}}}{N_{\text{cell}}} \phi_\alpha^D(\mathbf{r}_{\{n\}}), \quad (3.15)$$

where $N_{\text{cell}} = N_1 \times N_2 \times N_3$.

The choice of psinc functions to express NGWFs has some advantages as discussed in more detail in Refs. 31,32. The direct relation between the grid spacing of the psinc functions to the number of the plane-wave provides that the kinetic energy cut-off in Eq. (2.31) in plane-wave KS-DFT implementations remains applicable. Furthermore, the psinc functions are advantageous for efficient FFT, which is more suitable to evaluate the kinetic energy operator in reciprocal space without losing the linear-scaling feature by limiting the Fourier transform box to local unit regions centred on NGWFs^[12].

3.5 Energy minimisation with nested loops

The energy functional becomes a functional of the density kernel and the NGWFs through the density-matrix in Eq. (3.8) as

$$E[\rho] = E[K^{\alpha\beta}, \{\phi_\alpha\}] = E[K^{\alpha\beta}, C_{\{n\},\alpha}]. \quad (3.16)$$

The ground-state energy can be obtained by minimising this energy functional in two steps simultaneously updated in each iteration. Starting from an initial guess for $K^{\alpha\beta}$, the functional

of the expansion coefficient is optimised as

$$E_0 = \min_{C_{\{n\},\alpha}} L[C_{\{n\},\alpha}], \quad (3.17)$$

where

$$L[C_{\{n\},\alpha}] = \min_{K^{\alpha\beta}} E[K^{\alpha\beta}, C_{\{n\},\alpha}]. \quad (3.18)$$

The outer loop minimises the functional E for the fixed $K^{\alpha\beta}$, while the inner loop minimized the functional L for the updated $C_{\{n\},\alpha}$ with respect to $K^{\alpha\beta}$ [31].

3.6 The unoccupied bound states within LS-KS-DFT

ONETEP minimises the total energy with respect to the density-matrix and NGWFs, whereas the KS wave-functions are not constructed explicitly during the minimisation procedure. The final KS states can be recovered by directly diagonalising the KS Hamiltonian in the optimised NGWF basis at the very end of the SCF procedure. Hence, ONETEP only optimises the set of NGWFs for the occupied manifold, and a separate set of NGWFs are required to represent the unoccupied manifold. Since the orthogonality condition is hidden in the idempotency for the sake of linear-scaling effort, any NSCF procedure needs some special approaches suitable for linear-scaling.

Various methods to optimise NGWFs for the unoccupied manifold are presented and discussed in great detail in terms of their accuracy, computational cost and suitability for linear-scaling in Refs. 33–37. ONETEP uses *the projection method* [36,37] in practice to optimise the second set of NGWFs to represent unoccupied manifold.

In the projection method, the core idea is inspired by the fact that eigenvalues of the projected Hamiltonian, which is constructed by projecting the density-matrix operator

$$\hat{\rho} = \sum_i^N |\psi_i\rangle\langle\psi_i|, \quad (3.19)$$

on the KS Hamiltonian, are 1 for the occupied manifold. Similarly, eigenvalues of the projected Hamiltonian, which is constructed by projecting $(\hat{I} - \hat{\rho})$ on the KS Hamiltonian, are expected to be 1 for unoccupied manifold. However, such projection may lead to some non-Hermitian

matrix as both the density-matrix and the KS Hamiltonian are sparse matrices in a localised basis. Solution of eigenvalue problems with a non-Hermitian matrix are more challenging computationally^[38]. Such an issue can be avoided by double projections such as

$$\left(\hat{I} - \hat{\rho}\right) \hat{h}_{\text{KS}} \left(\hat{I} - \hat{\rho}\right) = \hat{h}_{\text{KS}} - \hat{\rho} \hat{h}_{\text{KS}} \hat{\rho}. \quad (3.20)$$

Within such a projection, eigenvalues of occupied states are 0, which is not an issue when the Fermi level is somewhere in the bound manifold, whereas unoccupied states have negative energies. However, a more robust protocol would be to shift all energies of occupied states until the lowest-energy occupied state exceeds the highest-energy unoccupied state in terms of energy. Such a correction is introduced by a shift to the KS Hamiltonian, which yields the effective projected Hamiltonian

$$\hat{h}_{\text{KS}} - \hat{\rho} \left(\hat{h}_{\text{KS}} - \sigma \right) \hat{\rho}, \quad (3.21)$$

where the shift σ is set higher than the highest-energy unoccupied state; hence, it mostly stays as constant. It can also be updated, if necessary, by considering the change in the energy of the highest unoccupied state during the minimisation process. Such a shift practically moves the energy of highest occupied state below zero. The shifted and projected Hamiltonian is expressed in ONETEP implementation as

$$\begin{aligned} (H_{\chi}^{\text{proj}})_{\alpha\beta} &= \langle \chi_{\alpha} | \hat{h}_{\text{KS}} - \hat{\rho} \left(\hat{h}_{\text{KS}} - \sigma \right) \hat{\rho} | \chi_{\beta} \rangle \\ (H_{\chi})_{\alpha\beta} &- \left(T^{\dagger} K H_{\phi} K T \right)_{\alpha\beta} - \sigma \left(T^{\dagger} K S_{\phi} K T \right)_{\alpha\beta}, \end{aligned} \quad (3.22)$$

where $\{\phi_{\alpha}\}$ and $\{\chi_{\alpha}\}$ are NGWFs basis sets for occupied and unoccupied manifolds respectively. The cross occupied-unoccupied overlap matrix is defined as $T_{\alpha\beta} = \langle \phi_{\alpha} | \chi_{\beta} \rangle$. The resolution of identity for occupied states are already present in the basis of $\{\phi_{\alpha}\}$ priorly from ground-state calculation. Hence, similar energy minimisation process can be performed for the $\{\chi_{\alpha}\}$ basis, and its corresponding density kernel, to obtain non-interacting unoccupied states. As expected, such an approach is not as robust as its plane-wave implementation counterpart due to its bypassing of the orthogonality conditions of KS states during the minimisation for the sake of the linear-scaling effort; hence, it requires very careful use in practical simulations.

3.7 Conclusion

In this chapter, a concise overview of the linear-scaling KS-DFT and its implementation within ONETEP were provided. While the scaling of the problem is reduced drastically, it is not suitable for metallic systems as it requires constant occupancies throughout system. Also, it is less robust for constructing the unoccupied manifold by due to the lack of the explicit orthogonality condition on KS wave-functions during simulation. However, it is a potent tool for certain classes of system such as spatially complex and large insulating systems. Within this overview, the main methods for obtaining ground-state electronic structures for perturbative approaches to spectra were introduced. In the next chapter, some limitations and systematic errors of KS-DFT, which become drastic in spectral simulations of transition-metal systems, will be discussed for a complete picture of our starting point.

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Chapter 4

Limitations and systematic errors of KS-DFT

KS-DFT provides an effective tool for ground-state electronic structure as well as an affordable starting point for perturbative approaches to spectra within LRT. However, KS-DFT has its limitations as it is a ground-state theory. It has also systematic errors due to (semi-) local approximations to xc-functionals. While such drawbacks can be negligible for some systems, they may become catastrophic for certain systems, such as many transition-metal systems.

In this chapter, these drawbacks will be addressed in order to attain well-controlled simulations starting from KS-DFT. First, some conceptual limitations of KS-DFT and KS wave-functions will be briefly discussed. Then, the major and well-known systematic errors in approximate KS-DFT, namely *self-interaction error* (SIE) and its consequences in many-body cases, i.e. the *delocalisation error*, will be described. The most effective and feasible approach to correct SIE using a Hubbard type model, namely DFT+ U , will be outlined in detail. Lastly, an essential correction to the canonical relation in Eq. (1.28) in the case of the pseudo-potential approximation will be explained.

4.1 The conceptual limitations of KS-DFT

By construction, DFT is principally restricted to ground-state properties by means of the second Hohenberg-Kohn theorem, which relies on the variational principles of quantum systems. Thus, any properties beyond the ground-state are not accessible even if the exact DFT were hypothetically possible in realistic applications. Moreover, KS-DFT maps an interacting many-body system to a non-interacting auxiliary many-body system with an identical density, where this auxiliary system is a mathematical tool rather than an actual physical system. KS wave-functions are mathematical constructions rather than physical electronic states^[1], unlike in Hartree-Fock theory^[2-4] by virtue of the absence of a generalised Koopmans' theorem^[5,6] except the highest occupied KS wave-function, which corresponds to the first ionisation energy (or chemical potential in metallic cases) by Janak's theorem^[7]. Consequently, connections of KS wave-functions and energies to physical observables such as single-particle transitions are not well established, even for simple cases. For instance, it is well established that the linear-response starting from KS-DFT with xc-functionals such as LDA overestimates the electric dipole polarisation of standard small molecules such as $(\text{H}_2)_n$

chains^[8–12] for increasing chain-length.

4.2 Systematic errors in KS-DFT

Beside the conceptual limitations of KS-DFT, LDA and GGA-based xc-functionals give rise to certain systematic errors leading to inaccurate descriptions of ground-state electronic structures and, consequently, of excited-state properties within the linear-response. Formally, such systematic errors can be illustrated by recalling the approximation to the two-particle density term in the Hartree interaction term in Eq. (2.12) in terms of the product of the single-particle densities with a corrective term encapsulated by the xc-functional. The single-particle density-density interaction term allows self-interaction of electron density with itself, whereas such an unphysical interaction is expected to be cancelled by the xc-hole term in Eq. (2.19), in principle. However, approximate xc-functionals fail to cancel out such errors particularly for inhomogeneous densities due to highly localised features in density as discussed in Subsec. 2.1.3. Infamously, this cancellation error namely *the single-particle SIE* has been demonstrated extensively in the single-electron cases such as the molecule H_2^+ ^[13–16]. Despite straightforward observation of SIE in the single electron case, it is more complicated in the many-body case; hence, the concept of *the many-body self-interaction error*, or *the delocalisation error*^[12,17–21] is developed to understand the consequences of the single-particle SIE in many-body systems.¹

4.2.1 Fractional charges

In principle, SIE occurs for any system; however, it becomes significant for certain systems such as the ones with fractional electron charges^[16,22,23]. The total energy curve with respect to the total occupation of an open quantum system has been demonstrated to be piece-wise linear for the exact xc-functionals^[22] as

$$E(N + q) = (1 - q)E(N) + qE(N + 1), \quad (4.1)$$

where $0 < q < 1$. For exact xc-functionals producing this feature, *the highest occupied molecular orbital* (HOMO) and *the lowest unoccupied molecular orbital* (LUMO) energies are

¹For avoiding any complication, the term ‘*SIE*’ will be used exclusively for the single-particle SIE, whereas ‘*the delocalisation error*’ will be used for the many-body SIE in this work.

equal to the first ionization energy^[22,24] and the electron affinity^[25] as

$$\epsilon_{HOMO} = -I, \quad \text{and} \quad \epsilon_{LUMO} = -A, \quad (4.2)$$

where I and A are connected to *the hardness* in molecules^[26,27], or *the fundamental band-gap* in solids with the help of Janak's theorem^[7] as^[25]¹

$$E_{\text{gap}} = I - A = \epsilon_{LUMO} - \epsilon_{HOMO}, \quad (4.3)$$

and *the chemical potential* as

$$\mu = \begin{cases} -I(N_0) = E(N_0) - E(N_0 - 1), & \text{if } N - 1 < N_0 < N \\ -A(N_0) = E(N_0 + 1) - E(N_0), & \text{if } N < N_0 < N + 1. \end{cases} \quad (4.4)$$

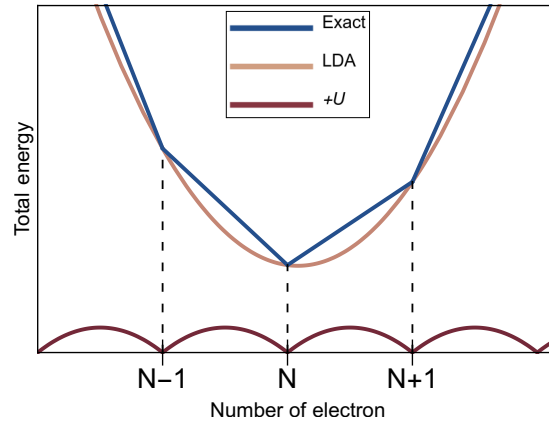


Figure 4.1: The total energy as a function of the electron count of an open quantum system within approximate DFT. Difference between two curves is approximately the $+U$ correction to approximate DFT provided by DFT+ U . This illustration is replicated from the Ph.D. dissertation of Cococcioni in Ref. 28.

The piece-wise linear feature of the total energy curve described in Eq. (4.1) is crucial to obtain

¹For approximate xc-functionals, Eq.(4.3) requires an additional terms to include the derivative discontinuity of the exact energy curve such as

$$E_{\text{gap}} = I - A = \epsilon_{LUMO} - \epsilon_{HOMO} + \Delta_{xc},$$

where Δ_{xc} is defined as

$$\Delta_{xc} = \lim_{q \rightarrow 0} \left(\left. \frac{\delta E}{\delta N} \right|_{N_0+q} - \left. \frac{\delta E}{\delta N} \right|_{N_0-q} \right).$$

the hardness of molecules, and the fundamental band-gap of solids, which play critical roles in determination of the response to EM radiation^[29]. LDA-based xc-functionals produce convex quadratic energy curves with respect to the occupancy rather than the piece-wise linear curves in Fig. 4.1. The difference between the energy curves produced by the exact xc-functional and LDA is here termed the delocalisation error.

4.2.2 The delocalisation error

The deviation from the piece-wise linear behaviour of the total energy curve with respect to the occupation number for the fractional charge in approximate KS-DFT becomes more significant with the increasing localisation of the electron density^[12]. This behaviour is expected for LDA as it favours fractional and delocalised charge distributions over integer and localised charge distributions by construction. Consequently, the delocalisation error is expected to be large for systems with the partially filled states of localised nature due to spatial confinement of charge density such as in transition-metal oxides (TMOs) and coordination complexes. However, delocalisation errors can be observed even for systems with less localised charge densities such the metallic solids^[12] and closed-shell organic molecules^[30,31].

4.3 The Hubbard U correction of SIE

The most widely used approach to correct SIE and delocalisation error for systems with highly localised orbitals is the computationally expedient Hubbard U correction (DFT+ U) method^[32–40]¹. The fundamental idea behind DFT+ U , within its modern interpretation, is to account the *overestimated* Coulomb interaction on the highly localised subspace by LDA-based functionals explicitly. The total energy is expressed in DFT+ U as

$$E_{\text{DFT}+U} = E_{\text{LDA}} + E_{\text{Hub}} - E_{\text{dc}}, \quad (4.5)$$

where E_{Hub} is the on-site energy known as the Hubbard energy and E_{dc} is the double-counting term, which cancels the LDA contribution for the target subspace to avoid double-counting. A

¹Despite the general consensus of the terminology, + U correction is indeed applied to the approximate KS-DFT with rather than DFT itself. It should be stressed that DFT is a complete theory itself; hence some literature prefer to use LDA+ U , GGA+ U , *etc.* depending on the approximate functional.

rotationally-invariant form is expressed as^[37,41,42]

$$\begin{aligned} E_U[\{n^{I\sigma}\}] &= E_{\text{Hub}}[\{n^{I\sigma}\}] - E_{\text{dc}}[\{n^{I\sigma}\}] \\ &= \frac{1}{2} \sum_{I\sigma} \sum_{m,m'} \left\{ (U^I - J^I) [n_{mm'}^{I\sigma} \delta_{mm'} - n_{mm'}^{I\sigma} n_{m'm}^{I\sigma}] + J^I n_{mm'}^{I\sigma} n_{m'm}^{I\sigma'} \right\} \end{aligned} \quad (4.6)$$

where I is the correlated site index, σ is the spin quantum number and $\{n_{mm'}\}$ is the KS density-matrix with the averaged on-site like-spin interaction U^I and unlike-spin interaction J^I . The KS density-matrix for the on-site localised subspace is represented as

$$n_{mm'}^{I\sigma} = \langle \varphi_m^I | \hat{\rho}^\sigma | \varphi_{m'}^I \rangle, \quad (4.7)$$

where $\rho^\sigma = \sum_i^{\text{occ}} |\psi_i^\sigma\rangle \langle \psi_i^\sigma|$ is the KS density operator for σ -spin channel and $\{\varphi_m\}$ is the set of some localised orbitals spanning the correlated site I . The full-form in Eq. (4.6) is called DFT+ $U + J$; however the unlike-spin interaction corrections are commonly ignored, or partially introduced via the single effective Hubbard parameter $U_{\text{eff}}^I = U^I - J^I$. Ignoring the unlike-spin interaction correction, the Hubbard functional is simplified to

$$E_U[\{n^{I\sigma}\}] = \frac{1}{2} \sum_{I\sigma} \sum_{m,m'} U^I [n_{mm'}^{I\sigma} \delta_{mm'} - n_{mm'}^{I\sigma} n_{m'm}^{I\sigma}]. \quad (4.8)$$

DFT+ U provides an effective approach to correct SIE and delocalisation error within first-principles methods, particularly by means of the direct calculation of the Hubbard $U(+J)$ parameters, for which a number of methods have been proposed^[38–40,43–45]. Moreover, it is compatible with linear-scaling methods^[46,47] for spatially complex systems.

4.3.1 The Hubbard U and J parameters

The efficiency and robustness of the DFT+ $U(+J)$ method is essentially dependent on the determination of the Hubbard parameters self-consistently within the KS-DFT scheme. A common approach is to use linear-response to determine the Hubbard parameters^[38,39], later also adopted for the $+J$ parameter^[48]. In this work, we employ the recently-introduced minimum-tracking variant of linear-response as implemented in the ONETEP code^[49], and in particular, its spin-specific extension introduced in Ref. 50. In this approach, each spin-channel in the selected-localised subspace is perturbed with some weak external potential one at a time and responses of each spin-channel are measured to determine linear-response

functions. Within LRT, responses of the up- and spin-down channels to applied external fields are expressed as¹

$$\delta n^\sigma(\mathbf{r}) = \int d\mathbf{r}' \chi^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \delta v_{\text{ext}}^{\sigma'}(\mathbf{r}') \implies \chi^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \frac{\delta n^\sigma(\mathbf{r})}{\delta v_{\text{ext}}^{\sigma'}(\mathbf{r}')}, \quad (4.9)$$

where $\{\sigma, \sigma'\} = \{\downarrow, \uparrow\}$. Similarly, another response function due to total change in KS potential can be defined as

$$\delta n^\sigma(\mathbf{r}) = \int d\mathbf{r}' \chi_{\text{KS}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \delta v_{\text{KS}}^{\sigma'}(\mathbf{r}') \implies \chi_{\text{KS}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \frac{\delta n^\sigma(\mathbf{r})}{\delta v_{\text{KS}}^{\sigma'}(\mathbf{r}')}, \quad (4.10)$$

where $\delta v_{\text{KS}}^\sigma = \delta v_{\text{Hxc}}^\sigma + \delta v_{\text{ext}}^\sigma$. Using these two definitions of perturbation to the density,

$$\begin{aligned} \int d\mathbf{r}''' \chi^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}''') \delta v_{\text{ext}}^{\sigma'}(\mathbf{r}''') &= \int d\mathbf{r}''' \chi_{\text{KS}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}''') \delta v_{\text{KS}}^{\sigma'}(\mathbf{r}''') \\ &= \int d\mathbf{r}''' \chi_{\text{KS}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}''') \left[\delta v_{\text{Hxc}}^{\sigma'}(\mathbf{r}''') + \delta v_{\text{ext}}^{\sigma'}(\mathbf{r}''') \right] \\ &= \iint d\mathbf{r}''' d\mathbf{r}'' \chi_{\text{KS}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}''') F_{\text{Hxc}}^{\sigma'\sigma}(\mathbf{r}''', \mathbf{r}'') \delta n^\sigma(\mathbf{r}'') \\ &\quad + \int d\mathbf{r}''' \chi_{\text{KS}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}''') \delta v_{\text{ext}}^{\sigma'}(\mathbf{r}'''), \end{aligned} \quad (4.11)$$

where the Hartree+xc (Hxc) interaction kernel $F_{\text{Hxc}}^{\sigma'\sigma}$ is defined as

$$F_{\text{Hxc}}^{\sigma'\sigma}(\mathbf{r}''', \mathbf{r}'') = \frac{\delta v_{\text{Hxc}}^{\sigma'}(\mathbf{r}''')}{\delta n^\sigma(\mathbf{r}'')}. \quad (4.12)$$

Taking functional derivative of both sides in Eq. (4.11) with respect to $\delta v_{\text{ext}}^{\sigma'}(\mathbf{r}')$ and using the Eq. (4.9)

$$\chi^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \chi_{\text{KS}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') + \iint d\mathbf{r}'' d\mathbf{r}''' \chi_{\text{KS}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}''') F_{\text{Hxc}}^{\sigma'\sigma}(\mathbf{r}''', \mathbf{r}'') \chi^{\sigma\sigma'}(\mathbf{r}'', \mathbf{r}'), \quad (4.13)$$

which is Dyson's equation. Re-writing Eq. (4.13) in matrix form

$$\chi = \chi_{\text{KS}} + \chi_{\text{KS}} F_{\text{Hxc}} \chi \implies F_{\text{Hxc}} = \chi_{\text{KS}}^{-1} - \chi^{-1} \quad (4.14)$$

¹Dropping the site label I for the notational simplicity.

where the explicit form by recalling Eq. (4.9) and Eq. (4.10) becomes

$$F_{\text{Hxc}} = \begin{pmatrix} f^{\uparrow\uparrow} & f^{\uparrow\downarrow} \\ f^{\downarrow\uparrow} & f^{\downarrow\downarrow} \end{pmatrix} = \begin{pmatrix} \frac{\delta n^{\uparrow}}{\delta v_{\text{KS}}^{\uparrow}} & \frac{\delta n^{\uparrow}}{\delta v_{\text{KS}}^{\downarrow}} \\ \frac{\delta n^{\downarrow}}{\delta v_{\text{KS}}^{\uparrow}} & \frac{\delta n^{\downarrow}}{\delta v_{\text{KS}}^{\downarrow}} \end{pmatrix}^{-1} - \begin{pmatrix} \frac{\delta n^{\uparrow}}{\delta v_{\text{ext}}^{\uparrow}} & \frac{\delta n^{\uparrow}}{\delta v_{\text{ext}}^{\downarrow}} \\ \frac{\delta n^{\downarrow}}{\delta v_{\text{ext}}^{\uparrow}} & \frac{\delta n^{\downarrow}}{\delta v_{\text{ext}}^{\downarrow}} \end{pmatrix}^{-1}. \quad (4.15)$$

where the averaged Hubbard parameters are expressed as^[51]

$$U = \frac{1}{4} \left(f^{\uparrow\uparrow} + f^{\uparrow\downarrow} + f^{\downarrow\uparrow} + f^{\downarrow\downarrow} \right), \quad (4.16)$$

$$J = -\frac{1}{4} \left(f^{\uparrow\uparrow} - f^{\uparrow\downarrow} - f^{\downarrow\uparrow} + f^{\downarrow\downarrow} \right), \quad (4.17)$$

$$U_{\text{eff}} = U - J = \frac{1}{2} \left(f^{\uparrow\uparrow} + f^{\downarrow\downarrow} \right), \quad (4.18)$$

and we note that U_{eff} concerns only like-spin interactions, much like the DFT+ U functional itself.

4.3.1.1 Uncoupled-spin response

The simplest approach to determine the Hubbard parameters can be proposed by ignoring the coupling of the unlike spins. In such case, the Hubbard J becomes zero, and the Hubbard U parameter is simply the averaging of like-spin terms as

$$U_{\cancel{\sigma\sigma}} = \frac{1}{2} \left(f_{\cancel{\sigma\sigma}}^{\uparrow\uparrow} + f_{\cancel{\sigma\sigma}}^{\downarrow\downarrow} \right), \quad (4.19)$$

where $f_{\cancel{\sigma\sigma}}^{\sigma\sigma}$ are the uncoupled screened interactions for each spin, which simply becomes reciprocals of scalar quantities rather than being calculated by matrix inversion. This effectively decouples the spin populations into distinct sites, reflecting the DFT+ U functional. Each spin channel, for a given localised subspace, then forms part of the screening both for the other channel. In practical attempts to determine the Hubbard U parameters, the perturbative external potential $\delta v_{\text{ext}}^{\sigma}$ is the input parameter to measure response of a system;

hence, any response should be expressed as direct response to this potential as

$$\begin{aligned}
 f_{\mathcal{A}}^{\sigma\sigma} &= \left(\frac{\delta n^\sigma}{\delta v_{\text{KS}}^\sigma} \right)^{-1} - \left(\frac{\delta n^\sigma}{\delta v_{\text{ext}}^\sigma} \right)^{-1} \\
 &= \left(\frac{\delta n^\sigma}{\delta v_{\text{ext}}^\sigma} \right)^{-1} \left(\frac{\delta v_{\text{ext}}^\sigma}{\delta v_{\text{KS}}^\sigma} \right)^{-1} - \left(\frac{\delta n^\sigma}{\delta v_{\text{ext}}^\sigma} \right)^{-1} \\
 &= \left(\frac{\delta n^\sigma}{\delta v_{\text{ext}}^\sigma} \right)^{-1} \left[\left(\frac{\delta v_{\text{KS}}^\sigma}{\delta v_{\text{ext}}^\sigma} \right) - 1 \right].
 \end{aligned} \tag{4.20}$$

Furthermore, responses of spin-channels are *de facto* identical for closed-shell systems; hence, the Hubbard U parameter can be calculated by just perturbing one of spin-channels as

$$U_{\mathcal{A}}^{\uparrow\downarrow} = f_{\mathcal{A}}^{\uparrow\uparrow} = f_{\mathcal{A}}^{\downarrow\downarrow}. \tag{4.21}$$

4.3.1.2 Coupled-spin response for closed-shell systems

For the closed shell systems, where $n_{mm'}^{I\sigma} \approx n_{mm'}^{I\sigma'}$, the effective Hubbard U parameter can be approximated in a more accurate manner by employing this approximation to the DFT+ U + J functional of Eq. (4.6), yields

$$\begin{aligned}
 E_U[\{n^{I\sigma}\}] &= \frac{1}{2} \sum_{I\sigma} \sum_{m,m'} \left\{ (U^I - J^I) [n_{mm'}^{I\sigma} \delta_{mm'} - n_{mm'}^{I\sigma} n_{m'm}^{I\sigma}] + J^I n_{mm'}^{I\sigma} n_{m'm}^{I\sigma'} \right\} \\
 &= \frac{1}{2} \sum_{I\sigma} \sum_{m,m'} \left\{ (U^I - 2J^I) [n_{mm'}^{I\sigma} \delta_{mm'} - n_{mm'}^{I\sigma} n_{m'm}^{I\sigma}] \right\},
 \end{aligned} \tag{4.22}$$

where the effective U parameter becomes more accurately as

$$U'_{\text{eff}} = U - 2J = \frac{1}{4} \left(3f^{\uparrow\uparrow} - f^{\uparrow\downarrow} - f^{\downarrow\uparrow} + 3f^{\downarrow\downarrow} \right). \tag{4.23}$$

4.4 The non-local velocity commutator term

The pseudo-potential approximation is essential for routine applications of KS-DFT as discussed in Subsec. 2.2.2. In this approximation, the KS Hamiltonian acquires an explicit non-local contribution, as shown in Eq. (2.29). Hence, transition dipole moments in

momentum space cannot be expressed in position space with just a phase factor. The canonical commutation relation becomes^[52]

$$\langle \psi_f | \hat{\mathbf{p}} | \psi_i \rangle \propto \langle \psi_f | \hat{\mathbf{r}} | \psi_i \rangle + \langle \psi_f | [\hat{\mathbf{r}}, v_{\text{nl}}(\mathbf{r}, \mathbf{r}')] | \psi_i \rangle, \quad (4.24)$$

where $v_{\text{nl}}(\mathbf{r}, \mathbf{r}')$ is the non-local contribution to the pseudo-potential. The effects of the non-local commutator term in Eq. (4.24) highly depend on the construction of the pseudo-potential, and particularly on the choice of angular momentum selected for the pseudo-potential's local part. For instance, in the case of this work, this term contributes significantly, as shown in Fig. 4.2, to the optical spectra of noble metals such as Au¹.

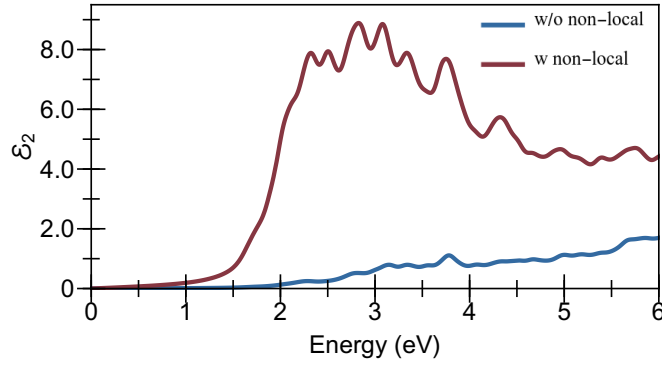


Figure 4.2: Effect of the non-local velocity commutator term in the optical spectrum of bulk Au from FGR.

As seen in Fig. 4.2, the non-local velocity term can be crucial for spectral simulations, depending on the particular construction of the pseudo-potential.

4.5 Conclusion

DFT and the approximate KS-DFT formalism have certain limitations and unavoidable systematic errors in currently available approximations, which lead to inaccurate descriptions of ground-state electronic structures. Such ill-definition of starting points is inevitably expected to cause inaccurate first-principles spectra, particularly of transition-metal systems. However, the most relevant systematic error namely, SIE, and its manifestation in many-body quantum systems, the delocalisation error, are well studied errors, which can be corrected with

¹See Subsec. 6.1.1 and App. A for details on the pseudo-potential for Au.

a feasible, self-consistent approach, namely DFT+ U (+ J). In Part III, SIE and DFT+ U will be extensively demonstrated both in the static limit and the time-domain. Also, the non-local velocity commutator term due to non-local potentials in canonical relations is shown to be crucial in spectral simulations.

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Part II

Optical Spectroscopy of Noble Metals Alloys

Chapter 5

The optical spectra of metallic solids

First-principles simulations of optical spectra of metallic solids are relatively challenging due to their requirement for very accurate descriptions of dense electronic states close to the Fermi level, which strongly contribute at the IR-vis-UV spectral range, as well as the presence of high density nearly-free electrons. The macroscopic dielectric function, which is the most central function here due to its direct connections to other optical function as well observable spectra, is constituted by two main parts

$$\mathcal{E}(\omega) = \mathcal{E}^{\text{inter}}(\omega) + \mathcal{E}^{\text{intra}}(\omega), \quad (5.1)$$

where $\mathcal{E}^{\text{inter}}(\omega)$ and $\mathcal{E}^{\text{intra}}(\omega)$ are due inter-band transitions and intra-band transitions, or the so-called the Drude plasmon, respectively.

In this chapter, the fundamental phenomena contributing to optical spectra of solids, particularly metallic solids will be discussed within classical theories and LRT. First, an averaging process for vanishing momentum transfer conditions will be derived to connect the microscopic dielectric function, due to inter-band transitions, to its macroscopic dual. Then, the most commonly used approach, namely the random-phase approximation (RPA), to obtain the microscopic dielectric function will be discussed. The second contribution to the macroscopic dielectric function, which is due to intra-band transitions, will also be investigated within classical models. Lastly, some corrective methods to RPA to include partially non-local quantum many-body effects will be formulated.

5.1 Inter-band transitions

Inter-band transitions are electronic transitions between valence and conduction bands contributing to optical spectra. As solids are treated as infinite objects, such transitions occur throughout solids simultaneously for a given energy of EM radiation. Observable spectra are spatial averages of these transitions, whereas electronic transitions are microscopic events. Naturally, an averaging process is needed that is starting from microscopic quantities to observable macroscopic quantities.

5.1.1 The micro-macro connection

The inverse microscopic dielectric function is defined as^[1]

$$\varepsilon(\mathbf{r}, \mathbf{r}', t, t')^{-1} = \frac{\delta V_{\text{tot}}(\mathbf{r}, t)}{\delta V_{\text{ext}}(\mathbf{r}', t')}, \implies \varepsilon(\mathbf{r}, \mathbf{r}', t, t') = \frac{\delta V_{\text{ext}}(\mathbf{r}, t)}{\delta V_{\text{tot}}(\mathbf{r}', t')}, \quad (5.2)$$

where V_{ext} is the external potential due to the applied field, and V_{tot} is the sum of V_{ext} and the potential due to the induced charge density, given by

$$V_{\text{tot}}(\mathbf{r}, t) = V_{\text{ext}}(\mathbf{r}, t) + V_{\text{ind}}(\mathbf{r}, t), \quad (5.3)$$

where V_{ind} can be expressed, by solving Poisson's equation, as

$$V_{\text{ind}}(\mathbf{r}, t) = \int dt' \int d\mathbf{r}' v(\mathbf{r}, \mathbf{r}') \rho_{\text{ind}}(\mathbf{r}', t'), \quad (5.4)$$

where $v(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$ is just the bare Coulomb interaction. By these relations, the microscopic dielectric functions and its inverse can be expressed as

$$\begin{aligned} \varepsilon(\mathbf{r}, \mathbf{r}', t, t') &= 1 - v(\mathbf{r}, \mathbf{r}') \frac{\rho_{\text{ind}}(\mathbf{r}, t)}{V_{\text{tot}}(\mathbf{r}', t')} = 1 - v(\mathbf{r}, \mathbf{r}') \tilde{\chi}(\mathbf{r}, \mathbf{r}', t, t') \\ \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t, t') &= 1 + v(\mathbf{r}, \mathbf{r}') \frac{\rho_{\text{ind}}(\mathbf{r}, t)}{V_{\text{ext}}(\mathbf{r}', t')} = 1 + v(\mathbf{r}, \mathbf{r}') \chi(\mathbf{r}, \mathbf{r}', t, t'), \end{aligned} \quad (5.5)$$

where $\tilde{\chi}$ and χ are called *the irreducible polarization* and *the reducible polarization*, respectively¹. While V_{ext} varies with respect to position slowly for the large wavelength limit, V_{ind} in Eq. (5.3), so V_{tot} vary rapidly. Hence, an averaging process through the inverse dielectric function is the appropriate route to obtain the macroscopic dielectric function appropriately in momentum space for the vanishing momentum transfer^[2,3]

$$\mathcal{E}^{\text{inter}}(\omega) = \frac{1}{\lim_{\mathbf{q} \rightarrow 0} \left[\varepsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega) \right]_{\mathbf{G}, \mathbf{G}'=0}}, \quad (5.6)$$

¹ χ is connected to $\tilde{\chi}$ through Dyson's equation with the bare Coulomb interaction v as

$$\chi = \tilde{\chi} + \tilde{\chi} v \chi.$$

where

$$\varepsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q},\omega) = \int d\tau e^{i\omega\tau} \sum_{\mathbf{q},\mathbf{G},\mathbf{G}'} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \varepsilon^{-1}(\mathbf{r},\mathbf{r}',\tau) e^{i(\mathbf{q}'+\mathbf{G}')\cdot\mathbf{r}'} \quad (5.7)$$

where $\tau = t - t'$. $\mathbf{G}$ and $\mathbf{G}'$ are the reciprocal lattice vectors, and $\mathbf{q}$ is the transferred momentum. As the limit in Eq. (5.6) implies, the transferred momentum from the incoming photon to excited electron is assumed to be negligible; thus, the only vertical excitations occurring at the same point of the reciprocal space are accounted. In such an averaging process, non-local effects are assumed to be negligible.

5.1.2 Random-phase approximation

For a non-interacting system, the independent-particle microscopic function is given by within FGR, or the so-called *independent-particle random phase approximation* (IP-RPA)^[4], as

$$\varepsilon_{\mathbf{G},\mathbf{G}'}^0(\mathbf{q},\omega) = 1 + v_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) \frac{\delta [\rho_{\text{ind}}(\omega)]_{\mathbf{G}}}{\delta [V_{\text{tot}}(\omega)]_{\mathbf{G}'+\mathbf{q}}} = 1 - v_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) \chi_{\mathbf{G},\mathbf{G}'}^0(\mathbf{q},\omega), \quad (5.8)$$

where the bare Coulomb interaction in the reciprocal space takes the approximate form

$$v_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \frac{4\pi}{|\mathbf{q} + \mathbf{G}| |\mathbf{q} + \mathbf{G}'|}. \quad (5.9)$$

Within LRT^[5], the non-interacting response function due to inter-band excitations is expressed in terms of KS wave-functions in momentum space as^[2,3]

$$\chi_{\mathbf{G}\mathbf{G}'}^0(\mathbf{q},\omega) = 2 \sum_{c,v,\mathbf{k}} (f_{v,\mathbf{k}} - f_{c,\mathbf{k}-\mathbf{q}}) \frac{\langle \psi_{c,\mathbf{k}-\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{v,\mathbf{k}} \rangle \langle \psi_{v,\mathbf{k}} | e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | \psi_{c,\mathbf{k}-\mathbf{q}} \rangle}{\omega - \omega_{cv,\mathbf{k}} + i\Gamma}, \quad (5.10)$$

where $\omega_{cv} = (\epsilon_{c,\mathbf{k}-\mathbf{q}} - \epsilon_{v,\mathbf{k}})$ and $\mathbf{q}$ is the transferred momentum vector, which is in the first Brillouin zone, and the factor 2 is for accounting the spin degeneracy. The interacting-particle

response function is, by definition,

$$\begin{aligned}\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) &= \frac{\delta [\rho_{\text{ind}}(\omega)]_{\mathbf{G}}}{\delta [V_{\text{ext}}(\omega)]_{\mathbf{G}'+\mathbf{q}}} = \frac{\delta [\rho_{\text{ind}}(\omega)]_{\mathbf{G}}}{\delta [V_{\text{tot}}(\omega)]_{\mathbf{G}'+\mathbf{q}}} \frac{\delta [V_{\text{tot}}(\omega)]_{\mathbf{G}}}{\delta [V_{\text{ext}}(\omega)]_{\mathbf{G}'+\mathbf{q}}} \\ &= \chi_{\mathbf{G}\mathbf{G}'}^0(\mathbf{q}, \omega) (1 + v_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) \chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)),\end{aligned}\quad (5.11)$$

which is Dyson's equation to obtain the interacting response-function. This approach is called *the random-phase approximation* (RPA)^[6-9]. Rearranging Eq. (5.11), a compact form emerges, given by

$$\chi^{-1} = \chi_0^{-1} - v, \quad (5.12)$$

for the interacting response function. Finally, the inverse macroscopic dielectric function is expressed as

$$\varepsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q}, \omega) = \delta_{\mathbf{G},\mathbf{G}'} + v_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) \chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega). \quad (5.13)$$

5.2 Intra-band transition

In metallic solids, intra-band transitions, which give rise to *the Drude plasmon*, is described as the collective oscillations of the free electrons. The Drude plasmon can be illustrated as the electrons in the metallic bands oscillating back and forth at the Fermi level in phase with the longitudinal parts of the EM radiations. The Drude plasmon generally occurs at ~ 10 eV, and it can be directly excited by accelerated electrons with kinetic energies in 1-20 keV or using laser beams to achieve the desired large wavelength at smaller energies. Drude plasmons contribute significantly at the near-infra-red part of the spectra of metals. Description of Drude plasmons starting from the KS band-structure are extremely computationally costly due to the requirement of extremely dense Brillouin zone sampling containing the Fermi surface such of up to ~ 16000 grid points^[10]. Commonly, the Drude plasmon is discussed in terms of a classical model of the oscillating free electrons under the external field obtained, by solving equation of motion

$$m_e \ddot{x} + m_e \eta_p \dot{x} = -\mathbb{E} e^{-i\omega t}, \quad (5.14)$$

where the displacement is then

$$x = \frac{E_0}{m_e(\omega^2 + i\eta_p\omega)}. \quad (5.15)$$

The polarization of the free electron gas is defined as

$$\mathbb{P} = -n_c x = -\frac{n_c}{m_e(\omega^2 + i\eta_p\omega)}\mathbb{E}, \quad (5.16)$$

where n_c is the charge carrier density. In linear-response regime, the intra-band part of the macroscopic dielectric function becomes as

$$\mathcal{E}^{\text{intra}}(\omega) = \varepsilon_\infty - \frac{4\pi n_c}{m_e(\omega^2 + i\eta_p\omega)} = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 - i\eta_p\omega}, \quad (5.17)$$

where ω_p , η_p , and ε_∞ are the Drude plasmon energy, the phenomenological inverse life-time, and the electric permittivity at the infinite frequency limit due to positive ionic background, respectively. This model to describe oscillations of free electrons in the metals is called the Drude-Lorentz model^[11–14].

5.2.1 The Drude parameters

The set $\{\omega_p, \eta_p, \varepsilon_\infty\}$ contains the Drude parameters. Experimentally, common practice is to perform optical measurements at the infrared and the far infrared spectral range corresponding $\approx 0\text{--}2.0$ eV and to determine these parameters by fitting the Drude-Lorentz model to the spectra^[15–21]. In such a procedure, the contribution of $\mathcal{E}_{\text{inter}}(\omega)$ in these range is expected to be negligible. Unfortunately, the determination of the Drude parameters is not possible solely from KS-DFT directly; however a step-by-step semi-empirical approach can be used to approximate them.

We start from the Drude plasmon energy in Eq. (5.17), which can be expressed in atomic unit as^[11,12,22]

$$\omega_p^2 = \frac{4\pi N(E_F)}{m_{\text{eff}}}, \quad (5.18)$$

where $N(E_F)$ is the density of states (DOS) at the Fermi level and m_{eff} is the effective electron mass at the metallic bands. The effective mass is approximated for parabolic band dispersion

relations as^[23]

$$m_{\text{eff}}^{-1} \propto \langle v^2(E_F) \rangle = \frac{\sum_i \int_{S_F} d\mathbf{S} v_i^2(\mathbf{k})}{\int_{S_F} d\mathbf{S}}, \quad v_i^2(\mathbf{k}) = \left| \frac{\partial E_i(\mathbf{k})}{\partial \mathbf{k}} \right|^2, \quad (5.19)$$

where S_F is the Fermi surface, and i is index running over bands. Consequently, the Drude plasmon energy can be expressed within so called *the one-band theory* using the KS-DFT band-structure as^[23],

$$\omega_p^2 = \frac{4\pi}{3} N(E_F) \langle v^2(E_F) \rangle, \quad (5.20)$$

where $1/3$ factor is due to the averaging over the three reciprocal unit vectors.

Unlike the Drude plasmon energy, the phenomenological inverse life-time for Drude plasmon is beyond the realm of KS-DFT, since electron-phonon and electron-impurity scattering contribute dominantly to the DC conductivity σ_0 , whereas the contribution due to electron-electron scattering is relatively small^[22].

A semi-empirical scheme can be employed regarding linear dependence of σ_0 to $\sqrt{\langle v^2(E_F) \rangle}$; hence, η_p can be written with some arbitrary scaling factor as

$$\eta_p = \frac{N(E_F)}{\sigma_0 m_{\text{eff}}} = c_\eta N(E_F) \langle v^2(E_F) \rangle^{1/2}, \quad (5.21)$$

where c_η is the scaling coefficient. Expressing the real and imaginary part of $\mathcal{E}_{\text{intra}}(\omega)$ from Eq. (5.17), we arrive at

$$\begin{aligned} \Re[\mathcal{E}^{\text{intra}}] &= \mathcal{E}_1^{\text{intra}}(\omega, \omega_p, \eta_p, \varepsilon_\infty) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \eta_p^2}, \\ \Im[\mathcal{E}^{\text{intra}}] &= \mathcal{E}_2^{\text{intra}}(\omega, \omega_p, \eta_p) = \frac{\eta_p \omega_p^2}{\omega^3 + \eta_p^2 \omega}. \end{aligned} \quad (5.22)$$

For the first-principles ω_p , the imaginary part is parametrized only by η_p . The scaling factor for η_p in Eq. (5.21) can be determined by fitting $\mathcal{E}_2^{\text{intra}}$ to the experimental spectra at the near infra-red spectral range (≈ 0.8 - 1.2 eV). Consecutively, ε_∞ is determined by fitting $\mathcal{E}_1^{\text{intra}}$ to the experimental spectra with ω_p and η_p obtained in previous steps at the same spectral range.

5.3 Quantum many-body effects on the spectra

RPA starting from the approximate KS-DFT band-structure is a computationally moderate approach to study the optical spectra of a wide range of condensed matter systems. As it is built upon an auxiliary non-interacting system, RPA is unable to build any non-local quantum many-body effects into the single-particle states. The absence of such effects leads to inaccurate descriptions of the electronic bands in solids, which are required to construct optical spectra of solids, for which screening and correlation play significant roles. Such cases are well reported in the literature for various material classes such as insulators and semi-conductors^[24–28], transition-metal oxides^[29–31] and metallic solids^[32,33]. As pertains to this work, such quantum-many effects become crucial for the low-energy spectral ranges for noble metals, since there the electronic bands dominantly contributing to the spectra are the fully-filled d^{10} bands tightly packed in a narrow energy window close to the Fermi level. These electronic bands are poorly described within approximate KS-DFT for noble metals, and then such error become more pronounced in spectral simulations with RPA^[34–39]. However, as stressed throughout this work, this leads to a dilemma as the non-interacting picture is only partially successful even for properties at the static limit, while a fully interacting picture is not feasible within any current analytic or computational methods. Hence, an intermediate approach is needed to include the quantum-many effects approximately at a minimum additional computational cost with respect to the FGR or RPA methods built upon the approximate KS-DFT eigen-spectrum.

5.3.1 The quasiparticle formalism

The concept of *the quasiparticle* (QP) dates back to the works of Landau on the Fermi liquids^[40–42]. The fundamental idea in this formalism is a mapping of the interacting many-body systems of particles to a weakly interacting quantum many-body system of virtual particles, namely *the quasiparticles*¹^[43,44]. QP wave-functions and corresponding energy levels are determined by solving the QP equation

$$\left[-\frac{1}{2m_{\text{QP}}} \nabla_i^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \omega) \right] \psi_i^{\text{QP}}(\mathbf{r}, \omega) = \epsilon_i^{\text{QP}} \psi_i^{\text{QP}}(\mathbf{r}, \omega), \quad (5.23)$$

¹The term *quasiparticle* is used as a general term for virtual, composite particles in condensed matter theory. In this work, this term is used for electron quasiparticles, which are electrons surrounded with their positive screening clouds and *hole* quasiparticles, which are holes surrounded with negative screening clouds.

where $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$ is the *self-energy*, which is energy-dependent and spatially non-local. $\Psi_i^{QP}(\mathbf{r})$ and E_i^{QP} are the i^{th} QP wave-function and the corresponding QP energy. As seen in Eq. (5.23), the QP equations only differs from the KS equation in Eq. (2.17) by the self-energy term instead of locally defined xc-potential, where KS equation can be recovered by defining the xc-potential as the local part of the self-energy at the static limit as

$$v_{xc}(\mathbf{r}) = \lim_{\omega \rightarrow 0} \Sigma(\mathbf{r}, \mathbf{r}', \omega) \delta(\mathbf{r} - \mathbf{r}'). \quad (5.24)$$

In common practice, QP energies are calculated using *many-body perturbation theory* (MBPT)^[45] methods with Green's functions instead of explicit solution of Eq. (5.22).

5.3.2 The GW approximation

Formally, the self-energy is obtained in common practice by solving the set of the five closed, coupled integrable and differentiable equations namely the Hedin equations^[46,47]

$$\Sigma(1, 2) = i \int d(3, 4) G(1, 3) W(4, 1^+) \Gamma(3, 4, 2) \quad (5.25)$$

$$G(1, 2) = G^0(1, 2) + \int d(3, 4) G^0(1, 3) \Sigma(3, 4) G(4, 2) \quad (5.26)$$

$$\Gamma(1, 2, 3) = \delta(1, 2) \delta(2, 3) + \int d(4, 5, 6, 7) \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 5) G(7, 5) \Gamma(6, 7, 3) \quad (5.27)$$

$$\tilde{\chi}(1, 2) = -i \int d(3, 4) G(1, 3) \Gamma(3, 4, 2) G(4, 1^+) \quad (5.28)$$

$$W(1, 2) = v(1, 2) + \int d(3, 4) v(1, 3) \tilde{\chi}(3, 4) W(4, 2), \quad (5.29)$$

where the coordinates represent for non-spin polarized case $i = \{\mathbf{r}_i, t_i\}$ and $i^+ = \{\mathbf{r}_i, t_i + \delta t\}$. Here, Σ , G , Γ , $\tilde{\chi}$ and W are the *self-energy*, the *single-particle Green function*, the *vertex function*, the *irreducible polarization* and the *screened Coulomb interaction*, respectively, and v is the bare Coulomb interaction. The exact self-energy can be determined by solving the Hedin equations self-consistently as illustrated in Fig. 5.1. In practical applications, the self-energy is approximated by setting the vertex function to $\Gamma(1, 2, 3) = \delta(1, 2) \delta(2, 3)$, which yields the *GW approximation* (GWA). In the GWA, the vertex function is bypassed as illustrated in Fig. 5.1;

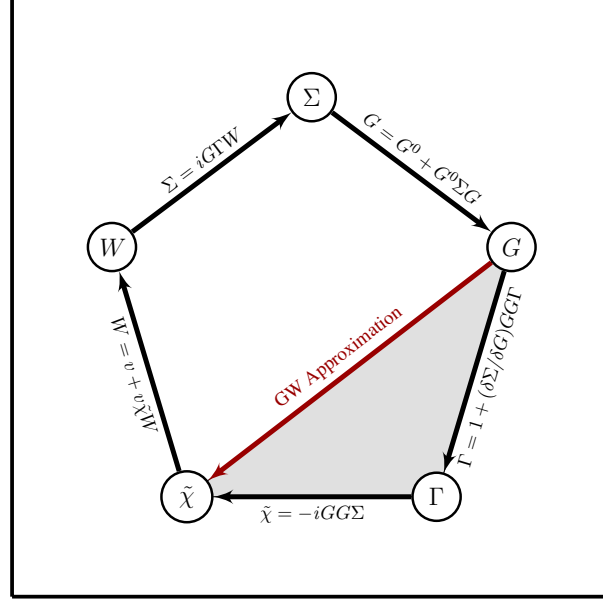


Figure 5.1: The Hedin pentagon.

hence the set of equations are reduced to

$$\Sigma(1, 2) = iG(1, 2)W(2, 1^+) \quad (5.30)$$

$$G(1, 2) = G^0(1, 2) + \int d(3, 4)G^0(1, 3)\Sigma(3, 4)G(4, 2) \quad (5.31)$$

$$\tilde{\chi}(1, 2) = -iG(1, 2)G(2, 1^+) \quad (5.32)$$

$$W(1, 2) = v(1, 2) + \int d(3, 4)v(1, 3)\tilde{\chi}(3, 4)W(4, 2). \quad (5.33)$$

To solve this, we should ideally start from the independent-particle Green's function G^0 constructed using the HF wave-functions. In practice, the $G^0 = G_{\text{KS}}$ of approximate KS-DFT is most widely used.

5.3.3 The one-shot, non-self-consistent GW: G_0W_0

The self-consistent GW method is a computationally expensive approach as it requires to solving Dyson's equations in Eq. (5.32) and Eq. (5.34) multiple times, which includes matrix inversion of large, complex matrices. Furthermore, it has been shown that it fails for systems

with over half-filled 3d bands^[48]. A more plausible, successful approximation is so called *the one-shot, non-self-consistent GW*, or G_0W_0 , which depends explicitly upon the input G_0 . In G_0W_0 , the self-energy is calculated in one-shot with

$$\Sigma = iG^0W^0, \quad (5.34)$$

where the product here is in real space and time. Formally, starting from G^0 , W^0 can be evaluated in the first iteration of the self-consistent GW. Naturally, determining QP energies perturbatively in KS wave-function basis is advantageous for realistic and high-throughput simulations, due to its relatively moderate computational cost, and since the approximate DFT density is usually reasonable, even if the KS-DFT eigen-spectrum is unphysical. Modifying the QP equation in Eq. (5.23) by adding and subtracting the xc-functional as

$$\begin{aligned} & \left[-\frac{1}{2m_e} \nabla_i^2 + v_{\text{KS}}(\mathbf{r}) \right] \psi_i^{\text{QP}}(\mathbf{r}, \omega) \\ & + \left[\int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \omega) - \delta(\mathbf{r} - \mathbf{r}') v_{\text{xc}}(\mathbf{r}, \mathbf{r}') \right] \psi_i^{\text{QP}}(\mathbf{r}, \omega) = \epsilon_i^{\text{QP}} \psi_i^{\text{QP}}(\mathbf{r}, \omega), \end{aligned} \quad (5.35)$$

we find that $\hat{\Sigma}' = \hat{\Sigma} - \hat{v}_{\text{xc}}$ is the correct self-energy, ensuring that any double-counting of the local part is cancelled. Assuming that $\langle \psi_i | \psi_i^{\text{QP}} \rangle \approx 1$, next, QP energies can be expressed as

$$\epsilon_i^{\text{QP}} = \epsilon_i + \langle \psi_i | \hat{\Sigma}'(\epsilon_i^{\text{QP}}) | \psi_i \rangle. \quad (5.36)$$

Expanding the self-energy operator as a function of the QP energies using its Taylor series around the KS energies, explicitly as

$$\hat{\Sigma}'(\epsilon_i^{\text{QP}}) = \hat{\Sigma}'(\epsilon_i) + (\epsilon_i^{\text{QP}} - \epsilon_i) \left. \frac{\partial \hat{\Sigma}'(\omega)}{\partial \omega} \right|_{\omega=\epsilon_i} + O[(\epsilon_i^{\text{QP}} - \epsilon_i)^2] + \dots, \quad (5.37)$$

the QP energies can be finally approximated as a first-order correction to the KS eigen-energies as

$$\epsilon_i^{\text{QP}} = \epsilon_i + Z_i \langle \psi_i | \hat{\Sigma}'(\epsilon_i) - \hat{v}_{\text{xc}} | \psi_i \rangle, \quad (5.38a)$$

$$Z_i = \left[1 - \left. \frac{\partial \hat{\Sigma}'(\omega)}{\partial \omega} \right|_{\omega=\epsilon_i} \right]^{-1}, \quad (5.38b)$$

where Z_i is called *the QP re-normalisation factor*. This factor can be thought of as the absolute value of the charge of the QP (e.g., of the electron and its screening cloud).

5.3.3.1 The independent-particle Green function: G_0

As QP energies are evaluated with first-order perturbation theory in the KS wave-functions basis, G^0 should be also expressed with KS wave-functions. The general form of the single-particle Green function is expressed in the second quantization as^[45,49]

$$G(\mathbf{r}, t; \mathbf{r}', t') = \begin{cases} -i \langle N | \hat{\Psi}(\mathbf{r}, t) \hat{\Psi}^\dagger(\mathbf{r}', t') | N \rangle & \text{for } t > t' \\ i \langle N | \hat{\Psi}^\dagger(\mathbf{r}', t') \hat{\Psi}(\mathbf{r}, t) | N \rangle & \text{for } t < t', \end{cases} \quad (5.39)$$

where $|N\rangle$ is the representation of the N -electron state in the configuration space, and where $\hat{\Psi}^\dagger$ and $\hat{\Psi}$ are the creation and the annihilation field operators. For $t > t'$, $G^0(\mathbf{r}, t; \mathbf{r}', t')$ is the probability of the annihilation of an electron at $(\mathbf{r}, t)$, while an electron is created at $(\mathbf{r}', t')$. For $t < t'$, it is the same procedure for the hole. We may expand the field operators in terms of the KS wave-functions as

$$\begin{aligned} \hat{\Psi}^\dagger(\mathbf{r}, t) &= \sum_{i, \mathbf{k}} e^{i\epsilon_{\text{KS}} t} \psi_{i, \mathbf{k}}(\mathbf{r}) \hat{c}_{i, \mathbf{k}}^\dagger \\ \hat{\Psi}(\mathbf{r}, t) &= \sum_{i, \mathbf{k}} e^{-i\epsilon_{\text{KS}} t} \psi_{i, \mathbf{k}}(\mathbf{r}) \hat{c}_{i, \mathbf{k}} \end{aligned} \quad (5.40)$$

where $\hat{c}_{i, \mathbf{k}}^\dagger$ and $\hat{c}_{i, \mathbf{k}}$ are creation and annihilation operators. In the KS wave-function basis, the non-interacting single-particle Green function becomes, for $t' > t$,

$$G^0(\mathbf{r}, t; \mathbf{r}', t') = 2i \sum_{i, \mathbf{k}} \psi_{i, \mathbf{k}}(\mathbf{r}) \psi_{i, \mathbf{k}}(\mathbf{r}') \left(f_{i, \mathbf{k}} e^{-i\epsilon_{i, \mathbf{k}}(t'-t)} + (1 - f_{i, \mathbf{k}}) e^{i\epsilon_{i, \mathbf{k}}(t'-t)} \right), \quad (5.41)$$

This becomes, in the frequency domain, by the Fourier transform^[10]

$$G^0(\mathbf{r}, \mathbf{r}', \omega) = 2i \sum_{i, \mathbf{k}} \psi_{i, \mathbf{k}}(\mathbf{r}) \psi_{i, \mathbf{k}}(\mathbf{r}') \left(\frac{f_{i, \mathbf{k}}}{\omega - \epsilon_{i, \mathbf{k}} + i\delta} + \frac{1 - f_{i, \mathbf{k}}}{\omega - \epsilon_{i, \mathbf{k}} - i\delta} \right). \quad (5.42)$$

5.3.3.2 The screened Coulomb interaction: W_0

Once G^0 is obtained, Σ can be achieved by calculating W^0 by using Eq. (5.5) in Eq. (5.33) with

$$\begin{aligned} W^0 &= v + v\tilde{\chi}W^0 \Rightarrow 1 = v(W^0)^{-1} + v\tilde{\chi} \Rightarrow (1 - v\tilde{\chi}) = v(W^0)^{-1} \Rightarrow \\ 1 &= (1 - v\tilde{\chi})^{-1}v(W^0)^{-1} \Rightarrow W^0 = (1 - v\tilde{\chi})^{-1}v \Rightarrow \\ &\boxed{W^0 = \varepsilon^{-1}v} \end{aligned} \quad (5.43)$$

where W^0 is a function of ω through the inverse dynamic dielectric function ε^{-1} . In reciprocal space, W_0 is expressed by Eq. (5.9) and Eq. (5.13) as the direct product

$$W_{\mathbf{G},\mathbf{G}}^0(\mathbf{q},\omega) = \varepsilon_{\mathbf{G},\mathbf{G}}^{-1}(\mathbf{q},\omega) \frac{4\pi}{|\mathbf{q} + \mathbf{G}||\mathbf{q} + \mathbf{G}'|}. \quad (5.44)$$

Computationally, the inversion of the dielectric function, which is a large matrix with frequency-dependent complex entities, is troublesome. Hence, the frequency-dependent complex entities are approximated by Lorentzian peaks within the so-called *plasmon-pole approximation* (PPA)^[50,51]. The idea behind the PPA is to replace the single-particle transitions making up $\varepsilon_{\mathbf{G},\mathbf{G}}^{-1}(\mathbf{q},\omega)$, which increase in number with the square of system size, with a smaller number of effective plasmon modes. Thus ε^{-1} is approximated in practice via

$$\varepsilon_{\mathbf{G},\mathbf{G}}^{-1}(\mathbf{q},\omega) = \delta_{\mathbf{G},\mathbf{G}} + \sum_{\lambda} \frac{\Omega_{\mathbf{G},\mathbf{G}}^{\lambda}}{\omega^2 - (\bar{\omega}_{\mathbf{G},\mathbf{G}}^{\lambda})^2}, \quad (5.45)$$

where $\Omega_{\mathbf{G},\mathbf{G}}$ and $\bar{\omega}_{\mathbf{G},\mathbf{G}}^{\lambda}$ are the strength and the frequency of plasmons fitted to the RPA inverse dielectric function.

5.3.4 Spectra with the quasiparticle formalism

Once the QP energies are determined, the non-interacting response function is evaluated using the expression

$$\chi_{\mathbf{G}\mathbf{G}'}^0(\mathbf{q}, \omega) = \sum_{c,v,\mathbf{k}} 2f_{v,\mathbf{k}}(1 - f_{c,\mathbf{k}-\mathbf{q}}) \frac{\langle \psi_{c,\mathbf{k}-\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{v\mathbf{k}} \rangle \langle \psi_{v\mathbf{k}} | e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | \psi_{c,\mathbf{k}-\mathbf{q}} \rangle}{\omega - \omega_{cv,\mathbf{k}}^{\text{QP}} + i\Gamma}, \quad (5.46)$$

where $\omega_{cv,\mathbf{k}}^{\text{QP}} = \epsilon_{c,\mathbf{k}}^{\text{QP}} - \epsilon_{v,\mathbf{k}}^{\text{QP}}$. Unfortunately, evaluation of quasiparticle energies at each point in the Brillouin zone for each band scales with $O(N_b^4)$. Instead of constructing the QP band-structure explicitly, an averaged scaling to the KS band-structure can be suggested assuming that the electronic bands contributing the spectra are similarly by the G_0W_0 correction. If this behaviour is found to hold in practice, then QP energies may be estimated for the relevant bands, for which linear regression can be used to determine some global scaling parameters for KS valence and conduction bands, namely *stretching parameters*. This expedient approach will be demonstrated in Chap. 6 in detail.

5.4 Conclusion

In this chapter, the main tools in the practical first-principles simulation of spectra in metallic solids were introduced within the linear-response regime. Inter-band transitions are described through the RPA, while Drude plasmon contributions are modelled using the classical Drude-Lorentz oscillator model. A semi-empirical approach to determine the Drude parameters is suggested by using KD-DFT band-structure and experimental spectra in the IR spectral range. The QP formalism and a feasible approach to obtain QP energies using G_0W_0 were discussed. In the next chapter, these tools will be applied to real systems starting from pure bulk Au, Ag, and Cu, in order to demonstrate their limitations and potentials.

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Chapter 6

Investigating the optical response of

$\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys

Noble metals and their alloys are compelling materials for many opto-electronic applications^[1–5] due to their strong optical response throughout the IR-vis-UV spectral range. Tailoring the plasmonic and optical properties of metallic systems via alloying processes is currently promising due to a high demand for novel and more efficient nano-materials for opto-electronic applications^[6–8]. Nano-structures of the pure Au, Ag and Cu are commonly used materials in diverse opto-electronic applications due to their good chemical and mechanical stabilities as well as their strong optical response in the low-energy spectral range; hence their alloys are naturally expected to be promising candidates for efficient opto-electronic applications. Spectroscopic measurements on alloys are mostly performed on their thin-film surfaces^[9–18], which are highly dependent on the alloying techniques^[19]. Hence, systematic first-principles studies of such alloys are crucial for fundamental insight on effects of alloying on optical properties as well as tailoring the optical response for designated applications.

In this chapter, various approaches to obtain optical and plasmonic properties of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ will be investigated comparatively. As starting point, bulk Au, Ag, and Cu will be used as theoretical laboratories for benchmarks to investigate accuracies of first-principles spectroscopy methods, which are introduced in Chap. 1 and Chap. 5, such as FGR and RPA starting from approximate KS-DFT and approximate QP band-structures. Furthermore, the Drude plasmon contributions, which are particularly crucial for low-energy spectral ranges, to optical spectra will be introduced within a semi-empirical approach starting from first-principles Drude plasmon energies. A standard work-flow will be suggested to construct the spectra of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ for the spectral range 0-6 eV. The macroscopic dielectric functions will be used to define quality measures for bulk and surface plasmons of these alloys. Finally, some predictions will be suggested on performances of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ for given wavelengths to determine most suitable stoichiometric ratios for plasmonic applications, which require strong and long-living plasmonic response.

6.1 Preliminary tests on Au

The optical properties of bulk Au have been well-studied experimentally throughout the IR-vis-UV spectral range^[20–25]; hence, it provides an excellent test laboratory to investigate the performance of both KS-DFT for the ground-state, as well as of spectra starting from it. Also,

Ag and Cu are expected to have similar electronic structures as they are iso-electronic elements to Au. Taking advantage of this, Au can be used to some extent as a laboratory to determine a common standard of optimised convergence parameters for KS-DFT simulations.

6.1.1 Computational details

Geometry optimisations, SCF and NSCF simulations were performed using Quantum Espresso software (QE)^[26,27]. The norm-conserving PBE pseudo-potentials¹ produced using the pseudo-potential generator OPIUM^[28] have configurations summarised in Table 6.1². The spectra simulations were performed with Yambo^[29].

Species	Configuration	Valence electron number
Au	Neutral, [Xe] (4f ¹⁴) 5d ¹⁰ 6s ¹	11
Ag	Neutral, [Kr] 4d ¹⁰ 5s ¹	11
Cu	Neutral, [Ar]3d ¹⁰ 4s ¹	11

Table 6.1: The details of pseudo-potentials used for Au, Ag, and Cu.

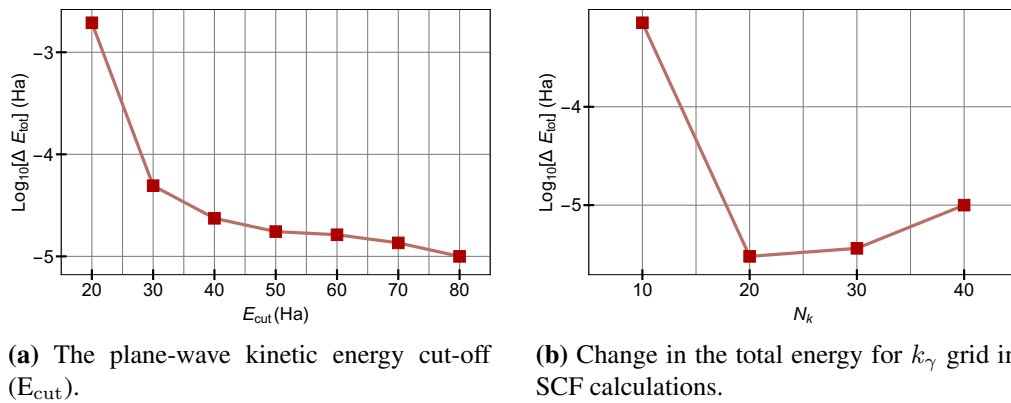


Figure 6.1: The relative change in the total KS energy (ΔE_{tot}) of bulk Au with single atom unit cell as functions of (a) the plane-wave kinetic energy cut-off in Eq. (2.31) and (b) the number of discrete uniform points in k_γ ($\gamma = x, y, z$) direction.

The initial crystallographic information for bulk Au (also for Ag, and Cu) in face-centred cubic structures were adopted from X-ray diffraction data at 1072 K from Ref. 30 for consistency

¹Yambo is only compatible with the norm-conserving pseudo-potentials.

²See App. A for the input file for OPIUM, including further details

with choice of smearing parameter for the Marzari-Vanderbilt cold smearing^[31] chosen, 0.1 eV. Full geometry relaxations were then performed with variable cell parameters at high E_{cut} (75 Ha) and $4 \times 4 \times 4$ automatically generated Monkhorst-Pack uniform grids for Brillouin zone sampling without imposing any crystal symmetry^{1 2}.

The initial convergence tests were performed in SCF level to determine E_{cut} and Brillouin zone sampling with respect to the change in the total energy shown in Fig. 6.1. Considering Fig. 6.1a, a sufficient E_{tot} of 25 Ha (~ 680 eV) using a set criteria of $\Delta E_{\text{tot}} \leq 0.001$ Ha per atom. Despite the fast convergence shown in Fig. 6.1b, a $21 \times 21 \times 21$ uniform grid was chosen for Brillouin zone sampling. This particular choice was due to limitations of various software used early stage testing simultaneously, for testing namely Yambo and BerkeleyGW^[32,33]. BerkeleyGW requires a shifted grid for NSCF calculations compared to the SCF grid to be able to include the non-local velocity term in Eq. (4.24) in spectral calculations³.

Yambo uses the KS band-structure as a starting point for simulating spectra within the various approaches introduced in Chap. 5. As discussed before, the simplest approach to obtain absorption spectra starting from KS-DFT is FGR; hence, it was used as a test tool to gain some insight about effects of initial choices imposed in SCF and NSCF levels on spectra. In Fig. 6.2a, the effect of including spin-orbit coupling (SOC) non-pertubatively at the KS-DFT level on the FGR absorption spectrum is demonstrated. The fully-relativistic pseudo-potential used in non-collinear spin-polarized calculations was generated by same input parameters of the scalar-relativistic pseudo-potential⁴. As expected, SOC splits peaks and creates smooth shoulders on the absorption spectrum due to the splitting of underlying KS states. This results in more defined peaks at lower energies. Inclusion of SOC increases computational costs drastically, especially RAM requirements; hence, the relatively small improvement of peak locations is not beneficial enough for high-throughput simulations, especially for the large inverse life-time Γ as in experiments as these additional peaks are smeared out. Hence, SOC was ruled out for the sake of constructing a more applicable scheme for larger sets of structures. Conversely, increasing the number of grid points in NSCF level smears out the peaks as in Fig. 6.2b by means of increasing number of excitation at a given energy window,

¹Yambo is restricted to uniform grids without any reduction in Brillouin zone sampling due to crystal symmetries.

²See App. A for details of the final crystallographic information.

³By the time early simulations performed, BerkeleyGW was in developing stage for the metallic systems. Despite its superiority in terms of more efficient parallelisation, it had some numerical instabilities leading to inaccurate results; hence, it was abandoned for further simulations.

⁴See App. A for the input files for OPIUM.

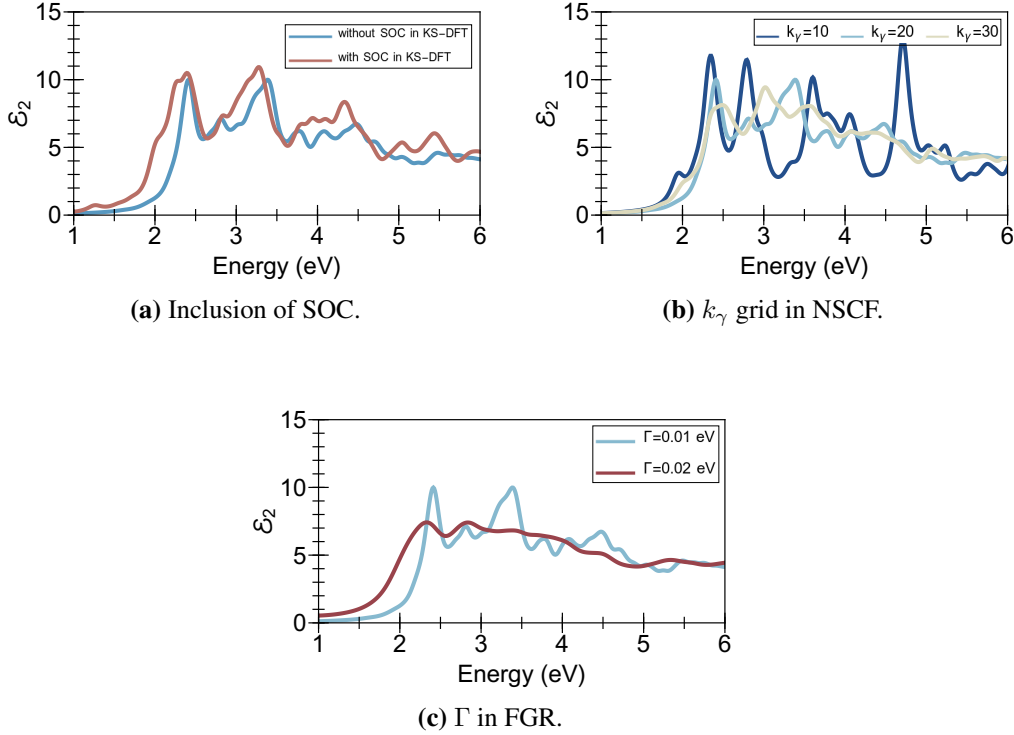


Figure 6.2: Preliminary test simulations of the absorption spectrum of bulk Au with FGR for comparison of (a) with and without spin-orbit coupling (SOC), (b) number of grid points in reciprocal unit vector direction in NSCF level, and (c) the inverse life-time Γ .

rather than moving peaks around. The inverse life-time Γ is already a free parameter without any further physical meaning in simulations with Yambo; hence, a $16 \times 16 \times 16$ uniform grid was chosen as the Brillouin zone sampling for pure metals at the NSCF level for finalised calculations. This particular choice will become more coherent in developing a systematic procedure consistently applicable for alloy systems in later sections. Strengthening this argument, the effect of Γ is shown in Fig. 6.2c by increasing it from 0.1 eV to 0.2 eV with a $20 \times 20 \times 20$ grid in NSCF. Observable spectra have large Γ values due to finite temperature effects and impurities in samples^[34–36]. Accordingly, a Lorentzian smearing parameter of full-width 0.2 eV was adopted for spectral simulation with Yambo.

Preliminary tests were performed to determine the limitations of the full simulation sequence both in terms of accuracy and computational cost. Decisions on related parameters for simulations were not determined solely by the preliminary test, but also in conjunction with high-throughput for feasible first-principles simulations of alloy systems within a well-controlled and systematic scheme. The final parameters used for pure metals are

summarised in Table 6.2.

	Level	Value	Unit
E_{cut}	SCF, NSCF	680	eV
k_{γ}	SCF	$21 \times 21 \times 21$	
Γ_{mv}	SCF, NSCF	0.1 (cold)	eV
k_{γ}	NSCF	$16 \times 16 \times 16$	
N_{b}	NSCF	100	
Γ	FGR, RPA	0.2	eV

Table 6.2: The final converged parameters used in the spectral simulations of pure Au, Ag, and Cu. E_{cut} , k_{γ} , Γ_{mv} , N_{b} are the kinetic energy cut-off in Eq. (2.31), the Brillouin zone sampling, the broadening in Marzari-Vanderbilt cold smearing^[31], and the number of bands, respectively.

6.2 Benchmark spectra of pure metals: Au, Ag, and Cu

Final simulations with the common set of parameters in Table 6.2 were performed on Au, Ag, and Cu for benchmarking using various levels of theories compared to observable spectra. The work-flow for simulations of spectra with FGR, RPA and G_0W_0 +RPA is illustrated in Fig. 6.3. For comparable spectra, stretching operators and the Drude parameters have to be determined first for each system.

6.2.1 Computation of stretching operators

In principle, G_0W_0 +RPA spectra are obtained by starting from Eq. (5.46), which requires a full QP band-structure, and solving Dyson's equation in Eq. (5.11). To be able to obtain QP band-structures, there is a need to evaluate QP energies for each point in the Brillouin zone for every band. For a given band and point in Brillouin zone $\{i, \mathbf{k}\}$, such an operation consists of summing both throughout the Brillouin zone and the bands to determine G_0 in Eq. (5.41) as well as W_0 through the inverse dynamic dielectric function in Eq. (5.44) for the self energy operator in Eq. (5.38a). Such a task is highly demanding both in terms of CPU hours as well as RAM. This operation needs to load all information about KS wave-functions in each processor unit, when using Yambo. Note that the eventual goal is constructing spectra rather than individual shapes of the bands, an averaged stretching to underlying KS band-structure via stretching operators close to the Fermi level can be sufficient, as well as more feasible for

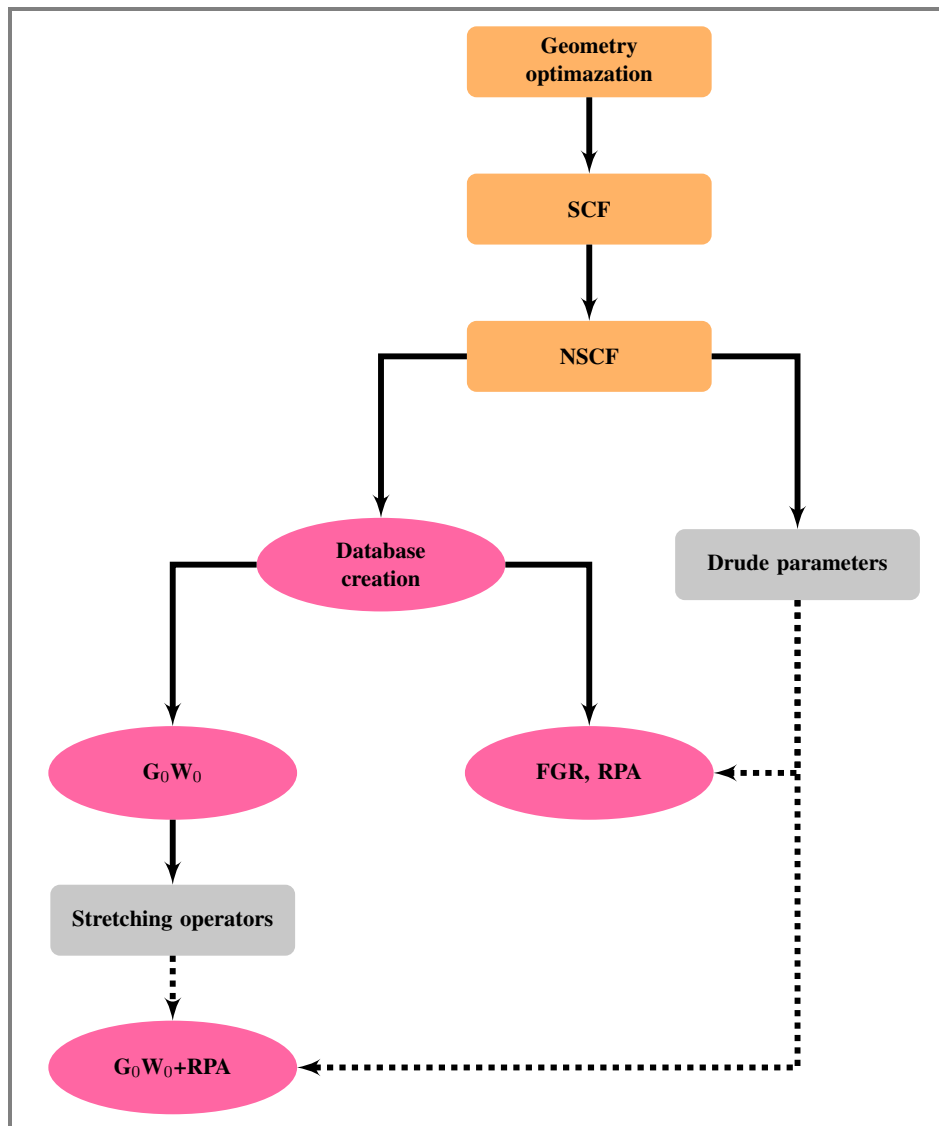


Figure 6.3: The work-flow followed to obtain spectra of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ with QE+Yambo. The colour codes are assigned to each software as QE with orange, Yambo with pink and original codes with gray.

the spectral range of interest. The idea of stretching operators is to approximate QP energies as linear functions of the KS energies, and for metals in particular we have simply

$$\epsilon_v^{\text{QP}} = s_v \epsilon_v, \quad \text{and} \quad \epsilon_c^{\text{QP}} = s_c \epsilon_c, \quad (6.1)$$

where s_v and s_c are the stretching operators for valence and conduction bands, respectively. Such an approach introduces averaged corrections to valence and conduction bands around Fermi level due to missing non-local electronic exchange-correlation, while keeping Fermi level fixed for metals.

	s_v	s_c
Au	1.419797	0.825253
Ag	1.376302	0.846172
Cu	1.735804	0.809883

Table 6.3: The stretching operators to stretch KS band-structures to imitate the QP band-structure for pure Au, Ag, and Cu.

Following this, the stretching operators can be determined by linear fitting on ϵ_i vs. ϵ_i^{QP} for some appropriately chosen set of grid points around the high-symmetry point Γ using chosen bands in the valence and conduction manifolds. For pure metals, QP energies were calculated for 6 valence bands and 6 conduction bands at 10 points at and around Γ , and the stretching operators were determined by linear fitting as shown in Fig. 6.4 with the values listed in Table 6.3. In Fig. 6.4, two main branches are observed in the valence manifolds. These distinctive branches are due to different non-local exchange contributions to s and d bands.

The stretching operators modify the KS band-structure as shown in Fig. 6.5. The Fermi-Dirac distribution for the chosen electronic temperature was used to interpolate between the distinct stretching parameters for the valence and conduction bands. KS-DFT tends to excessively flatten the fully-filled d -bands due to an absence of attractive short-ranged non-local exchange. In a sense, the stretching operator approximately corrects the dispersions of the bands, particularly for the occupied d -bands but also for the half-occupied s -band, which is made less dispersive on the other hand. In Fig. 6.5c, the bands close to the Fermi level are more narrowly packed and flattened compare to Ag, and Au cases; accordingly, s_v^{Cu} is largest among the three. The inverse behaviour is seen for the conduction stretching operators of pure

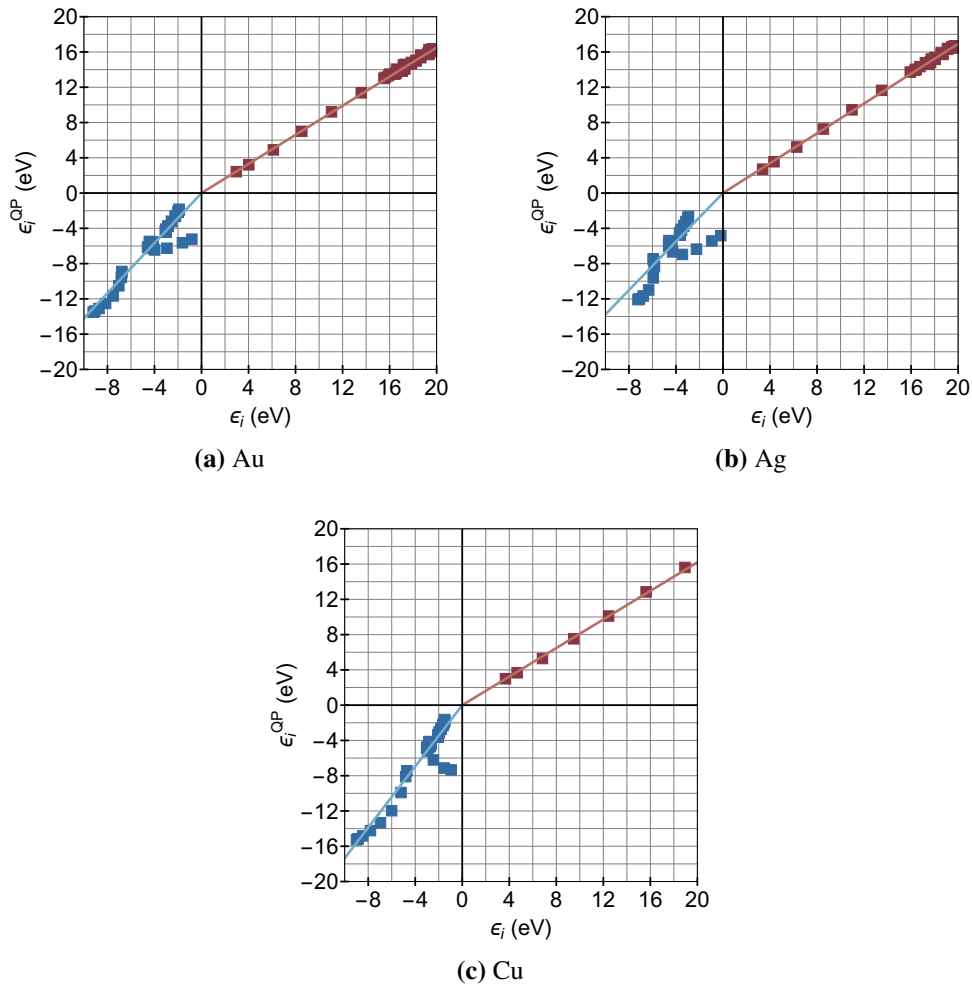


Figure 6.4: Stretching operator for Au, Ag, and Cu with linear fitting to KS-DFT vs. QP eigen-energies using 10 points around Γ for 6 valence (blue points) and 6 conduction (red points) bands. The Fermi levels are shifted to 0 eV for each case.

metals, which is due to correlation effects only, as Ag has the largest dispersion in the conduction manifold followed by Au, and then Cu.

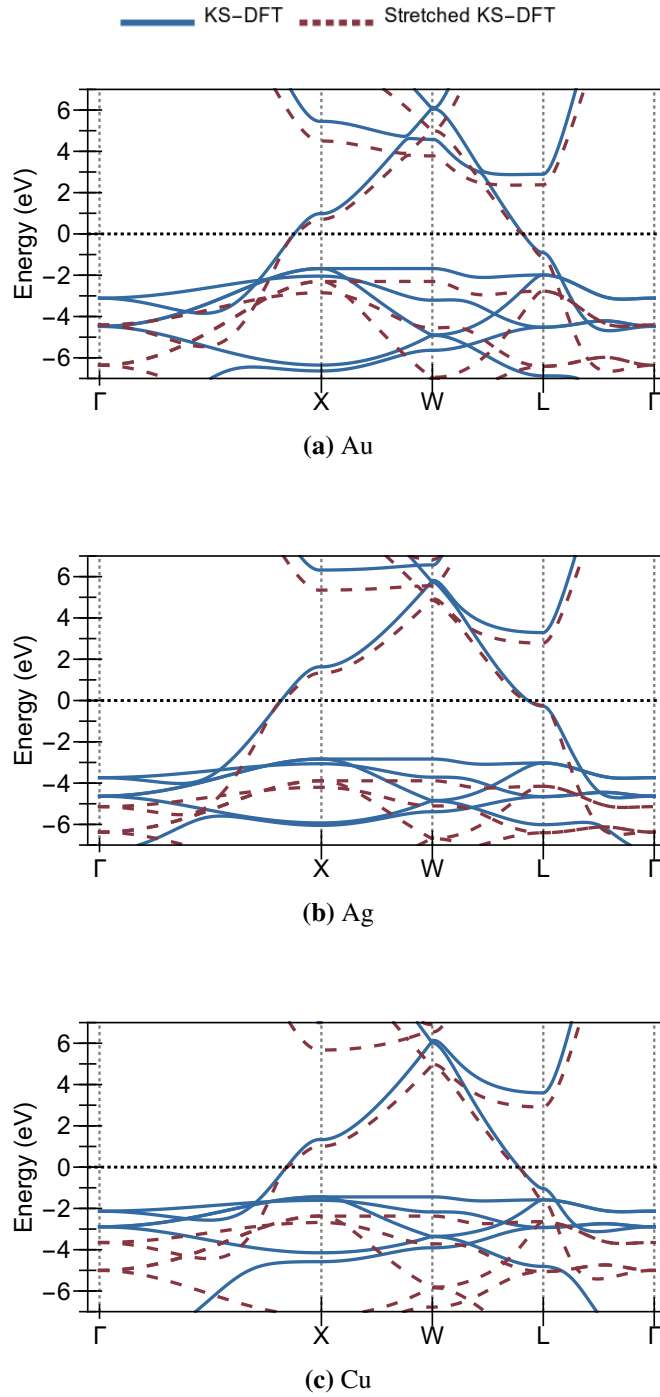


Figure 6.5: KS and QP band-structures for pure metals Au, Ag, and Cu along the high-symmetry point with 0.001 (in $1/a_0$ unit) step size.

6.2.2 Drude parameters for pure metals

Before constructing the final spectra, the Drude parameters introduced in Subsec. 5.2.1 are needed for the intra-band part of the dielectric function in Eq. (5.22). Our first step is to calculate the Drude plasmon energies using Eq. (5.20). For this purpose, the energies of bands crossing the Fermi level at each $\mathbf{k}$ -point were extracted from the outputs of NSCF calculations and interpolated on a fine grid in the Brillouin zone (601 points in each reciprocal-space direction), and the Fermi surface was located on this grid with a ± 0.01 eV tolerance for each system. Then, the square of the Fermi velocities, averaged over the Fermi surface, were calculated by Eq. (5.19). The average Fermi velocity itself is given by

$$v_F^{\text{KS}} = \sqrt{\langle v^2(E_F) \rangle} = \left[\frac{\sum_i \int_{S_F} d\mathbf{S} v_i^2(\mathbf{k})}{\int_{S_F} d\mathbf{S}} \right]^{1/2}, \quad v_i^2(\mathbf{k}) = \left| \frac{\partial \epsilon(\mathbf{k})}{\partial \mathbf{k}} \right|^2, \quad (6.2)$$

where S_F is the Fermi surface, are listed in Table 6.4 along with results in Ref. 37, which uses similar procedure with an extremely dense Brillouin zone sampling as $200 \times 200 \times 200$ rather than interpolating, as we have. Furthermore, the average Fermi velocity magnitudes for QP band-structures can be approximated by applying the geometric average of valence and conduction stretching operator directly to the velocity terms, as in

$$v_F^{\text{G}_0\text{W}_0} = \sqrt{s_v s_c} v_F^{\text{KS}} \quad (6.3)$$

by considering that stretching operators appear as constant coefficients in Eq. (6.2).

	$v_F^{\text{KS}} (10^5 \text{ m/s})$	$v_F^{\text{G}_0\text{W}_0} (10^5 \text{ m/s})$	$v_F (10^5 \text{ m/s})^{[37]}$
Au	13.476	14.588	13.82
Ag	13.912	15.014	14.48
Cu	10.794	12.798	11.09

Table 6.4: The average Fermi velocities for pure Au, Ag, and Cu comparing the work of Gall^[37](the third column), who evaluated the Fermi velocities at a $200 \times 200 \times 200$ Brillouin zone sampling.

The average Fermi velocities are slightly underestimated for KS band-structures with respect to Gall's results in the third column of Table 6.4. However, considering much smaller computational cost, these values are very reasonable estimates of the Drude plasmon energies.

Lastly, the DOS of pure metals based on the KS band-structure and QP band-structure are extracted by applying the Fermi-Dirac distribution function with a 0.1 eV Lorentzian broadening by using a post-processing tool of Yambo. Recalling Eq. (5.20),

$$\omega_p^2 = \frac{4\pi}{3} N(E_F) \langle v^2(E_F) \rangle,$$

the Drude plasmon energies can be estimated for the KS band-structure and QP band-structures with their respective DOS at the Fermi level, if the effective mass is known.

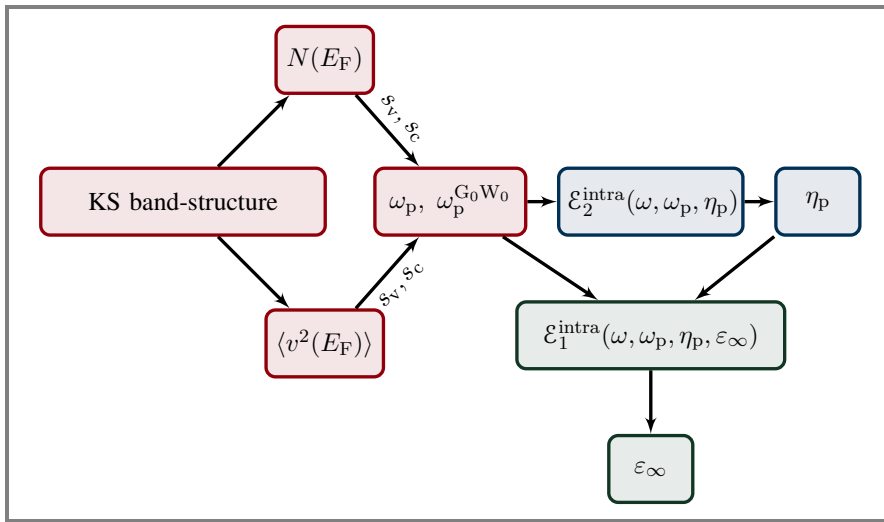


Figure 6.6: The semi-empirical method to obtain Drude parameters for pure metals starting from approximate KS-DFT band-structure.

The next step is to approximate the inverse life-time corresponding to the Drude plasmon, as well as the electric permittivity in the infinite frequency limit within a semi-empirical approach as illustrated in Fig. 6.6. Scaling factors for the inverse life-times η_p in Eq. 5.21 were determined by fitting the imaginary part of the dielectric function to the experimental curves in Ref. 25, and ϵ_∞ values were determined by fitting the real part of the dielectric function with sets of $\{\omega_p, \eta_p\}$ to the same experimental curves for Au, Ag, and Cu. The respective values for FGR, RPA and G_0W_0 +RPA are summarised in Table 6.5.

	ω_p	η_p^{FGR}	$\varepsilon_\infty^{\text{FGR}}$	η_p^{RPA}	$\varepsilon_\infty^{\text{RPA}}$	$\omega_p^{\text{G}_0\text{W}_0}$	$\eta_p^{\text{G}_0\text{W}_0}$	$\varepsilon_\infty^{\text{G}_0\text{W}_0}$
Au	8.911	0.01990	2.143	0.01991	3.775	8.947	0.02266	1.601
Ag	8.725	0.01896	-4.436	0.01896	-2.610	8.925	0.01918	-2.624
Cu	8.836	0.02756	-2.988	0.02758	-0.688	9.313	0.02426	0.104

Table 6.5: The Drude parameters $\{\omega_p, \eta_p, \varepsilon_\infty\}$ (in eV, eV and dimensionless, respectively) for spectra using FGR, RPA, and $\text{G}_0\text{W}_0+\text{RPA}$ for pure Au, Ag, and Cu.

In experimental studies, the Drude parameters are commonly determined by least-squares fitting of the Drude-Lorentz model in Eq. (5.22) to measurements in the IR spectral range. Such measurements are highly sensitive to the experimental details; experimental literature for the Drude parameters is not in good consensus. In Fig. 6.7, despite the relative simplicity of the approaches adopted in this work, the Drude parameters are comparable with experimental predictions.

6.2.3 Spectra of pure metals

The spectra of elemental metals are obtained by applying FGR and RPA to KS band-structures, and RPA on the QP band-structures. The real and imaginary part of the total dielectric function, and the EELS given by the relation in Eq. (1.65) are shown, along with the experimental spectra from the detailed work by Babar and Weaver in Ref. 25, for pure metals in Figs. 6.8, 6.9, and 6.10.

For all three systems, both FGR and RPA predict the lowest band-to-band absorptions, at energies of $\sim 0.5\text{-}1.5$ eV lower than those of the experimental absorption spectra. Furthermore, for higher energies, both approaches produce strong absorption peaks contradicting experiments. On the other hand, $\text{G}_0\text{W}_0+\text{RPA}$ locates the low-lying peaks at $\sim 3\text{-}4$ eV in Au, at $\sim 4\text{-}5$ eV in Ag, and at $\sim 2\text{-}3$ eV in Cu more accurately, as well as the overall curve trend, with respect to the experimental absorption spectra. Particularly, all three approaches reproduce the behaviour of $\varepsilon_1^{\text{Cu}}$ and $\varepsilon_1^{\text{Au}}$ successfully, whereas it works relatively well for $\varepsilon_1^{\text{Ag}}$. Such improvements, along with drastic improvements in ε_2 using $\text{G}_0\text{W}_0+\text{RPA}$, lead us to locate the first plasmonic peaks in all systems quite accurately in EELS, where FGR and RPA miss these features completely in Figs. 6.8, 6.9, and 6.10. As one can observe, improvements provided by $\text{G}_0\text{W}_0+\text{RPA}$ become less effective at higher energies, while still

6. Investigating the optical response of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys

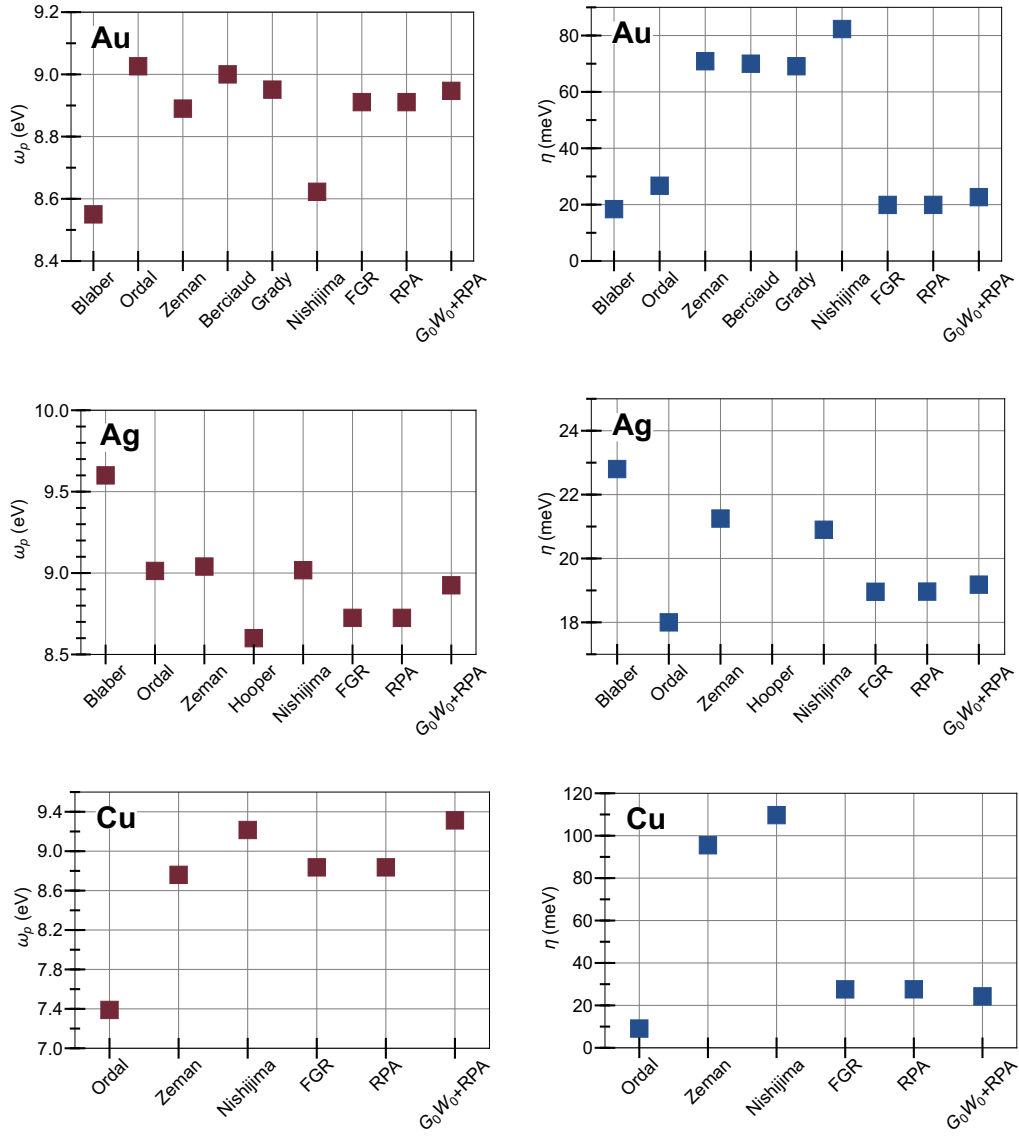


Figure 6.7: Comparison of the Drude plasmon energies and inverse life-times with commonly used experimental literature for these parameters, specifically from Blaber^[38], Ordal^[24], Zeman^[39], Berciaud^[40], Grady^[41], Hooper^[42], and Nishijima^[18].

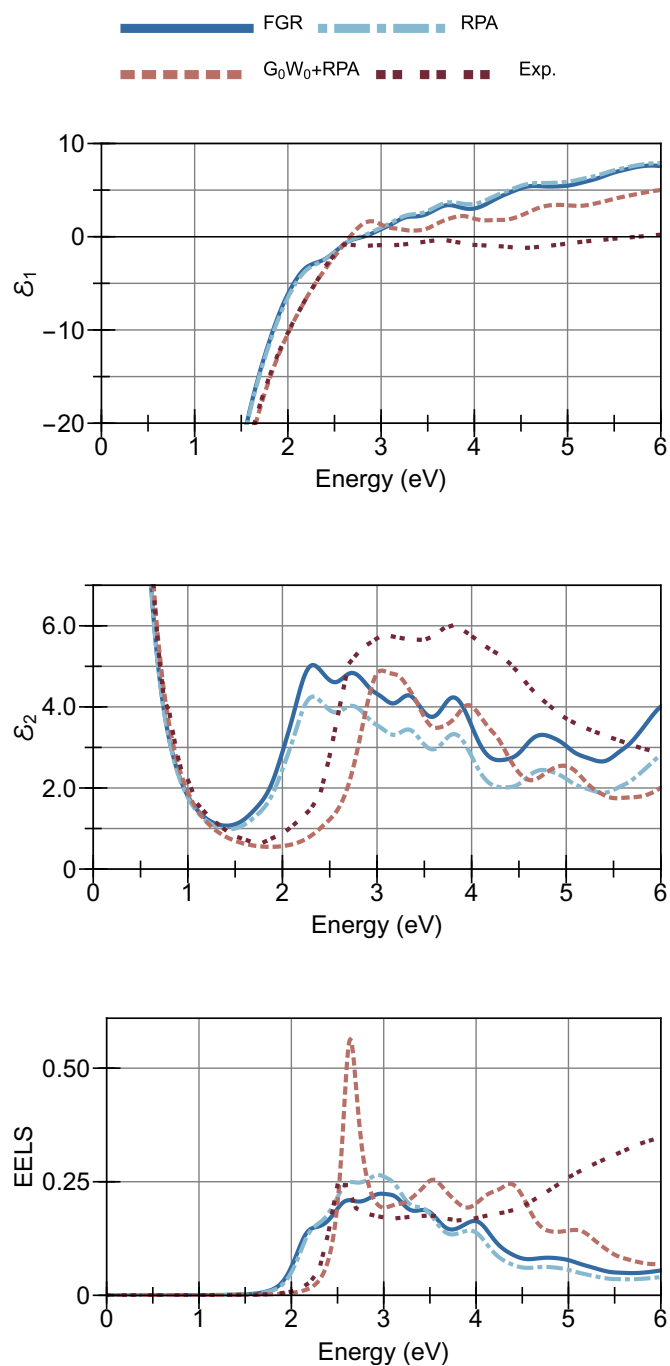


Figure 6.8: The real and imaginary parts of the dielectric function and EELS using FGR, RPA, G_0W_0 +RPA compared with the experimental data from Babar^[25] of bulk Au.

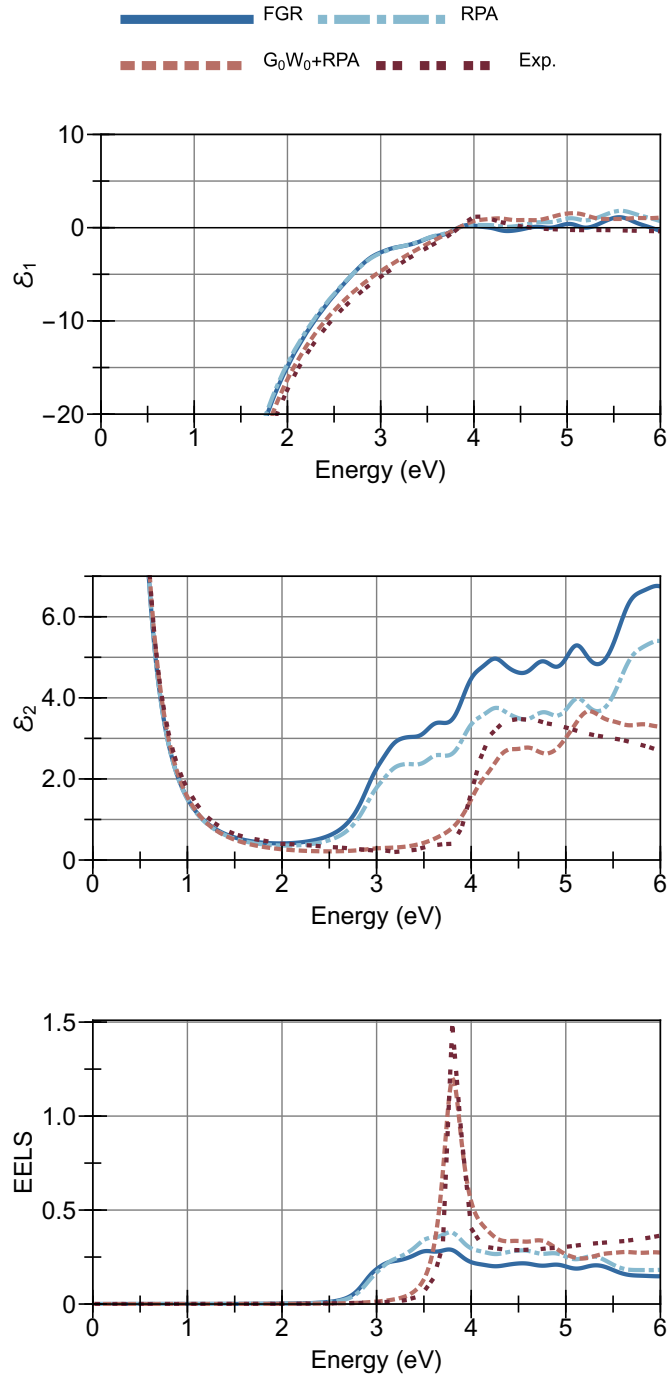


Figure 6.9: The real and imaginary parts of the dielectric function and EELS using FGR, RPA, G_0W_0 +RPA compared with the experimental data from Babar^[25] of bulk Ag.

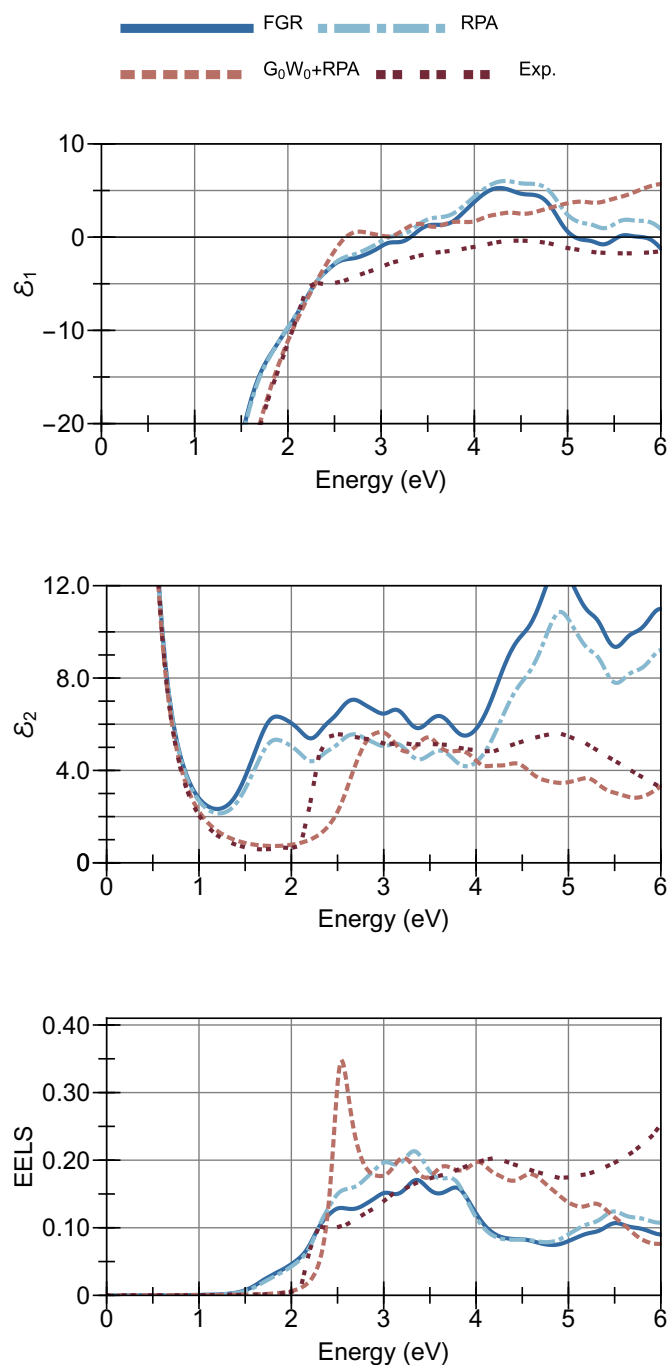


Figure 6.10: The real and imaginary parts of the dielectric function and EELS using FGR, RPA, G_0W_0 +RPA compared with the experimental data from Babar^[25] of bulk Cu.

some improvements are achieved compared to FGR and RPA. This is well expected as QP band-structures were approximated by an averaged stretching factor determined using the bands close to the Fermi level instead of using producing full QP band-structure. Hence, by construction, this simplified approach is more effective for the transitions occurring between the bands close to the Fermi level, which constitute the lower part of the spectra, which are in any case those relevant to plasmonic applications. However, regardless of its reducing effectiveness with increasing energy, G_0W_0 +RPA offers a feasible approach to describe the lower part of the spectra, as well as some improvement for higher energies as well. A further avenue for improvement of these spectra would be the incorporation of SOC, even at the stretching operator level.

6.3 Spectra of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys

Starting geometries for selected ordered alloys in multiples of 12.5% composition were constructed by using super cells of pure metals and substituting the desired number of other species to achieve the primitive unit cells for each stoichiometric ratio. Sample crystal structures for each stoichiometric ratio are shown in Fig. 6.11. Alloys with the stoichiometric ratios of $\{2 : 1 : 1\}$ and $\{6 : 1 : 1\}$ ¹ have 3 and 4 possible phases, respectively; and a total of 39 structures² were studied through the standardised work-flow in Fig. 6.3.

Recalling the particular choice of $16 \times 16 \times 16$ grid in Brillouin zones for pure metals, grid points for each stoichiometric ratio were chosen such as to keep pure metal primitive unit cell number equal in the super cells for convenience and comparability as summarised in Table 6.6.

	$\{1 : 0 : 0\}$	$\{1 : 1 : 0\}$	$\{3 : 1 : 0\}$	$\{2 : 1 : 1\}$	$\{7 : 1 : 0\}$	$\{6 : 1 : 1\}$
NSCF	$16 \times 16 \times 16$	$8 \times 16 \times 16$	$8 \times 8 \times 16$	$8 \times 8 \times 16$	$8 \times 8 \times 8$	$8 \times 8 \times 8$

Table 6.6: The uniform grids for Brillouin zones of alloys in NSCF calculations.

For systems with multiple primitive phases, the final spectra are obtained with a novel

¹The notation $\{a, b, c\}$ is used to refer to stoichiometric ratios with the integer values a, b, c among Au, Ag, and Cu for simplicity.

²See App. A for QE, NSCF input files including the final crystallographic information after geometry relaxations.

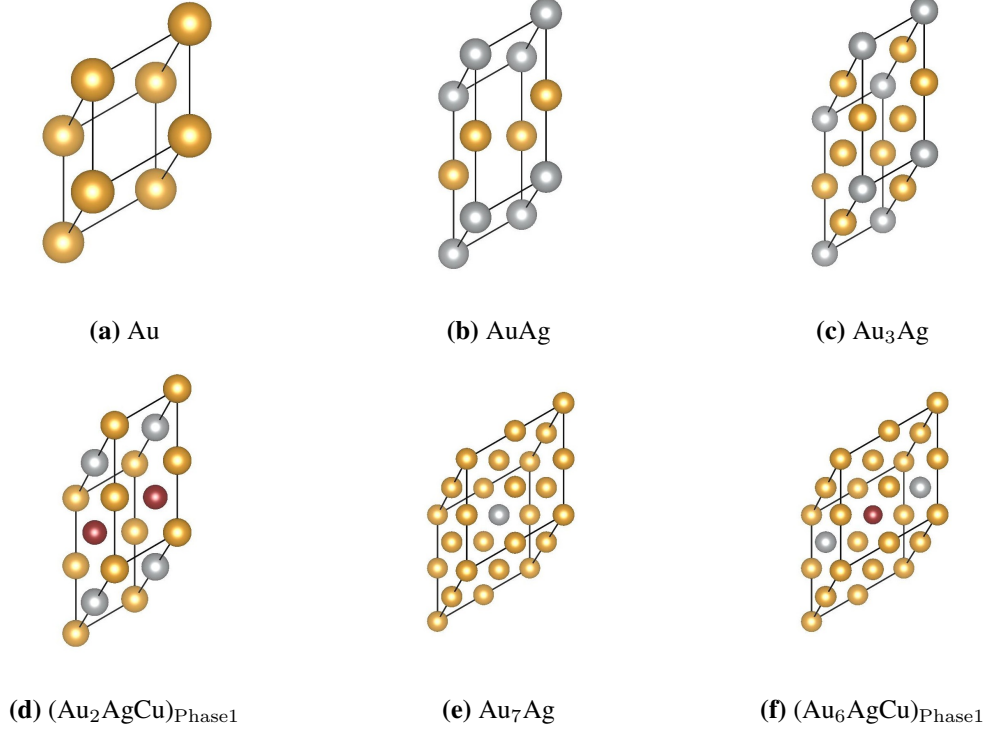


Figure 6.11: The sample structure for chosen stoichiometric ratios of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$.

thermodynamic averaging process using Boltzmann factor defined as

$$p_i = \frac{e^{-\frac{E_0 - E_i}{kT}}}{\sum_j e^{-\frac{E_0 - E_j}{kT}}}, \quad (6.4)$$

where j is the phase index, and E_0 and E_i , respectively, are the lowest ground-state energy among all phases and the ground-state energy of i^{th} phase. The final spectra of $\{2 : 1 : 1\}$ and $\{6 : 1 : 1\}$ are thus linear combinations of the spectra of their respective phases, with corresponding weighting constants.

6.3.1 Stretching operators for alloys

The stretching operators were calculated for all valence bands and an equal number of conduction bands at 10 points at and around the Γ point for each stoichiometric ratio, as summarised in Table 6.7.

6. Investigating the optical response of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys

	$\{1 : 0 : 0\}$	$\{1 : 1 : 0\}$	$\{3 : 1 : 0\}$	$\{2 : 1 : 1\}$	$\{7 : 1 : 0\}$	$\{6 : 1 : 1\}$
Number of bands (v+c)	6+6	12+12	24+24	24+24	46+46	46+46

Table 6.7: The number of bands used in G_0W_0 calculations for each stoichiometric ratio.

The renormalisation factors expressed in Eq. (5.38a) show a steady trend of decreasing with increasing Cu ratio both in the valence and the conduction manifolds, as shown in Fig. 6.12a and Fig. 6.12b. The valence stretching operator in Fig. 6.12c grows significantly larger for increasing Cu ratios. Pure Cu has the largest reciprocal unit cell, where the d -bands are spuriously flattened and narrowly packed the most by KS-DFT as also seen in Fig. 6.5c. Hence, larger stretching at the valence manifold is expected to result from an increasing Cu concentration.. The conduction stretching operators show inverse trends providing a slightly smaller stretching at the conduction manifold for increasing Cu concentrations. The stretching operators were applied to each alloy system, and further simulations were performed on the stretched (QP) band-structures individually; thus, the prefixes are subsequently dropped for the notational simplicity¹.

¹See App. B for the full list of the valence and the conduction stretching operators.

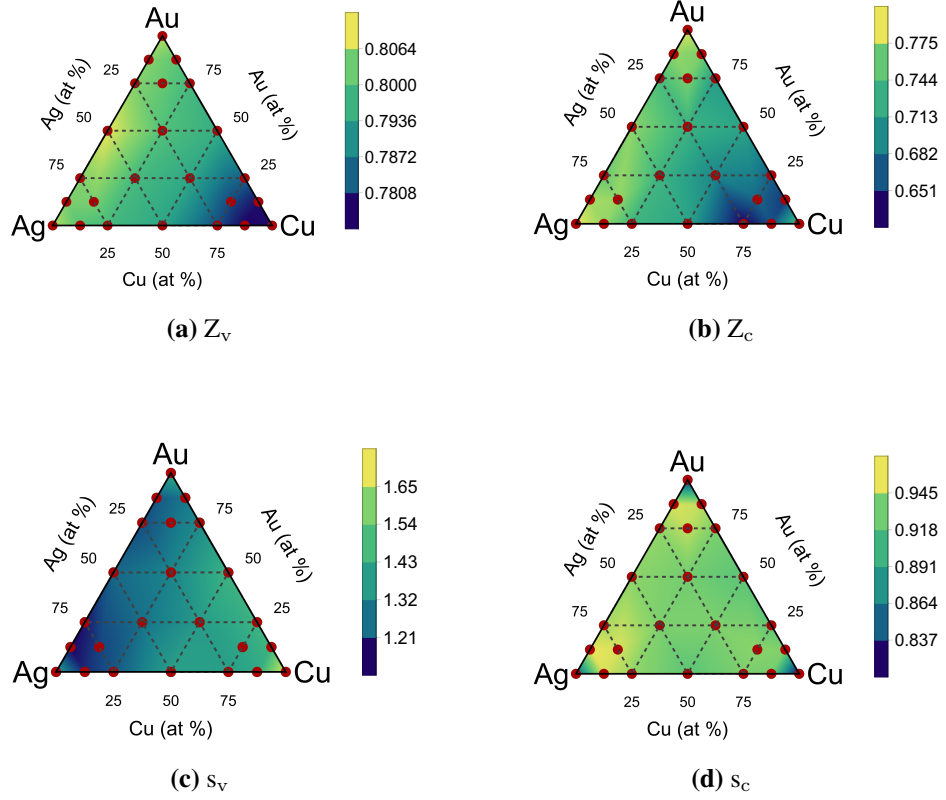


Figure 6.12: Stoichiometric dependence of the averaged QP renormalisation factors Z (a, and b), and corresponding stretching operators (c, and d) for chosen valence and conduction bands. The actual data points are marked with the red dots.

6.3.2 Drude parameters for alloys

Using a similar procedure to that for pure metals, the Fermi velocities and DOS at the Fermi level were computed for each alloy system. The stoichiometric dependence of the averaged QP Fermi velocities and DOS at the Fermi level are shown in Fig. 6.13. The Fermi velocities show some symmetric features, while they are lower in the case of predominantly Cu-based stoichiometric ratios. Conversely, the DOS becomes large for increasing Cu ratios as also the volumes of the systems are contracting with increasing Cu concentrations.

6. Investigating the optical response of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys

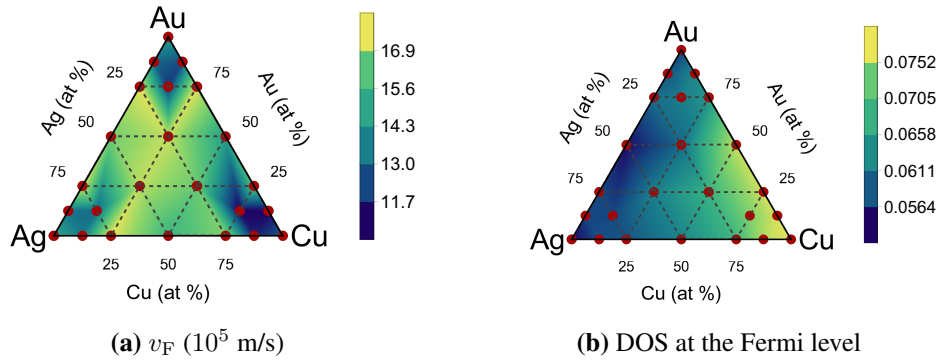


Figure 6.13: Stoichiometric dependence of the averaged QP Fermi velocities and DOS at the Fermi level (dimensionless). The actual data points are marked with the red dots.

Competing trends in the Fermi velocities in Fig. 6.13a and DOS in Fig. 6.13b compensate each other, and leading to a symmetric trend in the interpolated counter plot of the Drude plasmon energies in Fig. 6.14a. The inverse life-times in Fig. 6.14b were evaluated by using Eq. (5.21), where $\{c_\eta\}$ coefficients were produced via arithmetic averaging of the inverse-life times of pure metals Table 6.5 with respect to the stoichiometric ratios as

$$c_\eta^{(\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y})} = (xc_\eta^{\text{Au}} + yc_\eta^{\text{Ag}} + (1-x-y)c_\eta^{\text{Cu}}). \quad (6.5)$$

As the inverse life-times are proportional to the Fermi velocities and the DOS at the Fermi level, they show similar symmetries to the Drude plasmon energies. The electric permittivities at the infinite-frequency limit are simply approximated by the arithmetic averaging of values of pure metals in Table 6.5 with respect to the stoichiometric ratios; hence, the trend is a flat plane by construction.

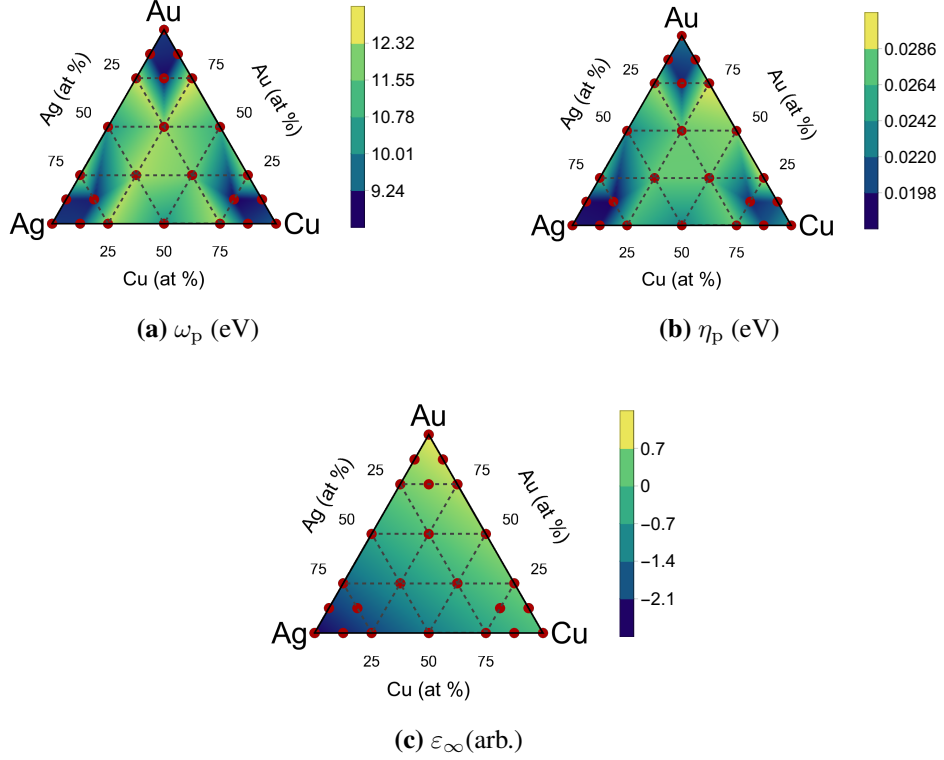


Figure 6.14: Stoichiometric dependence of the averaged Drude plasmon energies, the inverse lifetimes and electric permittivity in the infinite-frequency limit for the QP band-structures. The actual data points are marked with the red dots.

6.3.2.1 Binary alloys

Following the edges of Fig. 6.14a and Fig. 6.14b, starting from Cu to Ag passing through Au, the Drude plasmon energies and the inverse life-times as the function of alloying Au are shown in Fig. 6.15. The behaviours of ω_p and η_p show similar trends with the experimental works of Refs. 15,16, and 18, while the presented stoichiometric ratios are not perfectly matching ratios in their works.

6.3.3 Spectra of alloys

The inter-band parts of the dielectric function of alloys were calculated with FGR and RPA upon the KS band-structure and QP band-structure in the three Cartesian unit vectors. The total

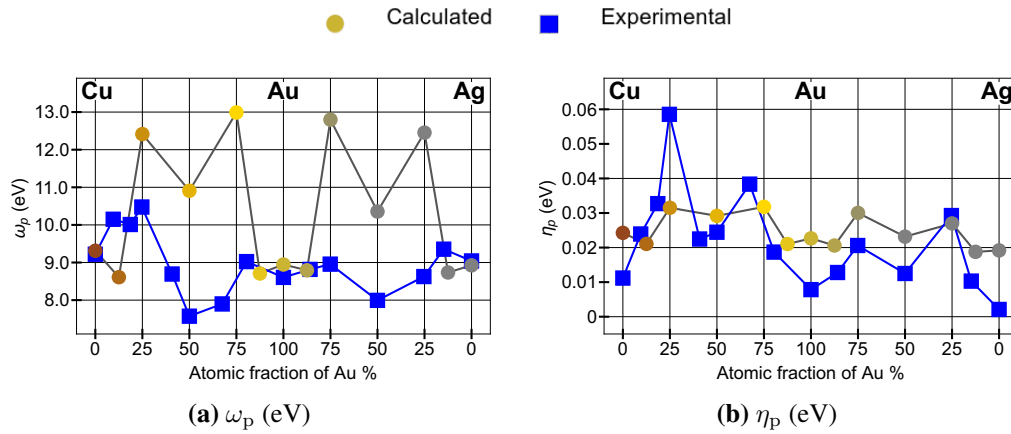


Figure 6.15: The calculates values (coloured circles), and the experimental values (blue squares) extracted from Ref. 16, of the Drude plasmon energy and the inverse-life time for the binary alloys of Au, Ag, and Cu as function of Au ratios in sample.

dielectric functions were obtained by adding the intra-band parts via Eq. (5.17) to arithmetically averaged inter-band parts over the unit vector directions together with averaging over crystal structures where necessary¹.

6.4 Investigation of plasmonic response of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys

Rapidly growing demand on strong, long-lived and well-controllable plasmons for various opto-electronic applications motivates for search of integrable and cost-effective plasmonic materials. Furthermore, technological limitations in laser technologies^[43] force us to design such systems within quite narrow energy ranges. Increasing accuracy of fabrication methods within shorter production time provides high-quality nano-materials; hence, plasmonic response become more dependent on fundamental limitations of underlying materials. Consequently, optical merits, which can be deduced using fundamental optical quantities, are crucial to determine intrinsic limitations of materials as well as engineering their plasmonic responses.

¹See App. B for the band-structures and the spectra of alloys.

6.4.1 Quality factors for plasmons

Even though plasmon production is highly dependent on size and geometry of nano-materials, some fundamental criteria can be suggested as universal conditions for strong plasmonic response. The primary requirement of a strong plasmon is the presence of a high-density of free electrons such as in noble and alkali metals, which are prominent systems for plasmonic applications^[44]. Moreover, plasmon quality is predominantly determined by loss^[45,46], which can occur through various phenomena such as radiative dumping, surface scattering, thermal loss^[47], and imperfections in materials such as surface roughness^[48], grain boundaries^[49]. Some approximate methods are proposed to sum individual contributions of these conditions to determine overall plasmon quality^[47]. As we work on perfectly ordered bulk systems, our aim is to determine some universal preliminary measures, which are independent of size and structural properties, for plasmon qualities starting from bulk dielectric functions. Plasmons in bulk systems are predominantly *bulk plasmons*, which is result of combination of both intra-band and inter-band transitions¹ [44]. The bulk plasmon energy Ω_p is expected to be at lower energy than the bare plasmon energy ω_p due to screening of inter-band transitions. Additionally to bulk plasmons, there are surface plasmons due to finite size of realistic systems. EELS, which is introduced in Subsec. 1.4.3, provides signature for bulk plasmons. Similarly, a slightly modified expression of EELS can be proposed for a signature for surface plasmons for noble metals such as^[50]

$$-\Im \left[\frac{1}{1 + \mathcal{E}} \right], \quad (6.6)$$

which impose the condition of $\mathcal{E}_1 \approx -1$ and $\mathcal{E}_2 \approx 0$ for significant surface plasmons. Furthermore, some measures for more specific plasmons such as *the localised surface plasmon* (LSP)^[51,52], and *the surface plasmon polaritons* (SPP)^[53], which are crucial many plasmonic applications^[54] such as optical circuits^[55] and switching^[56,57]. In Ref. 46, various measures using relations between $\mathcal{E}_1$ and $\mathcal{E}_2$ for LSP and SPP such at low-loss and the nearly electrostatic limit have been investigated for their respective optimised geometries. $\mathcal{E}_1$ provides preliminary condition of presence of free electrons, while $\mathcal{E}_2$ is related to loss due to decaying of plasmons to particle-hole pairs via absorption. Hence, the number of electrons going through inter-band transitions is desired to be small around plasmon frequencies. Blaber, and *et al.*^[44] suggest some universal quality factors for LSP and SSP in metallic

¹Conveniently, the Drude plasmon is also called *the bare plasmon*.

systems with optimised geometries

$$Q_{\text{LSP}}(\omega) = -\frac{\epsilon_1}{\epsilon_2}, \quad \text{and} \quad Q_{\text{SPP}}(\omega) = \frac{\epsilon_1^2}{\epsilon_2}. \quad (6.7)$$

These quality factors provide some preliminary insights on the capacity of metals to produce surface plasmons and life-times of such plasmons determined by dumping due to inter-band transitions.

6.4.2 Plasmons in binary alloys

Alloying noble metals among themselves is the commonly used method to modify plasmonic response of such materials, while decreasing cost and increasing chemical and thermal stabilities. Binary alloys of Au, Ag, and Cu are popular; since they have similar crystallographic properties and strong plasmonic responses. It has repeatedly been shown that modification of plasmonic response is far more complex than simple model as well as highly dependent on fabrication methods^[9–14,44]. However, signatures for bulk and surface plasmons as well as the quality factors can be used for preliminary plasmonic merits for such systems.

Bulk and surface EELS, Q_{LSP} , and Q_{SPP} at 200-1000 nm are presented for Au-Ag, Au-Cu, and Ag-Cu binary alloys in Figs. 6.16, 6.17, and 6.18, respectively. Also, amplitudes and wavelengths of global maxima between 200-1000 nm of surface EELS obtained from first-principles bulk dielectric functions using Eq. (6.6) are listed in Table 6.8, Table 6.9, and Table 6.10 alongside with Q_{LSP} and Q_{SPP} values at corresponding wavelengths.

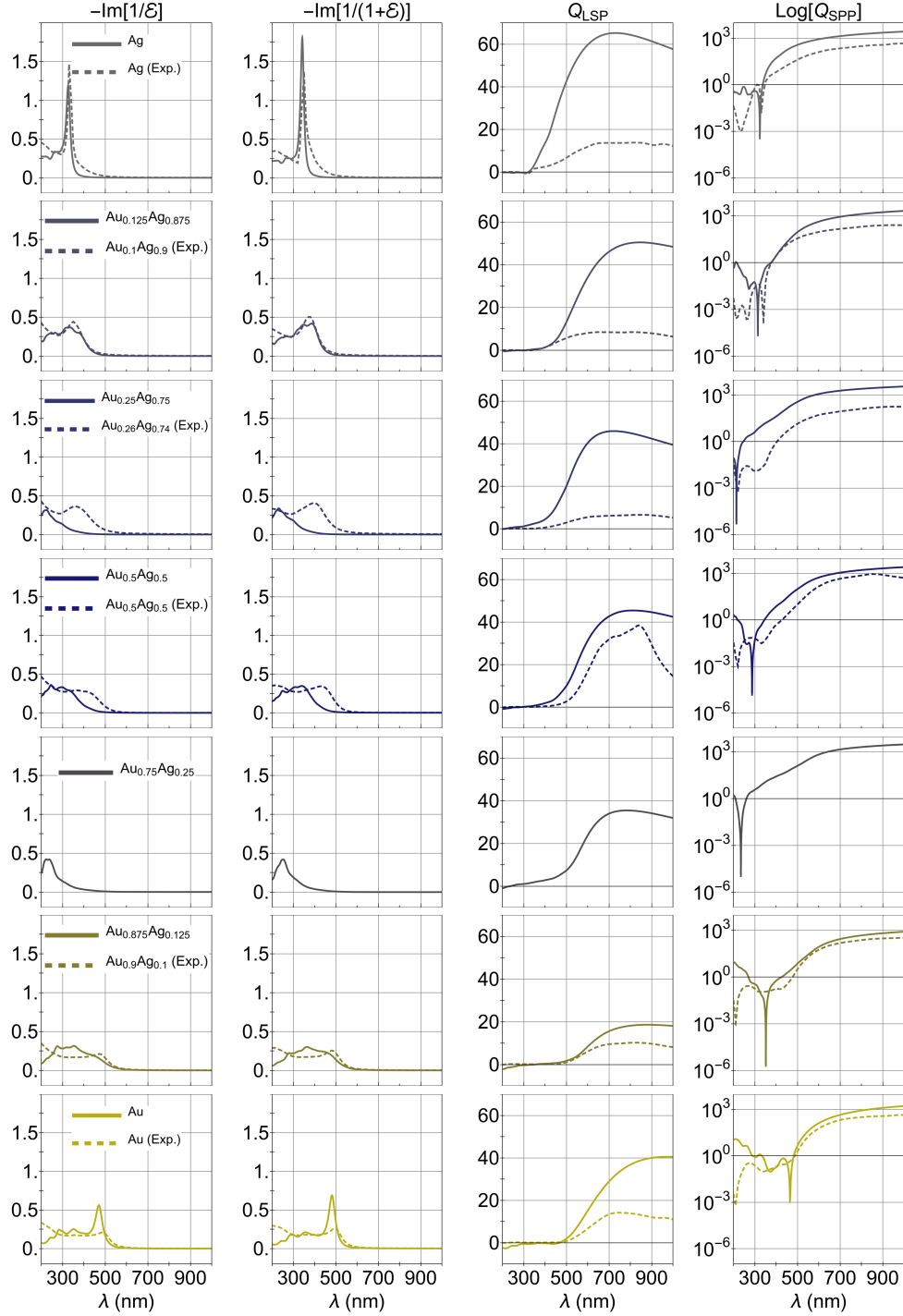


Figure 6.16: Bulk EELS (first column), surface EELS (second column), Q_{LSP} (third column) and Q_{SPP} (fourth column) from first-principles bulk dielectric functions (solid lines) and experimental SPP measurements on thin-films (dashed lines) of Au-Ag binary alloys with similar stoichiometric ratios extracted from Ref. 17.

6. Investigating the optical response of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys

	$-\Im\left[\frac{1}{(1+\epsilon)}\right]_{\max} \rightarrow \lambda \text{ (nm)}$	Q_{LSP}	Q_{SPP}
Ag	$1.81 \rightarrow 342$	2.02	2.21
AuAg_7	$0.42 \rightarrow 385$	0.83	1.46
AuAg_3	$0.34 \rightarrow 231$	0.36	0.39
AuAg	$0.35 \rightarrow 339$	0.53	0.79
Au_3Ag	$0.42 \rightarrow 250$	0.39	0.36
Au_7Ag	$0.30 \rightarrow 364$	0.17	0.09
Au	$0.69 \rightarrow 482$	0.84	1.00

Table 6.8: The amplitudes and wavelengths (in nm units) of global maxima between 200-1000 nm extracted from surface EELS in Fig. 6.16, which are constructed from first-principles bulk dielectric functions using Eq. (6.6), alongside with Q_{LSP} , and Q_{SPP} factors at corresponding wavelengths for Au-Ag binary alloys.

In Fig. 6.16, bulk and surface EELS are relatively successful to produce SSP measurements extracted from Ref. 17, while Q_{LSP} and Q_{SPP} are significantly overestimated. Such overestimation is expected as only radiative loss can be considered through dielectric function of pristine bulk systems, where any surface effects or thermal loss are not included with methods used in this work. The distinctive peaks in EELS of Au and Ag disappear in their binary alloys in both bulk and surface EELS. Alloying pushes minimums of ϵ_2 to larger wavelengths, while ϵ_1 has large values¹. Hence, plasmons energies are higher than inter-band transition edges for Au-Ag alloys. Consequently, damping of plasmons become larger due to fast decaying to particle-hole pairs. These are reflected both in Q_{LSP} and Q_{SPP} by lower qualities in binary alloys compared to pure Au and Ag. However, in Table 6.8, AuAg_7 still shows relatively strong plasmonic features at 385 nm, which is close plasmon wavelength of pure Ag at 342 nm, with significant Q_{LSP} (0.83) and Q_{SPP} (1.46) that are larger than of pure Au.

¹See Fig. B.1 for dielectric functions of Au-Ag binary alloys.

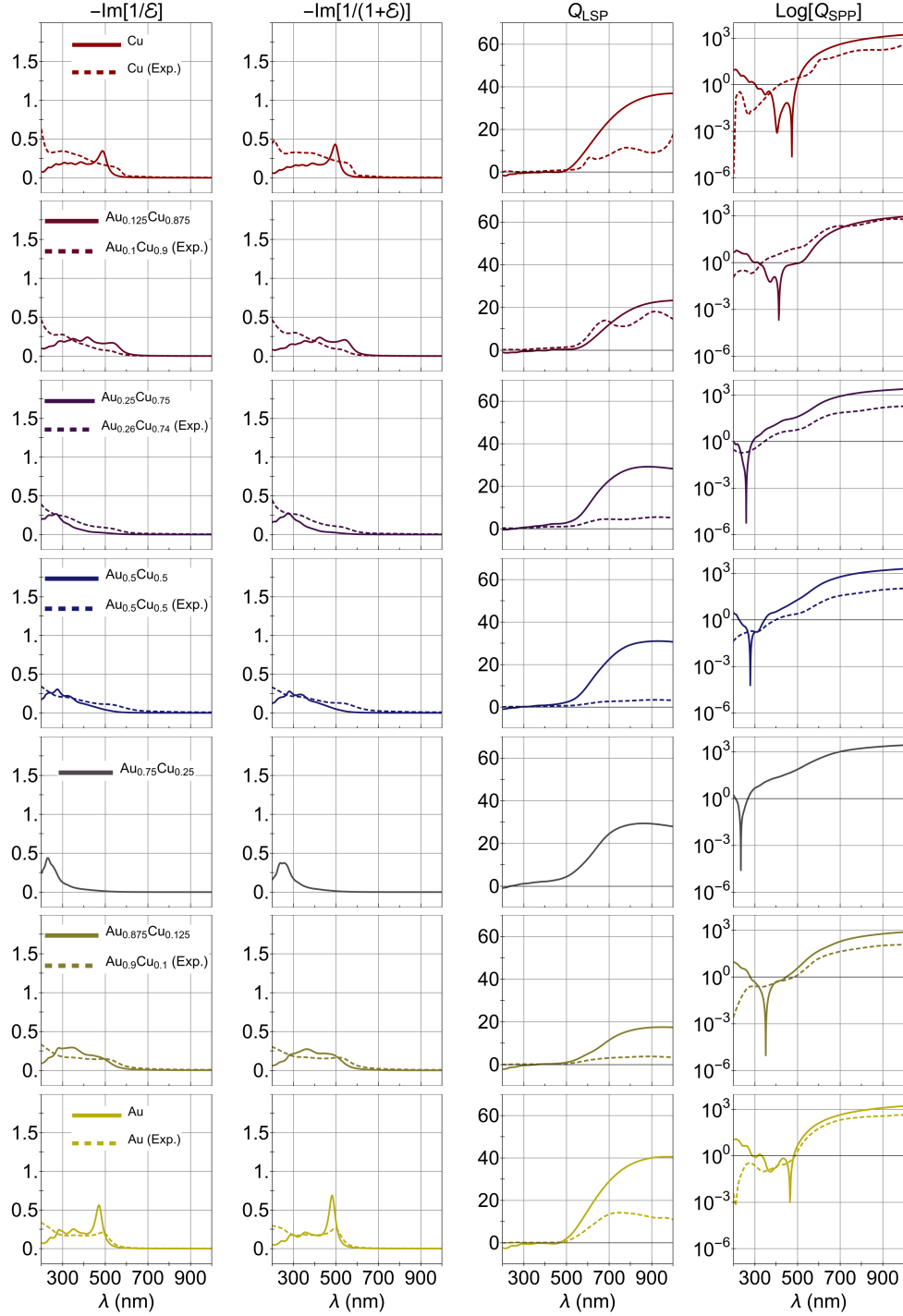


Figure 6.17: Bulk EELS (first column), surface EELS (second column), Q_{LSP} (third column) and Q_{SPP} (fourth column) from first-principles bulk dielectric functions (solid lines) and experimental SPP measurements on thin-films (dashed lines) of Au-Cu binary alloys with similar stoichiometric ratios extracted from Ref. 17.

6. Investigating the optical response of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys

	$-\Im\left[\frac{1}{(1+\varepsilon)}\right]_{\max} \rightarrow \lambda \text{ (nm)}$	Q_{LSP}	Q_{SPP}
Cu	$0.43 \rightarrow 496$	0.67	1.00
AuCu_7	$0.24 \rightarrow 423$	0.16	0.10
AuCu_3	$0.28 \rightarrow 276$	0.29	0.30
AuCu	$0.28 \rightarrow 281$	0.05	0.01
Au_3Cu	$0.37 \rightarrow 255$	0.37	0.36
Au_7Cu	$0.27 \rightarrow 364$	0.12	0.05
Au	$0.69 \rightarrow 482$	0.84	1.00

Table 6.9: The amplitudes and wavelengths (in nm units) of global maxima between 200-1000 nm extracted from surface EELS in Fig. 6.16, which are constructed from first-principles bulk dielectric functions using Eq. (6.6), alongside with Q_{LSP} , and Q_{SPP} factors at corresponding wavelengths for Au-Cu binary alloys.

In Fig. 6.17, pure Cu exhibits already weak plasmonic resonance, which disappears through alloying with Au. In this series, only pure Au shows strong surface plasmon resonance with relatively significant quality factors compared pure Au and Au-Cu binary alloys. Inter-band transition edges are pushed drastically to larger wavelengths (smaller energies) by alloying Au with Cu, where ε_1 of Au-Cu binary alloys have already quite large values¹. Particularly, AuCu exhibits only a very short-living plasmon resonance at ~ 4.41 eV with the worst performing LSP and SPP among Au-Cu binary alloys.

¹See Fig. B.2 for dielectric functions of Au-Cu binary alloys.

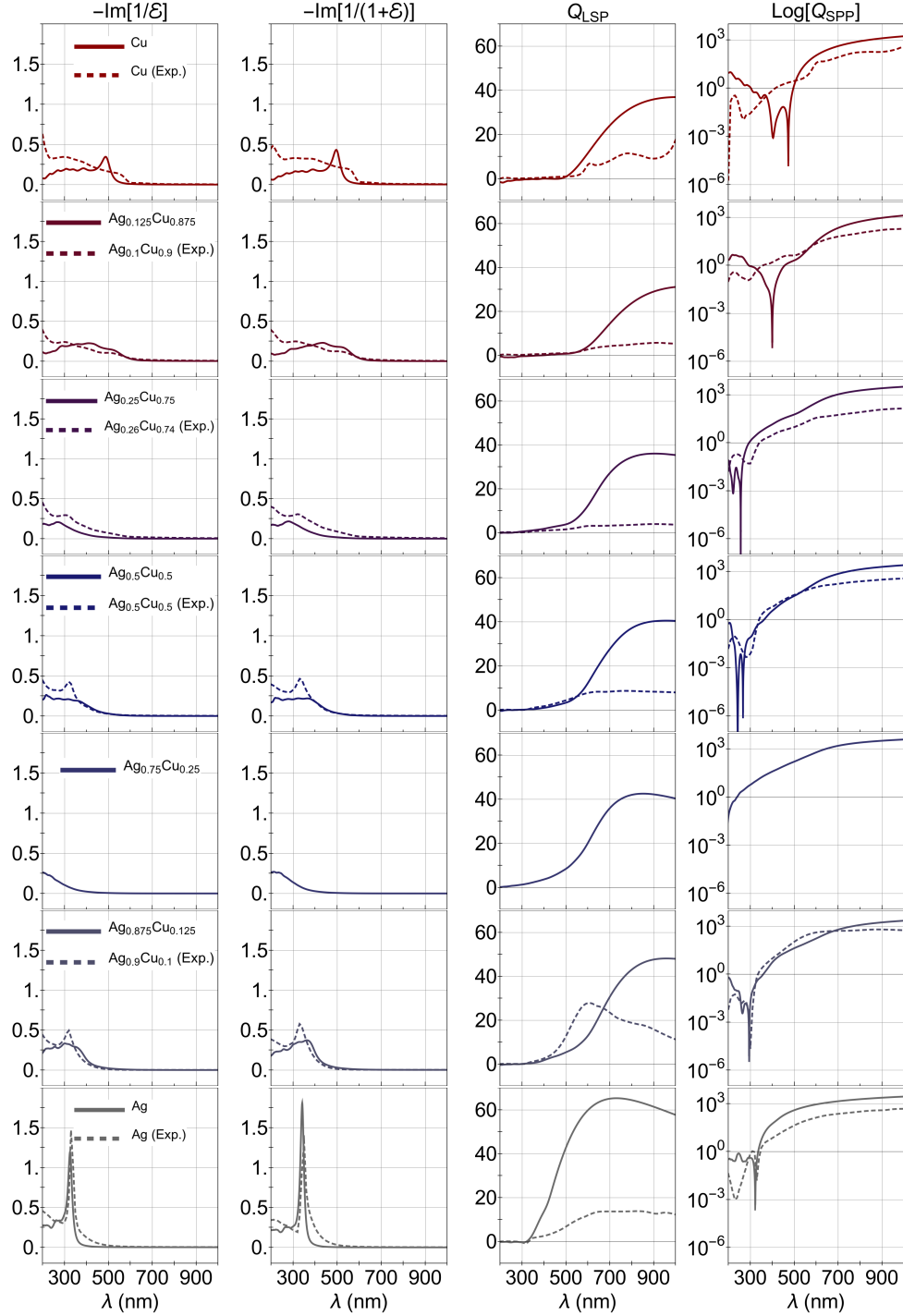


Figure 6.18: Bulk EELS (first column), surface EELS (second column), Q_{LSP} (third column) and Q_{SPP} (fourth column) from first-principles bulk dielectric functions (solid lines) and experimental SPP measurements on thin-films (dashed lines) of Ag-Cu binary alloys with similar stoichiometric ratios extracted from Ref. 17.

6. Investigating the optical response of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys

	$-\Im\left[\frac{1}{(1+\varepsilon)}\right]_{\max} \rightarrow \lambda \text{ (nm)}$	Q_{LSP}	Q_{SPP}
Cu	0.43 $\rightarrow$ 496	0.67	1.00
AgCu ₇	0.23 $\rightarrow$ 435	0.28	0.34
AgCu ₃	0.21 $\rightarrow$ 279	0.28	0.35
AgCu	0.23 $\rightarrow$ 219	-0.16	0.09
Ag ₃ Cu	0.27 $\rightarrow$ 212	0.27	0.28
Ag ₇ Cu	0.37 $\rightarrow$ 364	0.71	1.24
Ag	1.81 $\rightarrow$ 342	2.02	2.21

Table 6.10: The amplitudes and wavelengths (in nm units) of global maxima between 200-1000 nm extracted from surface EELS in Fig. 6.16, which are constructed from first-principles bulk dielectric functions using Eq. (6.6), alongside with Q_{LSP} , and Q_{SPP} factors at corresponding wavelengths for Ag-Cu binary alloys.

Similar to previous cases, alloying Ag with Cu leads to disappearance of distinctive peak in pure Ag. However, once again, AgCu₇ shows relatively strong plasmon peaks with both significant LSP and SPP quality factors, which have larger values than pure Cu. Once again, AgCu performs worst in terms of qualities of LSP and SPP with a negative factor for LSP. This pure performance is due to an inter-band transition edge at a very large wavelength ($\sim 800 \text{ nm}$)¹.

In summary, pure Ag exhibits strongest surface plasmon resonance at 342 nm with $Q_{\text{LSP}}=2.02$ and $Q_{\text{SPP}}=2.21$ factors. Such strong plasmons in pure Ag is expected as the inter-band transition edge is at the higher energy than the screened Drude plasmon energy as clearly seen in Fig. 6.9 by comparing EELS and ε_2 . Besides pure Ag, pure Au and Cu also show some weaker, but still distinctive plasmon resonance at 432 nm and 496 nm, respectively, with relatively large quality factors in LSP and SPP. Furthermore, AuAg₇ and Ag₇Cu produce significant plasmon resonances at wavelengths close to that of pure Ag with comparable amplitudes with longer life-times in LSP and SPP to these of pure Au and Cu, respectively.

¹ See Fig. B.3 for dielectric functions for Ag-Cu binary alloy.

6.4.3 Plasmonic response at common solid-state laser wavelengths

Three common solid-state laser wavelengths were chosen to demonstrate the plasmonic efficiencies of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$. The first wavelength is a common red laser at 650 nm (1.9074 eV) produced using InGaAIP^[43] and used in a wide range of applications such in imaging and sensing in biological systems in conjunction with a heterostructure of noble metals^[3,58].

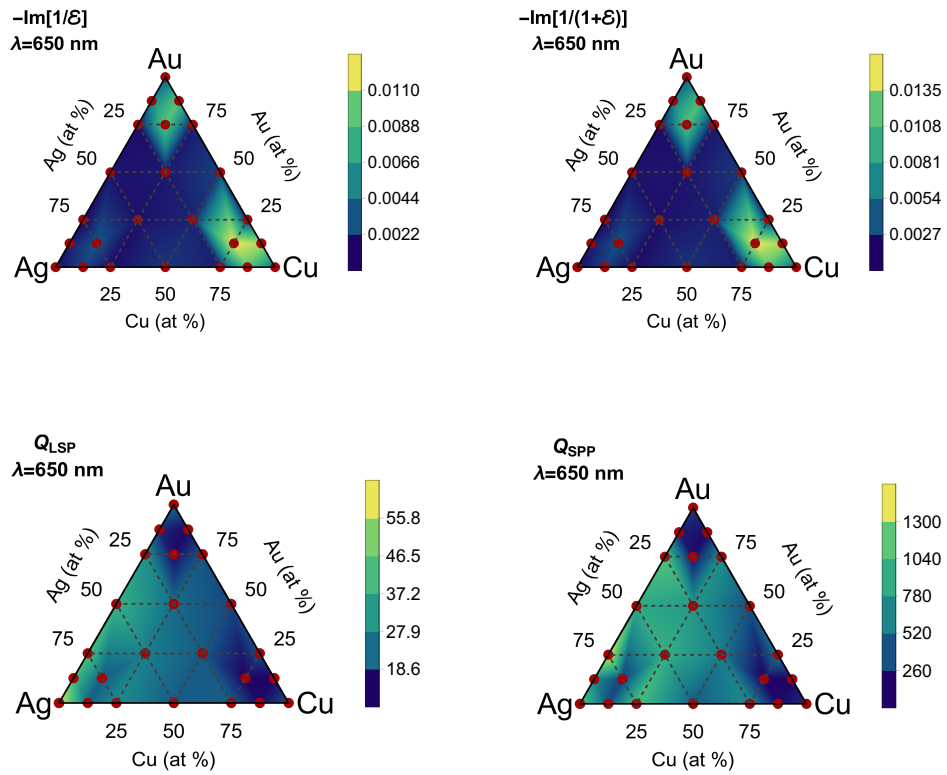


Figure 6.19: Stoichiometric dependence of the averaged plasmon descriptors of bulk and surface EELS, Q_{LSP} , and Q_{SPP} for $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ at the common red solid-state laser wavelength 650 nm.

In Fig. 6.19, $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys have weak bulk and surface plasmon resonances at orders of 10^{-2} - 10^{-3} . As this wavelength is commonly somewhere between the Drude tails and inter-band transition edges of ϵ_2 , these weak plasmons have long life-times due to small radiative dumpings, which result the large LSP and SPP factors. Au_6AgCu and AuAgCu_6 exhibits relatively strong plasmon resonance, whereas LSP and SPP have poor quality factors at these

stoichiometric ratios due to larger losses at this wavelength¹. Pure Ag exhibits large quality factors for LSP and SPP; however, plasmonic resonances are quite weak at 650 nm.

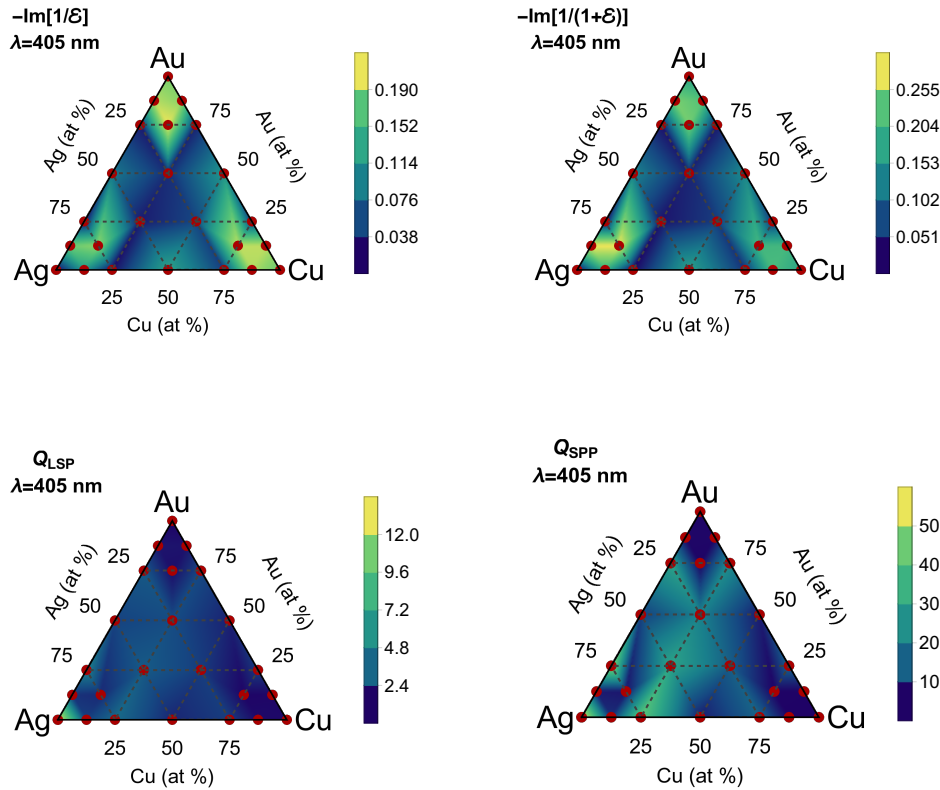


Figure 6.20: Stoichiometric dependence of the averaged plasmon descriptors of bulk and surface EELS, Q_{LSP} , and Q_{SPP} for $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ at the common blue-ray solid-state laser wavelength 405 nm.

The second frequency is that of the common lasers used in blu-ray devices at 405 nm (3.0613 eV), generally produced using InGaN^[59] for efficient optical recording in conjunction with noble metal nano-clusters^[60]. In Fig. 6.20, {7:1:0} stoichiometric ratios show relatively significant plasmon resonance alongside with {6:1:1} stoichiometric ratios in order of $\sim 10^{-1}$, which are comparable to these of maxima of plasmon peaks of binary alloys, with large quality factors of LSP and SPP. For LSP, Ag predominantly has long-lived localised surface plasmons, while AuAg_3 shows some longevity. QSP quality has a sharper gradient compared to the red laser case, as some QSP values fall after the global minimum points for some systems.

¹See App.B for ϵ_2 of phases in this stoichiometric ratios.

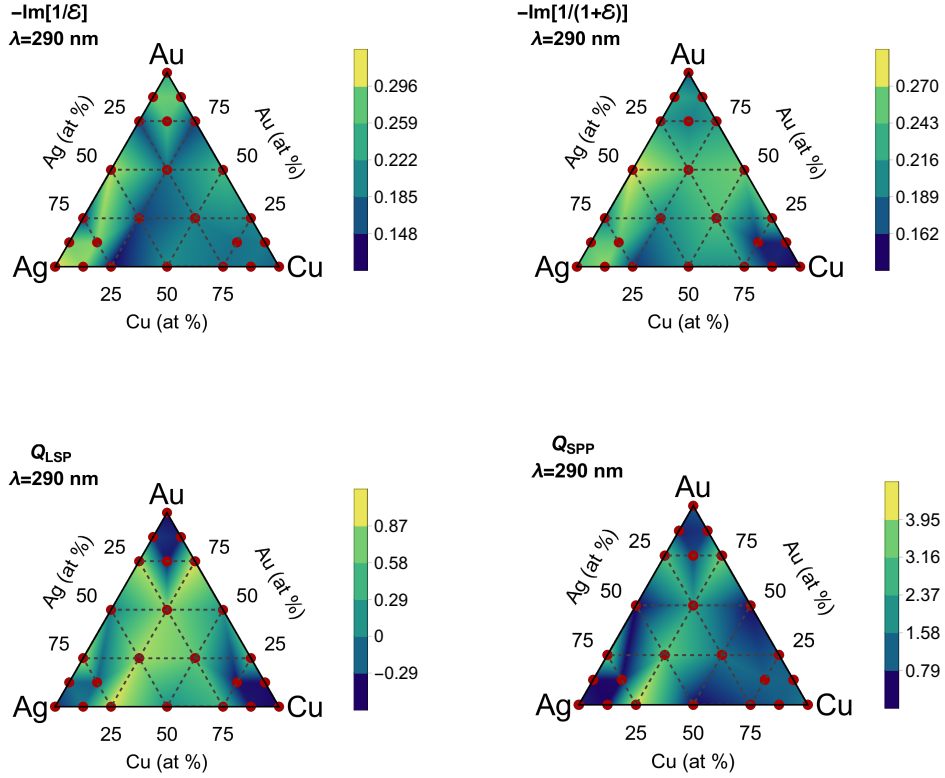


Figure 6.21: Stoichiometric dependence of the averaged plasmon descriptors of bulk and surface EELS, Q_{LSP} , and Q_{SPP} for $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ at the common deep-UV solid-state laser wavelength 290nm.

Lastly, the deep-UV laser at 290 nm (4.2753 eV) commonly produced in Ce:LiSAF / Ce:LiCAF media with Nd:YAG lasers^[61] was presented for the sake of discussion. In Fig. 6.21, the bulk and surface EELS profiles here have structures but a still stronger response in Ag, Au, Au_6AgCu , and AuAg_6Cu , with a newly emerging strong response in AuAg. Correspondingly, AuAg has short-lived LSPs and SPPs as does Ag, which performs relatively better in the former case of the blu-ray laser.

The plasmonic responses of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ have complex behaviours, which cannot be simple interpolated based on the stoichiometric ratios alone, despite the similar electronic structures of constituting atoms. Consistent first-principles simulations presented in this work are crucial to engineer and predict comprehensive alloys within well-controlled approximations at reasonable computational costs.

6.5 Conclusion

In this chapter, the optical and plasmonic responses of ordered $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ were investigated by using pure Au, Ag, and Cu as the test systems to determine an accurate and feasible approach for high-throughput simulations. It was shown that RPA starting from the KS band-structure fails to acceptably locate peaks in the absorption spectra of Au, Ag, and Cu, whereas RPA starting even from an approximate QP band-structure performs drastically better that locates low-energy peaks accurately in absorption spectra. Such an approximate QP band-structure can be achieved with little additional computational cost by applying average stretching to bands via stretching operators, which can be obtained within G_0W_0 for a small set of grid points in Brillouin zone and bands around the Fermi level. Furthermore, reasonable Drude parameters are required. KS-DFT alone is not sufficient to determine the Drude plasmon inverse life-times due to their dominant dependence on electron-phonon and impurity scattering processes; hence these quantities for the binary and ternary alloys were determined using the first-principles plasmon frequency in combination with experimental data.

Despite its lack of the finite size and surface effects, the bulk dielectric functions were used to determine some preliminary measures for LSP and SPP at plasmon resonance wavelengths. At the low-energy limit, the EELS and the surface-EELS, which is defined with a slight modification in EELS for noble metals due to presence of fully-filled d -bands by Eq. (6.6), were used as the signature prints of plasmon resonance in bulks and surface of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$, respectively. Comparing these quantities, which were obtained from the first-principles bulk dielectric functions, to the experimental SPP measurements on thin-films of binary alloys with the closest available stoichiometric ratios in Figs. 6.16, 6.17, and 6.18, Q_{LSP} and Q_{SPP} , the life-times of both SPP and LSP are overestimated in our simulations, especially at large wavelengths. In our simulations, the optical measures for plasmon resonances and life-times can only include the radiative dumping due to inter-band transitions; hence, such overestimations compared to experimental measurements are expected due to the absence of surface and corrosion effects as well as thermal loss in the former case.

It is shown that the distinctive plasmon peaks disappear in the EELS of the binary alloys. The main reason behind this behaviour during alloying is the shift of the band-edge transitions to lower energies, while the Drude plasmons energies shift either very slightly to lower energies, or to higher energies in Fig. 6.14. Hence, the radiative dumping becomes larger in the binary

alloys. Even though pure Au, Ag, and Cu perform best in terms of plasmonic performance at their respective plasmon resonance wavelengths compared to their alloys, a number of alloys perform better at a given wavelength. At the common solid-state red laser around 650 nm, AuAgCu₆, Au₆AgCu, AuCu₇, and Au₇Cu show relatively strong plasmon resonances, whereas higher Ag concentrations reduce plasmon resonance in general. AuAg₆Cu and AuAu₇ as well as AuAg, AuCu, and AgCu alloys start showing stronger plasmon resonances with significant quality factors for LSP and SPP at the common blu-ray laser at 405 nm. This trend at 405 nm becomes more distinctive at deep-UV laser wavelengths around 290 nm. Pure Ag, AuAg₇, Ag₇Cu produce significant plasmon resonances similar to these of global maximum of binary alloys of Au-Ag and Ag-Cu, even with higher LSP and SPP quality factors. at 290 nm.

In summary, RPA starting from an approximate QP band-structure with the Drude-Lorentz model using semi-classical Drude parameters provides a computationally feasible approach for spectra and plasmonic responses of the noble metals and their alloys. Despite its simplicity, some preliminary measures can be obtained that are useful as a starting point for tailoring plasmonic responses in such systems.

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Part III

Electronic and Optical Properties of Transition-Metal Systems with Large SIE

Chapter 7

Linear-scaling TDDFT with a Hubbard corrected interaction kernel: TDDFT+ U

DFT is an elegant theory that enables the realistic study of ground-state properties of practical many-body systems. Hence, a time-dependent extension is naturally an exciting prospect from both theoretical and applied perspectives. Early attempts to this end were demonstrated on the absorption of Si-layers^[1,2], the evolution of the orbitals of He^[3] and the photo-absorption spectra of certain rare gases^[4]. Also, the one-to-one correspondence between the time-dependent density and the time-dependent external potential was initially demonstrated for strict conditions by Deb and Gosh^[5]. However, the formal basis for the time-domain extension of DFT, namely *time-dependent density-functional theory* (TDDFT), was provided in the later work of Gross and Runge, particularly the Gross-Runge theorem^[6]. A practical scheme was proposed by Gross and Kohn via the generalisation of LDA to the time-domain^[7]. Despite the completeness of TDDFT as a theory, its practical applications rely on a set of approximations resulting in certain systematic errors, and they further inherit previously discussed systematic errors from KS-DFT in its approximate incarnations.

This chapter will begin by the theoretical background of TDDFT, introducing the Gross-Runge theorem. Then, the linear-response formalism of TDDFT will be introduced for practical applications, with a description of the xc-kernel constructed from the LDA in the adiabatic limit. This will be followed by the formalism known as the Casida equation^[8], which allows efficient evaluation of neutral excitation energies in the linear-response regime (LR-TDDFT). Some basic technical details of the computational implementation of the Casida equation will be discussed. In the next part, the linear-scaling formalism and prior implementation of LR-TDDFT within ONETEP will be described in preparation for our newly-implemented Hubbard U correction to the interaction kernel of TDDFT. Hence, the time-domain extension of DFT+ U , dubbed TDDFT+ U , will be derived and suitable strategies for its efficient implementation in ONETEP will be discussed. Finally, the effects of the + U correction on excitation energies at various levels of theory will be demonstrated with an illustrative four-level toy model.

7.1 Time-dependent density-functional theory

The evolution of the many-body system under the influence of a time-dependent potential is described by the time-dependent Schrödinger equation

$$\hat{\mathcal{H}}\Psi(t) = i \frac{\partial}{\partial t} \Psi(t), \quad (7.1)$$

where Ψ_t is the time-dependent many-body electronic wave-function, and the electronic Hamiltonian in the interaction picture for convenience is

$$\begin{aligned} \hat{\mathcal{H}}(t) &= \hat{\mathcal{T}}_e + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{\text{ext}}(t) \\ &= \frac{1}{2} \sum_i^N \hat{\mathbf{p}}_i^2 + \frac{1}{2} \sum_{i,j}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} + \sum_i^N \hat{v}_{\text{ext}}(\mathbf{r}_i, t). \end{aligned} \quad (7.2)$$

Such a complex problem cannot be tackled for any realistic system with current technologies. Analogously to the situation in ground-state DFT, if we can express an evolving system in terms of its time-dependent density instead of its multi-variable time-dependent wave-function, it will reduce the dimensionality of its computational treatment drastically.

7.1.1 The Gross-Runge theorem

The original work of Gross and Runge^[6] lays the foundations of TDDFT by generating analogous statements to those of the Hohenberg-Kohn theorems discussed in Chap. 2 for the time-domain.

The first deduction, which is also referred as the Gross-Runge theorem, of their work is that time-dependent densities $n(\mathbf{r}, t)$ and $n'(\mathbf{r}, t)$ evolving from a given stationary many-body state $\Psi(t_0) = \Psi_0$ due to corresponding external potentials $V_{\text{ext}}(\mathbf{r}, t)$ and $V'_{\text{ext}}(\mathbf{r}, t)$, which are expandable into a Taylor series around t_0 and differ more than just purely time-dependent term ($V_{\text{ext}}(\mathbf{r}, t) - V'_{\text{ext}}(\mathbf{r}, t) \neq c(t)$), are different for $t > t_0 = 0$. The postulate on the

external potentials can be summarised as

$$V_{\text{ext}}(\mathbf{r}, t) = \sum_k \frac{v_k(\mathbf{r})}{k!} (t - t_0)^k, \quad \text{and} \quad V'_{\text{ext}}(\mathbf{r}, t) = \sum_k \frac{v'_k(\mathbf{r})}{k!} (t - t_0)^k$$

$$\Downarrow$$

$$\frac{\partial^k}{\partial t^k} (V_{\text{ext}}(\mathbf{r}, t) - V'_{\text{ext}}(\mathbf{r}, t)) \neq c, \quad (7.3)$$

where c is a constant for some $k \geq 0$. This theorem can be summarised as

The Gross-Runge theorem:

There is a one-to-one mapping upto an additive scalar function $c(t)$ between the time-dependent external potential $V_{\text{ext}}(\mathbf{r}, t)$, which can be expanded into a Taylor series around t_0 , and the time-dependent density $n(\mathbf{r}, t)$ of interacting many-body systems, which is evolving from an initial state $\Psi(t_0) = \Psi_0$.

The proof of this statement is not as straightforward as the first HK theorem is. The first step is to show that the corresponding current densities differ under this condition. Subtracting equation of motions of the current densities gives, at $t = 0$,

$$\begin{aligned} \frac{\partial}{\partial t} (\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t))_{t=0} &= -i \left\langle \Psi_0 \left| \left[\hat{\mathbf{j}}(\mathbf{r}, 0) (V_{\text{ext}}(\mathbf{r}, 0) - V'_{\text{ext}}(\mathbf{r}, 0)) \right] \right| \Psi_0 \right\rangle \\ &= -n_0(\mathbf{r}) \nabla (V_{\text{ext}}(\mathbf{r}, 0) - V'_{\text{ext}}(\mathbf{r}, 0)), \end{aligned} \quad (7.4)$$

where $n_0(\mathbf{r}) = n(\mathbf{r}, t_0)$, since the corresponding Hamiltonians only differ in their external potentials. Applying partial derivatives with respect to t to each side of Eq. (7.4) k -times, the expression

$$\frac{\partial^{k+1}}{\partial t^{k+1}} (\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t))_{t=0} = -n_0(\mathbf{r}) \nabla \frac{\partial^k}{\partial t^k} (V_{\text{ext}}(\mathbf{r}, t) - V'_{\text{ext}}(\mathbf{r}, t))_{t=0} \quad (7.5)$$

can be obtained. Now, recalling the postulate expressed in Eq. (7.3), the relation between the current densities becomes

$$\mathbf{j}(\mathbf{r}, t) \neq \mathbf{j}'(\mathbf{r}, t), \quad (7.6)$$

as their time-derivatives at t_0 differs by more than a constant. Second, by the gradients of both sides of Eq. (7.5) and the continuity relation

$$\frac{\partial}{\partial t} n(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t), \quad (7.7)$$

the relation for corresponding densities is obtained as

$$\begin{aligned} \frac{\partial^{k+2}}{\partial t^{k+2}} (n(\mathbf{r}, t) - n'(\mathbf{r}, t))_{t=0} &= -\nabla \cdot \left(n_0(\mathbf{r}) \nabla \frac{\partial^k}{\partial t^k} (V_{\text{ext}}(\mathbf{r}, t) - V'_{\text{ext}}(\mathbf{r}, t))_{t=0} \right) \\ &= -\nabla \cdot (n_0(\mathbf{r}) \nabla f_k(\mathbf{r})), \end{aligned} \quad (7.8)$$

where $f_k(\mathbf{r}) = \frac{\partial^k}{\partial t^k} (V_{\text{ext}}(\mathbf{r}, t) - V'_{\text{ext}}(\mathbf{r}, t))_{t=0}$. It must be shown that the last term in Eq. (7.8) does not vanish as long as the postulate in Eq. (7.3) holds. This statement can be investigated indirectly through the identity^[9,10]

$$\int d\mathbf{r} f_k(\mathbf{r}) \nabla \cdot (n_0(\mathbf{r}) \nabla f_k(\mathbf{r})) = - \int d\mathbf{r} n_0(\mathbf{r}) (\nabla f_k(\mathbf{r}))^2 + \oint d\mathbf{S} \cdot n_0(\mathbf{r}) f_k(\mathbf{r}) \nabla f_k(\mathbf{r}), \quad (7.9)$$

where the last term can be shown to be vanishing. Indeed, the surface integral in Eq. (7.9) has been shown to vanish for an external potential arising from some finite normalisable external charge, or at least that it converges to zero with $1/r$ behaviour as $r \rightarrow \infty$ ^[11]. Next, the first term on the right-hand side has to be proved not to vanish. By the postulate $f_n(\mathbf{r}) \neq 0$ in Eq. 7.3, the integrand of the remaining integral on the right-hand side is ensured to be greater than zero at least somewhere; hence, $\nabla \cdot (n_0(\mathbf{r}) \nabla f_k(\mathbf{r}))$ is greater than zero at least for some $\mathbf{r}$. As a consequence, $n(\mathbf{r}, t) \neq n'(\mathbf{r}, t)$ for an infinitely small time $t > 0$, when they evolve from the same initial state Ψ_0 due to the time-dependent external potentials $V_{\text{ext}}(\mathbf{r}, t)$ and $V'_{\text{ext}}(\mathbf{r}, t)$, satisfying the postulate in Eq. (7.3).

The work of Gross and Runge also provides a minimisation scheme for TDDFT. The time-dependent wave-function is described by the time-dependent density of a system initially in the state Ψ_0 , up to a purely time-dependent phase factor, or mathematically

$$n(\mathbf{r}, t) \implies e^{-\alpha(t)} \Psi(t), \quad (7.10)$$

where the phase factor can be obtained by $c(t) = \partial\alpha(t)/\partial t$, and $c(t)$ is the additive scalar part

of $V_{\text{ext}}(\mathbf{r}, t)$. The purely time-dependent phase factor vanishes in the matrix element

$$\left\langle \Psi(t) \left| i \frac{\partial}{\partial t} - \hat{\mathcal{H}}(t) \right| \Psi(t) \right\rangle. \quad (7.11)$$

Hence, the quantum mechanical action of many-body system becomes a unique functional of the initial state and the time-dependent density as

$$A[\Psi(t)] = A[n, \Psi_0] = \int_{t_0=0}^t \left\langle \Psi[n, \Psi_0](t) \left| i \frac{\partial}{\partial t} - \hat{\mathcal{H}}(t) \right| \Psi[n, \Psi_0](t) \right\rangle \quad (7.12)$$

Similarly to the case of DFT, Eq. (7.12) only differs in terms of the external potentials of the two systems, therefore the universal and the time-dependent external potential parts can be partitioned such as

$$\begin{aligned} A[n, \Psi_0] &= \int_{t_0=0}^t \left\langle \Psi[n, \Psi_0](t) \left| i \frac{\partial}{\partial t} - \hat{\mathcal{T}} - \hat{\mathcal{V}}_{\text{ee}} \right| \Psi[n, \Psi_0](t) \right\rangle \\ &\quad - \int_{t_0=0}^t dt \int d\mathbf{r} n(\mathbf{r}, t) V_{\text{ext}}(\mathbf{r}, t) \\ &= B[n, \Psi_0] - \int_{t_0=0}^t dt \int d\mathbf{r} n(\mathbf{r}, t) V_{\text{ext}}(\mathbf{r}, t), \end{aligned} \quad (7.13)$$

where $B[n, \Psi_0]$ is a universal functional. In principle, the exact time-dependent density evolving from certain initial state can be determined by solving the Euler equations $\frac{\delta A[n]}{\delta n(\mathbf{r}, t)} = 0$ with the boundary conditions of $\delta \Psi[n](0) = 0$ and $\delta \Psi[n](t') = 0$, where $0 < t < t'$ [9].

7.1.2 The van Leeuwen theorem

The Gross-Runge theorem provides the conceptual basis for TDDFT, whereas an applicable scheme is provided by a special case of the van Leeuwen theorem^[12].

The van Leeuwen theorem:

If an external time-dependent potential $V_{\text{ext}}(\mathbf{r}, t)$ produces a time-dependent density $n(\mathbf{r}, t)$, which can be expanded into a Taylor series around t_0 , of a many-body system, which is interacting via $W(\mathbf{r}, \mathbf{r}')$ and evolving from a given initial state Ψ_0 , there exist a uniquely defined another time-dependent external potential $V'_{\text{ext}}(\mathbf{r}, t)$, which produces an identical time-dependent density for another many-body system, which is interacting via $W'(\mathbf{r}, \mathbf{r}')$ and evolving from a uniquely defined initial state Ψ'_0 producing $n(\mathbf{r}, t)$ and its time derivative at t_0 .

In more detail, this theorem proves that for an interacting many-body system with a v -representable time-dependent density $n(\mathbf{r}, t)$ evolving from the initial state Ψ_0 with the Hamiltonian

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{T}} + \hat{W}(\mathbf{r}, \mathbf{r}') + V_{\text{ext}}(\mathbf{r}, t),$$

there exists another interacting many-body system with an identical time-dependent density $n'(\mathbf{r}, t) = n(\mathbf{r}, t)$ and the Hamiltonian

$$\hat{\mathcal{H}}'(t) = \hat{\mathcal{T}}' + \hat{W}'(\mathbf{r}, \mathbf{r}') + V_{\text{ext}}(\mathbf{r}, t) + c(t),$$

evolving from an initial state chosen such that

$$n[\Psi_0](\mathbf{r}, 0) = n'[\Psi'_0](\mathbf{r}, 0), \quad \text{and} \quad \left. \frac{\partial}{\partial t} n[\Psi_0](\mathbf{r}, t) \right|_{t=0} = \left. \frac{\partial}{\partial t} n'[\Psi'_0](\mathbf{r}, t) \right|_{t=0}. \quad (7.14)$$

The special case of this theorem can be used to map an interacting system onto a non-interacting system by setting $\hat{W}(\mathbf{r}, \mathbf{r}') = \hat{V}_{\text{ee}}$ and $\hat{W}'(\mathbf{r}, \mathbf{r}') = 0$ with a given external potential and initial state.

7.1.3 The time-dependent KS equations

Using the van Leeuwen theorem, the time-dependent version of the KS equations in Eq. (2.17) can be written by taking the functional derivative of Eq. (7.13) with respect to the

time-dependent density, yielding

$$\left[-\frac{1}{2m} \nabla_i^2 + v_{tot}(\mathbf{r}, t) \right] \psi_i(\mathbf{r}, t) = \epsilon_i \psi_i(\mathbf{r}, t), \quad (7.15)$$

where the time-dependent $v_{tot}(\mathbf{r}, t)$ is given by

$$v_{tot}(\mathbf{r}, t) = \int d\mathbf{r}' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{ext}(\mathbf{r}, t) + v_{xc}(\mathbf{r}, t), \quad (7.16)$$

subject to the condition that $\psi_i(\mathbf{r}, 0) = \psi_i^0$, which are ground-state KS wave-functions. Thus, the time-dependent density can be obtained analogously to the ground-state case as

$$n(\mathbf{r}, t) = \sum_i^N |\psi_i(\mathbf{r}, t)|^2. \quad (7.17)$$

As in DFT, some approximations are needed for the time-dependent xc-potential

$$v_{xc}(\mathbf{r}, t) = \frac{\delta A_{xc}[n]}{\delta n(\mathbf{r}, t)}, \quad (7.18)$$

for which will be discussed in Subsec. 7.2.1.

7.2 Linear response TDDFT

In applications of real time TDDFT, the time-dependent KS equations in Eq. (7.15) need to be solved at each time step starting from ground-state KS wave-functions. However, EES and dipole-dipole absorption in Sec. 1.3 can be obtained using a single time-step from the ground-state in the linear-response regime^[13]. Hence, an explicit set of solutions of the time-dependent KS equations become a needless effort considering its high computational cost. Alternatively, TDDFT can be formulated within LRT starting from a ground-state for weak external time-dependent fields.

Within LRT, the time-dependent density can be expressed as

$$n(\mathbf{r}, t) = n_0(\mathbf{r}) + \delta n(\mathbf{r}, t), \quad (7.19)$$

where $n_0(\mathbf{r})$ is the ground-state density, and $\delta n(\mathbf{r}, t)$ is *the response density* defined

as^[14]

$$\delta n(\mathbf{r}, t) = \int dt' \int d\mathbf{r}' \chi(\mathbf{r}, t, \mathbf{r}', t') v_{\text{ext}}(\mathbf{r}', t'), \quad (7.20)$$

for which the linear-response function becomes

$$\chi(\mathbf{r}, t, \mathbf{r}', t') = \frac{\delta n(\mathbf{r}, t)}{\delta v_{\text{ext}}(\mathbf{r}', t')} = \int d\mathbf{r}'' dt'' \frac{\delta n(\mathbf{r}, t)}{\delta v_{\text{tot}}(\mathbf{r}'', t'')} \frac{\delta v_{\text{tot}}(\mathbf{r}'', t'')}{\delta v_{\text{ext}}(\mathbf{r}', t')} \quad (7.21)$$

where $v_{\text{tot}}(\mathbf{r}, t)$ is the total time-dependent KS potential in Eq. (7.16). On the other hand, the non-interacting response function is given by

$$\chi_0(\mathbf{r}, t, \mathbf{r}', t') = \frac{\delta n(\mathbf{r}, t)}{\delta v_{\text{tot}}(\mathbf{r}', t')} = \left. \frac{\delta n(\mathbf{r}, t)}{\delta v_{\text{KS}}(\mathbf{r}', t')} \right|_{v_{\text{KS}}[n_0]} \quad (7.22)$$

as the response of the corresponding KS system, since the time-dependent density produced by the corresponding ground-state KS system must be identical to the real system in the static limit.

Hence, Eq. (7.21) becomes

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}', \omega) = & \chi_0(\mathbf{r}, \mathbf{r}', \omega) \\ & + \iint d\mathbf{r}'' d\mathbf{r}''' \chi_0(\mathbf{r}, \mathbf{r}'', \omega) [v(\mathbf{r}'', \mathbf{r}''') + f_{\text{xc}}(\mathbf{r}'', \mathbf{r}''', \omega)] \chi(\mathbf{r}''', \mathbf{r}', \omega), \end{aligned} \quad (7.23)$$

which is just Dyson's equation. The interaction kernel is the sum of the bare Coulomb interaction $v(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$, and

$$f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) = \int d(t - t') e^{-i\omega(t' - t)} \frac{\delta^2 A_{\text{xc}}[n]}{\delta n(\mathbf{r}, t) \delta n(\mathbf{r}', t')} = \frac{\delta v_{\text{xc}}(\mathbf{r}, \omega)}{\delta n(\mathbf{r}', \omega)} \quad (7.24)$$

which is called *the exchange-correlation kernel*. Multiplying Eq. (7.23) with $v_{\text{ext}}(\mathbf{r}, t)$, then integrating over $\mathbf{r}$ and applying the Fourier transform, the expression

$$\begin{aligned} \delta n(\mathbf{r}, \omega) = & \int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}', \omega) v_{\text{ext}}(\mathbf{r}', \omega) \\ & + \iint d\mathbf{r}' d\mathbf{r}'' \chi_0(\mathbf{r}, \mathbf{r}', \omega) [v(\mathbf{r}', \mathbf{r}'') + f_{\text{xc}}(\mathbf{r}', \mathbf{r}'', \omega)] \delta n(\mathbf{r}'', \omega), \end{aligned} \quad (7.25)$$

is obtained for the response density only as a functional of non-interacting response function and the interaction kernel. In a more compact form, δn can be evaluated by working through

the equation

$$\begin{aligned}\delta n &= \chi_0 v_{\text{ext}} + \chi_0 [v - f_{\text{xc}}] \delta n \Rightarrow \\ \delta n &= \frac{1}{v_{\text{ext}}^{-1} \chi_0^{-1} - v_{\text{ext}}^{-1} [v - f_{\text{xc}}]}\end{aligned}\quad (7.26)$$

where the only unknown is the xc-kernel.

7.2.1 The exchange-correlation kernel

Similarly to the case of DFT, the most challenging part of practical TDDFT is to determine the xc-kernel, which includes quantum many-body effects throughout the evolution of a system; hence, the exact xc-kernel is a non-local and frequency-dependent object, whose exact analytical form is unknown. The most widely used xc-kernel is the time-domain extension of LDA at the adiabatic limit namely *the adiabatic local density approximation* (ALDA). Within the adiabatic approximation, the frequency-dependent xc-kernel is approximated by the xc-kernel of a density in the $\omega \rightarrow 0$ limit. Mathematically, it is expressed as

$$f_{\text{xc}}(\mathbf{r}, \mathbf{r}') = \lim_{\omega \rightarrow 0} \frac{\delta^2 E_{\text{xc}}[n]}{\delta n(\mathbf{r}, \omega) \delta n(\mathbf{r}', \omega)} = \frac{\delta^2 E_{\text{xc}}[n_0]}{\delta n_0(\mathbf{r}) \delta n_0(\mathbf{r}')} \quad (7.27)$$

The xc-kernel within ALDA is given using Eq. (7.23) by

$$f_{\text{xc}}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta E^{\text{LDA}}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \right|_{n=n_0} \delta(\mathbf{r} - \mathbf{r}'), \quad (7.28)$$

and thus $f_{\text{xc}}^{\text{ALDA}}$ is spatially and temporally local. Limitations and systematic errors of the ALDA will be discussed in more detail in Sec. 7.5.

7.3 Excitation energies within LR-TDDFT

Undoubtedly, the most practical use of LR-TDDFT is in determining electronic excitation energies of various finite-sized systems such as molecules or nano-clusters in low-energy spectral ranges. LR-TDDFT within the ALDA is not effective for extended systems, where long-ranged, non-local interactions play important roles as discussed in Sec. 5.3.

7.3.1 The Casida equation

The Casida equation is a non-Hermitian eigenvalue problem to obtain excitation energies of the coupled exciton and de-exciton¹ Hamiltonian. Hence, LR-TDDFT within the Casida formalism² determines the electronic transition energies $\{\omega_{ji}\}$ to construct EES and ABS using Eq. (1.38) and Eq. (1.39), respectively. Starting from KS system for $t < t'$, where $v_{\text{ext}} = 0$, Eq. (7.25) becomes

$$\delta n(\mathbf{r}, \omega) = \iint d\mathbf{r}' d\mathbf{r}'' \chi_0(\mathbf{r}, \mathbf{r}', \omega) f_{\text{Hxc}}(\mathbf{r}', \mathbf{r}'', \omega) \delta n(\mathbf{r}'', \omega), \quad (7.29)$$

where $f_{\text{Hxc}} = v + f_{\text{xc}}$ represents the total interaction kernel in a more compact form. Let us define an auxiliary object for notational simplicity as

$$g(\mathbf{r}, \omega) = \int d\mathbf{r}' f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}', \omega) \delta n(\mathbf{r}', \omega) \Rightarrow \quad (7.30a)$$

$$\delta n(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}', \omega) g(\mathbf{r}', \omega), \quad (7.30b)$$

where $g(\mathbf{r}, \omega)$ can be rewritten by substituting Eq. 7.30b into Eq. 7.30a as

$$g(\mathbf{r}, \omega) = \iint d\mathbf{r}' d\mathbf{r}'' f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}', \omega) \chi_0(\mathbf{r}', \mathbf{r}'', \omega) g(\mathbf{r}'', \omega). \quad (7.31)$$

Setting the initial states to KS-DFT states for $t < t'$, the non-interacting response function is expressed as discussed in Chap. 5 in Eq. (5.10) in the real space^[15,16], without any life-time broadening and assuming excitation energies differ from ω_{ji} for brevity, as

$$\begin{aligned} \chi_0(\mathbf{r}, \mathbf{r}', \omega) &= 2 \sum_{i,j} (f_i - f_j) \frac{\psi_j^*(\mathbf{r}) \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}') \psi_j(\mathbf{r}')}{\omega - \omega_{ji}} \\ &= \sum_{i,j} \bar{f}_{ji} \frac{\Phi_{ji}^*(\mathbf{r}) \Phi_{ji}(\mathbf{r}')}{\omega - \omega_{ji}}. \end{aligned} \quad (7.32)$$

¹The exciton is a finite-living quasiparticle composed of an excited electron and its hole interacting via the attractive Coulomb interaction with associated xc-effects. The term *de-exciton* is used for the sake of the terminological distinction to refer to a removed exciton (analogously to describing removed electron as holes).

²The derivation of the Casida equation is reproduced by following the procedure in Ref. 9.

where $\Phi_{ji}(\mathbf{r}') = \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})$, $\omega_{ji} = (\epsilon_j - \epsilon_i)$ and $\bar{f}_{ji} = 2(f_i - f_j)$. Defining yet another auxiliary objects as

$$H_{ji}(\omega) = \int d\mathbf{r} \Phi_{ji}(\mathbf{r})g(\mathbf{r}, \omega), \quad (7.33)$$

substituting Eq. (7.32) into Eq. (7.31), then multiplying with $\Phi_{j'i'}(\mathbf{r})$ and integrating over spatial coordinates, the following expression can be achieved

$$\begin{aligned} H_{ji}(\omega) &= \sum_{j',i'} \frac{\bar{f}_{j'i'}}{\omega - \omega_{j'i'}} \iint d\mathbf{r} d\mathbf{r}' \Phi_{ji}(\mathbf{r}) f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}', \omega) \Phi_{j'i'}^*(\mathbf{r}') H_{j'i'}(\omega) \\ &= \sum_{j',i'} \frac{\bar{f}_{j'i'}}{\omega - \omega_{j'i'}} K_{ji,j'i'}(\omega) H_{j'i'}(\omega), \end{aligned} \quad (7.34)$$

where $K_{ji,j'i'}(\omega)$ is called *the coupling matrix* and

$$K_{ji,j'i'}(\omega) = \iint d\mathbf{r} d\mathbf{r}' \Phi_{ji}(\mathbf{r}) f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}', \omega) \Phi_{j'i'}^*(\mathbf{r}'). \quad (7.35)$$

Lastly, defining another auxiliary object

$$\beta_{ji}(\omega) = \frac{H_{ji}(\omega)}{\omega - \omega_{ji}}, \quad (7.36)$$

and dropping the frequency variable for brevity, the final form becomes

$$\sum_{j',i'} [\delta_{ii'} \delta_{jj'} \omega_{j'i'} + \bar{f}_{j'i'} K_{ji,j'i'}] \beta_{j'i'} = \omega \beta_{ji}. \quad (7.37)$$

Using v and c to label states in the occupied and unoccupied manifolds, respectively¹, the two following coupled equations are obtained:

$$\begin{aligned} \sum_{c',v'} [\delta_{vv'} \delta_{cc'} \omega_{c'v'} + \bar{f}_{c'v'} K_{cv,c'v'}] \beta_{c'v'} &= \omega \beta_{cv}, \quad \text{and} \\ \sum_{c',v'} [\delta_{cv'} \delta_{vc'} \omega_{c'v'} + \bar{f}_{c'v'} K_{cv,v'c'}] \beta_{v'c'} &= \omega \beta_{cv}, \end{aligned} \quad (7.38)$$

¹These notational choices are only for consistency with previous parts of this work rather than referring to valence and conduction states in solids. It is more convenient to classify molecular electronic states through their occupancy as occupied or unoccupied.

which can be re-expressed in matrix form by substituting

$$X_{cv} = -\beta_{cv}, \quad Y_{cv} = \beta_{vc} \quad (7.39)$$

as a eigenvalue problem (in the adiabatic limit)

$$\begin{pmatrix} \mathbb{A} & \mathbb{B} \\ -\mathbb{B}^\dagger & -\mathbb{A}^\dagger \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \quad (7.40)$$

where

$$\begin{aligned} A_{cv,c'v'} &= \delta_{vv'} \delta_{cc'} \omega_{c'v'} + K_{cv,c'v'} \\ B_{cv,c'v'} &= K_{cv,v'c'}. \end{aligned} \quad (7.41)$$

Eq. (7.40) is called *the Casida equation*^[8]. The block matrix $\mathbb{A}$ in Eq. (7.40) couples the exciton-exciton pairs, while the block matrix $\mathbb{B}$ couples exciton-de-exciton pairs. In a fully interacting picture, an exciton interacts with remaining excitons as well as de-excitons through an interaction kernel. Physically, it can be illustrated as various absorption occurring spontaneously and interactively as well as various emissions; hence, absorption and emission are interacting phenomena rather than isolated processes.

Since $\mathbb{A}$ and $\mathbb{B}$ become real matrices for real KS wave-functions, the Casida equation can be expressed equivalently for frequency-independent xc-kernels as^[8]

$$\mathbb{C}\mathbf{Z} = \omega^2 \mathbf{Z}, \quad (7.42)$$

where

$$\begin{aligned} \mathbb{C} &= (\mathbb{A} - \mathbb{B})^{1/2} (\mathbb{A} + \mathbb{B}) (\mathbb{A} - \mathbb{B})^{1/2} \\ \mathbf{Z} &= (\mathbb{A} - \mathbb{B})^{1/2} (\mathbf{X} - \mathbf{Y}), \end{aligned} \quad (7.43)$$

from which oscillator strengths are extracted as^[9]

$$f_n = \frac{2}{3} \sum_i^3 \left| \mathbf{R}_i^T (\mathbb{A} - \mathbb{B})^{1/2} \mathbf{Z}_n \right|^2, \quad (7.44)$$

where $R_{i,vc} = \int d\mathbf{r} \ (\mathbf{r} \cdot \hat{\mathbf{e}}_i) \Phi_{vc}(\mathbf{r})$ with the Cartesian unit vectors $\{\hat{\mathbf{e}}_i\}$ and $\mathbf{Z}_n$ is the n^{th}

eigenvector of Eq. (7.42).

7.3.1.1 The Tamm-Dancoff approximation

Non-Hermitian eigenvalue problems are hard to tackle, requiring computationally relatively expensive and numerically unstable diagonalisation processes due to their non-orthogonal eigenvectors^[17]. The problem can be simplified by invoking the so-called *the Tamm-Dancoff approximation* (TDA)^[18] for LR-TDDFT^[19]. In the TDA, the coupling of excitons and de-excitons is neglected; hence, Eq. (7.40) is reduced to

$$\mathbb{A}\mathbf{X} = \omega\mathbf{X}, \quad (7.45)$$

which is a Hermitian eigenvalue problem. Furthermore, it is reported that TDA has some technical advantages over the Casida equation in some cases such as open-shell molecular systems with distorted geometries^[20].

7.4 The iterative solution of LR-TDDFT

Practically, excitation energies can be evaluated by using an inverse iteration of the generalised Rayleigh quotient^[21] for some trial vector $\mathbf{x}_i$ ¹ for the Hamiltonian in the product space of occupied and unoccupied KS wave-functions. For the simplified case using TDA, it is a minimum-value search for the first excitation energy with the matrix $\mathbb{A}$ as

$$\omega_1 = \min_{\mathbf{x}} \frac{\mathbf{x}^\dagger \mathbb{A} \mathbf{x}}{\mathbf{x}^\dagger \mathbf{x}}, \quad (7.46)$$

where the change in excitation energy is found by using by the directional partial derivative

$$\frac{\partial \omega_1}{\partial \mathbf{x}} = \frac{2}{\mathbf{x}^\dagger \mathbf{x}} [\mathbb{A}\mathbf{x} - \omega\mathbf{x}], \quad (7.47)$$

¹See Subsec. 2.2.4 for more details.

where the action $\mathbf{q} = \mathbb{A}\mathbf{x}$ is sufficient rather than an explicit construction of $\mathbb{A}$. Elements of the action are, in explicit form, by means of Eq. (7.41):

$$q_{cv} = \omega_{cv}x_{cv} + \sum_{c',v'} \bar{f}_{c'v'} \iint d\mathbf{r} d\mathbf{r}' \psi_c^*(\mathbf{r})\psi_v(\mathbf{r})f_{\text{Hxc}}(\mathbf{r},\mathbf{r}')\psi_{c'}(\mathbf{r}')\psi_{v'}^*(\mathbf{r}')x_{c'v'}. \quad (7.48)$$

The response density becomes for such trial vector^[22]

$$\delta n(\mathbf{r}) = \sum_{cv} \bar{f}_{cv}\psi_c(\mathbf{r})x_{cv}\psi_v^*(\mathbf{r}), \quad (7.49)$$

which can be used to define *the self-consistent field potential* (SCFP) as a functional of response density as

$$\hat{V}_{SCF}[\delta n](\mathbf{r}) = \int d\mathbf{r}' f_{\text{Hxc}}(\mathbf{r},\mathbf{r}')\delta n(\mathbf{r}'), \quad (7.50)$$

which lets one to express Eq. (7.48) in more compact form

$$\begin{aligned} q_{cv} &= \omega_{cv}x_{cv} + \left\langle \psi_c \left| \hat{V}_{SCF}[\delta n] \right| \psi_v \right\rangle \\ &= \omega_{cv}x_{cv} + (V_{SCF})_{cv}. \end{aligned} \quad (7.51)$$

7.4.1 Generalisation to the non-Hermitian problem

Despite its non-Hermitian nature, the latter approach can be extended to the Casida equation considering that block matrices $\mathbb{A}$ and $\mathbb{B}$ are Hermitian themselves^[23,24] via

$$\omega = \min_{\mathbf{q}, \mathbf{p}} \frac{\begin{pmatrix} \mathbf{p}^\dagger & \mathbf{q}^\dagger \end{pmatrix} \begin{pmatrix} \mathbb{A} - \mathbb{B} & 0 \\ 0 & \mathbb{A} + \mathbb{B} \end{pmatrix} \begin{pmatrix} \mathbf{p} \\ \mathbf{q} \end{pmatrix}}{|\mathbf{p}^\dagger \mathbf{q} + \mathbf{q}^\dagger \mathbf{p}|}, \quad (7.52)$$

where $\mathbf{p} = \mathbf{X} - \mathbf{Y}$ and $\mathbf{q} = \mathbf{X} + \mathbf{Y}$. Eq. (7.46) and Eq. (7.52) provide a minimisation scheme for the lowest excitation. For higher excitations, an additional constraint is needed that imposes the orthogonality of eigen-vectors

$$\left| \mathbf{p}_1^\dagger \mathbf{q}_2 + \mathbf{q}_1^\dagger \mathbf{p}_2 \right| = 0. \quad (7.53)$$

Hence, the j^{th} excitation can be calculated by enforcing this condition starting from the first excitation up to the $(j - 1)^{th}$ excitation.

7.5 Linear-scaling LR-TDDFT

LR-TDDFT with the ALDA and related semi-local functionals is spatially local by construction. Therefore, it is suitable for linear-scaling implementations introduced in Chap. 4 through some localised basis set in real space^[24–27]. As ONETEP^[26,28–34] was primarily used for performing linear-scaling first-principles simulations in this work, the linear-scaling formalism of LR-TDDFT will be introduced in terms of the ONETEP formalism. We refer the reader to Ref. 26 for a comprehensive overview of the implementation of the TDA in ONETEP prior to this work, and to Ref. 24 for its subsequent extension to treat the full Casida LR-TDDFT eigenvalue problem.

Starting from the TDA, linear-scaling effort can be achieved by representing q_{cv} in Eq. (7.51) in the optimised unoccupied NGWFs basis set $\{\chi_\alpha\}$ and the optimised occupied NGWFs basis set $\{\phi_\beta\}$ introduced in Chap. 3. For this purpose, the response density-matrix in this basis is expressed as

$$\begin{aligned}\delta\rho(\mathbf{r}, \mathbf{r}') &= \sum_{cv} \langle \mathbf{r} | \psi_c \rangle x_{cv} \langle \psi_v | \mathbf{r}' \rangle \\ &= \sum_{\alpha\beta} \chi_\alpha(\mathbf{r}) \left(\sum_{cv} \langle \chi^\alpha | \psi_c \rangle x_{cv} \langle \psi_v | \phi^\beta \rangle \right) \phi_\beta(\mathbf{r}') \\ &= \sum_{\alpha\beta} \chi_\alpha(\mathbf{r}) \delta P^{\alpha\beta} \phi_\beta(\mathbf{r}'),\end{aligned}\tag{7.54}$$

where $\delta n(\mathbf{r}) = \delta\rho(\mathbf{r}, \mathbf{r}')\delta(\mathbf{r} - \mathbf{r}')$ ¹. Similarly, the SCFP is represented as

$$(V_{SCF})_{cv} = \langle \psi_c | \chi^\alpha \rangle \langle \chi_\alpha | \hat{V}_{SCF}[\delta\rho(\mathbf{r})] | \phi_\beta \rangle \langle \phi^\beta | \psi_v \rangle.\tag{7.55}$$

Lastly, the diagonal terms in Eq. (7.51) are re-expressed in the relevant NGWFs basis sets

¹This notation will be needed in Sec. 7.6.

as

$$\begin{aligned}\omega_{cv}x_{cv} &= \epsilon_c x_{cv} - \epsilon_v x_{cx} = \sum_{c'} \langle \psi_c | \chi_\alpha \rangle \langle \chi^\alpha | \hat{H} | \chi^\beta \rangle \langle \chi_\beta | \psi_{c'} \rangle x_{c'v} \\ &\quad - \sum_{v'} x_{cv'} \langle \psi_{v'} | \phi_\alpha \rangle \langle \phi^\alpha | \hat{H} | \phi^\beta \rangle \langle \phi_\beta | \psi_v \rangle\end{aligned}\quad (7.56)$$

Finally, inserting Eq. (7.55) and Eq. (7.56) into Eq. (7.52), then multiplying with $\langle \chi^\alpha | \psi_c \rangle$ and $\langle \psi_v | \phi^\beta \rangle$ from the left and right, respectively and summing over c and v indices, $\mathbf{q} = \mathbb{A}\mathbf{x}$ in Eq. (7.47) becomes, in its most compact form

$$\mathbf{q} = \mathbf{P}^{\{c\}} \mathbf{H}^\chi \delta \mathbf{P} - \delta \mathbf{P} \mathbf{H}^\phi \mathbf{P}^{\{v\}} + \mathbf{P}^{\{c\}} V_{SCF}^{\chi\phi} [\delta \mathbf{P}] \mathbf{P}^{\{v\}}, \quad (7.57)$$

for which the necessary matrix elements are

$$\begin{aligned}\left(P^{\{c\}}\right)^{\alpha\beta} &= \sum_c \langle \chi^\alpha | \psi_c \rangle \langle \psi_c | \chi^\beta \rangle, & \left(P^{\{v\}}\right)^{\alpha\beta} &= \sum_v \langle \phi^\alpha | \psi_v \rangle \langle \psi_v | \phi^\beta \rangle, \\ (H^\chi)_{\alpha\beta} &= \langle \chi_\alpha | H | \chi_\beta \rangle, & (H^\phi)_{\alpha\beta} &= \langle \phi_\alpha | H | \phi_\beta \rangle, \\ \delta P^{\alpha\beta} &= \sum_{cv} \langle \chi^\alpha | \psi_c \rangle x_{cv} \langle \psi_v | \phi^\beta \rangle, & V_{SCF}^{\chi\phi} [\delta P^{\alpha\beta}] &= \langle \chi_\alpha | \hat{V}_{SCF} [\delta \rho(\mathbf{r})] | \phi_\beta \rangle.\end{aligned}\quad (7.58)$$

Within this representation of the action vector, the minimisation problem in Eq. (7.46) becomes

$$w_1 = \min_{\delta \mathbf{P}} \frac{\text{Tr} [\delta \mathbf{P}^\dagger \mathbf{S}^\chi \mathbf{q} \mathbf{S}^\phi \delta \mathbf{P}]}{\text{Tr} [\delta \mathbf{P}^\dagger \mathbf{S}^\chi \delta \mathbf{P} \mathbf{S}^\phi]}, \quad (7.59)$$

where $(S^\chi)_{\alpha\beta} = \langle \chi_\alpha | \chi_\beta \rangle$ and $(S^\phi)_{\alpha\beta} = \langle \phi_\alpha | \phi_\beta \rangle$ are overlaps of unoccupied and the occupied NGWFs.

The full Casida formalism in this is obtained by constructing the object in Eq. (7.57) for both $\mathbf{q}$ and $\mathbf{p}$ simultaneously such as

$$\begin{pmatrix} \mathbf{p} \\ \mathbf{q} \end{pmatrix} = \begin{pmatrix} \mathbf{P}^{\{c\}} \mathbf{H}^\chi \delta \mathbf{P}^{\{p\}} - \delta \mathbf{P}^{\{p\}} \mathbf{H}^\phi \mathbf{P}^{\{v\}} \\ \mathbf{P}^{\{c\}} \mathbf{H}^\chi \delta \mathbf{P}^{\{q\}} - \delta \mathbf{P}^{\{q\}} \mathbf{H}^\phi \mathbf{P}^{\{v\}} + 2\mathbf{P}^{\{c\}} V_{SCF}^{\chi\phi} [\delta \mathbf{P}^{\{q\}}] \mathbf{P}^{\{v\}}, \end{pmatrix}, \quad (7.60)$$

with two newly introduced vectors

$$\left(\delta P^{\{\mathbf{p}\}}\right)^{\alpha\beta} = \sum_{cv} \langle \chi^\alpha | \psi_c \rangle p_{cv} \langle \psi_v | \phi^\beta \rangle, \quad \left(\delta P^{\{\mathbf{q}\}}\right)^{\alpha\beta} = \sum_{cv} \langle \chi^\alpha | \psi_c \rangle q_{cv} \langle \psi_v | \phi^\beta \rangle, \quad (7.61)$$

where p_{cv} and q_{cv} are elements of the action vectors in Eq. (7.52). Additionally, $\delta \mathbf{P}^{\{\mathbf{p}\}}$ and $\delta \mathbf{P}^{\{\mathbf{q}\}}$ are expected to satisfy the invariance conditions

$$\begin{aligned} \delta \mathbf{P}^{\{\mathbf{p}\}'} &= \mathbf{P}^{\{c\}} \mathbf{S}^\chi \delta \mathbf{P}^{\{\mathbf{p}\}} \mathbf{S}^\phi \mathbf{P}^{\{v\}} = \delta \mathbf{P}^{\{\mathbf{p}\}} \\ \delta \mathbf{P}^{\{\mathbf{q}\}'} &= \mathbf{P}^{\{c\}} \mathbf{S}^\chi \delta \mathbf{P}^{\{\mathbf{q}\}} \mathbf{S}^\phi \mathbf{P}^{\{v\}} = \delta \mathbf{P}^{\{\mathbf{q}\}}, \end{aligned} \quad (7.62)$$

which are required to ensure some reasonable response density matrices implicitly carrying orthogonality of the KS states^[24]. Consequently, the minimisation problem in Eq. (7.52) is summarised as

$$w_1 = \min_{\{\delta \mathbf{P}^{\{\mathbf{p}\}}, \delta \mathbf{P}^{\{\mathbf{q}\}}\}} \left[\frac{\text{Tr} \left[(\delta \mathbf{P}^{\{\mathbf{p}\}})^\dagger \mathbf{S}^\chi \mathbf{P}^{\chi\phi} \mathbf{S}^\phi \right]}{2 \text{Tr} \left[(\delta \mathbf{P}^{\{\mathbf{p}\}})^\dagger \mathbf{S}^\chi \delta \mathbf{P}^{\{\mathbf{q}\}} \mathbf{S}^\phi \right]} + \frac{\text{Tr} \left[(\delta \mathbf{P}^{\{\mathbf{q}\}})^\dagger \mathbf{S}^\chi \mathbf{Q}^{\chi\phi} \mathbf{S}^\phi \right]}{2 \text{Tr} \left[(\delta \mathbf{P}^{\{\mathbf{p}\}})^\dagger \mathbf{S}^\chi \delta \mathbf{P}^{\{\mathbf{q}\}} \mathbf{S}^\phi \right]} \right], \quad (7.63)$$

where minimisation is carried out with the constraint analog to Eq. (7.53), namely

$$\text{Tr} \left[(\delta \mathbf{P}^{\{\mathbf{p}\}})^\dagger \mathbf{S}^\chi \delta \mathbf{P}^{\{\mathbf{q}\}} \mathbf{S}^\phi \right] = 1. \quad (7.64)$$

7.6 The Hubbard U corrected interaction kernel

The systematic errors in approximate KS-DFT level due to overestimation of Coulombic interactions of the localised orbitals, namely SIE^[35–38] and the delocalisation error^[39–44], were discussed in detail in Sec. 4.2. As the starting point of LR-TDDFT is the product space of underlying KS-DFT wave-functions of occupied and unoccupied manifolds together with the KS eigenvalues, it naturally inherits these systematic errors. The effects of SIE on first-principles simulations of the neutral excitations within LR-TDDFT have attracted increasing interest in recent years^[45–48]. Particularly, SIE becomes a matter of central importance in the first-principles spectroscopy of the systems comprising transition-metal ions^[49–54]. For approximated systems with a large SIE, state-of-art-approaches beyond

ALDA have been proposed to obtain more accurate description of spectra, such as hybrid-TDDFT^[55,56], or Green's function based methods such as GW + Bethe-Salpeter^[57]; however, computational costs of such approaches limit applicabilities of them on most realistic systems.

Inspired by the success and efficiency of DFT+ U , the time-domain extension of the Hubbard U correction to TDDFT, namely TDDFT+ U , is an intriguing prospect. To our knowledge, the first reported TDDFT+ U implementation was that of Ref. 58, combining real-time propagation and a plane-wave basis, followed by Ref. 59, which detailed the results of a linear-response implementation applied to bulk NiO. In this system, TDDFT+ U was shown to reproduce the experimentally observed, tightly-bound Frenkel excitons, whereas neither TDDFT with ALDA, nor RPA built from DFT+ U succeeded in recovering these to any extent. The role of DFT+ U as a starting point in simulations of excitation energies, particularly the explicit contribution from the Hubbard U term, has been explored in Ref. 60.

Despite widespread use of DFT+ U , particularly for transition-metal systems, the current literature is lacking of any systematic study of effects of SIE, DFT+ U , or much less TDDFT+ U on neutral excitation energies. For potentially more accurate first-principles spectral simulations of systems with localised orbitals, as well as for further theoretical understanding, we were motivated to investigate TDDFT+ U in detail.

In the most general description, a non-local interaction kernel is defined as the second functional derivative of the energy functional with respect to the density-matrix^[6]

$$f_{tot}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = \frac{\delta^2 E_{tot}[\rho^\sigma, \rho^{\sigma'}]}{\delta \rho^\sigma(\mathbf{r}'', \mathbf{r}''') \delta \rho^{\sigma'}(\mathbf{r}, \mathbf{r}')}, \quad (7.65)$$

which reduces via Eq. (4.5) for the non-spin-polarized systems within local and semi-local functionals to

$$f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2}{\delta n(\mathbf{r}') \delta n(\mathbf{r})} (E_H[n] + E_{\text{xc}}^{\text{LDA}}[n]), \quad (7.66)$$

where $\delta n(\mathbf{r}) = \delta \rho(\mathbf{r}, \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}')$ as in Sec. 7.5. Invoking the Hubbard U correction to the energy functional from Eq. (4.5), we propose the introduction of a Hubbard U corrected

interaction kernel

$$\begin{aligned} f_{Hxc+U}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') &= f_{Hxc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'') + f_U^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') \\ &= \frac{\delta^2 E_{Hxc}[n^\sigma, n^{\sigma'}]}{\delta n^\sigma(\mathbf{r}'') \delta n^{\sigma'}(\mathbf{r})} + \frac{\delta^2 E_U[\rho^\sigma, \rho^{\sigma'}]}{\delta \rho^\sigma(\mathbf{r}'', \mathbf{r}''') \delta \rho^{\sigma'}(\mathbf{r}, \mathbf{r}')}. \end{aligned} \quad (7.67)$$

Inserting Eq. (4.8) into the second term of this expression, the Hubbard U kernel in the localised basis set $\{\varphi_m\}$ spanning the localised subspace evaluates to

$$f_U^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = -U \sum_{mm'} \delta^{\sigma\sigma'} \varphi_m(\mathbf{r}) \varphi_{m'}^*(\mathbf{r}') \varphi_m^*(\mathbf{r}'') \varphi_{m'}(\mathbf{r}'''). \quad (7.68)$$

Inserting this to Eq. (7.35), a non-local Hubbard correction to the coupling matrix is obtained in the KS wave-function basis as

$$\begin{aligned} K_{cv, c'v'}^U &= -U \sum_{c'v'} \sum_{mm'} \langle \psi_c | \varphi_m \rangle \langle \varphi_{m'} | \psi_v \rangle (\langle \psi_{c'} | \varphi_m \rangle \langle \varphi_{m'} | \psi_{v'} \rangle)^\dagger \\ &= -U \sum_{c'v'} \sum_{mm'} \langle \psi_c | \varphi_m \rangle \langle \varphi_{m'} | \psi_v \rangle \langle \psi_{v'} | \varphi_{m'} \rangle \langle \varphi_m | \psi_{c'} \rangle \end{aligned} \quad (7.69)$$

For the special hypothetical case, where the localised subspace is spanned by KS wave-functions of as in $\{\varphi_m\} = \{\psi_m\}$, the contributions of f_U to the matrix elements of $\mathbb{A}$ and $\mathbb{B}$ become

$$\begin{aligned} A^U &= K_{cv, c'v'}^U = -U \delta_{cm} \delta_{m'v} \delta_{v'm'} \delta_{mc'} = -U \delta_{vv'} \delta_{cc'}, \quad \text{and} \\ B^U &= K_{cv, v'c'}^U = -U \delta_{cm} \delta_{m'v} \delta_{c'm'} \delta_{mv'} = 0. \end{aligned} \quad (7.70)$$

As seen in this special case, the only contribution is to the diagonal terms of $\mathbb{A}$ in such cases as it is indeed nothing but the direct exciton self-interaction. Neglecting interactions via Dyson's equation, the effect of included this in $\mathbb{A}$ would be to shift ω_{cv} in energy down by $-U$. In such an independent picture, SIE of excitons is purely due to the missing exchange terms, which is included through A_{cv}^U by practically shifting ω_{cv} down with $-U$.

7.6.1 A four-level toy model

For further insight, the effects of TDDFT+ U in conjunction with DFT+ U can be illustrated with a toy model both within TDA and the Casida equation. Let us consider four independent-particle KS-like states, of which two occupied and two unoccupied states are labelled with $\{v, v'\}$ and $\{c, c'\}$, respectively, with some arbitrary eigenenergies as illustrated in Fig. 7.1. The states shown in red corresponding to the pair $\{c, v\}$ is that which we target with a correction inspired by DFT+ U and TDDFT+ U .

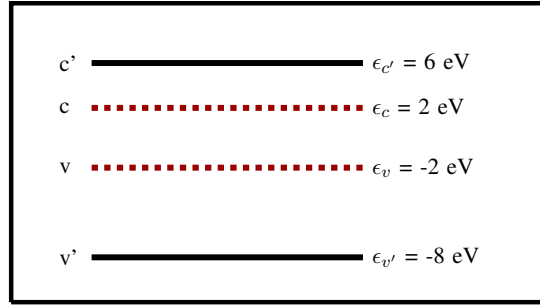


Figure 7.1: A four-level toy model for independent-particle KS-like states proposed as two levels affected by + U corrections illustrated with the dashed, red lines and two bystander levels illustrated with the black lines with the arbitrarily assigned energies, while avoiding any symmetry in energy differences.

The block matrices $\mathbb{A}$ and $\mathbb{B}$ in the Casida equation become 4×4 matrices with elements

$$A_{ji,j'i'}(U) = \left[(\epsilon_{j'} - \epsilon_{i'}) + \frac{U_1}{2} (\delta_{j'c} + \delta_{i'v}) - U_2 \delta_{j'i',cv} \right] \delta_{i'i} \delta_{jj'} + K_{ji,j'i'}^{\text{Hxc}}$$

$$B_{ji,j'i'} = K_{ji,i'j'}^{\text{Hxc}} \quad (7.71)$$

where j and j' run over $\{c, c'\}$, while i and i' run over $\{v, v'\}$. The Hubbard parameter U_1 imitates the effect of DFT+ U by pushing the targeted states away from the Fermi level via the term $U_1 (\delta_{j'c} + \delta_{i'v}) / 2$, whereas the Hubbard parameter U_2 includes the effect of TDDFT+ U via the term $-U_2 \delta_{j'i',cv}$. By making these two Hubbard parameters as U_1 and U_2 independent, the individual effects of the Hubbard corrections at the DFT and TDDFT levels can be observed by setting one of them to zero at a time. The Hartree+xc coupling matrix elements are assigned

to some arbitrary values as

$$K_{ji,j'i'}^{\text{Hxc}} = \begin{cases} 4.0 \text{ eV} & \text{for } \delta_{ji,j'i'} \\ 0.8 \text{ eV} & \text{otherwise,} \end{cases}$$

$$K_{ji,i'j'}^{\text{Hxc}} = \begin{cases} 4.0 \text{ eV} & \text{for } \delta_{ji,i'j'} \\ 0.8 \text{ eV} & \text{otherwise,} \end{cases} \quad (7.72)$$

where such a symmetric choice is a deliberate attempt to simplify the contributions due to f_{Hxc} .

The Casida equation in its full form and within the TDA was solved using an eigenvalue solver for various cases listed with corresponding acronyms in Table 7.1.

Acronym	U_1	U_2	Description
DFT+ U & TDDFT	0-20 eV	0 eV	TDDFT without f_U on DFT+ U eigenvalues
DFT & TDDFT+ U	0 eV	0-20 eV	TDDFT with f_U on DFT eigenvalues
DFT+ U & TDDFT+ U	0-20 eV	0-20 eV	TDDFT with f_U on DFT+ U eigenvalues

Table 7.1: The acronyms for the + U correction in DFT and TDDFT levels.

Additionally, FGR excitations energies are included and calculated as

$$\omega_{ji}^{\text{FGR}}(U_1) = (\epsilon_j - \epsilon_i) + \frac{U_1}{2} (\delta_{jc} + \delta_{iv}). \quad (7.73)$$

In Fig. 7.2 and Fig. 7.3, the principle effects of DFT+ U and TDDFT+ U are demonstrated via the amplitude densities of normalised EES using Eq. (1.38) with a life-time broadening $\Gamma = 0.1$ eV for high resolution on a grid of the Hubbard U parameters with 0.05 unit steps for 0-20 eV range versus frequencies (in eV units) with 0.05 unit steps for 0-25 eV range within FGR, TDA and the Casida equation in conjunction with the corrective approaches summarised in Table 7.1.

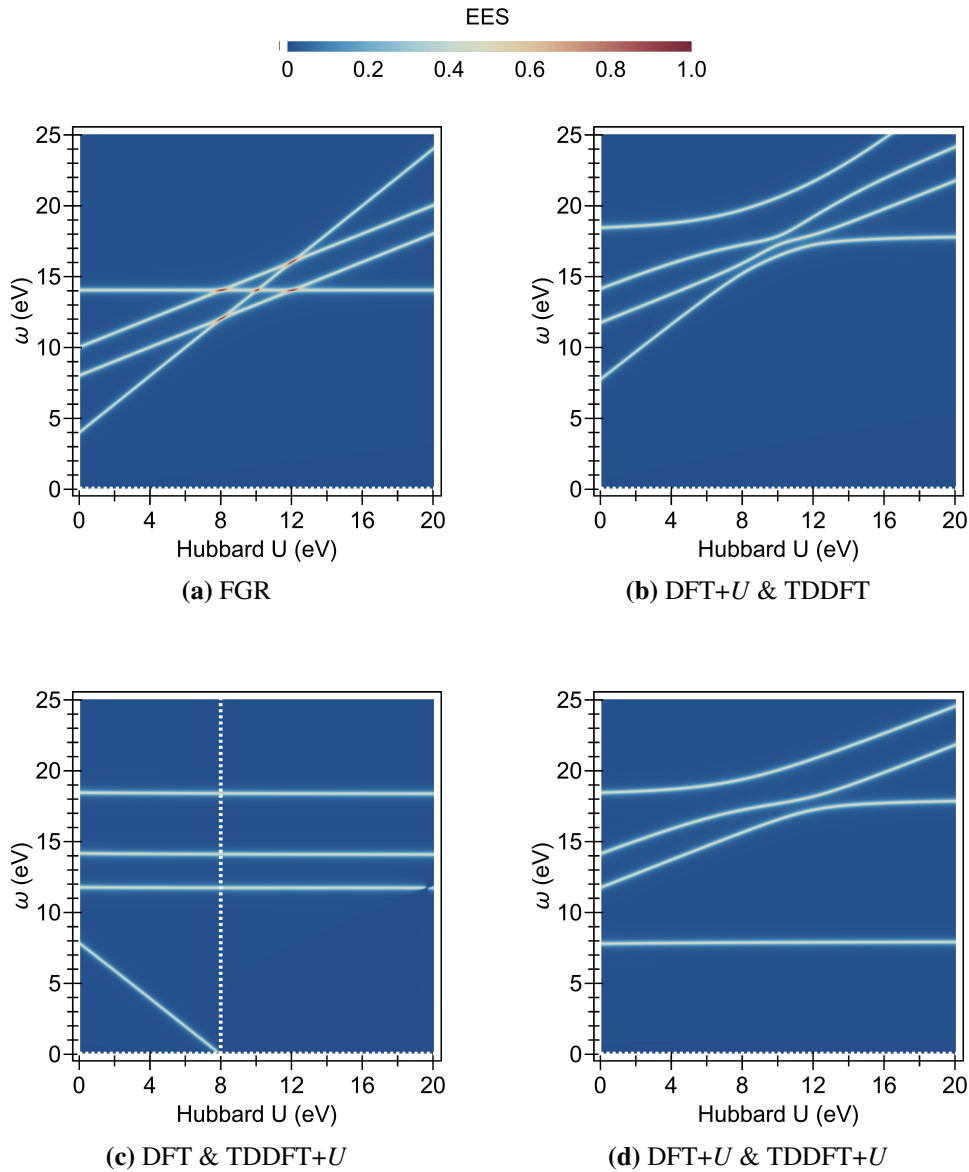


Figure 7.2: EES using the spectral function in Eq. (1.38) with $\Gamma = 0.1$ eV for excitation energies of the four-level toy model within FGR and TDA with the Hubbard U correction in various levels as a function of the Hubbard U parameter.

In Fig. 7.1, the increasing U value in DFT+ U pushes the targeted states (v, c) away from the Fermi level with $U/2$, while the remaining states remain intact. Consequently, in Fig. 7.2a, the excitation from v to c ($v \rightarrow c$) increases with U , while the energies of $v' \rightarrow c$ and $v \rightarrow c'$ increase by $U/2$ with the increasing U in DFT+ U level. The remaining excitation $v' \rightarrow c'$ is not affected as it is totally isolated due to lack of any kind of interaction between exciton pairs

within FGR. Comparing Figs. 7.2b, 7.2c, and 7.2d with FGR in Fig. 7.2a at $U=0$ eV, a global shift of ~ 4 eV on the excitation energies can be seen due to the interactions of exciton pairs within TDA that were introduced by the coupling matrix $K_{ji,j'i'}^{\text{Hxc}}$ in Eq. (7.72). However, the relative alignment of the excitation energies remain the same for each case at $U=0$ eV. Such a preservation of the relative alignment of excitation energies is due to perfectly symmetric definition of the coupling matrix in Eq. (7.72).

In Fig. 7.2b, the DFT+ U affects the excitation energies globally including the excitation $v' \rightarrow c'$ within TDA, unlike the case in Fig. 7.2a within FGR. This global effect is due to fact that DFT+ U modifies the underlying eigenvalues, which are reflected to the coupling matrix. On the contrary, in Fig. 7.2c, DFT+ U exclusively affects the excitation $v \rightarrow c$ by linearly pushing it down from ≈ 8 eV for increasing U values, when TDA is applied on the DFT eigenvalues. For $U=8$ eV, the excitation $v \rightarrow c$ becomes imaginary as $A_{cv,cv}$ becomes 0. Indeed, the excitation energy of $v \rightarrow c$ becomes imaginary at $U = 8$ eV, meaning that the excitation itself becomes purely transient. In Fig. 7.3c, the combined effects of DFT+ U and TDDFT+ U is seen as the total cancellation of the effect of DFT+ U on the excitation $v \rightarrow c$ by TDDFT+ U , while the remaining excitations still are affected by DFT+ U .

Excitations show similar behaviour in DFT+ U & TDDFT and DFT+ U & TDDFT+ U within the Casida equation with the TDA excitations with ~ 1 eV lower energies throughout the frequency range overall comparing Fig. 7.3a and Fig. 7.3c with their TDA counterparts. In Fig. 7.3b, we see that excitations, that are not directly affected by TDDFT+ U , exhibit identical behaviour in Fig. 7.3b. However, we note that DFT+ U has a more pronounced effect in the Casida equation than in the TDA equation, observing that, in Fig. 7.3b, the targeted eigenvalue becomes complex at $U=4$ eV rather than the previously mentioned $U=8$ eV, when the Hubbard U correction to exciton-de-exciton coupling is introduced in the $\mathbb{B}$ matrix.

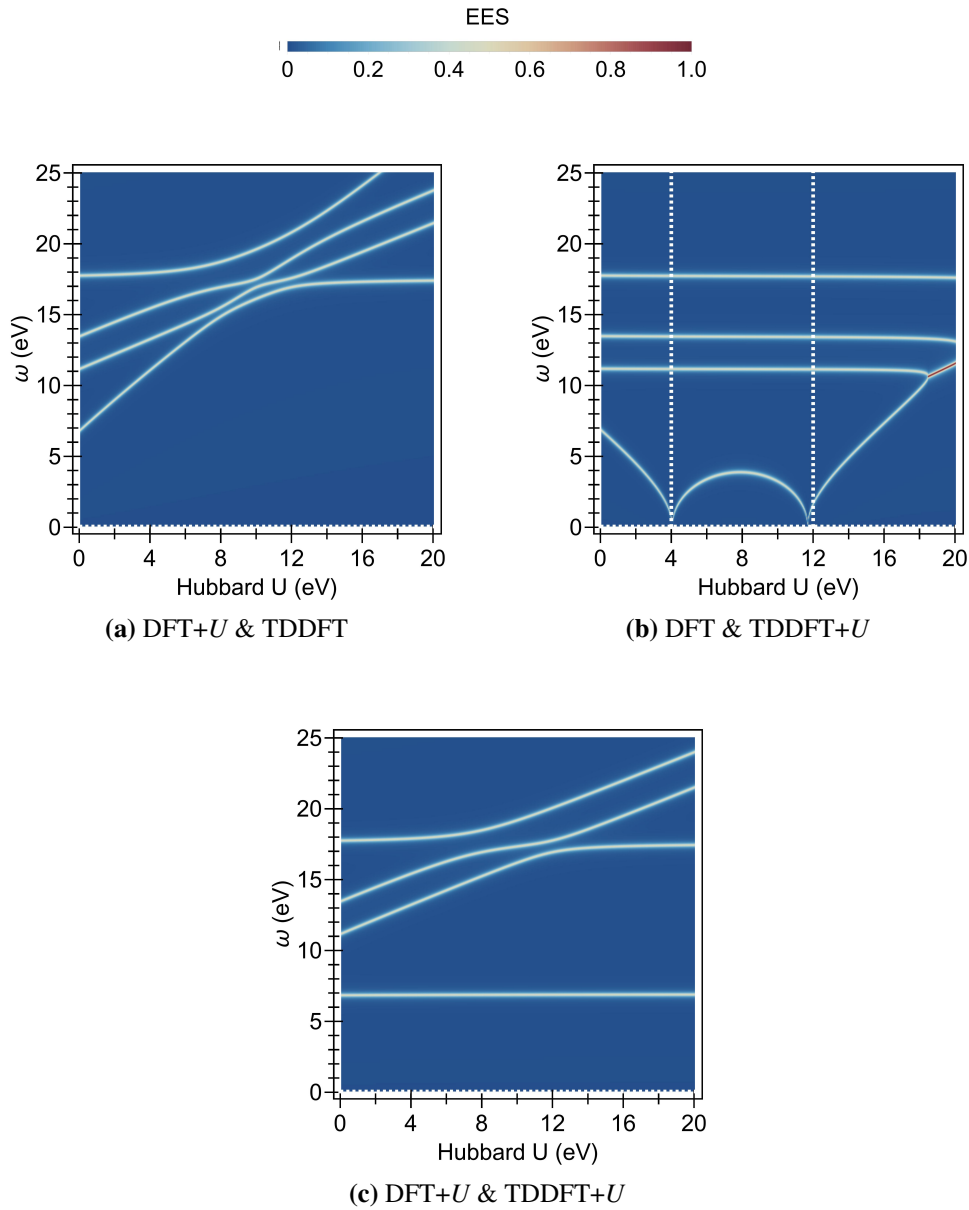


Figure 7.3: EES using Eq. (1.38) with $\Gamma = 0.1$ eV for excitation energies of the four-level toy model within the Casida equation with the Hubbard U correction in various levels as a function of the Hubbard U parameter. The norm of the complex values are presented.

7.6.2 The implementation of TDDFT+ U within ONETEP

We have implemented the TDDFT+ U kernel of Eq. 7.69 in ONETEP^[29,30,61]. The Hubbard U kernel brings an additional term to SCFB in Eq. (7.5), given by

$$V_{SCF+U}^{\chi\phi}[\delta P^{\alpha\beta}] = V_{SCF}^{\chi\phi}[\delta P^{\alpha\beta}] + V_U^{\chi\phi}[\delta P^{\alpha\beta}], \quad (7.74)$$

where the Hubbard U correction to SCFB for $\delta\rho(\mathbf{r}, \mathbf{r}')$ in Eq. (7.54) is

$$\begin{aligned} V_U[\delta P^{\alpha\beta}] &= - \sum_{\alpha'\beta'} \sum_{mm'} U \langle \chi_{\alpha} | \varphi_m \rangle \langle \varphi_m | \chi_{\alpha'} \rangle \delta P^{\alpha\beta} \langle \phi_{\beta'} | \varphi_{m'} \rangle \langle \varphi_{m'} | \varphi_{\beta} \rangle \\ &= - \sum_{\alpha'\beta'} \sum_{mm'} U S_{\alpha m}^{\chi\varphi} S_{m\alpha'}^{\varphi\chi} \delta P^{\alpha\beta} S_{\beta' m'}^{\phi\varphi} S_{m'\beta}^{\varphi\phi}. \end{aligned} \quad (7.75)$$

The TDDFT+ U contribution to $\mathbf{q}$ in Eq. (7.57) in its matrix form is then

$$V_U[\delta \mathbf{P}^{\{\mathbf{q}\}}] = -U \mathbf{S}^{\chi\varphi} \mathbf{S}^{\varphi\chi} \delta \mathbf{P}^{\{\mathbf{q}\}} \mathbf{S}^{\phi\varphi} \mathbf{S}^{\varphi\phi}, \quad (7.76)$$

where it takes an equivalent form for $\mathbf{p}$.

7.7 Conclusion

In this chapter, our main tools for studying the spectra of finite-sized transition-metal systems were introduced starting from the fundamentals of TDDFT. Its linear-scaling, linear-response formalism and implementation with the ALDA kernel within ONETEP were discussed. The TDDFT+ U approach was derived and its linear-scaling implementation within ONETEP was established. Furthermore, the effects of TDDFT+ U in conjunction with DFT+ U were demonstrated using an illustrative four-level toy model. From this simple toy model, we observe that DFT+ U modifies the coupling matrix of exciton-exciton pairs by shifting eigenvalues of underlying states in the targeted manifold; hence, transitions into, out of, and within this manifold are pushed to higher energies with the increasing Hubbard U values. On the other hand, TDDFT+ U acts exclusively on transitions within the targeted manifold by shifting its energy down with the increasing Hubbard U values, while the remaining transitions stay unaffected by TDDFT+ U . Hence, it can be inferred that TDDFT+ U is effective on a particular subset of the transitions that are affected by DFT+ U . For the

particular case in our toy-model, the effect of DFT+ U is precisely cancelled out by the effect TDDFT+ U . However, a general conclusion on the relative effects of DFT+ U and TDDFT+ U cannot be derived through such a toy-model, as coupling matrices were chosen as perfectly symmetric for the sake of simplicity. In the next two chapters, the performance of first-principles DFT+ U and TDDFT+ U will be demonstrated on some realistic transition-metal systems.

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Chapter 8

Molecular spectroscopy of finite-sized systems: coordination complexes with TDDFT+ U

Coordination complexes are a class of molecular systems with transition-metal centres and organic ligands. They have a wide range opto-electronic applications such as in dye-sensitized solar cells^[1,2], and photo-assisted water splitting^[3], due to their low-lying excitations. In coordination complexes, the $3d$ orbitals of metal centres are highly hybridised with π and π^* orbitals resulting in ligand-field splitting of $3d$ orbitals. As discussed in Chap. 4, approximate KS-DFT fails to describe such orbitals due to the large SIE and the de-localisation error. Hence, the first-principles simulations of low-lying excitations, which have commonly mixed metal-to-ligand and $3d \rightarrow 3d$ characters, are challenging when starting from approximate KS-DFT. More robust approaches such as hybrid TDDFT^[4,5], Green's function based methods such as GW + Bethe-Salpeter^[6], optimally-tuned range-separated hybrid functionals^[7-10], or coupled-cluster methods^[11] can more accurately describe these low-lying excitations; however, they are limited to smaller molecules due to their very high computational demand. By construction, DFT+ U is efficiently formulated for the sole purpose of improving the description and energies of localised orbitals. However, since the inaccuracies in DFT will be inherited by TDDFT, particularly in the interaction strengths among excitons, so TDDFT+ U is promising for use conjunction with DFT+ U . Otherwise, DFT+ U alone may worsen the accuracy by over-correcting in the product space of occupied and unoccupied manifolds.

In this chapter, the main objective is to demonstrate the effective domains of DFT+ U and TDDFT+ U in occupied and unoccupied manifolds for selected representative coordination complexes, as well as to determine the low-lying excitation energies of these systems accurately. First, the effects of the Hubbard U correction at various levels of theory will be investigated as functions of the Hubbard U parameter on two closed-shell Ni-centred coordination complexes. Then, the first-principles Hubbard parameters for an open-shell, high-spin Co-centred complex, addition to the two Ni-centred complexes, will be calculated using first-principles approaches described in Chap. 4. Finally, fully first-principles EES and ABS will be demonstrated for these three systems, for comparison with previous experimental and prior first-principles studies, including quantum chemistry works.

8.1 The Hubbard *U* dependence of spectra

Two small closed-shell Ni-centred coordination complexes, namely the planar tetracyanonickelate anion $\text{Ni}(\text{CN})_4^{2-}$ and tetrahedral nickel tetracarbonyl $\text{Ni}(\text{CO})_4$ shown in Fig. 8.1a and Fig. 8.1b, respectively, were chosen for study. The Hubbard *U* dependence of molecular spectra in both individual and combined effects of DFT+*U* and TDDFT+*U* were individually investigated. These systems provide a playground to investigate the effects of DFT+*U* and TDDFT+*U*, since they minimise any complex contributions from magnetic ordering and large ligand-field splittings, as both systems are closed-shell and centro-symmetric with strong ligands. Furthermore, these systems have previously been studied experimentally^[12–15] and within numerous first-principles methods^[16–19].

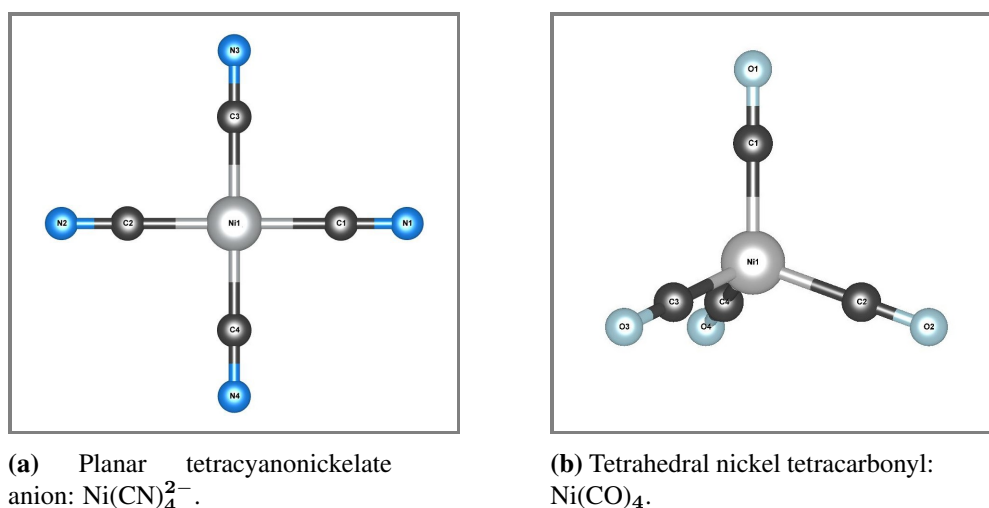


Figure 8.1: The molecular structures of selected Ni-centered closed-shell coordination complexes.

8.1.1 Computational details

First-principles simulations were performed within ONETEP^[20–22]. Terminologies used in ONETEP are adopted as ground-state simulation is referred as *single-point*, and the procedure of variationally optimising the second set of NGWFs to represent the unoccupied manifold is referred as *conduction*. TDA is labelled as such, whereas the Casida formalism is called *random-phase approximation* (RPA) for historical reasons; however it is crucial to emphasise that it differs from the previous description of RPA in Chap. 5, since the interaction kernel includes additionally xc- and TDDFT+*U* kernels. The general work-flow for obtaining

excitation energies and oscillator strengths within ONETEP is summarized in Fig. 8.2.

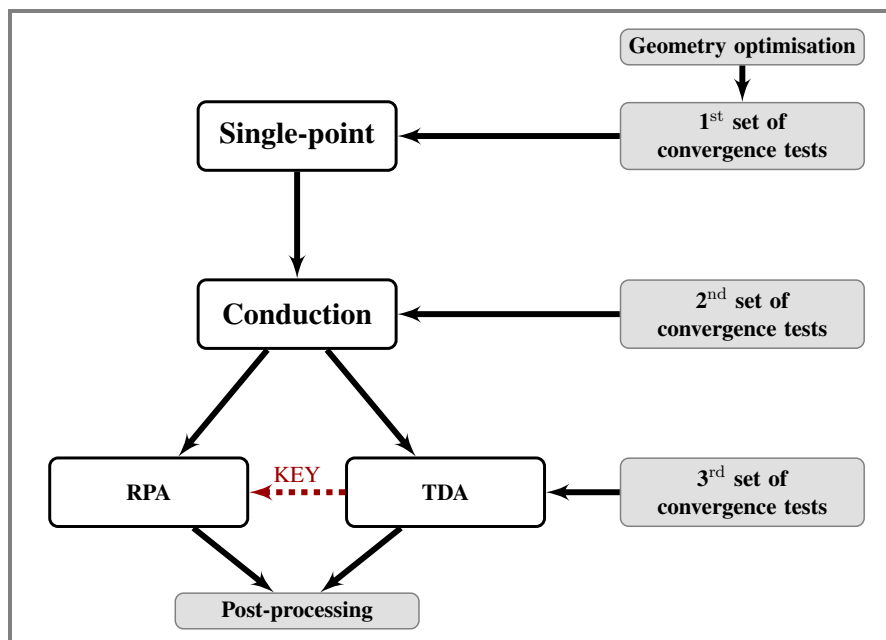


Figure 8.2: The work-flow for calculating spectra within the TDA and RPA in ONETEP.

The pseudo-potential construction

The scalar-relativistic, norm-conserving Perdew-Burke-Ernzerhof (PBE) pseudo-potentials^[23–25] produced with the pseudo-potential generator OPIUM^[26] were used for these simulations. General info about PBE pseudo-potentials produced for each atomic species are summarized in Table 8.1¹.

Species	Configuration	Valence electron number	Additional info
Ni	Neutral, [Ar]3d ⁸ 4s ² 4p ⁰	10	Non-linear core corr.
O	Neutral, [He]2s ² 2p ⁴	6	
C	Neutral, [He]2s ² 2p ²	4	
N	Neutral, [He]2s ² 2p ³	5	

Table 8.1: Details of pseudo-potentials for the atomic species in Ni-centred coordination complexes.

¹See App. A for the input files for OPIUM.

Construction of the simulation box

The initial geometries were adopted from the first-principles result for $\text{Ni}(\text{CN})_4^{2-}$ [27], and from experimental data for $\text{Ni}(\text{CO})_4$ [28]. The molecular structures were optimised iteratively by fulfilling three convergence criteria, on the atomic displacements, energy per atom, and total atomic forces for pre-defined values (0.005 bohr, 10^{-6} Ha, and 0.002 Ha/bohr, respectively) by means of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method [29,30]. The optimised geometries were positioned in cuboid simulation boxes centred on Ni atoms, with the available minimum dimensions needed to satisfy the requirements of the Martyna-Tockeman boundary condition (PBC) used, which was applied with the dimensionless parameter 7 [31]. For instance, assuming that the largest distance between atoms in x-direction is d_x a_0 of atoms A and B with NGWFs radii of r_A and r_B , then the minimum dimension of this simulation box in the x-direction has to be

$$R_x = 2(d_x + r_A + r_B).$$

Convergence tests

Three sets of convergence tests were performed to safeguard simulations. The first set of convergence tests were performed at the single-point level to determine a common set of values for an effective plane-wave kinetic energy cut-off (E_{cut}), and the radii of the variationally optimised NGWFs for single-point, namely $R_{\text{NGWFs}}^{\text{GS}}$. The per-atom total-energy convergences for $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$ are shown in Fig. 8.3a and Fig. 8.3b, respectively. Additionally, a total of 9 NGWFs for Ni atoms to complete the period up to Kr, and a total of 4 NGWFs for each C, O and N atoms to complete the period up to Ar, were optimised at the single-point level.

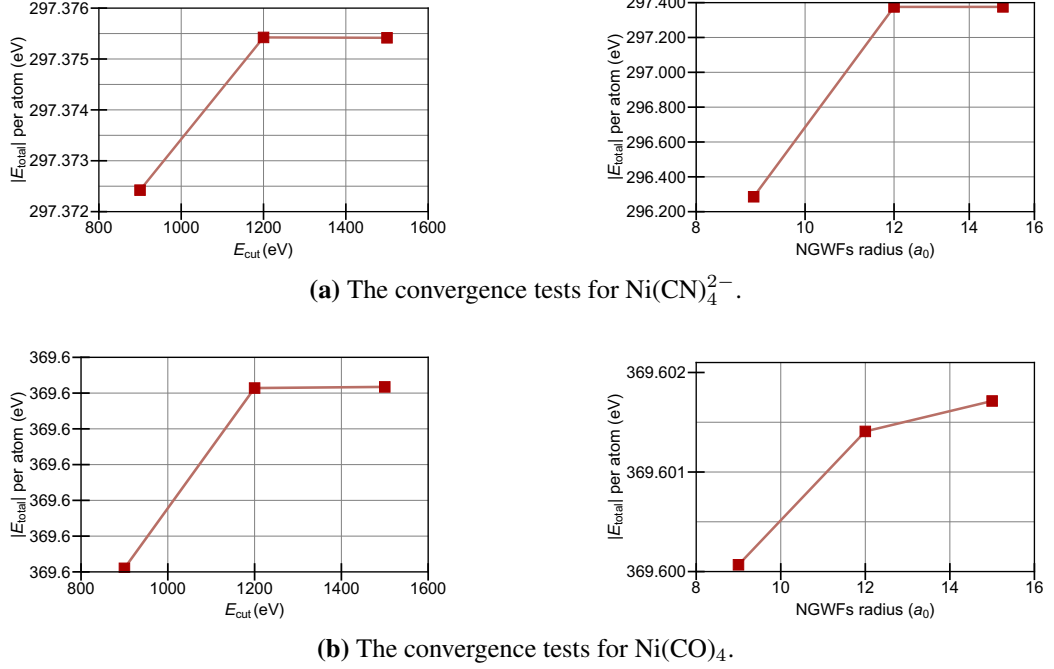


Figure 8.3: Convergence tests performed to determine the effective plane-wave kinetic energy cut-off energy (E_{cut}) and the single-point NGWFs radius ($R_{\text{NGWFs}}^{\text{SP}}$) for $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$. A criterion for change of total energy per atom of 1 meV ($\Delta(E_{\text{tot}}/N_a) \leq 1 \text{ meV}$) was used.

A second set of convergence tests were then performed at the conduction level to determine the NGWFs radius for conduction states, and minimum numbers of additional NGWFs needed to be optimised to represent the product space of occupied-unoccupied orbital pairs in a relevant spectral range, with respect to a set of criteria of eigenenergies of states, HOMO-LUMO gap positions, and occupancies of states. The increment of radius of conduction NGWFs does not significantly affect the set of criteria here; hence, it was chosen 12 a_0 at the single point level. In $\text{Ni}(\text{CN})_4^{2-}$, the HOMO-LUMO gap is positioned at the vacuum level; hence 20 additional states (equivalent to 10 additional NGWFs in non-spin-polarized cases) were optimised to represent the unoccupied manifold. Thus, the number of NGWFs for each species was doubled to 18 for Ni, and 8 for C, O, and N in order to have sufficient NGWFs to represent the product space, while closing sub-shells. In $\text{Ni}(\text{CO})_4$, it has found that there exist sufficient optimised NGWFs from single-point to represent the conduction manifold already.

A third set of convergence tests was required to determine the numbers of the optimised occupied and unoccupied states to be able to represent the respective product spaces for RPA

and TDA. In principle, this number should be adjusted down as small as possible to reduce dimensions of related matrices for lower computational costs, while maintaining the desired accuracy; however, for both $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$, all optimised occupied and unoccupied manifolds were used for the sake of benchmark simulations with TDDFT+ U . The common parameter set used consistently for both systems is summarised in Table 8.2.

Parameter	Level	Value	Unit
E_{cut}	All	1200	eV
PBC	All	7	
$R_{\text{NGWFs}}^{\text{SP}}$	All	12	a_0
$N_{\text{NGWFs}}^{\text{Ni}}$	SP (COND)	9 (18)	
$N_{\text{NGWFs}}^{\text{C}}$	SP (COND)	4 (8)	
$N_{\text{NGWFs}}^{\text{N}}$	SP (COND)	4 (8)	
$N_{\text{NGWFs}}^{\text{O}}$	SP (COND)	4 (8)	

Table 8.2: The common set of convergence parameters used for $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$.

Final converged calculations

Final calculations were performed with converged parameters for $U=0$ eV at integer values of the Hubbard U parameter in the range 0 – 10 eV for the first 50 singlet excitations of each system. The product spaces for LR-TDDFT calculations were constructed by using full valence manifolds, which are represented by 24 and 25 NGWFs for $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$, respectively, and conduction manifolds represented by 10 NGWFs¹.

Post-processing

EES and ABS were constructed by using Eq. (1.38) and Eq. (1.39) with a Lorentzian broadening $\Gamma = 0.1$ eV at integer values of the Hubbard U parameters and interpolated at 0.01 eV steps for intermediate values. While EES provides a count of all possible excitations without imposing any selection rules, ABS is the dipole-dipole allowed absorption spectra under Laporte’s selection rules^[32] discussed in Subsec. 1.2.2. EES was scaled by the global maximum of EES data within DFT& TDDFT, DFT+ U & TDDFT, and DFT+ U & TDDFT+ U . Similarly, ABS was scaled by the global maximum of ABS data within DFT& TDDFT, DFT+ U & TDDFT, and DFT+ U & TDDFT+ U . Such separate scaling factors enable

¹See App. A for the sample input files for ONETEP.

us to compare relative intensities within various methods as well as the comparabilities between EES and ABS within same method. EES within FGR was scaled by its own maximum as the larger number of energy differences of occupied and unoccupied states were used to show approximate behaviour beyond first 50 excitations.

8.2 The square-planar tetracyanonickelate anion: $\text{Ni}(\text{CN})_4^{2-}$

The square-planar $\text{Ni}(\text{CN})_4^{2-}$ is a low-spin coordination complex, with a Ni center of nominal charge 2+. $(\text{CN})^-$ is a π -acceptor strong-field ligand that leads to ligand-splitting at $3d$ -levels of Ni, following $d_{yz} \approx d_{xz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$, where $3d^8$ electrons occupy the first four levels and the remaining $3d_{x^2-y^2}$ forms a dsp^2 -hybrid with the ligands in the square-planar symmetry^[33]. As a deduction, the low-lying excitations are expected to be predominantly of a mixed $3d \rightarrow 3d$ and metal-to-ligand $3d \rightarrow \pi^*$ character, as suggested by previous works^[18].

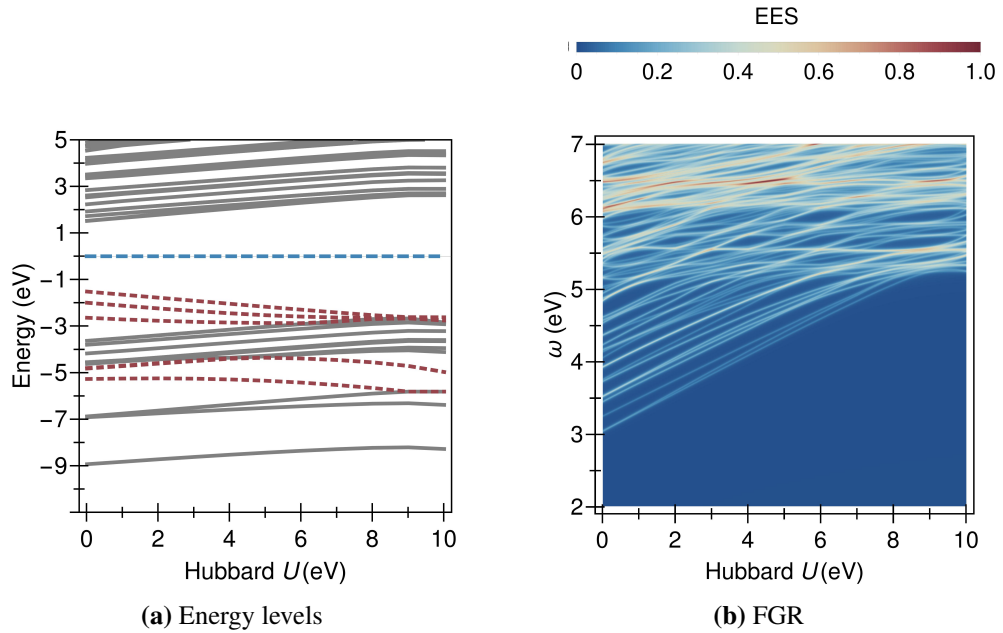


Figure 8.4: The energy levels and the singlet EES spectra using FGR for $\text{Ni}(\text{CN})_4^{2-}$ as functions of Hubbard U parameter. The Fermi level (dashed, blue line) is set to 0 eV. The states affected strongly by DFT+ U are shown with dashed, red lines.

The energy alignment of $3d$ states is shown as a function of U in Fig. 8.4a. For increasing U ,

the occupied $3d$ states move to deeper energies. The states close to the HOMO-LUMO gap (shown with red, dashed lines), which strongly contribute to low-lying excitations, fall to lower energetic states entirely at about $U \gtrsim 7$ eV. Thus, low-lying excitations are pushed upwards and ultimately combine with higher energy excitations of metal-to-ligand character, as seen in EES using FGR of Fig. 8.4b.

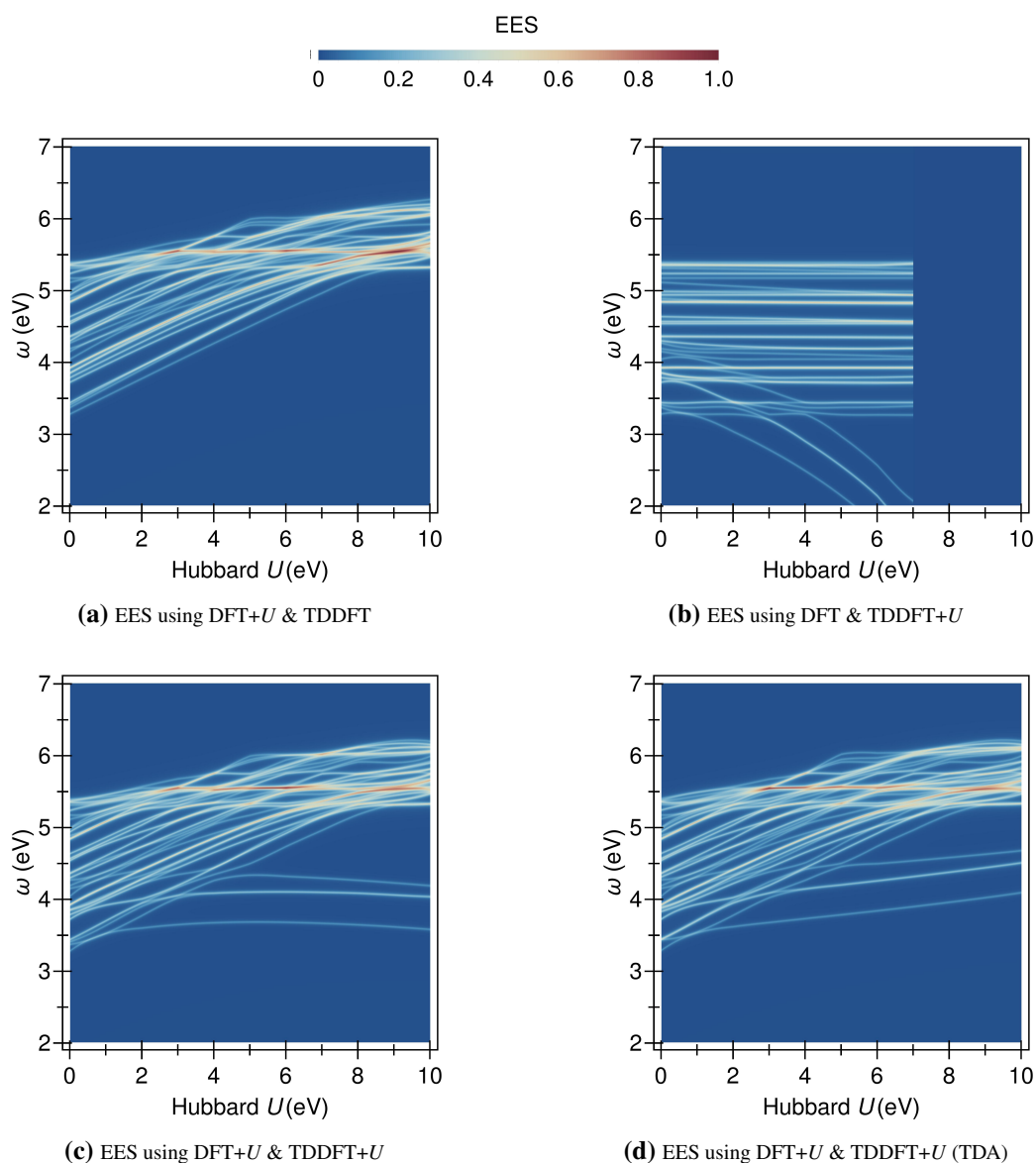


Figure 8.5: The singlet EES of $\text{Ni}(\text{CN})_4^{2-}$ using DFT+ U & TDDFT, DFT & TDDFT+ U , and DFT+ U & TDDFT+ U as functions of the Hubbard U parameter.

Hitherto, the Hubbard U has been used only to modify the under-lying KS-DFT states via DFT+ U . In Fig. 8.5, a more complete and consistent picture is represented by the EES for the first 50 singlet excitations using various combinations of DFT+ U and TDDFT+ U . In Fig. 8.5a, increasing U values in DFT+ U reduces the $3d \rightarrow 3d$ characters of the excitations, and combines them with excitations from deeper states similarly to the FGR case. Beyond that, DFT+ U is effective globally as it pushes other excitations to higher energies as well, by means of modifying the metal-to-ligand energy as seen in Fig. 8.4a. On the contrary, in Fig. 8.5b, TDDFT+ U affects specifically only the excitations carrying of $3d \rightarrow 3d$ type, while remaining excitations are intact as expected. Also, the affected excitations become non-physical for large value $U \gtrsim 7$ eV in DFT & TDDFT+ U , similar to what is observed in the four-level toy model of Subsec. 7.6.1, by virtue of exciton over-binding that is a result of extremely large U value. For these large values of U , TDDFT+ U contributions to coupling matrix elements $K_{cv,cv}^U$ in Eq. (7.69) over-compensate sums of energy differences ω_{cv} and coupling matrix elements $H_{cv,cv}^{Hxc}$ in Eq. (7.41), and lead to complex eigenvalues in Eq. (7.40). In Fig. 8.5c, when DFT+ U and TDDFT+ U are combined, consistently, TDDFT+ U primarily cancels the effects of DFT+ U on $3d \rightarrow 3d$ type of excitations that are at $\sim 3.5 - 4.5$ eV range. This cancellation of DFT+ U with TDDFT+ U is more quadratic in RPA compared to a more linear behaviour as a function U in TDA, comparing Fig. 8.5c and TDA in Fig. 8.5d, and also again recalling what was observed in our four-level toy model.

While DFT+ U is still effective in modifying the ABS by pushing low-lying optical transitions to higher energies as seen in Fig. 8.6a, Fig. 8.6c, and Fig. 8.6d, TDDFT+ U does not have any significant effect on ABS in Fig. 8.6 as TDDFT+ U acts solely on $3d \rightarrow 3d$ excitations directly, which are totally optically dark in $\text{Ni}(\text{CN})_4^{2-}$ in ideal square-planar symmetry.

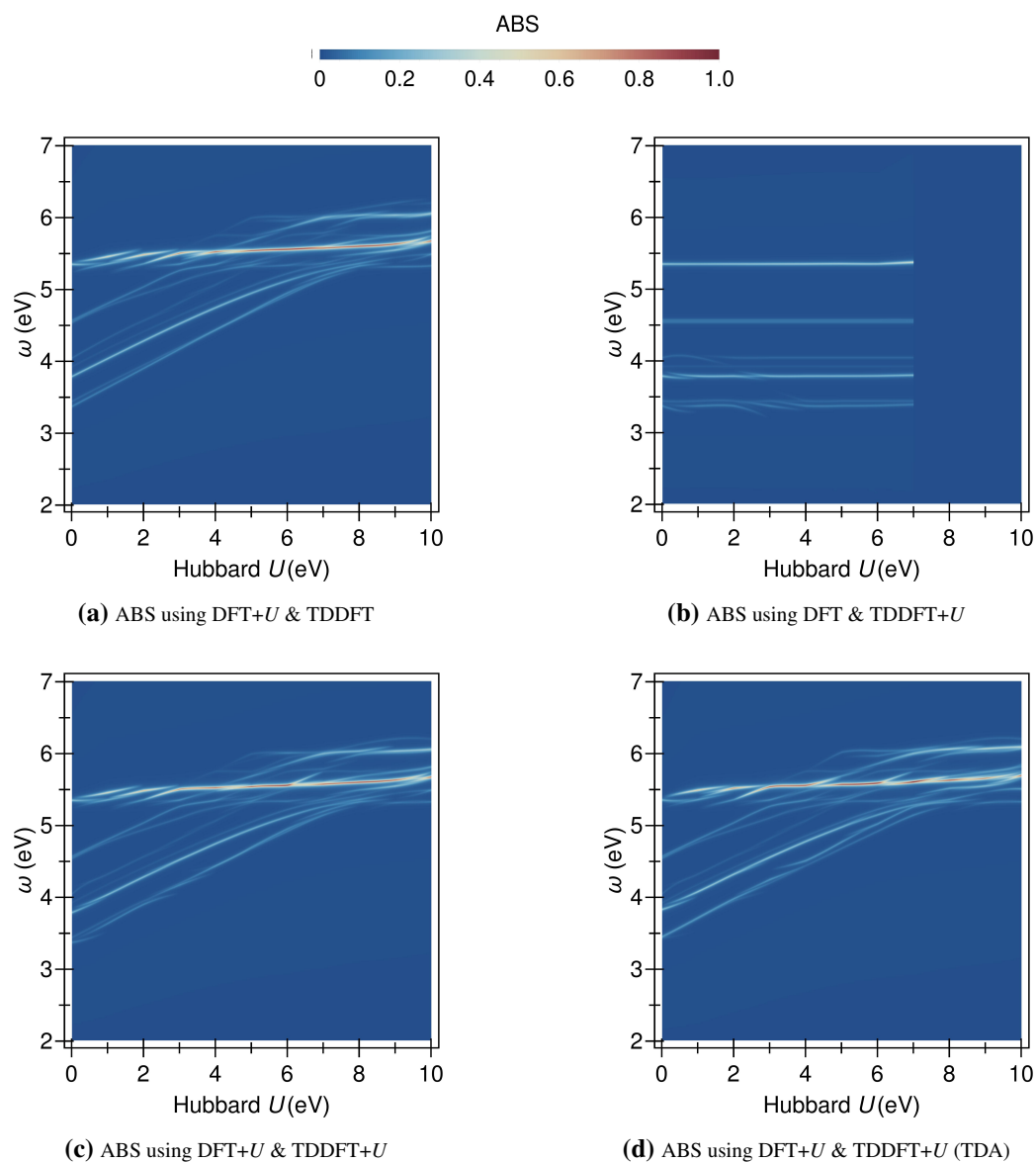


Figure 8.6: The dipole-dipole absorption spectra of $\text{Ni}(\text{CN})_4^{2-}$ using DFT+ U & TDDFT, DFT & TDDFT+ U , and DFT+ U & TDDFT+ U as functions of the Hubbard U parameter.

8.3 The tetrahedral nickel tetracarbonyl: Ni(CO)₄

The tetrahedral Ni(CO)₄ is another low spin coordination with a neutral Ni center, which has a full 3*d* sub-shell. The (CO)[−] ion is a strong-field π -acceptor ligand, which splits 3*d* states on Ni as $d_{z^2} \approx d_{x^2-y^2} < d_{xy} \approx d_{xz} \approx d_{yz}$ in a tetrahedral symmetry. The two-fold and the three-fold degenerate 3*d* splitting can be clearly distinguished by their response to DFT+*U* in Fig. 8.7a as they are pushed down to lower energies. Therefore, the low-lying singlet excitations are predominantly of a Ni 3*d* $\rightarrow$ π^* character^[15,34].

In Fig. 8.7a, the two-fold degenerate $d_{z^2} \approx d_{x^2-y^2}$ states (red, dashed line) at -2 eV and the three-fold degenerate $d_{xy} \approx d_{xz} \approx d_{yz}$ states (red, dashed lines) at -3 eV for $U = 0$ eV are pushed down for increasing U values with DFT+ U . In Fig. 8.7b, these immediate effects of DFT+ U on the low-lying excitations are hinted by the up-shifts in the singlet EES with FGR as functions of increasing U values. The 3*d* $\rightarrow$ π^* characteristic excitations at ~ 4.0 - 5.5 eV for $U = 0$ eV shift to higher energies for increasing U values due to down-shift of 3*d* states. Such shifts are larger particularly for excitations from d_{z^2} and $d_{x^2-y^2}$ as they are lowered more with DFT+ U .

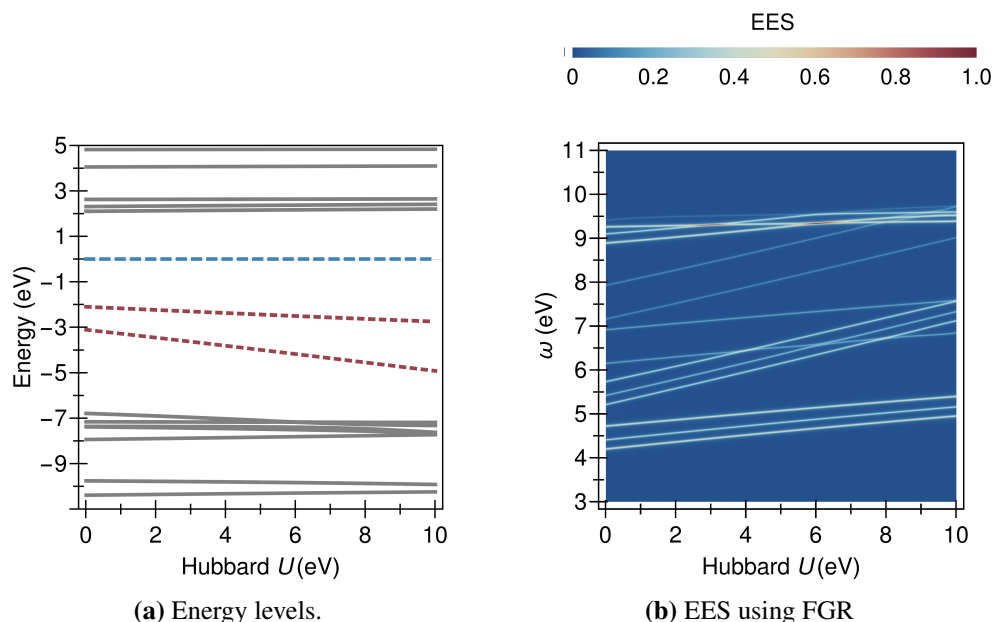


Figure 8.7: The energy levels and the singlet EES spectra using FGR of Ni(CO)₄ as functions of the Hubbard U parameter.

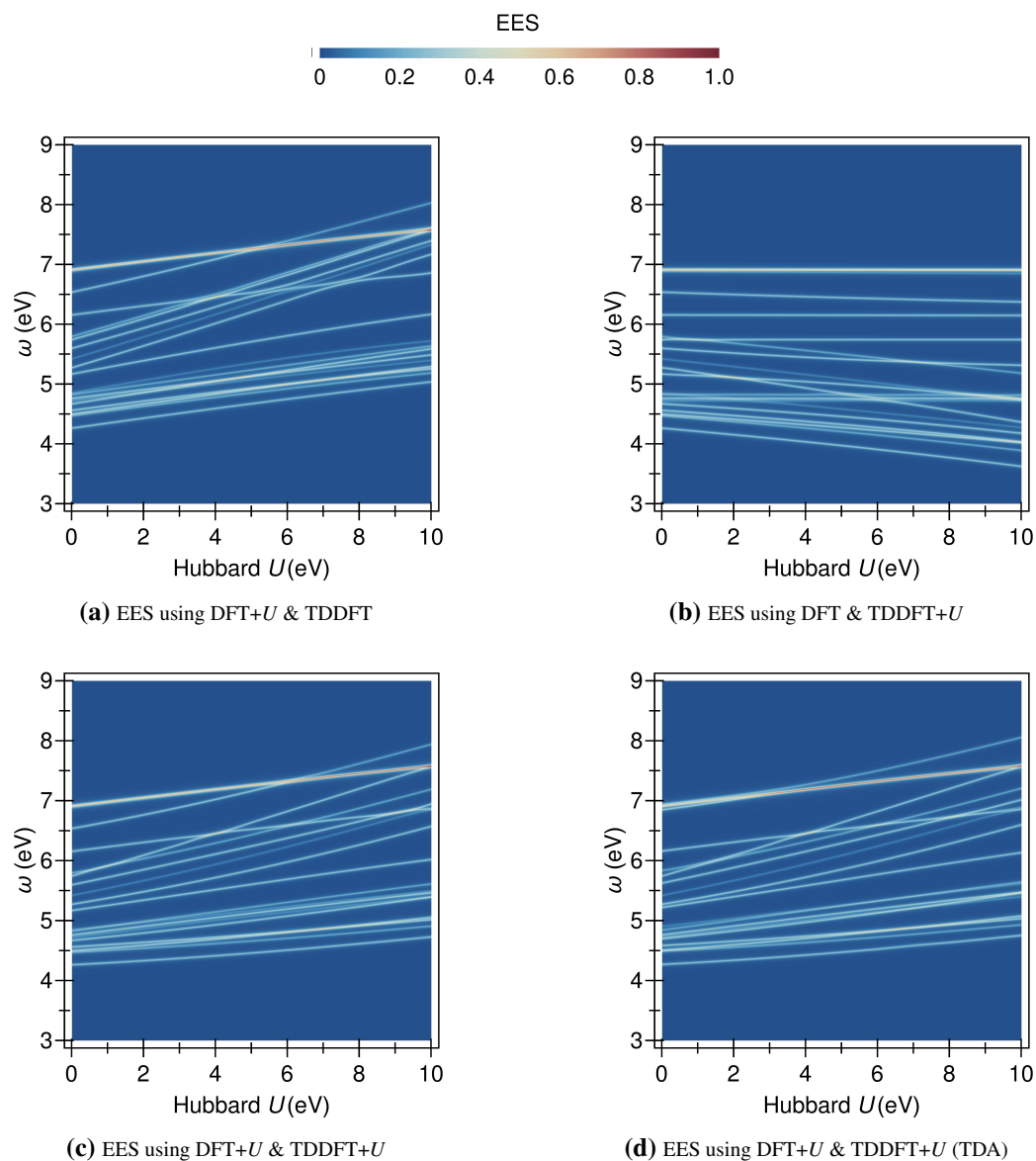


Figure 8.8: The singlet EES of $\text{Ni}(\text{CO})_4$ using DFT+ U & TDDFT, DFT & TDDFT+ U , and DFT+ U & TDDFT+ U as functions of the Hubbard U parameter.

The complete picture of behaviours of the first 50 excitations with DFT+ U and TDDFT+ U are presented in Fig. 8.8. The increasing U value of DFT+ U level affects excitation energies globally by pushing them to higher energies. In Fig. 8.5a, particularly, the excitations from the lower energetic $3d$ levels ($d_{z^2}/d_{x^2-y^2} \rightarrow \pi^*$) at $\sim 5-6$ eV for $U=0$ eV climb most strongly and cross-over with the excitations from the deeper states around $U \approx 4$ eV, as hinted in Fig. 8.4. A similar trend is also present with DFT+ U as it is more effective on the excitations from the

lower energetic $3d$ levels as seen in Fig. 8.5b, where some cross-overs occur with the lower energy batch of excitations. TDDFT+ U cancellation of effects of DFT+ U is more subtle in $\text{Ni}(\text{CO})_4$ for the relevant excitations compared to $\text{Ni}(\text{CN})_4^{2-}$, as expected due to the weaker $3d \rightarrow 3d$ character of the transitions, in Fig. 8.5c. Particularly, TDDFT+ U is less effective on the excitations affected by with DFT+ U . While it shifts the lowest batch of excitations as well as splitting these excitations, it does not lead to the splitting-off of distinct tight-bound excitons as observed in $\text{Ni}(\text{CN})_4^{2-}$. Indeed, it is an important implication, stressed in Chap. 7, that DFT+ U is effective in proportion to the $3d$ character of the KS manifold, whereas TDDFT+ U is proportional to the $3d$ character of product space of occupied $3d$ -unoccupied $3d$ subspaces. This product space is spanned by product wave-functions $|\psi_c^{3d}\psi_v^{3d}\rangle = |\psi_c^{3d}\rangle|\psi_v^{3d}\rangle$.

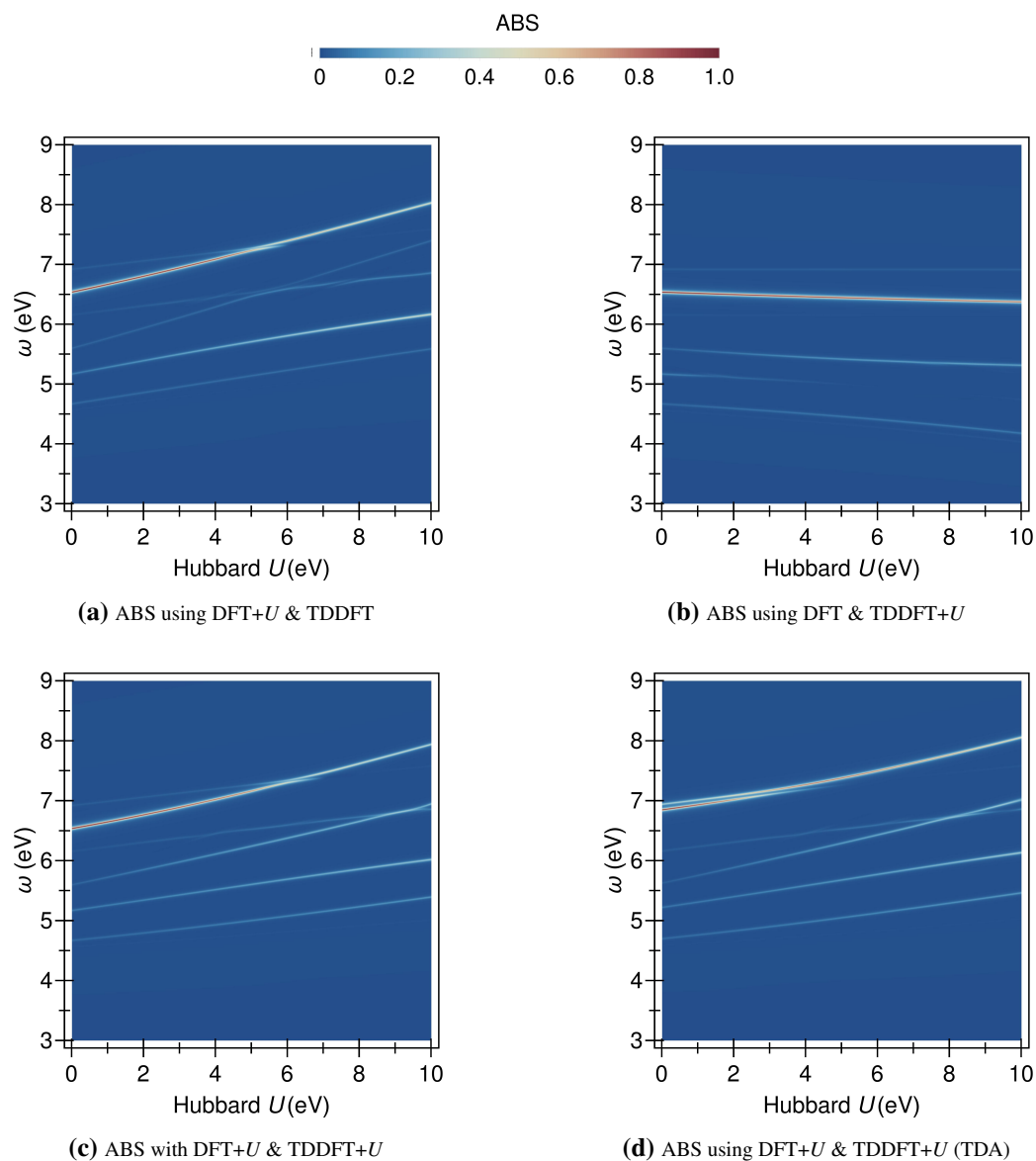


Figure 8.9: The dipole-dipole absorption spectra of $\text{Ni}(\text{CO})_4$ using DFT+ U & TDDFT, DFT & TDDFT+ U , and DFT+ U & TDDFT+ U as functions of the Hubbard U parameter.

As the dominant optically allowed transitions are almost purely $3d \rightarrow \pi^*$ character, DFT+ U naturally pushes bright excitations up as seen in Fig. 8.9a, where the effect of TDDFT+ U on these excitations is quite subtle, as previewed in Fig. 8.9b.

8.4 First-principles Hubbard U parameters for transition-metal centres

First-principles Hubbard parameters were calculated using LRT introduced in Sec. 4.3 within ONETEP for the $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$ introduced in Sec. 8.2 and Sec. 8.3, respectively. Additionally, the Hubbard parameters for an open-shell, high-spin Co-centred coordination complex namely, CoL_2Cl_2 (L=2-aminopyrimidine: $\text{C}_4\text{H}_5\text{N}_3$), which will be discussed in more detail in the next section, were calculated. Hubbard U parameters from the uncoupled-spin response approach in Eq. (4.20) were chosen for simulations. Since a more conventional approach yielded unphysically large values for U . Hence, only spin-up channels were perturbed in two closed-shell Ni-centred complexes by symmetry, whereas both spin-up and spin-down channels were separately perturbed for the open-shell Co-centred complex using a common $V_{\text{ext}}^{\sigma'}$ discrete mesh of $\{-0.10, -0.01, 0.00, 0.01, 0.10\}$. Total derivatives in Eq. 4.20 were determined by linear-fitting to responses of occupancies N_U^σ and projected KS potentials V_{KS}^σ for each spin channel of the Hubbard subspace, respectively, to the perturbative external potential $V_{\text{ext}}^{\sigma'}$.

As both $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$ are closed-shell systems, the respective responses of their spin-up and spin-down channels are identical; hence, the Hubbard U parameter is chosen as $U_{\uparrow\downarrow}^\uparrow$ in Eq. (4.21). Linear fittings of the spin-up occupancy and corresponding KS potential of $3d$ sub-shell of the Ni atom in $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$ versus the perturbative external potential are shown in Fig. 8.10. Also, Hubbard parameters with various schemes for the Ni-centred systems are summarized in Table 8.3. The adopted values of the Hubbard U parameter for Ni atoms in spectra calculations is 1.102 eV and 0.888 eV for $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$, respectively, as highlighted in the table.

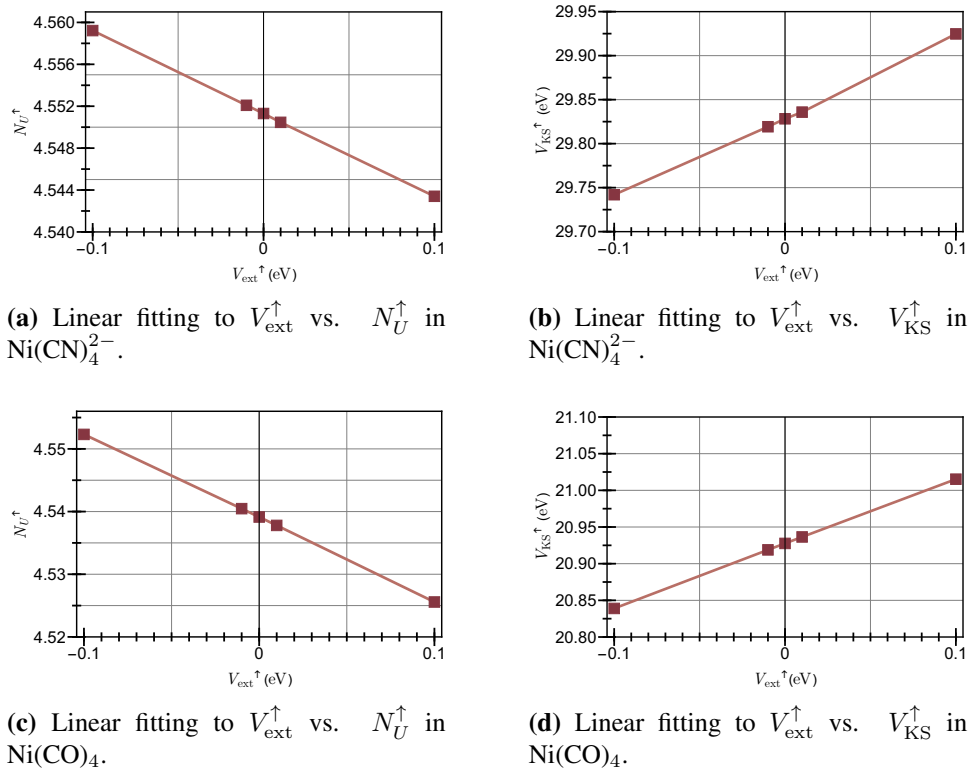


Figure 8.10: The linear-response of spin-up occupancy and the corresponding projected KS potential for the 3d sub-shell of the Ni atom in $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$.

Expression	Symbol	$\text{Ni}(\text{CN})_4^{2-}$	$\text{Ni}(\text{CO})_4$
Eq. (4.21)	$U_{\uparrow\uparrow}^{\uparrow}$	1.102	0.888
Eq. (4.15)	$f^{\uparrow\uparrow} (f^{\downarrow\downarrow}), f^{\uparrow\downarrow} (f^{\downarrow\uparrow})$	6.901, 8.456	9.849, 11.388
Eq. (4.16)	U	7.678	10.618
Eq. (4.17)	J	0.777	0.769
Eq. (4.18)	U_{eff}	6.901	9.849
Eq. (4.23)	U'_{eff}	6.123	9.079

Table 8.3: The Hubbard parameters (in eV) from self-consistent first-principles approaches for $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$.

As CoL_2Cl_2 is an open-shell system, responses of each spin channel need to be measured by perturbing the respective spin channels, separately, one at a time. Once again, the uncoupled-spin approach was used to determine the final averaged Hubbard U parameter for Co atom using linear fitting for spin-up and spin-down channels, as shown in Fig. 8.11.

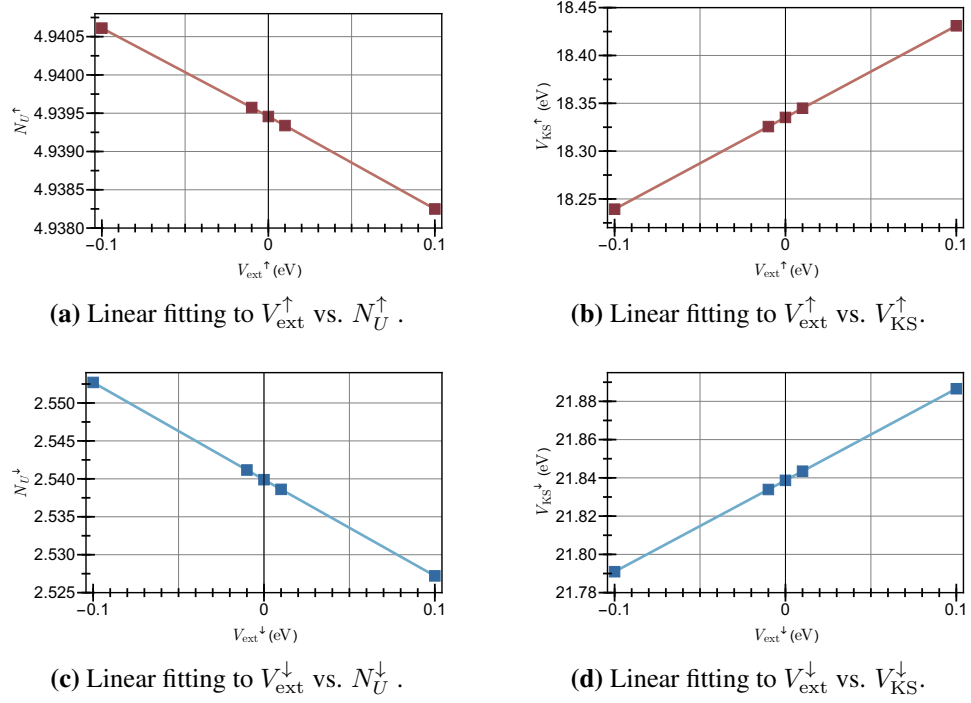


Figure 8.11: The linear-response of spin-up and spin-down occupancies and the corresponding projected KS potentials of the $3d$ sub-shell of the Co atom in CoL_2Cl_2 .

Hubbard parameters with various approaches for Co atom are summarised in Table 8.4. The adopted value of the Hubbard U parameter for Co atom in spectra calculations is 3.789 eV for Co highlighted in table.

Expression	Symbol	CoL_2Cl_2
Eq. (4.20)	$f_{\uparrow\uparrow}^{\uparrow\uparrow}, f_{\uparrow\downarrow}^{\uparrow\downarrow}$	3.503, 4.093
Eq. (4.19)	$U_{\uparrow\downarrow}$	3.798
Eq. (4.15)	$f_{\uparrow\uparrow}^{\uparrow\uparrow}, f_{\uparrow\downarrow}^{\uparrow\downarrow}, f_{\downarrow\uparrow}^{\downarrow\uparrow}, f_{\downarrow\downarrow}^{\downarrow\downarrow}$	13.711, 6.029, 15.268, 7.650
Eq. (4.16)	U	10.660
Eq. (4.17)	J	0.795
Eq. (4.18)	U_{eff}	9.870

Table 8.4: The Hubbard parameters (in eV) from first-principles approaches for CoL_2Cl_2 .

8.5 First-principles spectra of Ni-centred complexes

The EES and ABS of the three coordination complexes were constructed for using DFT+ U and TDDFT+ U with their respective first-principles Hubbard U parameters. The spectra of Ni-centred complexes were obtained from the cross-section of interpolated data in Sec. 8.2 and Sec. 8.3 at their respective first-principle Hubbard U parameters.

8.5.1 Excitation energies and spectra of $\text{Ni}(\text{CN})_4^{2-}$

The EES and ABS of $\text{Ni}(\text{CN})_4^{2-}$ are presented in Fig. 8.12 and Fig. 8.13 for the first-principles $U=1.102$ eV alongside experimental experimental excitation spectra extracted from Ref. 12. In Fig. 8.12, the experimental excitation energies are shown with vertical gray lines in Fig. 8.12. In Fig 8.13, these lines are scaled with respect to the maximum absorbance of highest energy excitation at 4.66 eV given as 10600 in $\text{M}^{-1}\text{cm}^{-1}$; hence, the heights of vertical gray lines represent relative maximum absorbances. The first-principles excitation energies were obtained from the peak positions of Fig. 8.12 with smaller peaks and shoulders removed, and the optically bright ones were assigned by matching the peaks of Fig. 8.13. All excitations were listed in Table 8.5 along with the experimental results ^[12] and TDDFT results^[18], where optically bright excitations are highlighted with bold fonts. The previous TDDFT calculations at Ref. 18 were performed with implicit solvation with a dielectric constant of 37.5, and this provides an important benchmark testing to evaluate the numerical validity of the TDDFT+ U implementation.

As seen Fig. 8.12, DFT+ U is effective throughout the spectral range. The excitation energies are shifted to higher energies as seen by comparing DFT+ U & TDDFT with DFT & TDDFT (PBE). TDDFT+ U , however, acts only at low-energy part, where there emerges some additional peaks surrounded by neighbouring peaks present in DFT & TDDFT. The combined effects of DFT+ U and TDDFT+ U is indeed nearly a combination of their respective individual effects, as seen in EES with DFT+ U & TDDFT+ U , where excitation energies are globally shifted and some additional peaks emerge. In terms of the optically bright excitations, TDDFT+ U has virtually no effect. In Fig. 8.13, DFT+ U still carries these excitations to higher energies with slightly larger shifts at lower energies. TDA and RPA predict spectra in close mutual agreement, with slightly higher energies emerging within TDA for both spectra.

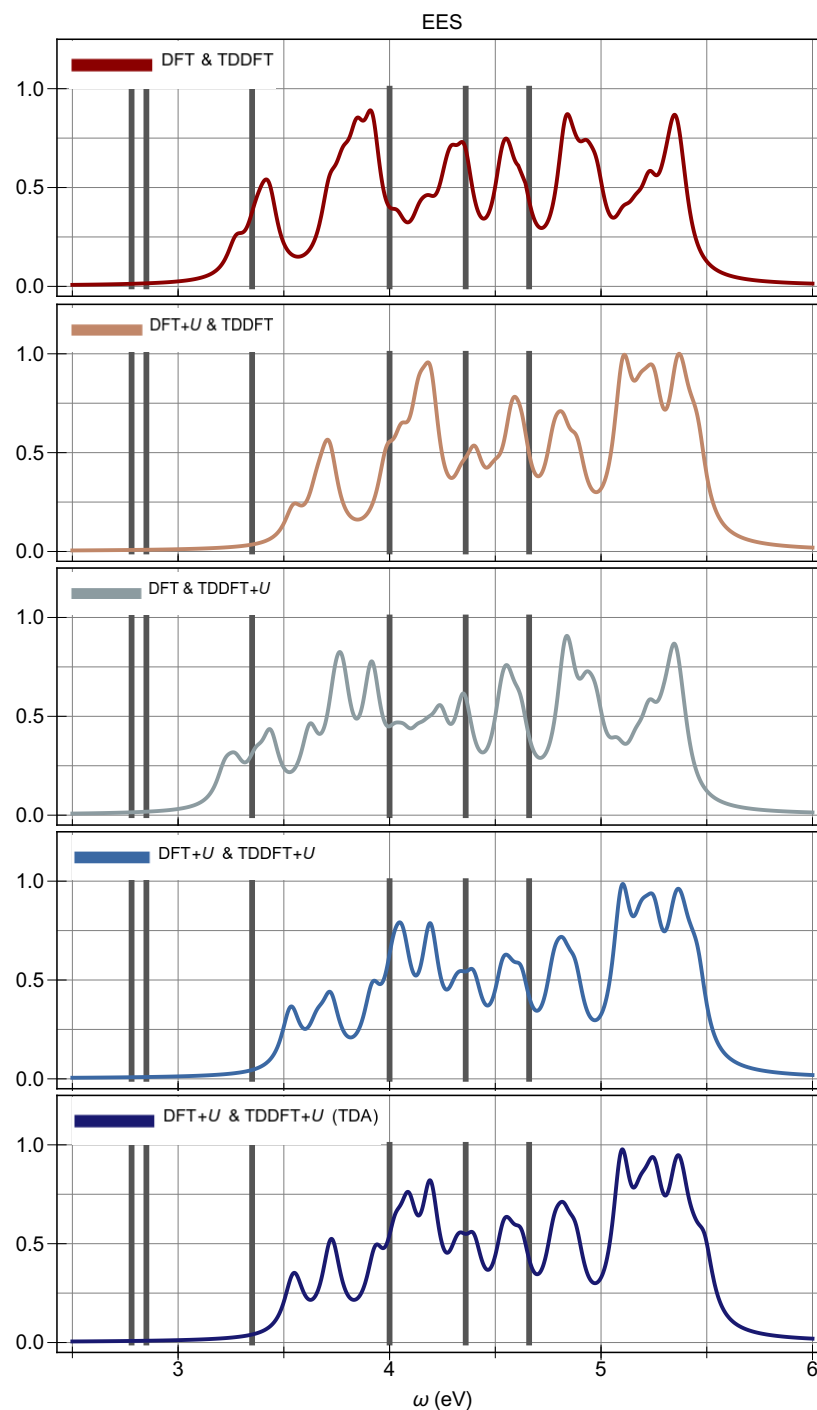


Figure 8.12: The singlet EES of Ni(CN)_4^{2-} extracted from Fig. 8.5 using the cross-section at the first-principles Hubbard $U=1.102$ eV, shown with a Lorentzian broadening of 0.1 eV. The experimental excitation energies extracted from Ref. 12 are shown with vertical gray lines.

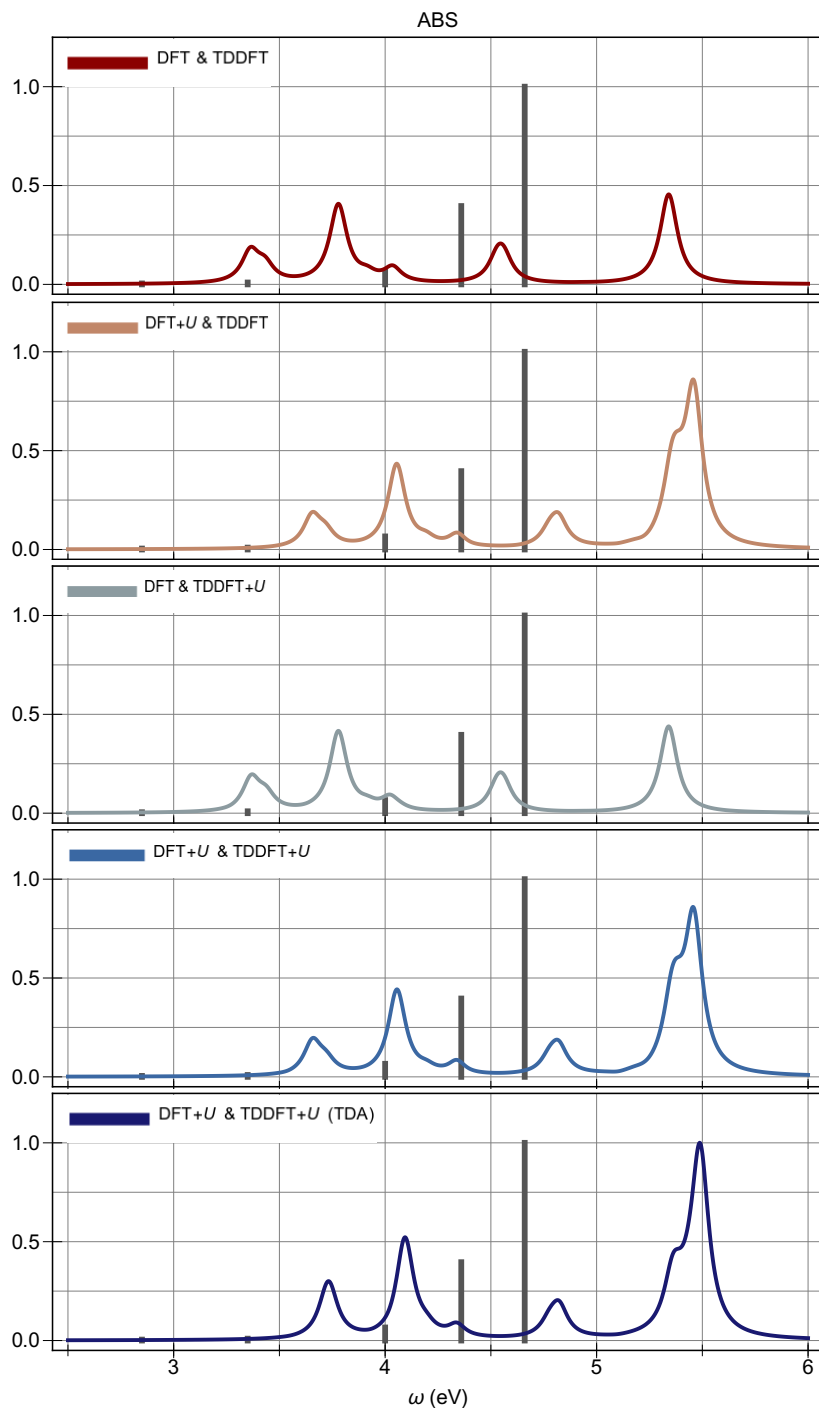


Figure 8.13: The singlet dipole-dipole ABS of $\text{Ni}(\text{CN})_4^{2-}$ extracted from Fig. 8.6 using the cross-section at the first-principles Hubbard $U=1.102$ eV, shown with a Lorentzian broadening of 0.1 eV. The experimental absorption energies extracted from Ref. 12 are shown with vertical gray lines that are scaled with respect to the maximum absorbance of the highest energy peak at 4.66 eV given as 10600 in $\text{M}^{-1}\text{cm}^{-1}$.

In Fig. 8.13 (also represented In Table 8.5), regardless of flavour, TDDFT fails to capture the optically bright excitation at 2.85 eV observed in experimental measurements, consistently with previous TDDFT studies using LDA and PBE. The hybrid-TDDFT, using B3LYP functional, performs relatively better than LDA or PBE, surely due to its better description of exciton binding via partial inclusion of the exact exchange interaction. DFT+ U worsens the agreement with experimental excitation energies by pushing excitations within DFT & TDDFT to higher energies such that the lowest optically bright excitation is carried to ~ 0.30 eV higher energy compared to DFT & TDDFT. While, TDDFT+ U shows some effects on excitations by locating an optically dark excitation at 3.26 eV, its effect is overshadowed by the dominating underlying DFT+ U within DFT+ U & TDDFT+ U . Such a result is not surprising as the $3d$ orbitals are mostly occupied, such that the transitions overlapping with the $3d \times 3d$ product space is quite small.

Method						
DFT & TDDFT (PBE)	3.37	3.42	3.78	3.85	3.91	4.03
	4.34	4.55	4.84	4.92	5.23	5.34

DFT+ U & TDDFT	3.55	3.66	3.71	4.06	4.34	4.40
	4.49	4.81	5.11	5.24	5.37	5.46

DFT & TDDFT+ U	3.26	3.37	3.43	3.63	3.78	3.92
	4.02	4.24	4.35	4.55	4.83	4.93
	5.06	5.23	5.34			

DFT+ U & TDDFT+ U	3.54	3.66	3.72	4.05	4.19	4.34
	4.55	4.81	5.10	5.24	5.37	5.46

DFT+ U & TDDFT+ U (TDA)	3.55	3.73	3.94	4.09	4.19	4.33
	4.55	4.82	5.10	5.24	5.37	5.49

Exp. ^[12]	2.85	3.35	4.00	4.36	4.66	-
TDDFT (PBE) ^[18]	3.99	4.19	4.48	3.76	4.12	4.53
TDDFT (LDA) ^[18]	3.98	4.17	4.46	3.78	4.13	4.55
TDDFT (B3LYP) ^[18]	3.29	3.57	3.92	4.75	5.07	5.59

Table 8.5: Energies (in eV) of the singlet excitations of $\text{Ni}(\text{CN})_4^{2-}$, as obtained without symmetry assignment from the peak positions of Fig. 8.12, with smaller peaks and shoulders removed. Coinciding peaks in Fig. 8.13 are assigned as optically bright excitations highlighted with a bold font.

8.5.2 Excitation energies and spectra of $\text{Ni}(\text{CO})_4$

The EES and ABS of $\text{Ni}(\text{CO})_4$ are presented in Fig. 8.14 and Fig. 8.15, respectively, within various schemes, for the first-principles $U=0.888$ eV, alongside respective spectra using the experimental excitation energies and oscillator strengths extracted from Ref. 15. Neither DFT+ U nor TDDFT+ U affect the DFT & TDDFT spectra significantly. They produce very similar curves both in Fig. 8.14 and 8.15, with the exception of very highest optically bright peak, which is shifted up by ~ 0.20 eV with DFT+ U , and additionally by ~ 0.30 eV in TDA compared to RPA.

In Fig. 8.15, DFT & TDDFT overestimates the lowest optically bright excitation compared to the experimental values, also as represented in Table 8.6. DFT+ U slightly worsens DFT & TDDFT results, and TDDFT+ U marginally reduces this effect. As $3d$ states are again nearly fully filled, the conduction manifold has been left with a minuscule $3d$ character; hence, TDDFT+ U has very little effect for such small Hubbard parameters.

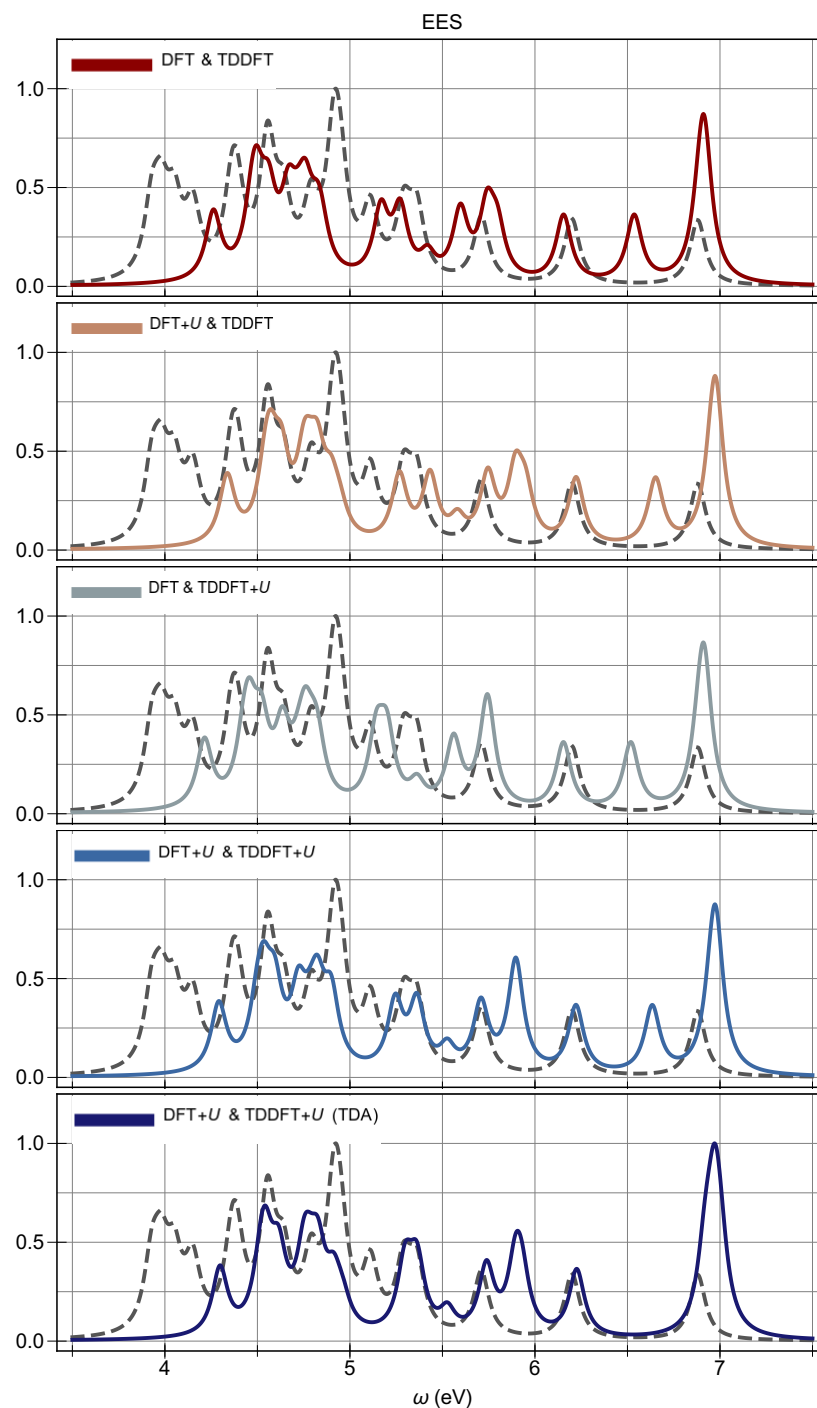


Figure 8.14: The singlet EES of $\text{Ni}(\text{CO})_4$ extracted from Fig. 8.8 using the cross-section at the first-principles Hubbard $U=0.888$ eV, shown with a Lorentzian broadening of 0.1 eV. The experimental EES (gray, dashed line) constructed from the experimental excitation energies extracted from Ref. 15, shown with a Lorentzian broadening of 0.1 eV.

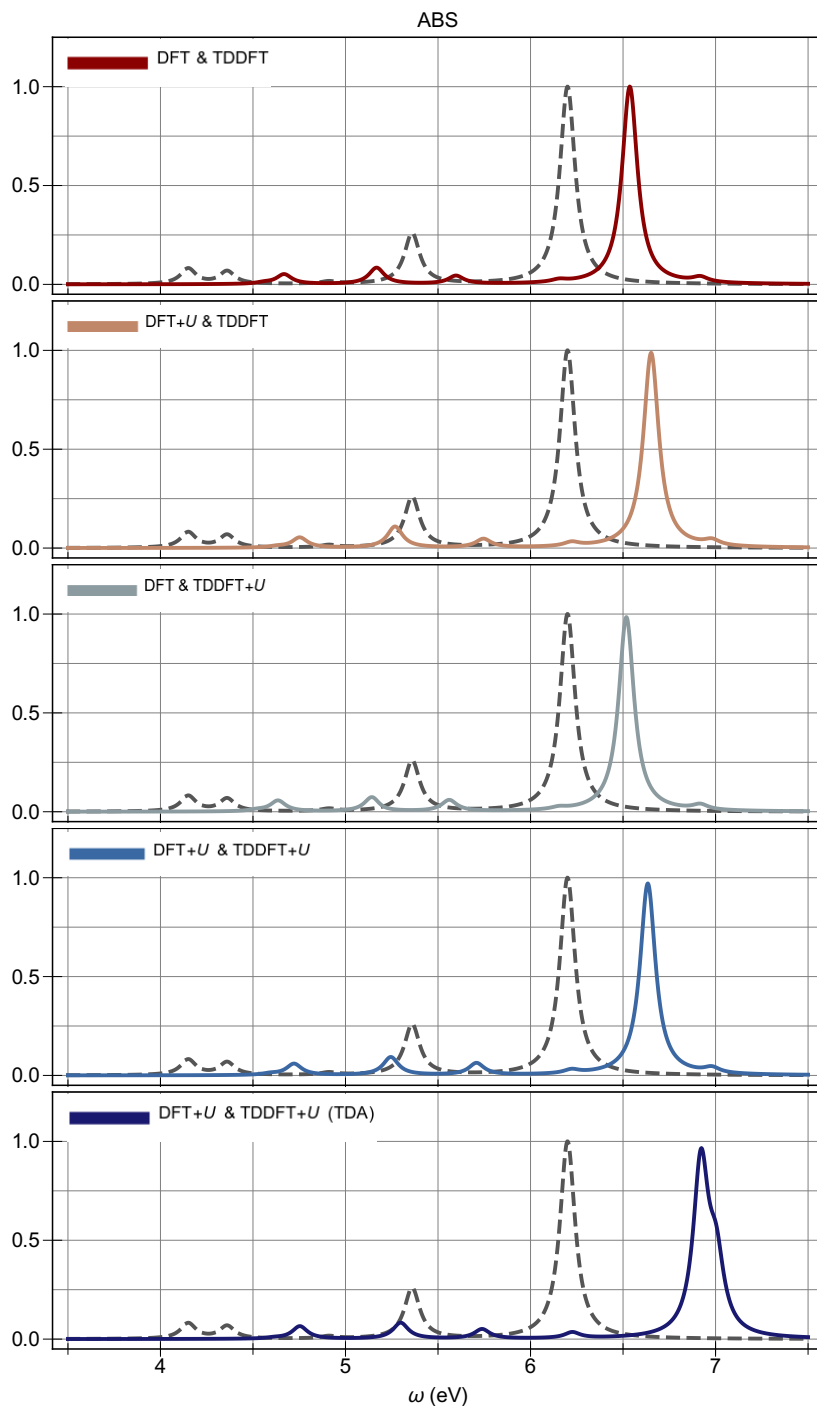


Figure 8.15: The singlet dipole-dipole ABS of $\text{Ni}(\text{CO})_4$ extracted from Fig. 8.9 using the cross-section at the first-principles Hubbard $U=0.888$ eV, shown with a Lorentzian broadening of 0.1 eV. The experimental ABS (gray, dashed line) constructed from the experimental excitation energies and oscillator strengths extracted from Ref. 15, shown with a Lorentzian broadening of 0.1 eV.

Method						
DFT & TDDFT (PBE)	4.26	4.50	4.67	4.75	5.17	5.27
	5.42	5.60	5.75	6.16	6.54	6.91
DFT+ <i>U</i> & TDDFT	4.34	4.57	4.75	5.27	5.43	5.58
	5.75	5.90	6.23	6.65	6.97	-
DFT & TDDFT+ <i>U</i>	4.22	4.46	4.63	4.76	5.14	5.36
	5.56	5.74	6.17	6.52	6.91	-
DFT+ <i>U</i> & TDDFT+ <i>U</i>	4.29	4.54	4.72	4.82	5.24	5.36
	5.52	5.71	5.90	6.23	6.63	6.97
DFT+ <i>U</i> & TDDFT+ <i>U</i> (TDA)	4.30	4.54	4.75	5.30	5.52	5.74
	5.91	6.23	6.92	-	-	-
Exp. (solvent) ^[13]	-	5.24	5.52	6.02	-	-
Exp. (matrix) ^[14]	4.54	5.17	-	-	-	-
Exp. (gas) ^[15]	4.5	5.4	-	-	-	-
TDDFT (LDA) ^[17]	4.36	4.60	4.62	4.70	4.82	4.95
	5.37	5.84	6.01	-	-	-
SAC-CI ^[35]	4.52	4.53	4.79	4.97	5.25	5.41
	5.51	5.72	5.76	6.07	6.28	-
CASPT2 ^[16]	3.58	3.72	4.04	4.34	4.88	5.14
	5.15	5.20	5.22	5.57	6.00	6.01

Table 8.6: Energies (in eV) of the singlet excitations of Ni(CO)₄, as obtained without symmetry assignment from the peak positions of Fig. 8.14, with smaller peaks and shoulders removed. Coinciding peaks in Fig. 8.15 are assigned as optically bright excitations highlighted with a bold font.

8.6 A high-spin coordination complex: CoL_2Cl_2 ($\text{L} = 2\text{-aminopyrimidine: C}_4\text{H}_5\text{N}_3$)

CoL_2Cl_2 ($\text{L} = 2\text{-aminopyrimidine: C}_4\text{H}_5\text{N}_3$) is a Co-centred distorted pseudo-tetrahedral complex with two types of ligands, as illustrated in Fig. 8.16. The center Co atom has a nominal charge of 2+, with a $3d$ sub-shell of 7 electrons. Cl^- is a π -donor weak-field ligand, leading to splitting of the $3d$ sub-shell of the Co atom into a high-spin configuration in a (pseudo-)tetrahedral symmetry^[33,36]. In its high-spin configuration, the higher energy $3d$ orbitals have unpaired electrons resulting in a nominal 3 unit spin of Co atom in this symmetry. The higher energy fully and partially filled molecular orbitals are predominantly hybridisations of $3d$ of the Co atom and the $3p$ of Cl atoms. Moreover, further splitting in the energy levels of $3d - 3p$ hybridisations occurs by means of the distortion due to the tilted L-ligands¹. Consequently, low-lying excitations are expected to have strong $3d \rightarrow 3d$ character.

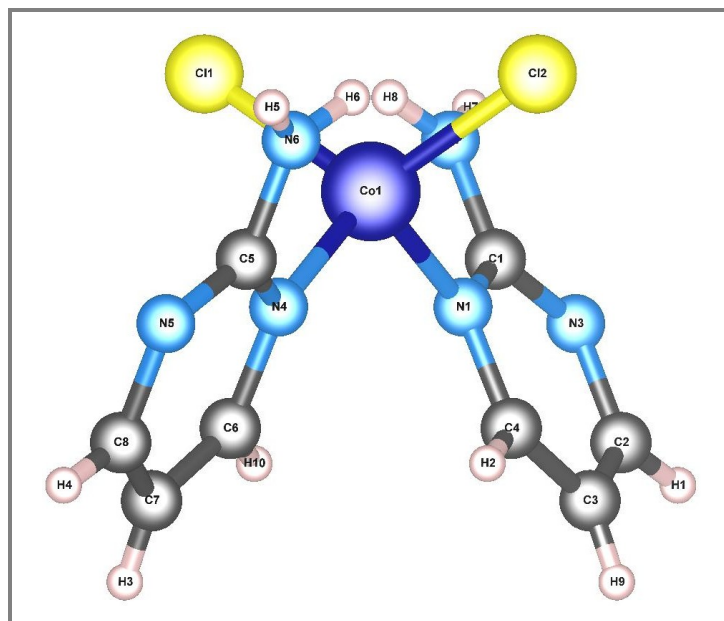


Figure 8.16: The molecular structure of CoL_2Cl_2 ($\text{L} = 2\text{-aminopyrimidine: C}_4\text{H}_5\text{N}_3$).

¹See App. C for the shapes of strongly $3d$ mixed KS-DFT orbitals.

Computational details

A norm-conserving PBE pseudo-potentials were generated for Co^{2+} , Cl, and H similarly to previous systems within OPIUM ¹,

Species	Configuration	Valence electron number	Additional info
Co2+	+2, [Ar]3d ⁷ 4s ⁰ 4p ⁰	7	Non-linear core corr.
Cl	Neutral, [Ne]3s ² 2p ⁵	7	
C	Neutral, [He]2s ² 2p ²	4	
O	Neutral, [He]2s ⁴ 2p ²	6	
N	Neutral, [He]2s ² 2p ³	5	
H	Neutral, 1s ¹	1	

Table 8.7: The details of pseudo-potentials for atomic species in CoL_2Cl_2 .

The geometry was directly adopted from Ref. 37 for the sake of preserving comparability of spectra for this particular distorted pseudo-tetrahedral structure studied in Ref. 38. An identical set of the converged parameters with Ni-centred complexes were used for single-point and conduction levels. Additionally, 9 (18) and 4 (13) NGWFs were variationally optimised for Co and Cl atoms during single-point (conduction) simulation, respectively. As CoL_2Cl_2 is an open-shell system, spin-polarised calculations were performed with a constrained total spin of 3 μ_B . Also, the initial configuration of Co for the pseudo-atomic solver was set to the theoretical high-spin configuration of $[\text{Ar}]4s^03d^7$, with an initial local 3 μ_B spin. In conduction band calculations, 11 NGWFs were optimised to represent the conduction manifold, where 11 extra NGWFs were used to improve descriptions of the first set of 11 conduction NGWFs. The first 20 excitations were calculated within TDA² for $U=0$ eV and the first-principles $U=3.798$ eV correction to the Co^3 .

8.6.1 Excitation energies and spectra of CoL_2Cl_2

In Table 8.8, experimental values of low-lying, spin-allowed optically bright excitations of CoL_2Cl_2 alongside with predictions using high-level quantum chemistry methods such as the complete active space self-consistent field (CASSCF) improved with the second-order N-electron valence perturbation theory (NEVPT2)^[39–42], which were extracted from Ref. 38,

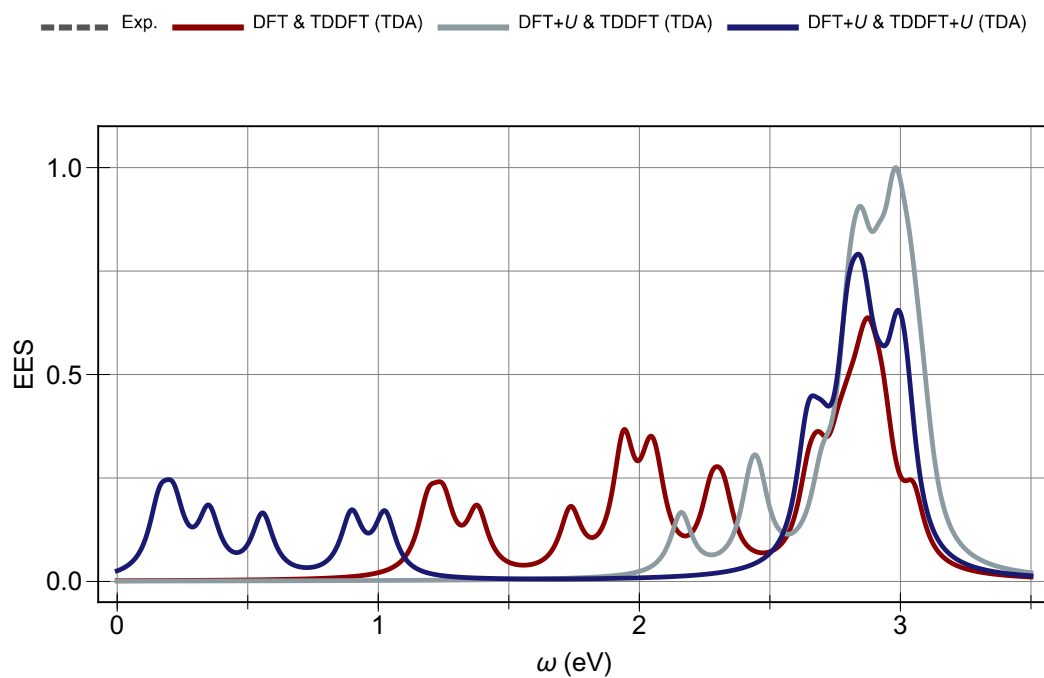
¹See App. A for the sample input files for OPIUM.

²The RPA routine for spin-polarised systems requires further testing to ensure numerical stability in ONETEP.

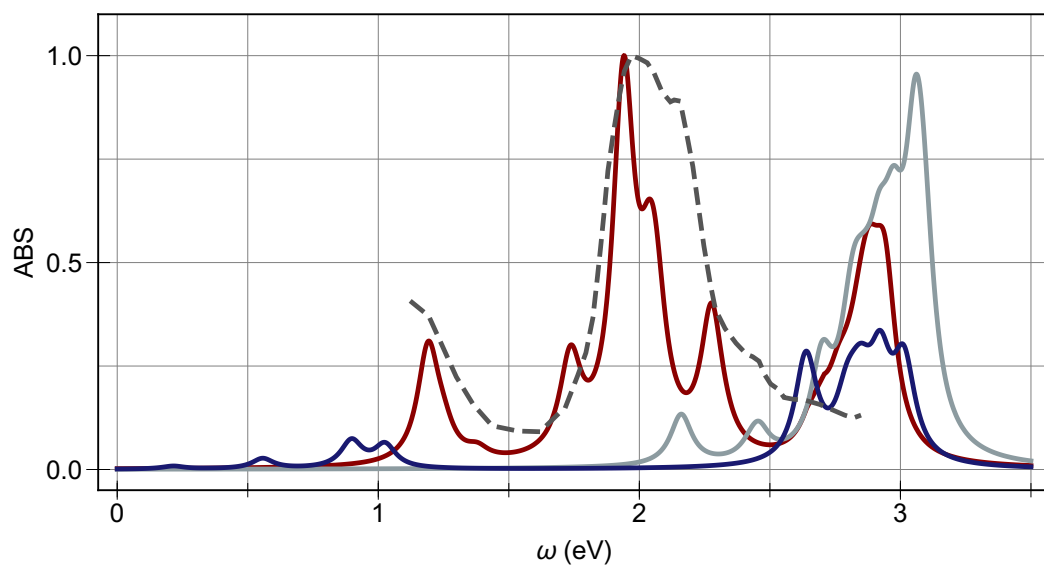
³See App. A for the sample input files for ONETEP.

are presented. In Fig. 8.17a, we see that DFT+*U* & TDDFT pushes excitation features at lower energies around $\sim 1 - 2$ eV higher by ~ 1.0 eV compared to DFT & TDDFT. While the two lowest excitations are still distinguishable, the intermediate excitations around ~ 2.0 eV in DFT & TDDFT are combined with higher energetic peaks at around ~ 2.8 eV in DFT+*U* & TDDFT. DFT+*U* & TDDFT+*U* brings these excitations to even lower energies than DFT & TDDFT, while higher-energy peaks remain similar to those of DFT & TDDFT within DFT+*U* & TDDFT+*U*. In Fig. 8.17a, DFT+*U* & TDDFT+*U* drastically changes the picture by pulling the excitations up to ~ 2 eV within DFT & TDDFT to ~ 1 eV lower energies compared to DFT & TDDFT, and to ~ 2 eV lower compared to DFT+*U* & TDDFT. Also, DFT+*U* & TDDFT+*U* produces three optically bright excitations with $\gtrsim 1$ eV energies, whereas neither DFT & TDDFT nor DFT+*U* & TDDFT could predict. Such a strong effect can be discussed with the help of ligand field theory^[33] for a simplified case in a perfect tetrahedral symmetry. In a perfect tetrahedral symmetry with a weak-field ligand, the $3d$ sub-shell of Co atom splits into two energy levels as $d_{x^2-y^2} = d_{z^2} < d_{xy} = d_{yz} = d_{xz}$ ^[36]. In this virtual case, the low-lying, spin-allowed excitations are expected to predominantly be a mixture of spin-down $d_{x^2-y^2}/d_{z^2} \rightarrow d_{xy}/d_{yz}/d_{xz}$ transitions. DFT+*U* is effective on the occupied spin-down manifold for $d_{x^2-y^2}/d_{z^2}$, while TDDFT+*U* is effective on the product space of $d_{x^2-y^2}/d_{z^2}$ and $d_{xy}/d_{yz}/d_{xz}$, representing a larger manifold; hence, TDDFT+*U* may have a larger effective domain. As expected, in the case of CoL_2Cl_2 , the excitations have more mixed characters due to hybridisation and the distortion, which leads to further splitting in the energy levels with diverse orbital shapes^[38].

Quantitative accuracy improvements on lower-energy excitations offered by DFT+*U* & TDDFT+*U* are clearly seen in Table 8.8. Both DFT & TDDFT and DFT+*U* & TDDFT fail to capture the lowest three-fold degenerate excitation (highlighted with light pink) between $\sim 0.50 - 0.75$ eV calculated by the NEWPT2-corrected CASSCF (CASSCF+NEWPT2) method. Moreover, DFT+*U* & TDDFT also overestimates the second three-fold degenerate excitations (highlighted with light blue) around $\sim 0.90 - 1.40$ eV, both when compared to the experimental value of 1.12 eV and the CASSCF+NEWPT2 prediction of $\sim 0.95 - 1.13$ eV. DFT+*U* & TDDFT+*U* determines the lowest optically bright excitation energy with relatively high accuracy at 0.56 eV, comparing to both CASSCF and CASSCF+NEWPT2. Furthermore, it performs well by locating the second three-fold degenerate excitations (highlighted with light blue) at 0.90 eV and 1.02 eV, comparing again to both the experimental measurement and CASSCF+NEWPT2. However, DFT+*U* & TDDFT performs better for the third three-fold degenerate excitations (highlighted with light purple) at 2.45 eV, comparing to the



(a)



(b)

Figure 8.17: The singlet EES and ABS of CoL_2Cl_2 calculated using a first-principles Hubbard $U=3.798$ eV, shown with a Lorentzian broadening of 0.1 eV. The experimental absorption spectra (gray, dashed line) extracted from Ref. 38. The experimental spectra was scaled by setting the global peak to unit value.

experimental value, than both DFT+*U* & TDDFT+*U* and CASSCF+NEWPT2. Consequently, DFT+*U* & TDDFT+*U* performs better for low-lying excitations, whereas DFT+*U* & TDDFT may perform better for higher excitations.

Method					
DFT & TDDFT (TDA)	1.19 2.28	1.38 2.68	1.74 2.92	1.94 -	2.04 -
DFT+ <i>U</i> & TDDFT (TDA)	2.16 3.06	2.45 -	2.71 -	2.85 -	2.98 -
DFT+ <i>U</i> & TDDFT+ <i>U</i> (TDA)	0.20 2.64	0.35 2.85	0.56 2.93	0.90 3.00	1.02 -
Exp. (solvent) ^[38]	-	1.12	2.46	-	-
CASSCF ^[38]	0.35 1.06	0.43 2.76	0.56 2.80	0.72 2.84	0.87 -
CASSCF+NEWPT2 ^[38]	0.49 1.36	0.58 2.67	0.75 2.72	0.95 2.75	1.13 -

Table 8.8: Energies (in eV) of the singlet excitations of CoL_2Cl_2 , as obtained without symmetry assignment from the peak positions of Fig. 8.17a, with smaller peaks and shoulders removed. Coinciding peaks in Fig. 8.17b are assigned as optically bright excitations, highlighted with a bold font.

8.7 Conclusion

In this chapter, benchmark tests of a newly-developed methodology, namely TDDFT+*U*, were demonstrated on two Ni-centred closed-shell and one Co-centred open-shell, high spin coordination complexes, together with their respective first-principles calculated Hubbard parameters. DFT+*U* shifts excitation energies of transitions into, out of and within the localised subspace by modifying underlying energy levels proportionally to the Hubbard *U* parameter. Meanwhile, TDDFT+*U* affects exclusively transitions within the localised subspace by modifying the coupling matrix elements of these transitions proportionally to the product of densities of the occupied and the unoccupied localised subspaces and the Hubbard *U* parameter.

In the case of Ni-centred coordination complexes, in Fig. 8.4a and Fig. 8.7a, the increasing U values opens the HOMO-LUMO gaps within DFT+ U leading to shifts in the transitions from $3d$ states to higher energies. In $\text{Ni}(\text{CN})_4^{2-}$, the lower energy transitions are a mixture of $3d \rightarrow \pi^*$ and $3d \rightarrow 3d$ characters; hence, increasing U values used in DFT+ U level push such transitions to higher energies. However, the states, spanning unoccupied localised subspace, has very small $3d$ character; hence, TDDFT+ U shows very small effects on the transitions by lowering exclusively the energies $3d \rightarrow 3d$ character transitions. Since $3d \rightarrow 3d$ character transitions are forbidden by Laporte's selection rule, the effects of TDDFT+ U are not observable in the dipole-dipole absorption spectra shown in Fig. 8.6. In the case of $\text{Ni}(\text{CO})_4$, TDDFT+ U is less effective due to a very small density-density product of $3d \times 3d$ states of the occupied and the unoccupied localised subspaces., respectively. In such a case, the dipole-dipole absorption spectra is not affected by TDDFT+ U as the low-energy, optically bright transitions are $3d \rightarrow \pi^*$ characters.

In the case of the Co-centred coordination complex, TDDFT+ U becomes effective as both the edges of occupied and unoccupied localised subspaces are strongly $3d$ character; therefore, the density product becomes large enough to overcompensate the shift in the transitions due to opening of the HOMO-LUMO gap by DFT+ U . By doing so, DFT+ U & TDDFT+ U with the first-principles Hubbard $U=3.798$ eV predicts the lowest optically bright excitation at 0.56 eV, which is comparable to the computationally more expensive quantum chemistry methods, and the second lowest optically bright transition at 0.90 - 1.02 eV, which is comparable both to the experimental value at 1.12 eV and the computationally more expensive quantum chemistry methods presented in Table 8.8. However, in Fig. 8.17b, DFT & TDDFT performs better for the higher energy peak at 2.04 - 2.28 eV, comparing to the experimental peak at 2.46 eV. As the first-principle Hubbard U parameters for these systems were calculated at the static limit, + U correction for TDDFT level is expected to be more accurate for lower energy excitations.

Consequently, TDDFT+ U is needed for the sake of both consistency and accuracy in first-principles spectra of systems with highly localised states. Clearly, however, its most promising applications are to systems with a localised subspace where is partially-filled at least for one spin-channel. It remains to be seen what effect TDDFT+ $U+J$ will here, e.g, in LR-TDDFT triplet calculations; how it will affect excited-state ionic forces, or whether it is useful to apply DFT+ U e.g. to rather less localised ligand $2p$ orbitals. In the following chapter, we will see that applying ground-state DFT+ U to O $2p$ orbitals can yields very rewarding results.

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Chapter 9

Band gaps of TiO₂ systems from first-principles DFT+ U^d + U^p

Titanium dioxide (TiO₂) has been a widely used material for decades in various industrial applications such as pigmentations, coating, synthetic fibres, *etc.*^[1–3] due to its non-toxicity, low-cost production and thermal stability. However, TiO₂ became the scope of intense research activity after the ground-breaking work of Fujishima and Honda demonstrating water splitting in TiO₂ photo-chemical cells in the UV spectral range in 1972^[4]. Since then, various TiO₂-based structures have been engineered for diverse opto-electronic applications such as photo-catalysis, photo-voltaics, sensors *etc.* commonly used in energy and environmental applications. We refer interested readers to the comprehensive reviews on TiO₂ and its applications in Ref. 5–7.

In this chapter, we will investigate the competences of DFT+ U and TDDFT+ U with first-principles Hubbard U parameters to describe band-gaps and lowest excitation energies of pristine and O vacant TiO₂ systems using the ONETEP code. As starting point, the well-known band-gap problem in bulk pristine TiO₂ in its two most common phases, namely *rutile* and *anatase*, within approximate KS-DFT^[8] will be discussed in details in conjunction with various approaches to determine suitable Hubbard U parameters. The conventional DFT+ U method is commonly used to correct SIE on $3d$ state of Ti atoms. As will be shown, such an approach is not effective in these systems; hence, the DFT+ U method will be extended to $2p$ states of O atoms using first-principles Hubbard parameters for Ti and O atoms. This is symbolically referred as DFT+ U^d + U^p . The appropriate Hubbard parameters will be used in both in TDDFT+ U and TDDFT+ U^d + U^p in conjunction with DFT+ U and DFT+ U^d + U^p , respectively, to study the lowest excitation energies of two TiO₂ nano-clusters with similar structural properties of bulk TiO₂-rutile and TiO₂-anatase. Lastly, single point defects of neutral O vacancy type will be introduced to bulk TiO₂-rutile and TiO₂-anatase to test the capacity of DFT+ U^d + U^p to determine defects states in band-gaps of the pristine systems.

9.1 Bulk TiO₂ in the rutile and anatase phases

TiO₂ has three polymorphs found in nature with crystal structures named *rutile*, *anatase*, and *brookite*^[9]. While TiO₂-rutile and TiO₂-anatase are commonly used in industrial applications, the brookite phase is less stable and hard to synthesise in large volumes^[10]. The electronic

structure and optical properties of TiO₂-rutile and TiO₂-anatase have been extensively studied both experimentally^[11–15] and with first-principles methods^[16–19]. TiO₂-rutile and TiO₂-anatase are suggested experimentally to have band-gaps of ~ 3.0 eV^[13,14] and $\sim 3.2 - 3.4$ eV^[12,20], respectively. It is well known that approximate KS-DFT drastically underestimates band-gaps of TMOs^[21–23], and the predicted band-gaps of TiO₂-rutile and TiO₂-anatase^[8] within approximate KS-DFT are no exception. Commonly, DFT+ U is used to improve the TiO₂-rutile and TiO₂-anatase band-structures by reducing SIE on the Ti atom with Hubbard U parameters historically varying in the range $\sim 2.5 - 10$ eV^[24] determined by tuning to some observed quantities^[25–31]. Even overlooking the question of the consistency of DFT+ U applications using some U values that are determined by tuning to some observable quantities, a problem arises by virtue of that $3d$ -bands of Ti atoms being located at lower energies than $2p$ -states of O atoms. Applying the Hubbard U corrections on these $3d$ -states is thus not fully effective even with unreasonably large U values, as $2p$ -states at the valence band edge are barely affected^[32]. Consequently, the conventional DFT+ U approach of correcting SIE error for only $3d$ -state still underestimates the gaps of TiO₂-rutile and TiO₂-anatase.

DFT+ U^d+U^p provides a more accurate description of the band-structure around the Fermi level as well as a more consistent scheme^[33–36]; since the band-edges of these systems are a mixture of $3d$ -states of Ti and $2p$ -states of O atoms. Although $2p$ states of O atoms are not as localised as $3d$ states, they still do exhibit localisation. Taking advantage of the capability within ONETEP^[37–39] to determine the Hubbard U parameters as discussed in Chap. 4 for arbitrary atomic sub-shells, the band-gaps of TiO₂-rutile and TiO₂-anatase are investigated by using a fully first-principles approach.

9.1.1 Computational details

Initial crystallographic information for TiO₂-rutile and TiO₂-anatase were adopted from Refs. 40 and 41, as illustrated in Fig. 9.1.

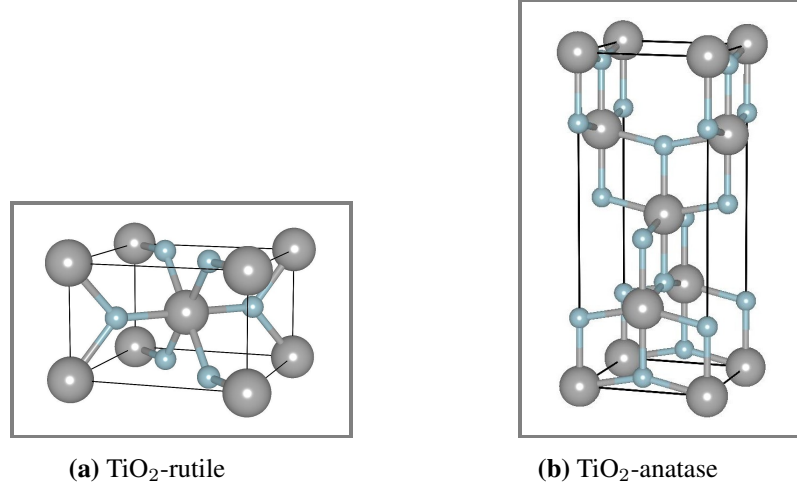


Figure 9.1: The tetragonal ($4/mmm$) crystal structures of TiO₂-rutile and TiO₂-anatase with space groups $P4_2/mnmD_{4h}^{14}$ and $I4_1/amdD_{4h}^{19}$.

Norm-conserving LDA pseudo-potentials were produced using the pseudo-potential generator OPIUM^{[42]1} for configurations summarised in Table 9.1. Ti³⁺ configuration was chosen to represent the oxidation configuration of Ti for the case of O vacancy in TiO₂^[43], which will be discussed in later sections.

Species	Configuration	Valence electron number
Ti	3+, [Ne]3s ² 3p ⁶ 3d ¹ 4s ⁰ 4p ⁰	9
O	Neutral, [He] 2s ² 2p ⁴	6

Table 9.1: Details of pseudo-potentials for ionic Ti³⁺ and atomic O with LDA.

Full geometry relaxations were performed with variable cell parameters at a high E_{cut} (75 Ha) and commonly used grids of $3 \times 3 \times 5$ and $5 \times 5 \times 3$ automatically generated uniform grids for Brillouin zone sampling within QE^[44,45]. The unit cell with converged cell parameters was used to construct super-cells with 270 and 900 atoms corresponding to $3 \times 3 \times 5$ and $5 \times 5 \times 3$ grids in the Brillouin zone sampling for TiO₂-rutile and TiO₂-anatase, respectively.

The strategy to choose grid samplings for psinc basis functions to achieve an effective kinetic energy cut-off was briefly introduced in Sec. 3.4. In the ONETEP input file, grid sampling for the psinc basis function is set by some uniform psinc spacing in each direction. Indeed, the

¹See App. A for the input files.

only restriction in determining the spacing parameters for a given direction is that

$$\Delta r_i = \frac{R_i}{2J_i + 1}, \quad (9.1)$$

where R_i is the norm of the unit cell vector in i -direction. The form of $2J_i + 1$ ensures an odd number of grid points for FFT purposes. Despite being not a necessary condition, it is intuitively more convenient to choose the spacing parameters such that the psinc grid is commensurate with the grid of primitive unit cells in the supercell. Such a choice, whenever possible, provides some advantages in post-processing such as in illustration of NGWFs as matching periodic discrete points with periodicities of NGWFs. For instance, the psinc spacing for TiO₂-rutile in the x -direction can be chosen for $3 \times 3 \times 5$ super-cell as

$$\Delta x = \frac{3 a_x}{3^k 5^l 7^m \dots}, \quad (9.2)$$

where a_x is the norm of the unit vector of the primitive unit cell in x -direction and $k, l, m \in \mathbb{N}$. As 3 primitive unit cells were used in the x -direction in the super cell, the number of grid points desired is a multiple of 3, while also satisfying the necessary condition in Eq. (9.1). Following this approach, the numbers of grid point for psinc functions were converged as $3^1 5^2 = 75$ in all directions for TiO₂-rutile corresponding to the effective kinetic energy cut-offs of ~ 1776 eV, ~ 1776 eV and ~ 1552 eV respectively, while $3^1 5^2 = 75$ in x - and y -directions and $3^1 7^2 = 147$ in z -direction for TiO₂-anatase corresponded to the effective kinetic energy cut-offs of ~ 945 eV, ~ 945 eV and ~ 1578 eV respectively. A number of 13 NGWFs for Ti atom to complete the second and third periods upto Kr, and a number of 4 NGWFs for O atom to complete the period up to Ar. These were been variationally optimised with cutoff radii of 12 a_0 .

9.1.2 Computation of the Hubbard parameters

The first-principles Hubbard parameters for the Ti $3d$ sub-shell and O $2p$ sub-shell were calculated using LRT introduced in Sec. 4.3 by perturbing each Hubbard subspace one at a time with a perturbative external potential (in eV) on the mesh of

$$\{-1.00, -0.50, -0.10, -0.01, 0.00, 0.01, 0.10, 0.50, 1.00\}.$$

As both TiO₂-rutile and TiO₂-anatase are closed-shell systems, only a single-spin channels was perturbed, since the responses of spin-channels are identical¹. Two sets of Hubbard parameters were calculated for TiO₂-rutile with atomic projections on the subspace configurations of atomic Ti⁰ and Ti³⁺.

Expression	Symbol	Ti ⁰ conf.		Ti ³⁺ conf.	
		Ti	O	Ti	O
Eq. (4.21)	$U_{\uparrow\downarrow}^{\uparrow\downarrow}$	1.325	2.986	1.853	3.126
Eq. (4.15)	$f^{\uparrow\uparrow} (f^{\downarrow\downarrow}), f^{\uparrow\downarrow} (f^{\downarrow\uparrow})$	3.270, 3.846	7.657, 9.486	5.204, 5.971	7.683, 9.458
Eq. (4.16)	U	3.558	8.571	5.587	8.571
Eq. (4.17)	J	0.288	0.915	0.384	0.887
Eq. (4.18)	U_{eff}	3.270	7.657	5.204	7.683
Eq. (4.23)	U'_{eff}	2.982	6.742	4.820	6.796

Table 9.2: The Hubbard parameters (in eV) from first-principles approaches for Ti and O in TiO₂, rutile phase for the neutral and 3+ atomic projection on the subspace of 3d-states of Ti atom.

The Hubbard parameters for TiO₂-rutile with various schemes are summarised in Table 9.2. Comparing the first and second block columns, the Hubbard parameters for Ti in Ti³⁺ configuration is ~ 2 eV larger compared to that of the neutral configuration, whereas the Hubbard parameters for O are not affected significantly for the given atomic configuration of Ti. Indeed larger Hubbard parameters for the Ti³⁺ configuration is not surprising as the atomic orbitals are more spatially compact. Conversely, a larger Hubbard parameter is required to correct SIE when the more compact Hubbard subspace is used to define DFT+ U [24].

Expression	Symbol	Ti	O
Eq. (4.21)	$U_{\uparrow\downarrow}^{\uparrow\downarrow}$	1.361	3.076
Eq. (4.15)	$f^{\uparrow\uparrow} (f^{\downarrow\downarrow}), f^{\uparrow\downarrow} (f^{\downarrow\uparrow})$	3.282, 3.856	7.656, 9.469
Eq. (4.16)	U	3.569	8.562
Eq. (4.17)	J	0.287	0.907
Eq. (4.18)	U_{eff}	3.282	7.656
Eq. (4.23)	U'_{eff}	2.996	6.749

Table 9.3: The Hubbard parameters (in eV) from first-principles approaches for Ti and O in TiO₂, anatase phase for the neutral atomic projection on the subspace of 3d-states of Ti atom.

¹See App. D for the linear fitting to the response of the KS potentials and occupancies at the Hubbard subspace to the perturbative external potential of each spin-channel.

The Hubbard parameters for TiO₂-anatase for Ti and O in the Ti⁰ configuration is presented in Table 9.3. The Hubbard parameters of TiO₂-anatase are quite similar to the Hubbard parameters of TiO₂-rutile; since, quite a comparable SIE are experienced by both systems due to their similar electronic structures.

9.2 Band-gaps with DFT+ U^d + U^p

In TiO₂-rutile and TiO₂-anatase, the unoccupied 3*d*-states of Ti split into $d_{xy} \approx d_{xz} = d_{yz} < d_{x^2-y^2} = d_{z^2}$ due to crystal-field splitting in octahedral molecular symmetry^[19,46,47]. These states are highly hybridised with the 2*p*-states of O; therefore, they are expected to contribute partially to predominantly π character states in the valence manifold around the Fermi level, where the unoccupied states at the conduction manifold close to the Fermi level are mostly unoccupied 3*d*-states with some hybridisation with π^* orbitals^[46].

9.2.1 TiO₂-rutile

The total DOS and the local DOS (LDOS) projected on Ti and O were shown for the Ti⁰ configuration in Fig. 9.2 and Fig. 9.3 using DFT+ U^d and DFT+ U^d + U^p , respectively, alongside DFT (LDA). As expected, the valence manifold around the Fermi level is predominantly constituted by 2*p*-states of O with a small contribution from the 3*d*-states of Ti, whereas 3*d*-states of Ti reside mostly in the conduction manifold close to the Fermi level regardless of applied methods as observed in both Fig. 9.2 and Fig. 9.3. In the left panel, DFT+ U^d shifts the occupied 3*d*-states to lower energies with various first-principles U parameters. Of course, the largest shift occurs for $U^d = {}^{\text{Ti}}U$ as it provides the largest Hubbard parameter. DFT+ U^d is more effective for deeper energies $\lesssim -4$ eV, whereas the total DOS at the valence manifold close to the Fermi level only changes slightly as the 2*p*-states of O, which are dominant close to the Fermi level, stay mostly unaffected. As a result, the HOMO-LUMO gap, corresponding to a direct band-gap at Γ , is still underestimated with DFT+ U^d , as listed in Table 9.4, compared to both experiments and more demanding first-principles methods. Even for the supposedly most elaborate approximation to the Hubbard U value by Eq. (4.23) in Table 9.3, the gap is predicted at 2.19 eV, which is lower than the 3.0 eV experimental gap.

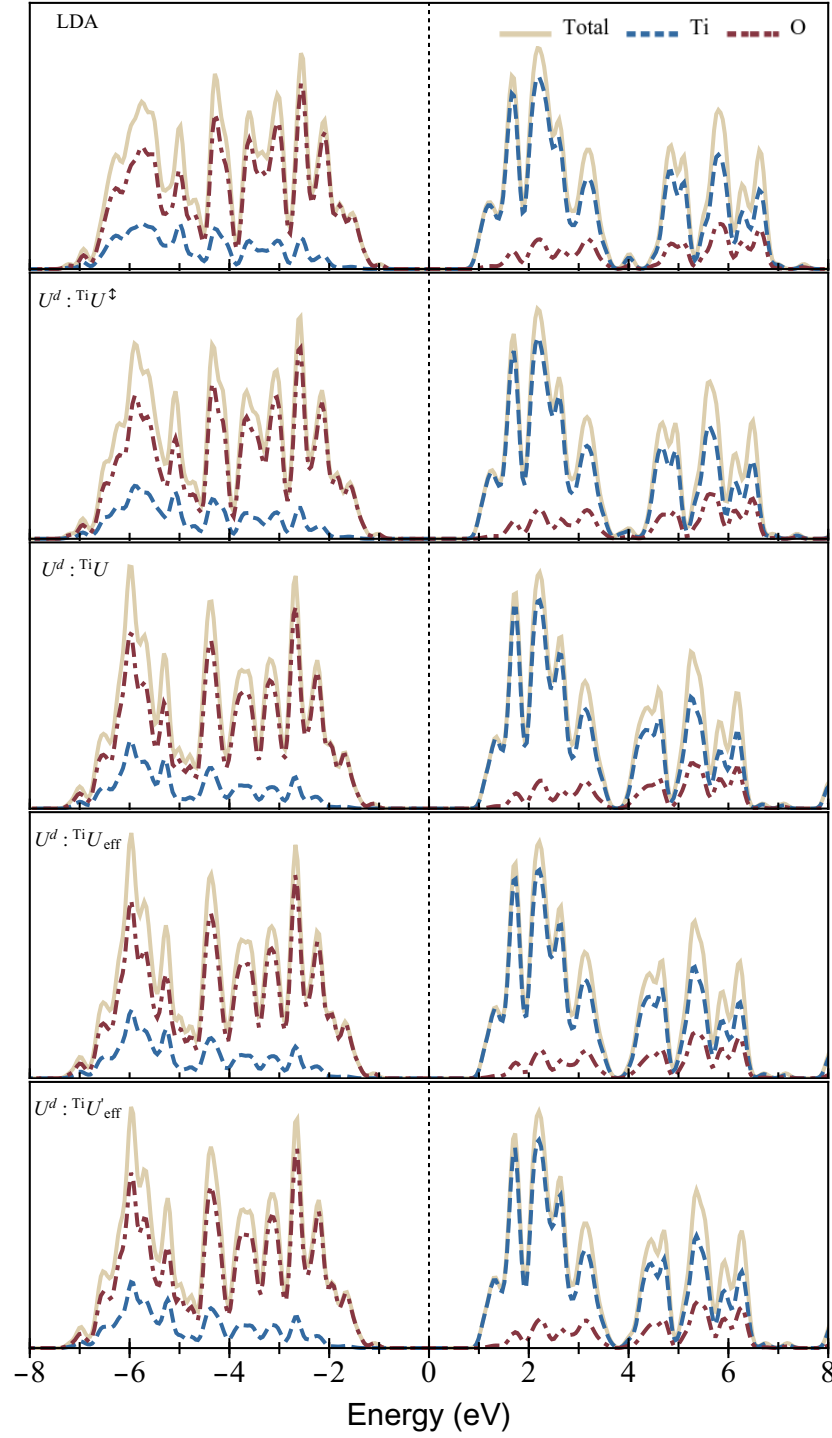


Figure 9.2: DOS of TiO₂-rutile using DFT+ U^d with the Hubbard U parameters using various methods summarised in Table 9.2 for $3d$ -states of Ti ($U^d : {}^{\text{Ti}}U$), shown with a Gaussian broadening of 0.1 eV.

9. Band gaps of TiO_2 systems from first-principles DFT+ U^d+U^p

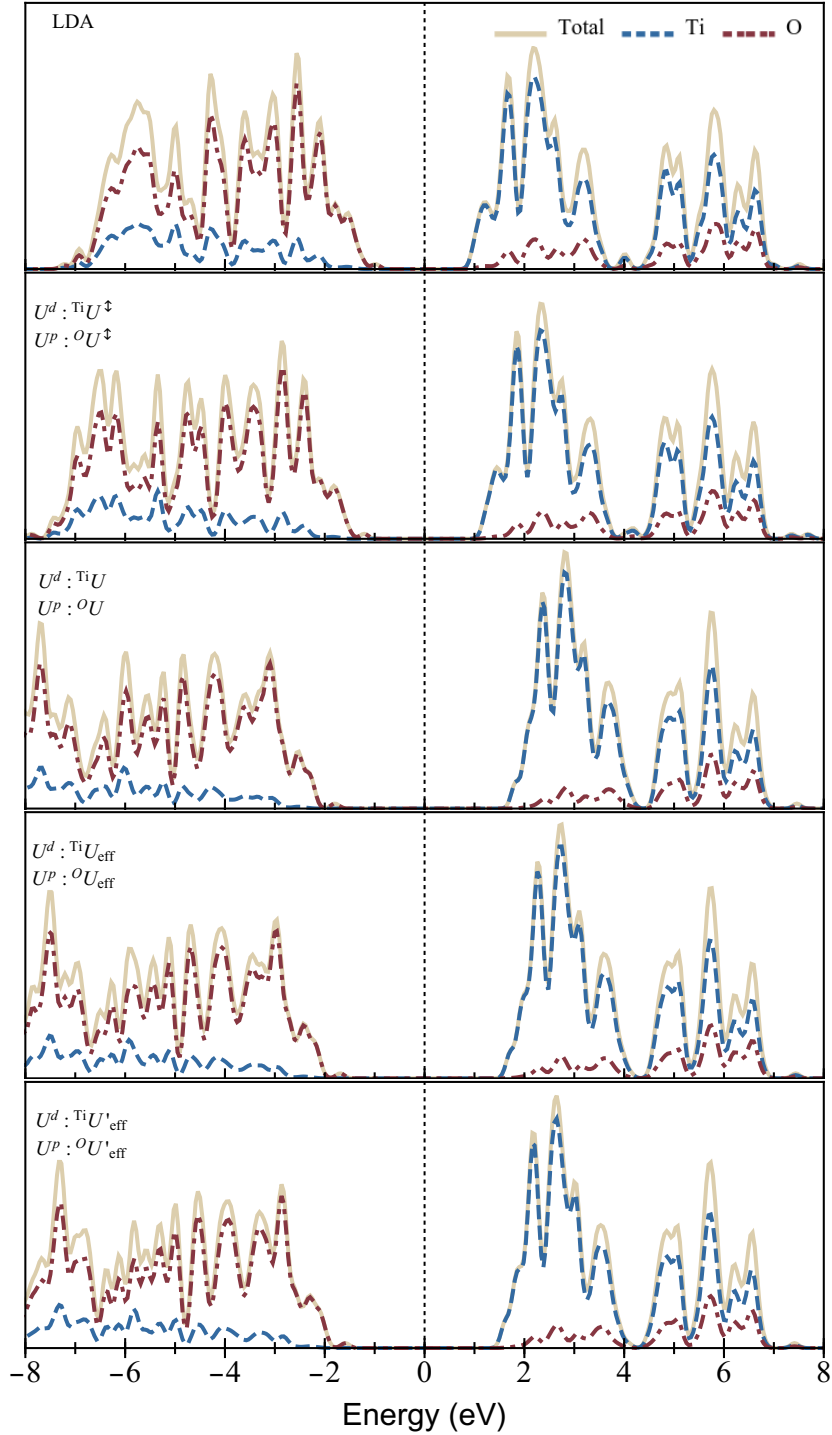


Figure 9.3: DOS of TiO_2 -rutile using DFT+ U^d+U^p with the Hubbard U parameters using various methods summarised in Table 9.2 for $3d$ -states of Ti ($U^d : \text{Ti}U$) and for $2p$ -states for O atom ($U^p : \text{O}U$), shown with a Gaussian broadening of 0.1 eV.

	Ti ⁰ conf.		Ti ³⁺ conf.	
LDA	1.97		2.09	
	DFT+ U^d	DFT+ U^d+U^p	DFT+ U^d	DFT+ U^d+U^p
$U_{\uparrow\downarrow}^{\uparrow\downarrow}$	2.05	2.42	2.30	2.69
U	2.24	3.59	2.83	4.33
U_{eff}	2.22	3.38	2.78	4.07
U'_{eff}	2.19	3.18	2.72	3.82
Exp. ^[13,14]	3.00			
LDA ^[36]	1.79			
PBE ^[19]	1.88			
HSE ^[19]	3.39			
PBE+G ₀ W ₀ ^[19]	3.46			
HSE+G ₀ W ₀ ^[19]	3.73			
GW ^[48]	4.80			
GW ^[18]	3.38			
DFT+ U ($U=7.5$ eV) ^[49]	2.83			
DFT+ U ($U=10$ eV) ^[50]	2.97			

Table 9.4: The direct band-gaps ($\Gamma \rightarrow \Gamma$) (in eV) TiO₂-rutile from experimental and first-principles methods.

In Fig. 9.3, the primary effect of DFT+ U^d+U^p is to down-shift both the $3d$ -states of Ti and $2p$ -states with their respective Hubbard U corrections. Moreover, the large shift in $2p$ -states increases the $3d$ -character at the valence manifold, while conversely reducing it in the conduction manifold close to the Fermi level. In Table 9.4, even DFT+ U^d+U^p with the “vanilla” Hubbard parameter from Eq. (4.21), which is determined solely by using the uncoupled response of single-spin channel, performs better than DFT+ U^d , predicting a direct band-gap of 2.42 eV. Ignoring the unlike-spin interaction of the Hubbard subspaces, which results from a larger Hubbard U parameter, from Eq. (4.16), leads to slight overestimation of the band-gap, while still performing relatively well compared to high level first-principles methods involving non-local exchange such as the hybrid functionals or various GW approximations listed in Table 9.4 but with a drastically lower computational cost. DFT+ U^d+U^p with the best available approximation to the Hubbard U parameter for closed-shell systems, via Eq. 4.23, gives a direct band-gap of 3.18 eV, out-performing other first-principles approaches in terms of accuracy compared to the experimental band gap. In

conclusion, $\text{DFT}+U^d+U^p$ with U'_{eff} is chosen as best performing approximation for future reference.

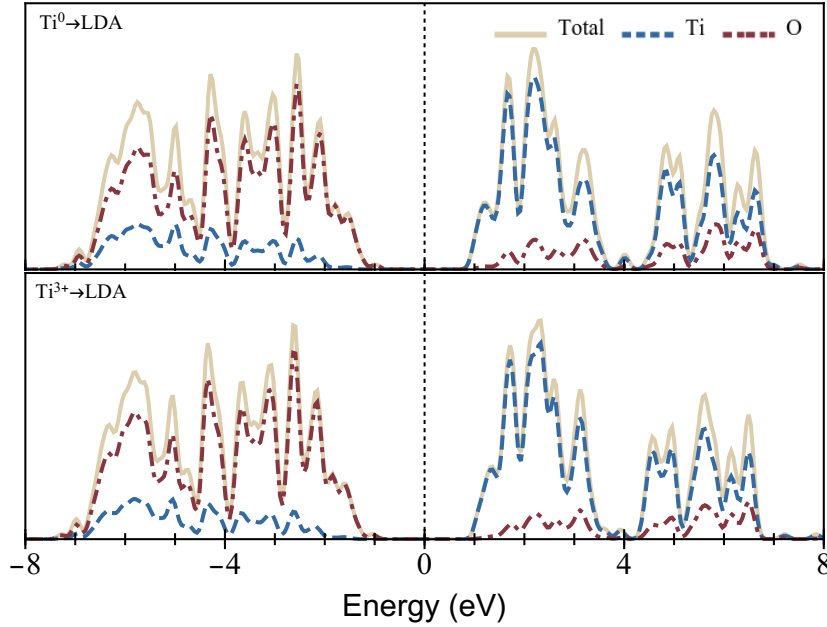


Figure 9.4: DOS of TiO_2 -rutile using DFT (LDA) for the neutral (top panel) and 3+ (bottom panel) atomic projection on the subspace of 3d-states of Ti atom, shown with a Gaussian broadening of 0.1 eV.

Lastly, for the sake of discussion, the effects of the charge configuration of Ti for atomic projection on the subspace of 3d-states are addressed as the Ti^{3+} configuration is used in the pseudo-potential generation for practical purposes of later simulations. When Ti^0 and Ti^{3+} configurations used for atomic projection on the subspace 3d-states, the DOS are quite similar within DFT (LDA) in Fig. 9.4 (top and bottom panels, respectively) with a slightly narrower band-gap of 1.97 eV for Ti^0 compared to a band-gap of at 2.09 eV for Ti^{3+} . This is due to the non-optimised nature of the conduction band, and hence its residual dependence on the initial guesses for the NGWFs. Furthermore, in Fig. 9.5, the shifts on 2p states of O atoms by $\text{DFT}+U^d+U^p$ are nearly identical as the 2p subspaces are not significantly affected by the choice of atomic configurations of Ti atoms as it can be observed in the linear fittings of the responses of the subspace 2p-states of O atom in App. D and the corresponding Hubbard parameters in Table 9.3 for the given atomic configurations of Ti atom. However, the Ti^{3+} choice leads to a larger localisation of the subspace of 3d-states, and a larger Hubbard U^d parameter due to a tighter confinement of the localised density in this charged configuration.

In Fig. 9.5, the larger ${}^{\text{Ti}}U'_{\text{eff}}=4.820$ eV for the Ti^{3+} configuration compared to the ${}^{\text{Ti}}U'_{\text{eff}}=2.982$ eV for the neutral configuration shifts $3d$ states more. The direct band-gap at the high symmetry point Γ is predicted with a slightly larger overestimation with DFT+ U^d+U^p with U'_{eff} parameters for the Ti^{3+} configuration, at 3.82 eV, while still performing relatively well compared to other first-principles methods listed in Table 9.4.

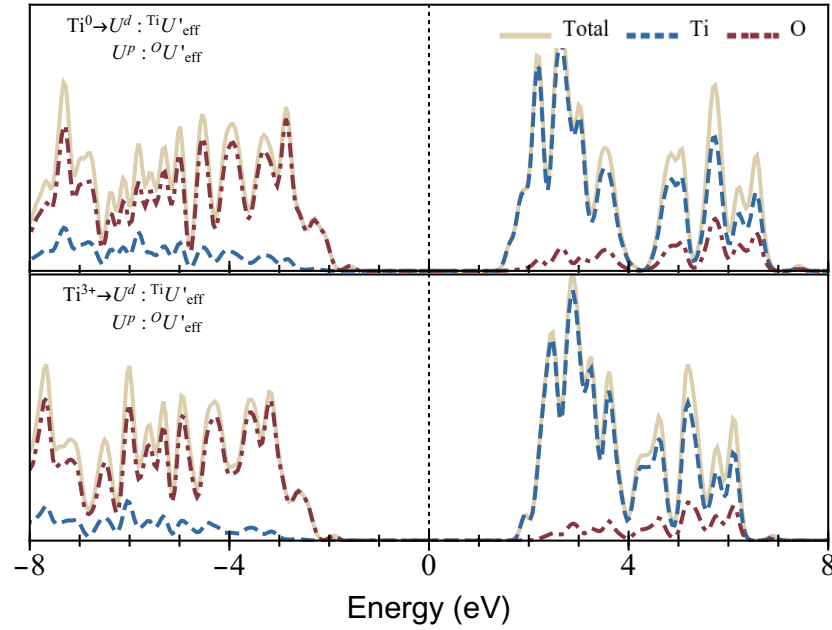


Figure 9.5: DOS of TiO_2 -rutile using DFT+ U^d+U^p for the neutral atomic projection of the subspaces of $3d$ -states of Ti atoms (top panel) with the Hubbard U'_{eff} parameters for $3d$ -states of Ti ($U^d : {}^{\text{Ti}}U'_{\text{eff}}=2.982$ eV) and for $2p$ -states for O atoms ($U^p : {}^{\text{O}}U'_{\text{eff}}=6.742$ eV), and the $3+$ atomic projection of the subspaces of $3d$ -states of Ti atoms (bottom panel) with the Hubbard U'_{eff} parameters for $3d$ -states of Ti ($U^d : {}^{\text{Ti}}U=4.820$ eV) and for $2p$ -states for O atoms ($U^p : {}^{\text{O}}U=6.796$ eV), shown with a Gaussian broadening of 0.1 eV.

The Ti^{3+} configuration gives rise to orbitals that are more localised than their neutral-configuration counterpart. Hence, the neutral atomic configuration of Ti for projection provides a more suitable description of the states around the Fermi level, and this choice is used for further simulations.

9.2.2 TiO₂-anatase

Within a similar approach for TiO₂-anatase, the total DOS and the local DOS (LDOS) projected on Ti and O were shown for the Ti⁰ configuration in Fig. 9.6 and Fig. 9.7 using DFT+ U^d and DFT+ U^d + U^p , respectively, alongside with DFT (LDA). Once again, DFT+ U even with largest applied Hubbard U parameter is ineffective for increasing the band-gap, and it underestimates it by $\sim 0.80 - 1.20$ eV compared to the experimental values listed in Table 9.5. DFT+ U^d + U^p with U'_{eff} predicts a band-gap of 3.82 eV, which is slightly overestimated compared to the experimental gap at 3.2 – 3.4 eV and the hybrid functional result of 3.60 eV. The fully GW scheme overestimates the direct band-gap as 4.14 eV as well; however, an indirect band-gap with lower energy is proposed in the same work as 3.56 eV with GW^[18] comparable to the band-gap predicted by the hybrid functional approximation.

LDA	2.21	
	DFT+ U^d	DFT+ U^d + U^p
$U_{\nearrow\searrow}^{\uparrow\downarrow}$	2.31	2.78
U	2.51	4.13
U_{eff}	2.48	3.89
U'_{eff}	2.45	3.65
Exp. ^[12,20]	3.2-3.4	
PBE ^[19]	1.94	
HSE ^[19]	3.60	
GW ^[18]	4.14	
DFT+ U^d ($U=7.5$ eV) ^[49]	3.27	

Table 9.5: The direct band-gaps ($\Gamma \rightarrow \Gamma$) (in eV) TiO₂-anatase from experimental and first-principles methods.

Despite its slight overestimation, DFT+ U^d + U^p with the U'_{eff} improves the descriptions of band-gaps both in TiO₂-anatase and in TiO₂-rutile drastically considering its small additional computational cost. It agrees very well with the Heyd-Scuseria-Ernzerhof functional (HSE), for instance. It is a promising achievement to enable the study of spatially more complex systems such as nano-clusters produced starting from spatial symmetries of TiO₂-rutile or TiO₂-anatase, and the key step here is the careful calculations of effective Hubbard U parameters for closed-shell systems.

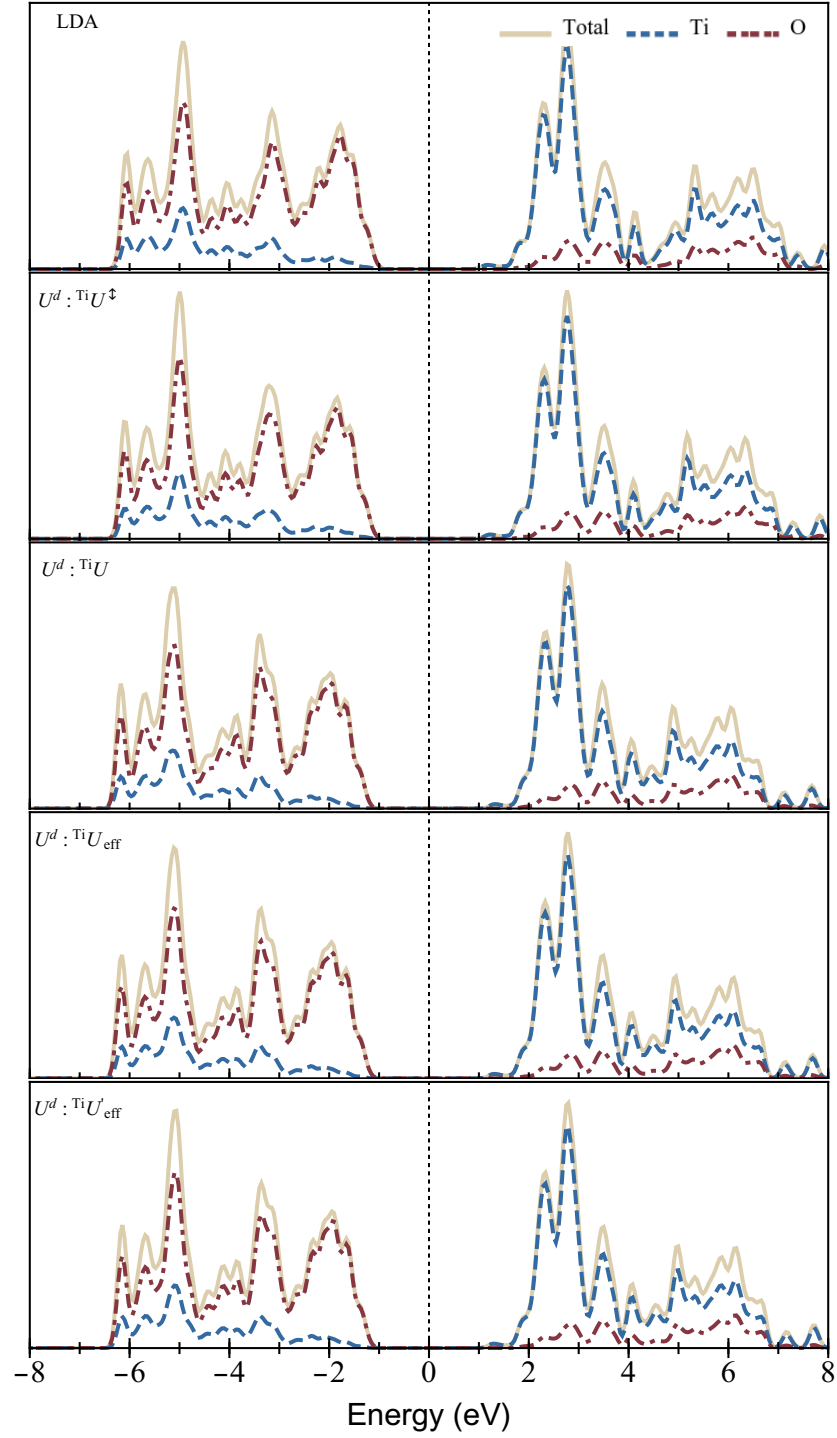


Figure 9.6: DOS of TiO₂-anatase using DFT+ U^d with the Hubbard U parameters using various methods summarised in Table 9.3 for $3d$ -states of Ti ($U^d : {}^{\text{Ti}}U$), shown with a Gaussian broadening of 0.1 eV.

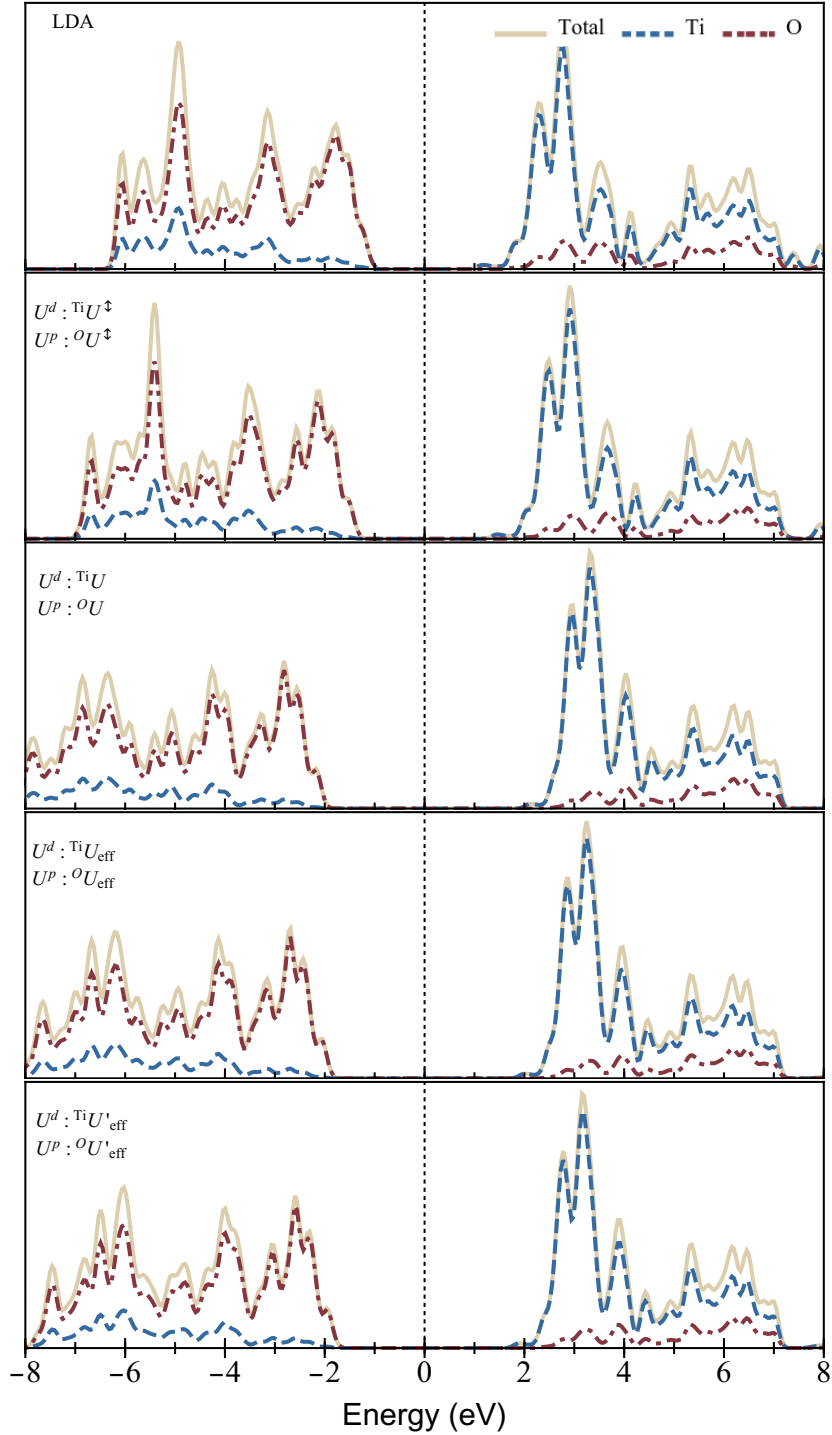


Figure 9.7: DOS of TiO₂-anatase using DFT+ U^d + U^p with the Hubbard U parameters using various methods summarised in Table 9.3 for $3d$ -states of Ti ($U^d : {}^{\text{Ti}}U$) and for $2p$ -states for O atom ($U^p : {}^{\text{O}}U$), shown with a Gaussian broadening of 0.1 eV.

9.3 Energies and oscillator strengths of the first electronic excitations of TiO_2 nano-clusters

Two small, neutral nano-clusters of TiO_2 , which were previously studied with first-principles methods, were chosen for investigating the performance of $\text{DFT}+U^d+U^p$ combined with $\text{TDDFT}+U$. $(\text{TiO}_2)_{12}$ shown in Fig. 9.8a was proposed by Chen and Dixon^[51] as a stable nano-cluster constructed by using the hybrid genetic algorithm combined with the hybrid functional approximation in DFT. They also showed that the clustering energy of nano-clusters $(\text{TiO}_2)_n$ grown with their approach shows a slow, but steady convergence to bulk TiO_2 -rutile values, whereas the disassociation energies converge rapidly to the bulk TiO_2 -rutile value for increasing n . Hence, $(\text{TiO}_2)_{12}$ is classified as TiO_2 -rutile like. The second nano-cluster $(\text{TiO}_2)_{48}$ shown in Fig. 9.8b was proposed by same authors using similar approaches^[52]. This nano-cluster is predicted as having an anatase-like structure with the second lowest ground-state energy for $n=48$. One of the objectives of this chapter is to propose an effective scheme for investigating the low-lying excitations of nano-structures. Hence, rather than discovering novel nano-clusters of TiO_2 , these nano-cluster were chosen for the sake of convenience.

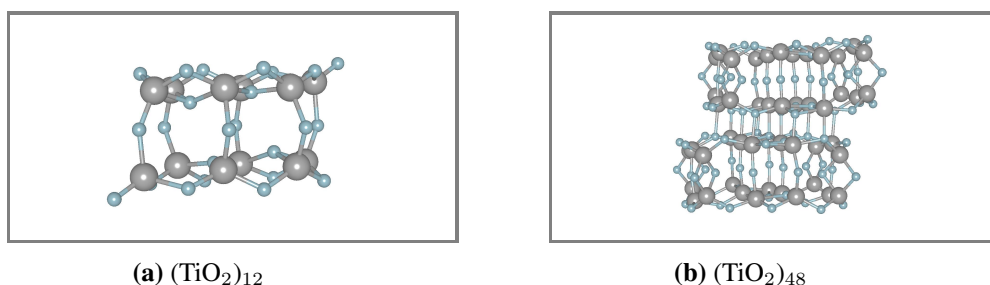


Figure 9.8: The structures of $(\text{TiO}_2)_{12}$ and $(\text{TiO}_2)_{48}$ nano-clusters.

The geometries were directly adopted from the original works in Ref. 51 and Ref. 52. An effective 1200 eV E_{cut} and a dimensionless parameter 7 for PBC^[53] were used, whereas other parameters are set the identical to the bulk TiO_2 simulations.

9.3.1 The first excitations of $(\text{TiO}_2)_{12}$ and $(\text{TiO}_2)_{48}$

In Fig. 9.9, the valence and the conduction band-edges are the predominantly $2p$ -states of O atom and $3d$ -states of Ti atom, respectively, within DFT (LDA). Comparing the top and middle panels in Fig. 9.9, $\text{DFT}+U$ shifts the conduction band-edge with the $3d$ character to slightly higher energy by ~ 0.2 eV and the $3d$ characteristic valence states at around ~ -1.75 eV, which are at deeper energies compared to the valence band-edge with the $2p$ character at ~ -1.5 eV. As expected, $\text{DFT}+U^d+U^p$ leads to a similar shift of $2p$ -states of O atom on top of the shift of $3d$ -states of Ti atom.

In Table 9.6, the excitation energies and the corresponding oscillator strengths using various methods from spectral simulations on top of DFT (LDA), $\text{DFT}+U^d$, and $\text{DFT}+U^d+U^p$ are presented. The first excitation energy is predicted by both TDA and RPA starting from the DFT (LDA) electronic states as 2.71 eV, with similar oscillator strengths. Indeed, the excitation energies are not affected by various methods applied in spectral simulations for the cases that are starting from identical electronic states. As also demonstrated in Chap. 8, TDA and RPA predict quite similar excitations for low-energy spectral range. Furthermore, the first excitation is expected to be the $2p \rightarrow 3d$ character considering the characters of valence and conduction band-edges as seen in Fig. 9.9. Hence, neither $\text{TDDFT}+U^d$ nor $\text{TDDFT}+U^d+U^p$ are effective on the first excitation energy as they exclusively act on excitations with $3d \rightarrow 3d$ and $2p \rightarrow 2p$ characters, respectively. However, $\text{DFT}+U^d$ and $\text{DFT}+U^d+U^p$ have significant effects on both excitation energies and oscillator strengths of the first excitation by modifying both the energies and the characters of valence and conduction manifold edges. $\text{DFT}+U^d$ shifts the first excitation energy to 3.02 eV by mostly shifting the $3d$ character conduction manifold edge to higher energy. As such shift does not significantly change the character of valence and conduction band-edges, the oscillator strengths using various methods starting from $\text{DFT}+U^d$ are predicted as quite similar to the ones starting from DFT (LDA). The first excitation energy is shifted further at 3.27 eV with $\text{DFT}+U^d+U^p$. Such an additional shift is expected as the valence band-edge is also shifted to a lower energy by the $+U^p$ correction. Furthermore, this shift of $2p$ -states is slightly larger compared to the shift of $3d$ -states at the valence manifold that leads to less $2p$ and more $3d$ character at the valence band-edge. Hence, the first excitation becomes less of $2p \rightarrow 3d$ character and more of $3d \rightarrow 3d$ character, which is optically weaker due to some spatial symmetries of the $(\text{TiO}_2)_{12}$ nano-cluster. As a result, the oscillator strengths become smaller with $\text{DFT}+U^d+U^p$ compared to DFT and $\text{DFT}+U^d$.

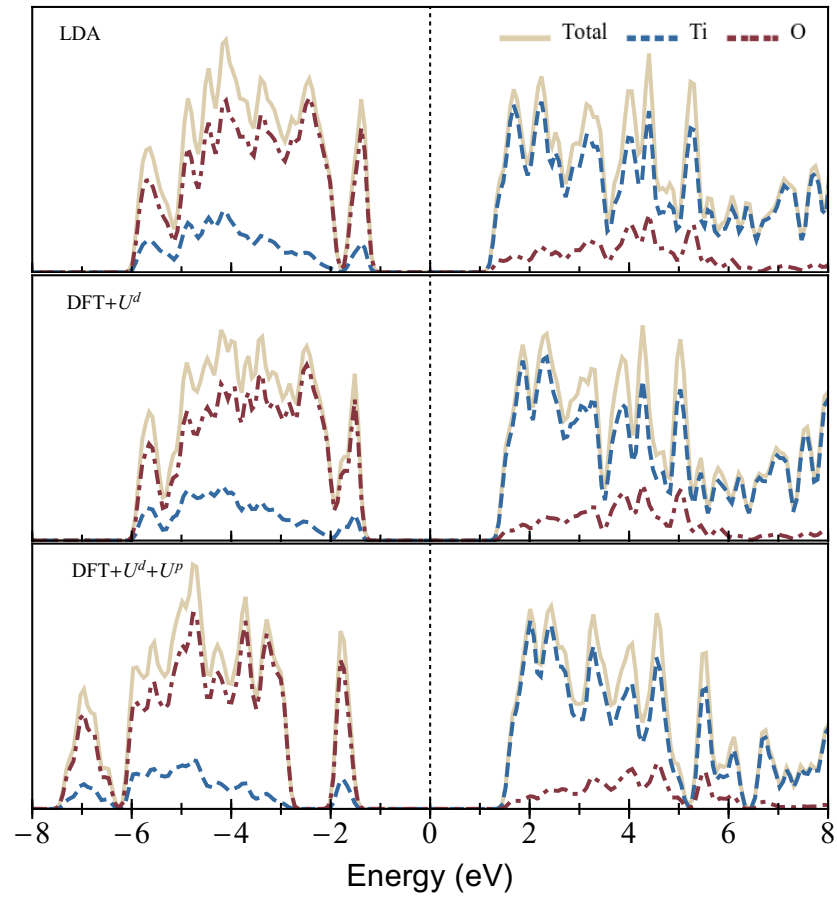


Figure 9.9: DOS of $(\text{TiO}_2)_{12}$ using DFT (LDA), $\text{DFT}+U^d$ and $\text{DFT}+U^d+U^p$ with the Hubbard U_{eff}' parameters for $3d$ -states of Ti (U^d : ${}^{\text{Ti}}U_{\text{eff}}'=2.982$ eV) and for $2p$ -states for O atom (U^p : ${}^{\text{O}}U_{\text{eff}}'=6.742$ eV) from the values of bulk TiO_2 -rutile , shown with a Gaussian broadening of 0.1 eV.

9. Band gaps of TiO_2 systems from first-principles DFT+ U^d + U^p

SP + COND	LR-TDDFT	Excitation energy (eV)	Oscillator str. ($\times 10^{-4}$)
DFT (LDA)	TDA	2.71	2.80
	RPA		2.71
DFT+ U^d	TDA	3.02	2.76
	TDA+ U^d		7.40
	RPA		2.30
	RPA+ U^d		3.61
DFT+ U^d + U^p	TDA	3.27	0.19
	TDA+ U^d + U^p		0.26
	RPA		0.11
	RPA+ U^d + U^p		0.20

Table 9.6: The first electronic excitation energy and the corresponding oscillator strength of the $(\text{TiO}_2)_{12}$ nano-cluster using LR-TDDFT, TDDFT+ U^d , and TDDFT+ U^d + U^p starting from DFT (LDA), DFT+ U^d , and DFT+ U^d + U^p with the Hubbard U'_{eff} parameters for $3d$ -states of Ti (U^d : $^{\text{Ti}}U'_{\text{eff}}=2.982$ eV) and for $2p$ -states for O atom (U^p : $^{\text{O}}U'_{\text{eff}}=6.742$ eV) from the values of bulk TiO_2 -rutile.

In Fig. 9.10, the valence and conduction band-edges of $(\text{TiO}_2)_{48}$ have very distinctive $2p$ and $3d$ characters, respectively, as seen in DOS with DFT (LDA). Similar to previous case, DFT+ U^d leads to a small shift at the conduction band-edge to a higher energy with ~ 0.10 eV due to its predominantly $3d$ character while the valence band-edge stays mostly intact. Likewise for DFT+ U^d + U^p : the valence band-edge is shifted to lower energy along with an additional shift of the conduction band-edge to a higher energy. Consequently, the first excitation energies $(\text{TiO}_2)_{48}$ starting from DFT, DFT+ U^d , and DFT+ U^d + U^p exhibit an expected trend that DFT+ U^d leads to a slightly higher excitation energy at 2.80 eV compared to the excitation energy with DFT at 2.63 eV, whereas the excitation energy starting from DFT+ U^d + U^p is located at a much higher energy at 3.73 eV. Once again, all methods result similar excitation energies when they are applied on top of identical electronic states. However, in the case of $(\text{TiO}_2)_{48}$, the characters of valence and conduction manifold edges are modified neither by DFT+ U^d nor DFT+ U^d + U^p ; hence, the oscillator strengths are similar within all combinations of methods at DFT and TDDFT levels.

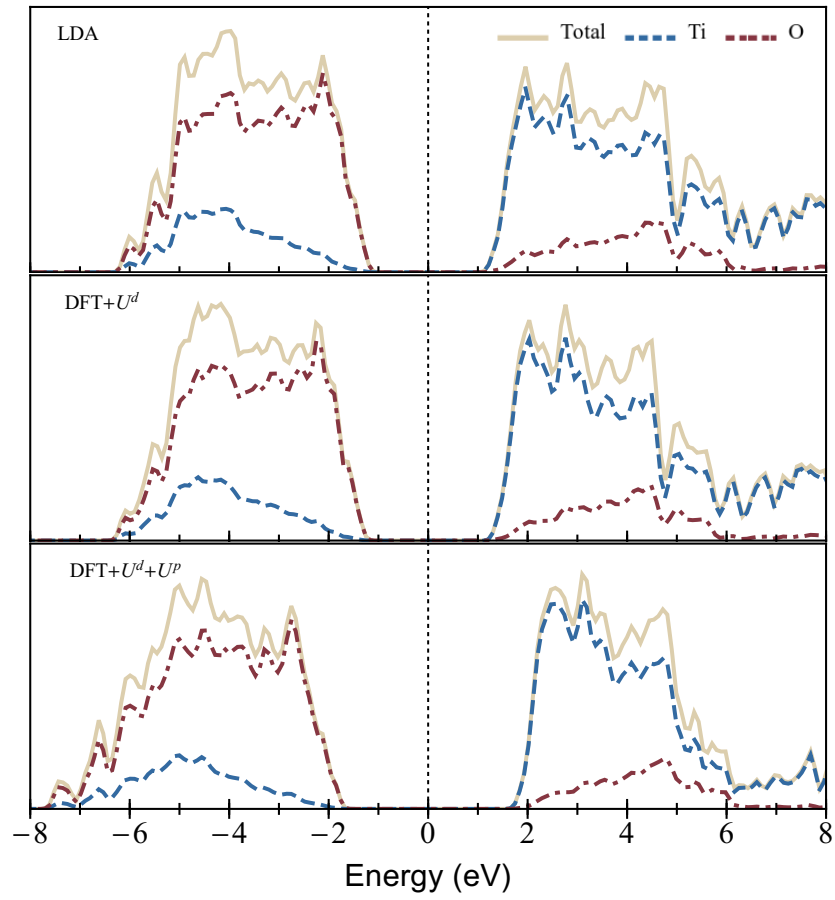


Figure 9.10: DOS of $(\text{TiO}_2)_{48}$ using DFT (LDA), DFT+ U^d and DFT+ U^d+U^p with the Hubbard U'_{eff} parameters for 3d-states of Ti (U^d : ${}^{\text{Ti}}U'_{\text{eff}}=2.996$ eV) and for 2p-states for O atom (U^p : ${}^{\text{O}}U'_{\text{eff}}=6.749$ eV) from the values of bulk TiO_2 -anatase, shown with a Gaussian broadening of 0.1 eV.

9. Band gaps of TiO₂ systems from first-principles DFT+ U^d + U^p

SP + COND	LR-TDDFT	Excitation energy (eV)	Oscillator str. ($\times 10^{-4}$)
LDA	TDA	2.63	0.25
	RPA		0.19
DFT+ U^d	TDA, TDA+ U^d	2.80	0.36
	TDA+ U^d		0.36
	RPA		0.24
	RPA+ U^d		0.28
	TDA		0.41
DFT+ U^d + U^p	TDA+ U^d + U^p	3.73	0.54
	RPA		0.35
	RPA+ U^d + U^p		0.42

Table 9.7: The first electronic excitation energy and the corresponding oscillator strength of the (TiO₂)₄₈ nano-cluster using LR-TDDFT, TDDFT+ U^d , and TDDFT+ U^d + U^p starting from DFT (LDA), DFT+ U^d , and DFT+ U^d + U^p with the Hubbard U'_{eff} parameters for 3d-states of Ti (U^d : ${}^{\text{Ti}}U'_{\text{eff}}$ =2.996 eV) and for 2p-states for O atom (U^p : ${}^{\text{O}}U'_{\text{eff}}$ =6.749 eV) from the values of bulk TiO₂-anatase.

9.4 Oxygen vacancies in TiO₂

Despite their highly promising features, both TiO₂-rutile and TiO₂-anatase have band-gaps in the UV spectral range, whereas the desired energy for most of opto-electronic applications is around ~ 2 eV. Various strategies have been proposed in the literature to engineer the band-gaps of TiO₂ and its nano-structures, as discussed in detail in the comprehensive reviews of Refs. 6 and 7. Single point defects such neutral O vacancy (V_{O}) in bulk TiO₂-rutile and TiO₂-anatase have attracted attention as many optical measurements suggest lower band gaps in such reduced TiO₂ systems^[29,54–60]. The lower band-gaps are predicted as resulting from the defect states of neighbouring O deficient Ti³⁺ centers^[61,62] with highly localised electronic densities^[63].

Similar to the case of pristine bulk, DFT+ U^d and DFT+ U^d + U^p are commonly used to simulate these phenomena within first-principles approaches^[64–68] as the Hubbard U correction is advantageous to describe localised states by construction. However, there is no consensus about choices of the Hubbard parameters and their first-principles determinations, and it is not necessarily the same set of parameters of pristine bulk cases and V_{O} rich

TiO₂^[64].

Three types of V_O are suggested by considering the locations of extra 2 electrons due to the vacancy. These three cases can be summarised such as

The types of V_O:

- V_O(0,0) : Extra electrons are paired at same Ti atom; hence, a closed-shell case, where $s = 0, \mu_s = 0$ (in μ_B units) → Non-spin-polarised simulation.
- V_O(2,0) : Extra electrons are restricted on Ti_A and Ti_B with opposite spins; hence, an open-shell, low-spin configuration, where $s = 2, \mu_s = 0$ (in μ_B units) → Spin-polarised simulation with spins of Ti_A and Ti_B set to 1 and -1, respectively. A broken-symmetry initial guess must be used.
- V_O(2,2) : Electrons are globally restricted to have same spin without any local restriction; hence, an open-shell, high-spin configuration, where $s = 2, \mu_s = 2$ (in μ_B units) → Spin-polarised simulation with global spin constrained to 2.

9.4.1 Single V_O in bulk TiO₂-rutile

A neutral O vacancy was added to the super-cell of TiO₂-rutile of Subsec. 9.2.1, as shown in Fig. 9.11, where, the vacant O is coloured with red, and the closest neighbouring Ti atoms, which are spatially symmetric relative to the vacant O, are coloured with black and labelled as Ti_A and Ti_B. In Fig. 9.12, DOS are presented for the pristine TiO₂-rutile and TiO₂-rutile with the three types of V_O within DFT+ U^d+U^p using the first-principles U'_{eff} parameters of the pristine TiO₂-rutile. Also, the Fermi levels of V_O systems are aligned to the Fermi level of the pristine TiO₂-rutile.

V_O(0,0) and V_O(2,0) produce identical ground-states, which are favourable over V_O(2,2) with ~ 0.01 eV lower ground-state energy. In Fig. 9.12, both V_O(0,0) and V_O(2,0) form defect states at 1.10 eV, which is 2.70 eV from the valence band-edge and 0.48 eV from the conduction band-edge. The defect states, which are 2.70 eV from the valence band-edge in the cases of V_O(0,0) and V_O(2,0), are in agreement with the previous DFT+ U^d and DFT+ U^d+U^p simulations with some tuned Hubbard parameters to obtain experimental predictions^[64–68]. In the case of V_O(2,2), the defect state, which is centred at 0.35 eV, is 1.95

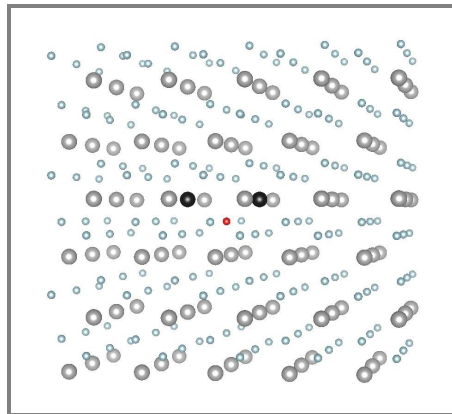


Figure 9.11: Super-cell structure of TiO_2 -rutile with a single neutral V_O (coloured with red). Two closest neighbouring Ti atoms to the vacant O are highlighted with black.

eV from the valence band-edge and 0.95 eV from the conduction band-edge. Furthermore, in the $V_O(2,2)$ case, another shoulder starts to form at the conduction band-edge centred at 1.30 eV. The formation of the defect state in the $V_O(2,2)$ case is comparable with photoelectron spectroscopy measurements^[29,55,69] and EELS measurement^[70], which are predicting such a defect state ~ 2 eV above the valence band-edge and ~ 1 eV below the conduction band-edge. Moreover, the $V_O(2,2)$ case locates the defect state very similarly to HSE simulations that predicts such defect state at 2.15 eV from the valence band-edge and 0.9 eV from the conduction band-edge^[71].

In all cases, the defect states formed are due to two unpaired electrons in the band-gap and they are predominantly the $3d$ character. Even in the case of $V_O(2,2)$, which does not impose any restriction on the local magnetic ordering, two unpaired electrons prefer to localise on the empty $3d$ orbitals of the neighbouring Ti_A and Ti_B that were in their $4+$ charge states in the pristine TiO_2 -rutile and became Ti^{3+} . The strong $3d$ characters of the defect states also agree with the absorption spectra measurement, where the blue colour of O-poor TiO_2 -rutile is predicted due to the low-energy $3d \rightarrow 3d$ transitions from the defect states to the $3d$ character conduction band-edge^[72]. Furthermore, the electron diffraction pattern shows the $3d^1$ electrons in O vacant TiO_2 -rutile^[63].

In TiO_2 -rutile with the single and neutral O vacancy, the unpaired two electrons localise on the empty $3d$ -states of the closed neighbouring Ti atoms and lead to a n-type donor defect states in the band-gap of the pristine TiO_2 -rutile^[65]. The Heyd-Scuseria-Ernzerhof functional (HSE06) simulations in Ref. 73 suggests that this is due to self-trapping of the two additional electrons

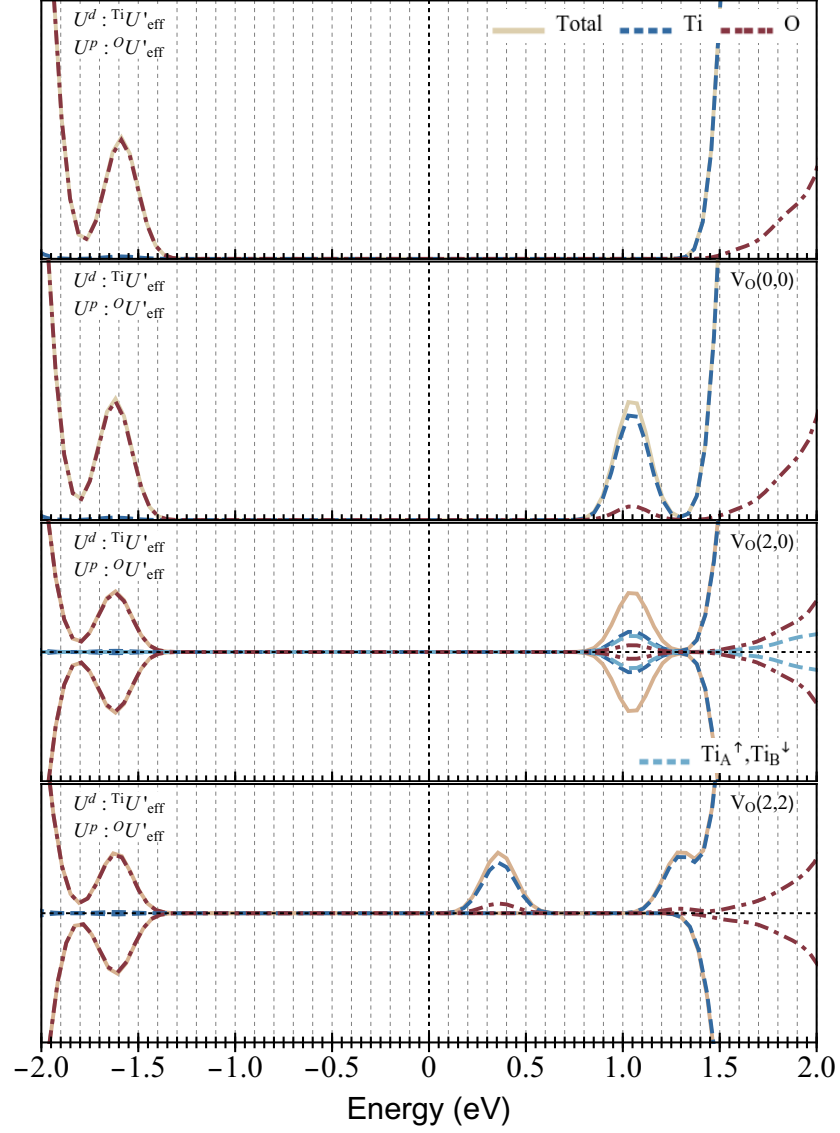


Figure 9.12: Magnified DOS of (from top to bottom) pristine TiO₂-rutile, the V_O(0,0), the V_O(2,0), the V_O(2,2) vacancy in TiO₂-rutile with DFT+ U^d+U^p with the Hubbard U'_{eff} parameters for 3d-states of Ti ($U^d : {}^{\text{Ti}}U'_{\text{eff}}=2.982$ eV) and for 2p-states for O atom ($U^p : {}^{\text{O}}U'_{\text{eff}}=6.742$ eV), shown with a Gaussian broadening of 0.1 eV.

that are weakly bounded.

9.4.2 Single V_O in bulk TiO_2 -anatase

Similarly to the previous case, the same types O vacancies were introduced to the super-cell of TiO_2 -anatase studied in Subsec. 9.2.2 as shown in Fig. 9.13, where the vacant O is coloured with red, and the closest neighbouring Ti atoms, which are spatially symmetric relative to the vacant O, are coloured with black and labelled as Ti_A and Ti_B . In Fig. 9.14, DOS are presented for the pristine TiO_2 -anatase and TiO_2 -anatase with the three types of V_O within DFT+ U^d+U^p using the first-principles U'_{eff} parameters of the pristine TiO_2 -anatase. Also, the Fermi levels of V_O systems are aligned to the Fermi level of the pristine TiO_2 -anatase.

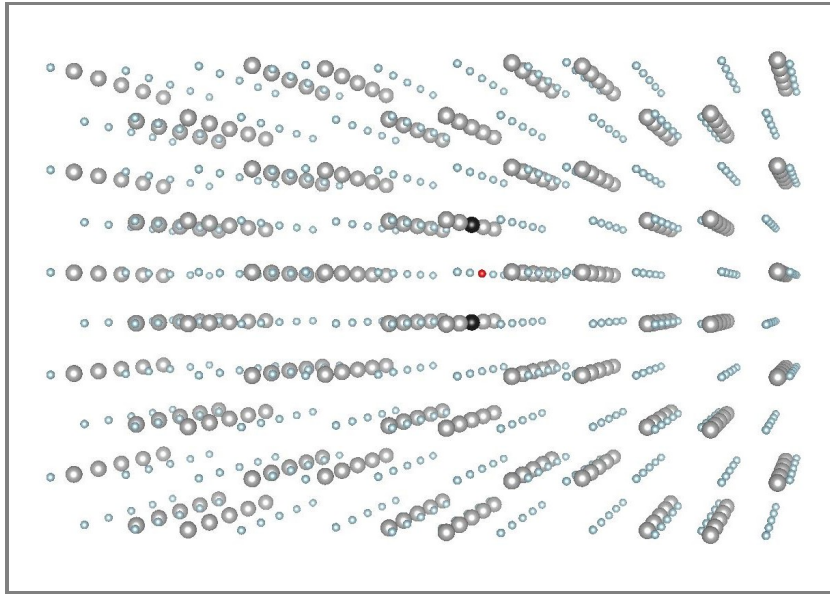


Figure 9.13: Super-cell structure of TiO_2 -anatase with a single neutral V_O (coloured with red). Two closest neighbouring Ti atoms to the vacant O are highlighted with black.

$V_O(0,0)$ and $V_O(2,0)$ again produce identical ground-states, whereas $V_O(2,2)$ has ~ 0.03 eV higher total energy. $V_O(0,0)$ and $V_O(2,0)$ create defect states at the same location 2.95 eV above the valence band-edge and ~ 0.30 eV below the conduction band-edge of the pristine TiO_2 -anatase. This defect state is predicted with slightly lower energy by previous hybrid functional (B3LYP) with an energy of 2.60 eV^[65]. The occupied spin-up defect state is n-type similarly to the case in the O vacant TiO_2 -rutile. Additionally, there exists a defect state due

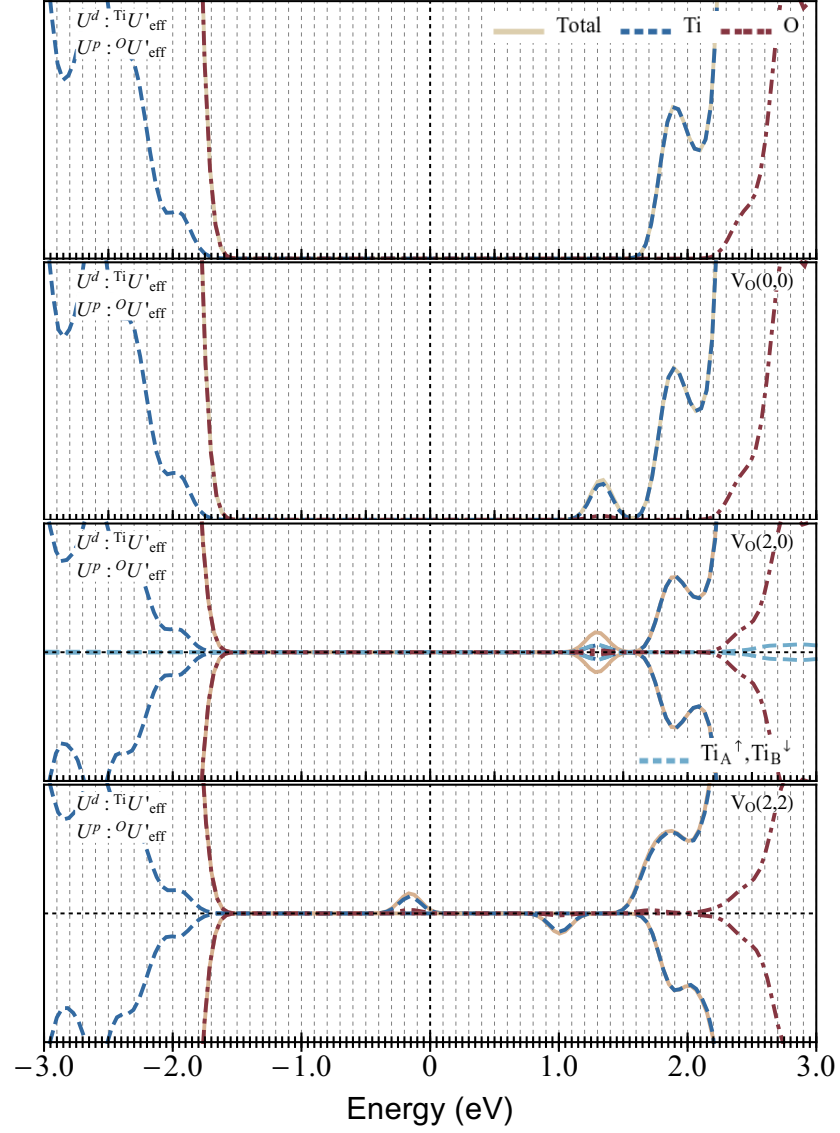


Figure 9.14: Magnified DOS of (from top to bottom) pristine TiO₂-anatase, the V_O(0,0), the V_O(2,0), the V_O(2,2) vacancy in TiO₂-anatase with DFT+ U^d+U^p with the Hubbard U'_{eff} parameters for 3d-states of Ti ($U^d : {}^{\text{Ti}}U'_{\text{eff}}=2.996$ eV) and for 2p-states for O atom ($U^p : {}^{\text{O}}U'_{\text{eff}}=6.746$ eV), shown with a Gaussian broadening of 0.1 eV.

to a localised excited state on the vacancy that is also observed with the HSE06 simulations in Ref. 73. The $V_{\text{O}}(2,2)$ locates these defect states at 1.40 eV and 2.55 eV from the valence band-edge. While the defect state at 1.40 eV is occupied, the defect state at 2.55 eV is unoccupied. This situation is similar to previous $\text{DFT}+U^d$ simulations with $U=3$ eV in Ref. 65, where these defect states are predicted at 1.85 eV and 2.64 from the valence band-edge compared to the B3LYP simulations in Ref. 65, where they are predicted at 2.76 eV and 2.88 from the valence band-edge.

9.5 Conclusion

In this chapter, the electronic structures of various TiO_2 were investigated within $\text{DFT}+U^d+U^p$ with first-principles Hubbard parameters. KS-DFT substantially underestimates the direct band-gaps of bulk TiO_2 -rutile and TiO_2 -anatase at the LDA level, whereas attempts to improve electronic bands with $\text{DFT}+U$ requires unreasonably large Hubbard U parameters, which are commonly tuned by hand. As the valence and the conduction band-edges are predominantly the $2p$ -state of O and the $3d$ -state of Ti atoms, respectively, in both TiO_2 -rutile and TiO_2 -anatase, applying the Hubbard correction both $3d$ sub-shell of Ti and $2p$ sub-shell of O simultaneously, with their respective Hubbard parameters, giving $\text{DFT}+U^d+U^p$, results in a far more accurate description of band-structures. Using $\text{DFT}+U^d+U^p$ with the first-principles coupled-spin response for closed-shell systems, a U'_{eff} parameters, the band-gaps were predicted as 3.18 eV and 3.65 eV comparable to the experimental values of 3.0 eV and 3.2-3.4 eV for the pristine TiO_2 -rutile and TiO_2 -anatase, respectively. Also, the electronic configuration for the atomic projection on the subspace of $3d$ -states of Ti atoms has to be chosen as neutral; since, the charged configuration such as $3+$ leads to over-localisation of $3d$ -states and correspondingly larger Hubbard parameters due to a tighter confinement, and overestimation on the band-gap of TiO_2 -rutile within $\text{DFT}+U^d+U^p$.

Taking advantage of this effective approach, the first excitations of two nano-clusters $(\text{TiO}_2)_{12}$ and $(\text{TiO}_2)_{48}$ with rutile-like and anatase-like properties at the large size limit, respectively, were studied using $\text{TDDFT}+U^d$ and $\text{TDDFT}+U^d+U^p$ alongside TDA and RPA. In Fig. 9.9 and Fig. 9.10, the valence and conduction band-edges of both nano-clusters are predominately $2p$ -states of O and $3d$ -state of Ti atoms, respectively. Hence, the first excitations of these systems are expected to be $2p \rightarrow 3d$ character. Consequently, while $\text{DFT}+U^d$ and $\text{DFT}+U^d+U^p$ push the first-excitation energies to higher energies by increasing the band-gaps, neither $\text{TDDFT}+U^d$

nor TDDFT+ U^d+U^p do not have any effect on the first-excitations of these systems.

Lastly, DFT+ U^d+U^p was applied to investigate the defect states in TiO₂-rutile and TiO₂-anatase with single, neutral O vacancies. Both in O-vacant TiO₂-rutile and TiO₂-anatase, the anti-ferromagnetic ordering of two unpaired electrons localised on the closest neighbouring two Ti atoms have lower total energies regardless of the initial conditioning of the local magnetic orderings compared to the case that the global spins are restricted to 2 (μ_B). V_O(0,0) and V_O(2,0) produce identical 3d character defect states in the band-gap 2.70 eV and 2.95 eV above the valance band-edges of the pristine TiO₂-rutile and TiO₂-anatase, respectively. In the O vacant TiO₂-rutile, V_O(2,2) creates a 3d character defect state 1.95 eV above the valance band-edge of the pristine TiO₂-rutile comparable to spectroscopic measurements suggesting a defect state ~ 2 eV above the valance band-edge. In the case of the O-vacant TiO₂-anatase, V_O(2,2) created two defect states 1.40 eV and 2.55 eV above the valance band-edge of the pristine TiO₂-anatase. The former one is due to the localised unpaired electrons, whereas the latter one is a localised excited state.

In conclusion, DFT+ U^d+U^p was shown to be a computationally feasible and effective approach, when it is combined with first-principles Hubbard parameters, to study electronic structure of TiO₂ systems that are particularly challenging using conventional KS-DFT.

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Part IV

Concluding Remarks

Chapter 10

Conclusion

This work focused on the first-principles simulations of electronic and optical spectra with quantitative accuracy within corrective, highly-efficient approaches starting from approximate KS-DFT. It placed a particular emphasis on transition-metal systems in the linear-response optical regime. In this dissertation, some drawbacks of contemporary approaches, and some novel methods to address these were introduced. There exists room for further developments, however we have newly enabled the high-throughput screening of metallic alloys and put in place the necessary tools to explore and correct for strong correlation effects among localised excitons.

In this last chapter, some key findings in this work will be summarised. Some suggestions for new research directions opened up by this work will also be discussed.

10.1 Synopsis

In Part I, the fundamental background was established for the theoretical and computational laboratories used to investigate problems within the scope of this work. It was started with Chap. 1, which formulated the conceptual and practical framework used for light-matter interactions modelling from first-principles. Then, the general problem was reduced to that of perturbing purely electronic many-body systems from their ground-states, using weak time-dependent external potentials. The description of some common spectroscopic signatures in molecular and solid-state spectroscopy were introduced to define our target observables. In Chap. 2 and Chap. 3, the theoretical and computational background of the ground-state theory, DFT, were introduced both in the conventional and linear-scaling formalisms. Also, we discussed what is necessary to obtain approximate conduction/unoccupied electronic states. The last chapter of this part, Chap. 4, was dedicated to diagnosing the limitations and the systematic errors of approximate KS-DFT, which particularly challenge the first-principles simulation of transition-metal systems. As KS-DFT relies on local-density type approximations for the xc-interactions among electrons, fully non-local effects cannot be included in first-principles spectra built upon approximate KS-DFT. Such non-local effects have been shown to be crucial for the accurate spectra of extended systems such as transition-metal solids. Also, SIE and its consequences in the many-body case, namely the delocalisation error, which becomes particularly large for transition-metals systems, were addressed with the widely used corrective approach DFT+ U , with an emphasis on calculating Hubbard U and Hund's J parameters from first-principles in

order to retain a first-principles methodology.

In Part II, the optical and plasmonic responses of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ were studied. For this purpose, our main methodology was introduced in Chap. 5. While inter-band contributions to spectra were formulated within the RPA, the intra-band contribution was described within the Drude-Lorentz model. Also, the QP formalism was introduced to tackle problems due to the lack of non-local interactions within KS-DFT, as mentioned in Chap. 4. In Chap. 6, benchmark tests were performed on pure Au, Ag, and Cu to measure the accuracies and efficiencies of various approaches introduced in previous chapters. It was demonstrated that both FGR and RPA fail to describe the inter-band part of the optical spectra of pure Au, Ag, and Cu by overestimating the band-edge transitions as well as the general trends of the spectra. This is due to over-flattening of the fully-filled *d*-bands of these systems within approximate KD-DFT, which does not include any non-local electronic exchange-correlation. Hence, an approximate approach to imitate the QP formalism was suggested, namely the stretching operators, which increase dispersions of the electronic bands. While using the stretching operators instead of evaluating the full QP band-structures decreases computational cost, it has its own drawback that it is mostly effective for the electronic bands close to the Fermi levels, whereas the dispersions of lower-energy valance bands are overestimated. This drawback can be seen particularly in spectra of pure metals at higher-energy spectral range comparing to the experimental spectra. Despite this slight overestimations, using the stretching operators is advantageous in terms of high-throughput simulations. Furthermore, Drude plasmon energies were obtained from first-principles by approximating the inverse effective electron masses via the Fermi velocities calculated from KS-DFT band-structures. These first-principles Drude plasmon energies are in good agreement with experimental values for Au, Ag, and Cu. Also, the Drude parameters of the $\text{Cu} \rightarrow \text{Au} \rightarrow \text{Ag}$ binary alloys have a M-shape trends with respect to increasing ratios that are comparable with the experimental trend for such binary alloys with similar stoichiometric ratios.

The final spectra for 24 stoichiometric ratios, with 39 structures in total, were evaluated using RPA on top approximate QP band-structures, namely, G_0W_0 +RPA. Their respective Drude parameters were generated using novel, semi-empirical approaches. Using the dielectric functions of the bulk $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys, the bulk and surface EELS were calculated as strength measures for bulk and surface plasmon resonances, whereas the quality factors for LSP and SPP, namely Q_{LSP} and Q_{SPP} , were used as measures for life-times. Comparing our results to the experimental SPP measurements on thin-films of binary alloys with the closest available stoichiometric ratios, the life-times of both LSP and SPP are overestimated in our

simulations due to the lack of surface and corrosion effects. However, our results offer preliminary fundamental measures for plasmonic performance for these systems. The distinctive plasmon resonance peaks in the case of the pure metals disappear through alloying. The pure metals show the strongest plasmonic response at their respective plasmon frequency compared to any other stoichiometric ratios. However, a number of alloy stoichiometries with promising characteristics at selected wavelengths were predicted. For instance, AuAgCu₆, Au₆AgCu, AuCu₇, and Au₇Cu show relatively strong plasmon resonances at the common solid-state red laser around 650 nm. Also, AuAg, AuCu, and AgCu alloys start showing relatively significant plasmonic resonance at smaller wavelengths such as common blu-ray laser around 405 nm and the deep-UV laser wavelengths around 290 nm.

Part III focused on the electronic and optical properties of transition-metal systems with large SIE within approximate KS-DFT. In Chap. 7, the background of TDDFT and its linear-response formalism were introduced. Then, the time-domain extension of DFT+*U*, namely TDDFT+*U*, was developed to counter the large SIE self-consistently within TDDFT, in conjunction with DFT+*U*. The key insight introduced is the concept of excitons self-interaction error, which is manifested by a tendency to under-bind excitons due to the delocalisation error. The effects and domains of applicability of DFT+*U* and TDDFT+*U* were demonstrated via calculated EES of an instructive four-level toy model. As expected, DFT+*U* acts on localised subspaces by splitting occupied and unoccupied levels energetically; hence, any electronic transitions within that subspace are shifted to higher energies with *U*. TDDFT+*U* modifies exclusively the electronic excitations from localised subspaces of occupied manifold to localised subspaces of unoccupied manifold by shifting excitations to lower energies, conversely. Naturally, TDDFT+*U* is effective on a subset of the excitations affected by DFT+*U*.

The newly developed TDDFT+*U* was implemented within the linear-scaling DFT code ONETEP. In Chap. 8, our TDDFT+*U* approach was demonstrated on previously well-studied coordination complexes. The Hubbard *U* dependence of EES and ABS were studied on two centro-symmetric, closed-shell Ni-centred complexes Ni(CN)₄²⁻ and Ni(CO)₄, at various levels. DFT+*U* & TDDFT shifts excitations with $3d \rightarrow \pi^*$ and $3d \rightarrow 3d$ character to higher energies by means of shifting $3d$ states in the occupied manifold to lower energies for increasing *U* values. The individual effects of TDDFT+*U* can be seen by invoking DFT & TDDFT+*U*, which moves down excitations with predominantly $3d \rightarrow 3d$ character. DFT+*U* & TDDFT+*U* exhibits the combined effects of DFT+*U* and TDDFT+*U*. As $3d \rightarrow 3d$ transitions are optically dark for centro-symmetric environments by Laporte's selection rules,

the effects of TDDFT+ U are quite small in the dipole-dipole absorption spectra of the Ni-centred coordination complexes studied in this work. Also, the Casida equation predicts very similarly to those of the TDA. First-principles EES and ABS were presented for these two Ni-centred systems with the addition of an open-shell, high-spin Co-centred complex, CoL_2Cl_2 ($\text{L} = 2\text{-aminopyrimidine: C}_4\text{H}_5\text{N}_3$), using their respective first-principles Hubbard U parameters for Ni and Co atoms. The Hubbard U parameters for Ni atoms in $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$ are 1.102 eV and 0.888 eV, respectively. Thus, both the effects of DFT+ U and TDDFT+ U are numerically subtle for EES, and particularly the ABS of these systems. However, TDDFT+ U predicts some additional peaks at lower energies compared to DFT+ U & TDDFT in the EES. These correspond to newly-bound excitons. On the other hand, both DFT+ U and TDDFT+ U have drastic impacts on the EES and ABS of CoL_2Cl_2 . Such effects of DFT+ U are expected as the $3d^7$ subspace is corrected with a larger first-principles Hubbard U parameter of 3.798 eV. Hence, low-energy excitations are shifted to higher energies compared to DFT & TDDFT, by ~ 1 eV. However, TDDFT+ U has the more dominant qualitative effect of bringing spatially localised excitations to lower energies in DFT+ U & TDDFT+ U , compared to DFT & TDDFT, again by ~ 1 eV. This larger effect can be explained though an idealistic picture, where TDDFT+ U acts product space of $d_{x^2-y^2}/d_{z^2}$ and $d_{xy}/d_{yz}/d_{xz}$ for ideal ligand-field splitting of $3d^7$ with the high-spin configuration in perfect tetrahedral symmetry. In principle, such a configuration leads to 2 occupied and 3 unoccupied down-spin $3d$ -states. Hence, TDDFT+ U modifies the corresponding coupling matrix elements proportionally to the density product of the occupied and the unoccupied $3d$ subspace manifolds, which becomes quite large in the Co-centred system. Consequently, DFT+ U & TDDFT+ U predict the first two three-fold degenerate optically bright excitation energies at 0.56 eV and 0.90-1.02 eV, which are comparable to experimental and quantum chemistry results.

In the last chapter of this part, the electronic structure of various TiO_2 systems were investigated by taking advantage of the first-principles Hubbard U parameters within the ONETEP code. We started by addressing the well-known band-gap problem of the pristine TiO_2 -rutile and TiO_2 -anatase within approximate KS-DFT. Conventional KS-DFT underestimates the band-gaps of TiO_2 -rutile and TiO_2 -anatase as 1.97 eV and 2.21 eV, whereas these systems have experimental band-gaps of 3.0 eV and 2.2-3.4 eV, respectively. Furthermore, the conventional DFT+ U applying the Hubbard U correction on the subspace of $3d$ -states of Ti atoms, namely DFT+ U^d , requires an unphysically large U values such as ~ 7.5 -10 eV, which are commonly determined by tuning with respect to some experimental

quantities. Such approaches to determine Hubbard U parameters are not first-principles and highly dependent on tuning quantities. Examining the DOS of TiO_2 -rutile and TiO_2 -anatase within DFT (LDA), the valence and the conduction band-edges are predominantly $2p$ -states of O atoms and $3d$ -states of Ti atoms, respectively. Both of these subspace exhibit de-localisation errors. Hence, DFT+ U^d using the first-principles Hubbard U parameters are not effective to increase the band-gaps of TiO_2 -rutile and TiO_2 -anatase as the valence band-edges stay mostly intact. Applying the Hubbard U corrections simultaneously on both the $2p$ -states of O and the $3d$ -states of Ti atoms, namely DFT+ U^d+U^p , with their respective first-principles Hubbard U parameters, provides an effective corrective approach. To our knowledge, this work provides the first linear-response first-principles Hubbard U and Hund's J parameters for Ti $3d$ and O $2p$ states in TiO_2 . DFT+ U^d+U^p with appropriate first-principles Hubbard parameters predicts the band-gaps of TiO_2 -rutile and TiO_2 -anatase accurately as 3.18 eV and 3.65 eV (comparing to 3.0 eV and 3.2 – 3.4 eV experimental band-gaps, respectively).

Taking advantage of this robust approach, various schemes were applied to determine the first excitation energies of two small nano-clusters $(\text{TiO}_2)_{12}$ and $(\text{TiO}_2)_{48}$, which exhibit TiO_2 -rutile and TiO_2 -anatase like properties, respectively. In both cases, the Hubbard U corrections to DFT levels are the determining factors of the properties of the first excitations, whereas the Hubbard U corrections to TDDFT levels have only slight effects on the oscillator strengths. In $(\text{TiO}_2)_{12}$, DFT+ U^d and DFT+ U^d+U^p push the first excitation energies to 0.31 eV and 0.56 eV higher energies, respectively, with respect to the first excitation energy within DFT & TDDFT. While DFT+ U^d does not significantly effect the oscillator strength, DFT+ U^d+U^p leads to weaker oscillator strengths. This is due to larger shift on the $2p$ -states compared to the $3d$ -states on the valence band-edge, so a larger $3d \rightarrow 3d$ character, which is optically less bright compared to $2p \rightarrow 3d$ character due to some spatial symmetries of $(\text{TiO}_2)_{12}$, in the first excitation. In $(\text{TiO}_2)_{48}$, DFT+ U^d and DFT+ U^d+U^p push the first excitation energies to 0.17 eV and 0.90 eV higher energies, respectively, with respect to the first excitation energy within DFT & TDDFT, whereas they do not have any significant effects on the oscillator strengths.

Lastly, in Chap. 9, single neutral O vacancies were introduced into TiO_2 -rutile and TiO_2 -anatase. In both systems, two unpaired electrons prefer to localise on the closest two neighbouring Ti atoms of the O vacancies with anti-ferromagnetic ordering. This creates defect states with 2.70 eV and 2.90 eV above the valence band-edges of the pristine TiO_2 -rutile and TiO_2 -anatase, respectively. In the O vacant TiO_2 -rutile with a total magnetisation of 2 (μ_B), the defect state is formed 1.95 eV above the valence band-edge of the pristine TiO_2 -rutile, that is comparable to ~ 2 eV, which are suggested by experimental

spectroscopy measurements. On the other hand, two defect states with 1.40 eV and 2.55 eV above the valance band-edge of the pristine in the O vacant TiO₂-anatase with a total magnetisation of 2 (μ_B). The low-energy defect states are due to two unpaired electrons, whereas the high-energy defect state is an excited state localised on the neighbouring Ti atoms.

10.2 Directions for further research

In this work, the development and testing of various novel methodologies has been done with a view to enabling, in the medium term, high-throughput simulations of realistic, but electronically challenging systems at a reasonable computational effort. Taking advantage of the well-tested approaches developed in this work, a large set of systems can now be studied in order to establish some general relations between initial structural and electronic properties, and excited state properties, such as optical and plasmonic figures of merit.

For the optical and plasmonic properties of Au_xAg_yCu_{1-x-y}, some further investigations can be suggested as a trivial continuation of this work. Using a single set of stretching operators has its own drawback as it modifies different types of electronic bands with an average, identical trend. Using separate sets of stretching operators for different electronic bands such as *s*, *p*, or *d*-bands would enable more accurate approximations. However, the Yambo code is currently limited to a single set of stretching operators, which can be modified in the source codes. In the current state, spectral simulations are limited to ordered alloys. Introduction of disorderedness is challenging as it requires large super-cells that increase computational cost and memory requirements. Alternatively, the virtual crystal approximation^[1-3] can be promising via cleverly constructed pseudo-potentials. Furthermore, our simulations do not include any effects due to thermal properties of alloys that can be approximated by using the semi-classical Boltzmann transport equation using BoltzWann code^[4], which is the post-processing tool compatible with QE and the Wannier90 code^[5]. Moreover, the post-processing tool to approximate the Fermi velocities was developed with serial and straightforward algorithms compatible with the NSCF output of QE. This tool can be optimised and generalised for some of the most commonly used KS-DFT software in a parallelised fashion to create a more effective and user-friendly post-processing tool. Using the Comsol package^[6], coupling various physics such as optical and thermal processes in alloys for a more realistic picture would be desirable. Furthermore, the ground-state

properties and plasmonic properties of the calculated stoichiometric ratios can be used within machine learning algorithms to predict the relationship between composition, structure, and plasmonic response.

Some further improvements and tests can be suggested for our TDDFT+ U implementation and for its applications. Particularly, the Hubbard U parameters used in simulations were derived from ground-state properties of systems; hence, they provide a correction in the adiabatic limits. In the case of CoL_2Cl_2 , DFT+ U & TDDFT+ U is sufficiently accurate to identify the lowest excitations, even exceeding the performance of quantum chemistry, whereas it over-corrects the higher energetic ones. Frequency-dependent Hubbard parameters would be more appropriate for applicability to excitations throughout the spectral range. Furthermore, TDDFT+ $U+J$ has already been implemented within ONETEP. This feature needs further testing for numerical stability.

Using DFT+ U^d+U^p , the Hubbard corrections were applied for two subspaces separately with their respective first-principles Hubbard parameters, which were obtained via perturbing each subspace independently. A more comprehensive scheme can be achieved, perhaps, by describing two subspaces as coupled, and applying a non-local Hubbard correction to correct the hybridisation between them. In DFT+ U^d and DFT+ U^d+U^p simulations of the nano-clusters and the O vacant systems, the first-principles Hubbard parameters of the pristine bulk systems were adopted, whereas the Hubbard parameters of these systems may differ from those pristine bulk values. Hence, some systematic benchmark tests should be performed to examine possible effects of individual properties of these systems such as structures, local magnetic ordering and charge states of neighbouring Ti atoms in O vacant bulk TiO_2 systems. Furthermore, investigations on the engineering of band-gaps of TiO_2 systems can be expanded by introducing more complex O vacancies, and doping with other transition-metals^[7]. Ultimately, our results show that first-principles Hubbard U and Hund's J parameters are an essential ingredient in the DFT+ U description in systems such as TiO_2 , where particular care is required to account for its closed-shell nature. A promising avenue would be to revisit systems that have been previously been judged not to be amenable to correction by DFT+ U , in the light of the promising results presented here.

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Appendix A

Representative input files

A.1 The input files for OPIUM

```
#####  
# Opium Parameter File #  
#####  
  
[Atom]  
Au # chemical symbol (max. 2 characters)  
15 # norb: number of orbitals  
# reference configuration  
100 2.00 -643.0 # rlm occ eigen(- means auto-generate)  
200 2.00 -77.4  
210 6.00 -68.4  
300 2.00 -10.0  
310 6.00 -6.0  
320 10.0 -6.4  
400 2.00 -6.4  
410 6.00 -6.0  
500 2.00 -2.4  
510 6.00 -2.0  
420 10.0 -6.0  
430 14.0 -6.4  
600 1.00 -1.0  
610 0.00 -1.0  
520 10.00 -1.0  
  
[Pseudo]  
3 2.05 2.3 2.05  
opt  
  
[Optinfo]  
7 07 10 # rc[a.u.] qc[sqrt(Ry)] Nb  
7 07 10  
7 07 10  
  
[XC]  
gga  
  
[Config]  
5  
#  
600 1.00 -1.0  
610 0.00 -1.0  
520 8.50 -1.0 # number of valence configurations  
#  
600 0.00 -1.0 # rlm occ eigen(- means auto-generate)  
520 9.00 -1.0  
#  
600 1.00 -1.0  
610 0.00 -1.0  
520 9.00 -1.0  
#  
600 0.00 -1.0 # rlm occ eigen(- means auto-generate)  
610 0.00 -1.0  
520 8.50 -1.0  
#  
600 0.00 -1.0  
610 0.00 -1.0  
520 10.0 -1.0  
  
[Relativity]  
srl # rel / srl / tl  
  
#Pcc  
#1.8  
#fuchs  
  
[XC]  
pbe_gga  
0.05
```

Au (PBE)

```
#####  
# Opium Parameter File #  
#####  
  
[Atom]  
Ag # chemical symbol (max. 2 characters)  
11 # norb: number of orbitals  
# reference configuration  
100 2.00 -643.0 # rlm occ eigen(- means auto-generate)  
200 2.00 -77.4  
210 6.00 -68.4  
300 2.00 -10.0  
310 6.00 -6.0  
320 10.0 -6.4  
400 2.00 -6.4  
410 6.00 -6.0  
500 1.00 -2.4  
510 0.00 -1.0  
420 10.0 -6.0  
  
[Pseudo]  
3 2.00 2.2 2.2  
opt  
  
[Optinfo]  
7 07 10 # rc[a.u.] qc[sqrt(Ry)] Nb  
7 07 10  
7 07 10  
  
[XC]  
gga  
  
[Config]  
5  
#  
500 1.00 -1.0  
510 0.00 -1.0  
420 8.50 -1.0 # number of valence configurations  
#  
500 0.00 -1.0 # rlm occ eigen(- means auto-generate)  
510 0.00 -1.0  
420 9.00 -1.0  
#  
500 1.00 -1.0  
510 0.00 -1.0  
420 9.00 -1.0  
#  
500 0.00 -1.0 # rlm occ eigen(- means auto-generate)  
510 0.00 -1.0  
420 8.50 -1.0  
#  
500 0.00 -1.0  
510 0.00 -1.0  
420 10.0 -1.0  
  
[Relativity]  
srl # rel / srl / tl  
  
#Pcc  
#1.8  
#fuchs  
  
[XC]  
pbe_gga  
0.05
```

Ag (PBE)

A. Representative input files

```
#####
# Oplum Parameter File #
#####

[Atom]
Cu #chemical symbol (max. 2 characters)
# #
# norb: number of orbitals
# reference configuration
100 2.00 - # nrm occ eigen(- means auto-generate)
200 2.00 -
210 6.00 -
300 2.00 -
310 6.00 -
400 1.00 -
410 0.00 -
320 10.00 -

[Pseudo]
3 1.9 2.5 2.1
opt

[Optinfo]
7.9 10
7.9 10
7.9 10

[Configs]
5
#
# 400 1.50 -
# 410 0.00 -
# 320 9.50 -
#
# 400 1.50 -
# 410 0.00 -
# 320 8.50 -
#
# 400 2.00 -
# 410 0.00 -
# 320 9.00 -
#
# 400 1.50 -
# 410 0.00 -
# 320 8.50 -
#
# 400 2.00 -
# 410 0.00 -
# 320 9.00 -
#
# 400 1.75 -
# 410 0.00 -
# 320 9.25 -

[Relativity]
srl # rel / srl / hrl

#Pec]
#1.8
#tuchs

[KC]
plogga
0.05
```

Cu (PBE)

```
#####
# Oplum Parameter File #
#####

[Atom]
Ni
# #
# norb: number of orbitals
# nrm occ eigen(- means auto-generate)
100 2.00 -
200 2.00 -
210 6.00 -
300 2.00 -
310 6.00 -
400 2.00 -
410 0.00 -
320 8.00 -

[Pseudo]
3 1.85 1.95 2.05
opt

[Optinfo]
7.9 10
7.9 10
7.9 10

[Configs]
7
#
# 400 0.00 -
# 410 0.00 -
# 320 7.00 -
#
# 400 1.00 -
# 410 0.00 -
# 320 8.00 -
#
# 400 2.00 -
# 410 0.00 -
# 320 7.00 -
#
# 400 2.00 -
# 410 0.00 -
# 320 8.00 -
#
# 400 1.00 -
# 410 0.00 -
# 320 8.00 -
#
# 400 0.50 -
# 410 0.00 -
# 320 9.50 -
#
# 400 0.00 -
# 410 0.00 -
# 320 10.00 -

[KC]
0pp 0.1

[Pec]
1.3
ffc # or fs

[Relativity]
srl

[KBdesign]
0 # local orb
```

Ni (PBE)

```
#####
# Oplum Parameter File #
#####

[Atom]
C
# #
# norb: number of orbitals
# reference configuration
100 2.00 -
200 2.00 -
210 2.00 -

[Pseudo]
2 1.95 1.45
opt

[Optinfo]
7.9 10
7.9 10

[Configs]
1
#
# 200 2.00 -
# 210 2.00 -

[KC]
gga 0.1

[Relativity]
srl
```

C (PBE)

```
#####
# Oplum Parameter File #
#####

[Atom]
O
# #
# norb: number of orbitals
# reference configuration
100 2.00 -
200 2.00 -
210 4.00 -

[Pseudo]
2 1.4 1.5
opt

[Optinfo]
7.9 10
7.9 10

[Configs]
3
#
# 200 2.00 -
# 210 4.20 -
#
# 200 2.00 -
# 210 4.40 -
#
# 200 2.00 -
# 210 4.60 -

[KC]
gga 0.1

[Relativity]
srl
```

O (PBE)

A.1 The input files for OPIUM

```
#####
# Opium Parameter File #
#####

[Atom]
N
3
100 2.00 -
200 2.00 -
210 3.00 -

[Pseudo]
2 1.35 1.45
opt

[Optinfo]
7.9 10
7.9 10

[Configs]
2
#
200 2.00 -
210 3.20 -
#
200 2.00 -
210 3.40 -

[KC]
gga 0.1

[Relativity]
sr1
```

N (PBE)

```
#####
# Opium Parameter File #
#####

[Atom]
Co
8
# norb: number of orbitals
100 2.00 - # nrm occ: eigen(- means auto-generate)
200 2.00 -
210 6.00 -
300 2.00 -
310 5.00 -
400 0.00 -
410 0.00 -
320 7.00 -

[Pseudo]
3 1.8 2.1 2.1
opt

[Optinfo]
7.90 10
7.90 10
7.90 10

[Configs]
6
# neutral
400 2.00 -
410 0.00 -
320 7.00 -
# plus 2 - Representation
400 0.00 -
410 0.00 -
320 7.00 -
# plus 2
400 2.00 -
410 0.00 -
320 5.00 -
# plus 2
400 1.00 -
410 0.00 -
320 6.00 -
# plus 3
400 0.00 -
410 0.00 -
320 6.00 -
# plus 3
400 1.00 -
410 0.00 -
320 5.00 -
# plus 3
400 2.00 -
410 0.00 -
320 4.00 -

[KC]
gga 0.05 # lda[PZ] or gga[PBE]

[pcc]
1.35
llc

[Relativity]
sr1
```

Co²⁺ (PBE)

```
#####
# Opium Parameter File #
#####

[Atom]
Cl
5
# norb: number of orbitals
100 2.00 - # nrm occ: eigen(- means auto-generate)
200 2.00 -
210 6.00 -
300 2.00 -
310 5.00 -

[Pseudo]
2 1.2 1.32
opt

[Optinfo]
7.90 10
7.90 10

[Configs]
2
#
300 2.00 -
310 5.50 -
#
300 1.50 -
310 6.00 -

[KC]
gga 0.05 # lda[PZ] or gga[PBE]

[pcc]
1.05
llc

[Relativity]
sr1
```

Cl (PBE)

```
#####
# Opium Parameter File #
#####

[Atom]
H
1
100 1.00 -

[Pseudo]
1 0.8
opt

[Optinfo]
7.9 10

[Configs]
1
#
100 1.00 -

[KC]
gga 0.1

[Relativity]
sr1
```

H (PBE)

A. Representative input files

<pre>##### # Opium Parameter File # ##### [Atom] Ti # element # number of orbitals # reference configuration 100 2.00 -135.0 200 2.00 -19.4 210 6.00 -19.4 300 2.00 -13.0 310 6.00 -6.0 320 1.00 -6.0 400 0.00 -6.0 410 0.00 -6.0 [Pseudo] 5 1.54 1.70 1.82 1.54 1.70 opt [XC] lda [Cintnl] 7.970 10 # rc[a.u.] Qc[sqrt(Ry)] Nb 7.970 10 7.970 10 7.970 10 [Configs] # number of valence configurations 4 # 300 2.00 -1.4 # test configuration 310 6.00 -0.4 # test configuration 320 2.00 -0.4 # test configuration 400 0.00 -0.4 # test configuration 410 0.00 -0.4 # test configuration # 300 2.00 -1.4 # test configuration 310 6.00 -0.4 # test configuration 320 1.00 -0.4 # test configuration 400 1.00 -0.4 # test configuration 410 0.00 -0.4 # test configuration # 300 2.00 -1.4 # test configuration 310 6.00 -0.4 # test configuration 320 1.00 -0.4 # test configuration 400 2.00 -0.4 # test configuration 410 0.00 -0.4 # test configuration # 300 2.00 -1.4 # test configuration 320 2.00 -0.4 # test configuration 400 2.00 -0.4 # test configuration 410 0.00 -0.4 # test configuration [Relativity] sr</pre>	<pre>##### # Opium Parameter File # ##### [Atom] O 3 100 2.00 - 200 2.00 - 210 4.00 - [Pseudo] 2 1.4 1.5 opt [Cintnl] 7.9 10 7.9 10 [Configs] 4 # 200 2.00 - 210 4.20 - # 200 2.00 - 210 4.40 - # 200 2.00 - 210 4.60 - # 200 2.00 - 210 4.80 - [XC] lda [Relativity] sr</pre>
Ti ³⁺ (LDA)	O (LDA)

Figure A.1: The input files of the atomic species for the pseudo-potential generator OPIUM.

A.2 The input files used for NSCF of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ using QE

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='au',
  outdir='./out-au'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.812127237,
  nat= 1,
  ntyp= 1,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Au 1.0 Au_PBE.upf
ATOMIC_POSITIONS
Au 0.000000000 0.000000000 0.000000000
K_POINTS {automatic}
16 16 16 0 0 0
CELL_PARAMETERS
0.503243024 0.000000000 0.503243024
0.000000000 0.503243024 0.503243024
0.503243024 0.503243024 0.000000000
```

Au

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag',
  outdir='./out-ag'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 1,
  ntyp= 1,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
K_POINTS {automatic}
16 16 16 0 0 0
CELL_PARAMETERS
0.503218093 0.000000000 0.503218093
0.000000000 0.503218093 0.503218093
0.503218093 0.503218093 0.000000000
```

Ag

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='cu',
  outdir='./out-cu'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 6.93907383,
  nat= 1,
  ntyp= 1,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Cu 0.000000000 0.000000000 0.000000000
K_POINTS {automatic}
16 16 16 0 0 0
CELL_PARAMETERS
0.504112672 0.000000000 0.504112672
0.000000000 0.504112672 0.504112672
0.504112672 0.504112672 0.000000000
```

Cu

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag-au',
  outdir='./out-ag-au'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 2,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Au 0.501479254 -0.001735674 0.501479254
K_POINTS {automatic}
16 16 16 0 0 0
CELL_PARAMETERS
1.002958507 -0.003471348 1.002958507
0.000000000 0.499743580 0.499743580
0.499743580 0.499743580 0.000000000
```

AuAg

A.2 The input files used for NSCF of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ using QE

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='au-cu',
  outdir='./out-au-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.81212724,
  nat= 2,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Au 0.000000000 0.000000000 0.000000000
Cu 0.469348825 0.021695058 0.469348825
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.938697650 0.043390116 0.938697650
0.000000000 0.491043883 0.491043883
0.491043883 0.491043883 0.000000000
```

AuCu

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag-cu',
  outdir='./out-ag-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 2,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Cu 0.473156913 0.008646977 0.473156913
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.946313826 0.017293954 0.946313826
0.000000000 0.481803890 0.481803890
0.481803890 0.481803890 0.000000000
```

AgCu

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag-au3',
  outdir='./out-ag-au3'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 4,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Au 0.498373684 -0.000809087 0.502650952
Au -0.000809087 0.498373684 0.502650952
Au 0.497572797 0.497572797 1.005301903
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.996747369 -0.001601775 1.005301903
-0.001601775 0.996747369 1.005301903
0.497572797 0.497572797 0.000000000
```

Au₃Ag

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='au3-cu',
  outdir='./out-au3-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.81212724,
  nat= 4,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Au 0.000000000 0.000000000 0.000000000
Au 0.494092986 0.006440721 0.488717332
Au 0.006440721 0.494092986 0.488717332
Cu 0.500533707 0.500533707 0.977434665
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.988185972 0.012881442 0.977434665
0.012881442 0.988185972 0.977434665
0.500533707 0.500533707 0.000000000
```

Au₃Cu

A. Representative input files

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag3-au',
  outdir='./out-ag3-au'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 4,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Ag 0.500000000 0.000000000 0.503243013
Ag 0.000000000 0.500000000 0.503243013
Au 0.500120827 0.500120827 1.006486026
K_POINTS {automatic}
8 8 16 0 0 0
CELL_PARAMETERS
1.001600976 -0.001359321 1.006486026
-0.001359321 1.001600976 1.006486026
0.500120827 0.500120827 0.000000000
```

AuAg₃

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='au-cu3',
  outdir='./out-au-cu3'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.81212724,
  nat= 4,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Au 0.000000000 0.000000000 0.000000000
Cu 0.468404894 0.007235298 0.457730302
Cu 0.007235298 0.468404894 0.457730302
Cu 0.475640192 0.475640192 0.915460605
K_POINTS {automatic}
8 8 16 0 0 0
CELL_PARAMETERS
0.936809788 0.014470596 0.915460605
0.014470596 0.936809788 0.915460605
0.475640192 0.475640192 0.000000000
```

AuCu₃

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag3-cu',
  outdir='./out-ag3-cu'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 4,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Ag 0.492656462 0.001658124 0.487599485
Ag 0.001658124 0.492656462 0.487599485
Cu 0.494314586 0.494314586 0.975198970
K_POINTS {automatic}
8 8 16 0 0 0
CELL_PARAMETERS
0.905312925 0.003316247 0.975198970
0.003316247 0.905312925 0.975198970
0.494314586 0.494314586 0.000000000
```

Ag₃Cu

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag-cu3',
  outdir='./out-ag-cu3'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 4,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Cu 0.464227902 0.002966854 0.456924806
Cu 0.002966854 0.464227902 0.456924806
Cu 0.467194756 0.467194756 0.913849611
K_POINTS {automatic}
8 8 16 0 0 0
CELL_PARAMETERS
0.928455804 0.005933708 0.913849611
0.005933708 0.928455804 0.913849611
0.467194756 0.467194756 0.000000000
```

AgCu₃

A.2 The input files used for NSCF of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ using QE

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag-au2-cu',
  outdir='./out-ag-au2-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 4,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Au      0.000000000  0.000000000  0.000000000
Ag      0.492203171  0.001871223  0.488479130
Au      0.005393090  0.488681304  0.484943731
Cu      0.497596262  0.490552526  0.973422862
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.984406343  0.003742445  0.976958261
0.010786181  0.977362607  0.969887463
0.494074394  0.494074394  0.000000000
```

$(\text{AuAg}_2\text{Cu})_{\text{Phase1}}$

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag-au2-cu',
  outdir='./out-ag-au2-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 4,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag      0.000000000  0.000000000  0.000000000
Au      0.480847642  0.002989124  0.489062615
Au      0.002989124  0.488847642  0.489062615
Cu      0.491036766  0.491036766  0.978125231
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.976095284  0.005978248  0.978125231
0.005978248  0.976095284  0.978125231
0.491036766  0.491036766  0.000000000
```

$(\text{AuAg}_2\text{Cu})_{\text{Phase2}}$

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag-au2-cu',
  outdir='./out-ag-au2-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 4,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Au      0.000000000  0.000000000  0.000000000
Ag      0.480846058  0.002990101  0.489065583
Cu      0.002998191  0.488846058  0.489065583
Au      0.491044159  0.491044159  0.978131165
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.976092116  0.005996203  0.978131165
0.005996203  0.976092116  0.978131165
0.491044159  0.491044159  0.000000000
```

$(\text{AuAg}_2\text{Cu})_{\text{Phase3}}$

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag2-au-cu',
  outdir='./out-ag2-au-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 4,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag      0.000000000  0.000000000  0.000000000
Ag      0.480860239  0.003656152  0.482905066
Au      -0.001776872  0.494113263  0.488445346
Cu      0.486915367  0.497769415  0.971430412
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.977372479  0.007312304  0.965970131
-0.003541744  0.988226526  0.976890693
0.492342391  0.492342391  0.000000000
```

$(\text{Au}_2\text{AgCu})_{\text{Phase1}}$

A. Representative input files

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag2-au-cu',
  outdir='./out-ag2-au-cu'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  celldm(1)= 7.872598468,
  nat= 4,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Au      0.000000000  0.000000000  0.000000000
Ag      0.489231311  0.003767844  0.494090008
Ag      0.003767844  0.488231311  0.494090008
Cu      0.491999155  0.491999155  0.988180015
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.976462622  0.007535688  0.988180015
0.007535688  0.976462622  0.988180015
0.491999155  0.491999155  0.000000000
```

(Au₂AgCu)_{Phase2}

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag2-au-cu',
  outdir='./out-ag2-au-cu'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  celldm(1)= 7.872598468,
  nat= 4,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag      0.000000000  0.000000000  0.000000000
Au      0.488264331  0.003763890  0.494115729
Cu      0.003763890  0.488264331  0.494115729
Ag      0.492028221  0.492028221  0.988231458
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.976528662  0.007527779  0.988231458
0.007527779  0.976528662  0.988231458
0.492028221  0.492028221  0.000000000
```

(Au₂AgCu)_{Phase3}

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag-au-cu2',
  outdir='./out-ag-au-cu2'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  celldm(1)= 7.872598468,
  nat= 4,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Cu      0.000000000  0.000000000  0.000000000
Cu      0.482948263  0.000064722  0.487827821
Ag      0.015903156  0.467109829  0.472116414
Au      0.498851418  0.467174551  0.959944235
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.965896525  0.000129444  0.975655642
0.031806311  0.934219658  0.944232828
0.483012985  0.483012985  0.000000000
```

(AuAgCu₂)_{Phase1}

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag-au-cu2',
  outdir='./out-ag-au-cu2'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  celldm(1)= 7.872598468,
  nat= 4,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag      0.000000000  0.000000000  0.000000000
Cu      0.486350925 -0.000661314  0.452169471
Cu      -0.000661314  0.486350925  0.452169471
Au      0.485689611  0.485689611  0.904338941
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.972701849 -0.001322627  0.904338941
-0.001322627  0.972701849  0.904338941
0.485689611  0.485689611  0.000000000
```

(AuAgCu₂)_{Phase2}

A.2 The input files used for NSCF of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ using QE

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag-au-cu2',
  outdir='./out-ag-au-cu2',
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 4,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Cu 0.000000000 0.000000000 0.000000000
Ag 0.486361016 -0.000659307 0.452180262
Au -0.000659307 0.486361016 0.452180262
Cu 0.485701710 0.485701710 0.904360524
K_POINTS (automatic)
8 8 16 0 0 0
CELL_PARAMETERS
0.972722033 -0.001318614 0.904360524
-0.001318614 0.972722033 0.904360524
0.485701710 0.485701710 0.000000000
```

(AuAgCu₂)_{Phase3}

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag-au7',
  outdir='./out-ag-au7',
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 8,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
ATOMIC_POSITIONS
Au 0.000000000 0.000000000 0.000000000
Au 0.499666813 0.000000000 0.499666813
Au 0.000000000 0.499666813 0.499666813
Au 0.499666813 0.499666813 0.000000000
Au 0.499666813 0.999333627 0.499666813
Au 0.999333627 0.499666813 0.499666813
Au 0.499666813 0.499666813 0.999333627
Ag 0.999333627 0.999333627 0.999333627
K_POINTS (automatic)
8 8 0 0 0
CELL_PARAMETERS
0.999333627 0.000000000 0.999333627
0.000000000 0.999333627 0.999333627
0.999333627 0.999333627 0.000000000
```

Au₇Ag

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='au7-cu',
  outdir='./out-au7-cu',
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.81212724,
  nat= 8,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Cu 1.0 Cu_PBE.upf
Au 1.0 Au_PBE.upf
ATOMIC_POSITIONS
Au 0.000000000 0.000000000 0.000000000
Au 0.497883023 0.000000000 0.497883023
Au 0.000000000 0.497883023 0.497883023
Au 0.497883023 0.000000000 0.000000000
Au 0.497883023 0.995766047 0.497883023
Au 0.995766047 0.497883023 0.497883023
Au 0.497883023 0.497883023 0.995766047
Cu 0.995766047 0.995766047 0.995766047
K_POINTS (automatic)
8 8 0 0 0
CELL_PARAMETERS
0.995766047 0.000000000 0.995766047
0.000000000 0.995766047 0.995766047
0.995766047 0.995766047 0.000000000
```

Au₇Cu

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag7-au',
  outdir='./out-ag7-au',
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 8,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Ag 0.502331981 0.000000000 0.502331981
Ag 0.000000000 0.502331981 0.502331981
Ag 0.502331981 0.502331981 0.000000000
Ag 0.502331981 1.004663963 0.502331981
Ag 1.004663963 0.502331981 0.502331981
Ag 0.502331981 0.502331981 1.004663963
Au 1.004663963 1.004663963 1.004663963
K_POINTS (automatic)
8 8 0 0 0
CELL_PARAMETERS
1.004663963 0.000000000 1.004663963
0.000000000 1.004663963 1.004663963
1.004663963 1.004663963 0.000000000
```

AuAg₇

A. Representative input files

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='au-cu7',
  outdir='./out-au-cu7'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.81212724,
  nat= 8,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Cu 1.0 Cu_PBE.upf
Au 1.0 Au_PBE.upf
ATOMIC_POSITIONS
Cu      0.000000000    0.000000000    0.000000000
Cu      0.456503584    0.000000000    0.456503584
Cu      0.000000000    0.456503584    0.456503584
Cu      0.456503584    0.456503584    0.000000000
Cu      0.456503584    0.913007167    0.456503584
Cu      0.913007167    0.456503584    0.456503584
Cu      0.456503584    0.456503584    0.913007167
Au      0.913007167    0.913007167    0.913007167
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.913007167    0.000000000    0.913007167
0.000000000    0.913007167    0.913007167
0.913007167    0.913007167    0.000000000
```

AuCu₇

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag7-cu',
  outdir='./out-ag7-cu'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 8,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag      0.000000000    0.000000000    0.000000000
Ag      0.497153270    0.000000000    0.497153270
Ag      0.000000000    0.497153270    0.497153270
Ag      0.497153270    0.497153270    0.000000000
Ag      0.497153270    0.994306540    0.497153270
Ag      0.994306540    0.497153270    0.497153270
Ag      0.497153270    0.497153270    0.994306540
Cu      0.994306540    0.994306540    0.994306540
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.994306540    0.000000000    0.994306540
0.000000000    0.994306540    0.994306540
0.994306540    0.994306540    0.000000000
```

Ag₇Cu

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag-cu7',
  outdir='./out-ag-cu7'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 8,
  ntyp= 2,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Cu      0.000000000    0.000000000    0.000000000
Cu      0.453273191    0.000000000    0.453273191
Cu      0.000000000    0.453273191    0.453273191
Cu      0.453273191    0.453273191    0.000000000
Cu      0.453273191    0.906546381    0.453273191
Cu      0.906546381    0.453273191    0.453273191
Cu      0.453273191    0.453273191    0.906546381
Ag      0.906546381    0.906546381    0.906546381
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.906546381    0.000000000    0.906546381
0.000000000    0.906546381    0.906546381
0.906546381    0.906546381    0.000000000
```

AgCu₇

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag-au6-cu',
  outdir='./out-ag-au6-cu'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 8,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Au      0.000000000    0.000000000    0.000000000
Au      0.494143780    0.001238400    0.494812439
Au      0.001238400    0.494143780    0.494812439
Au      0.495382180    0.495382180    0.000000000
Au      0.496620580    0.989525960    0.494812439
Au      0.989525960    0.496620580    0.494812439
Ag      0.495382180    0.495382180    0.989624877
Cu      0.990764360    0.990764360    0.989624877
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.988287560    0.002476800    0.989624877
0.002476800    0.988287560    0.989624877
0.990764360    0.990764360    0.000000000
```

(Au₆AgCu)_{Phase1}

A.2 The input files used for NSCF of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ using QE

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag-au6-cu',
  outdir='./out-ag-au6-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  celldm(1)= 7.872598468,
  nat= 8,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Au 0.000000000 0.000000000 0.000000000
Au 0.495348010 0.000000000 0.495348010
Au 0.001198610 0.494787152 0.494149400
Au 0.494149400 0.494787152 0.001198610
Ag 0.495348010 0.989574304 0.495348010
Au 0.989497410 0.494787152 0.495348010
Au 0.495348010 0.494787152 0.989497410
Cu 0.990696020 0.989574304 0.990696020
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.990696020 0.000000000 0.990696020
0.002397220 0.989574304 0.988298799
0.988298799 0.989574304 0.002397220
```

$(\text{Au}_6\text{AgCu})_{\text{Phase2}}$

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag-au6-cu',
  outdir='./out-ag-au6-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  celldm(1)= 7.872598468,
  nat= 8,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Au 0.000000000 0.000000000 0.000000000
Au 0.494212207 0.001049649 0.494732628
Au -0.001049649 0.494212207 0.494732628
Ag 0.493162557 0.493162557 0.000000000
Au 0.492112908 0.987374764 0.494732628
Au 0.987374764 0.492112908 0.494732628
Au 0.493162557 0.493162557 0.989465257
Cu 0.986325115 0.986325115 0.989465257
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.988424414 -0.002099299 0.989465257
-0.002099299 0.988424414 0.989465257
0.986325115 0.986325115 0.000000000
```

$(\text{Au}_6\text{AgCu})_{\text{Phase3}}$

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag-au6-cu',
  outdir='./out-ag-au6-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  celldm(1)= 7.872598468,
  nat= 8,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Au 0.493908611 0.000000000 0.493908611
Au 0.000000000 0.493908611 0.493908611
Au 0.493908611 0.493908611 0.000000000
Au 0.493908611 0.987817222 0.493908611
Au 0.987817222 0.493908611 0.493908611
Au 0.493908611 0.493908611 0.987817222
Cu 0.987817222 0.987817222 0.987817222
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.987817222 0.000000000 0.987817222
0.000000000 0.987817222 0.987817222
0.987817222 0.987817222 0.000000000
```

$(\text{Au}_6\text{AgCu})_{\text{Phase4}}$

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE.,
  prefix='ag6-au-cu',
  outdir='./out-ag6-au-cu'
  etot_conv_thr= 1.0D-7,
  forc_conv_thr= 1.0D-6,
/
&system
 ibrav= 0,
  celldm(1)= 7.872598468,
  nat= 8,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Ag 0.495730075 0.001268416 0.497608015
Ag -0.001268416 0.495730075 0.497608015
Ag 0.494461659 0.494461659 0.000000000
Ag 0.493193244 0.990191734 0.497608015
Ag 0.990191734 0.493193244 0.497608015
Au 0.494461659 0.494461659 0.995216031
Cu 0.988923318 0.988923318 0.995216031
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.991460149 -0.002536831 0.995216031
-0.002536831 0.991460149 0.995216031
0.988923318 0.988923318 0.000000000
```

$(\text{AuAg}_6\text{Cu})_{\text{Phase1}}$

A. Representative input files

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag6-au-cu',
  outdir='./out-ag6-au-cu'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 8,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Ag 0.494436570 0.000000000 0.494436570
Ag -0.001268418 0.497594568 0.495704988
Ag 0.495704988 0.497594568 -0.001268418
Au 0.494436570 0.995189135 0.494436570
Au 0.990141558 0.497594568 0.493168152
Ag 0.493168152 0.497594568 0.990141558
Cu 0.988873140 0.995189135 0.988873140
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.988873140 0.000000000 0.988873140
-0.002536836 0.995189135 0.991409976
0.991409976 0.995189135 -0.002536836
```

(AuAg₆Cu)_{Phase2}

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag6-au-cu',
  outdir='./out-ag6-au-cu'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 8,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Ag 0.000000000 0.000000000 0.000000000
Ag 0.495674138 0.001319249 0.497681061
Ag 0.001319249 0.495674138 0.497681061
Au 0.496993388 0.496993388 0.000000000
Ag 0.498312637 0.992667526 0.497681061
Ag 0.992667526 0.498312637 0.497681061
Ag 0.496993388 0.496993388 0.995362121
Cu 0.993986775 0.993986775 0.995362121
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.991348277 0.002638499 0.995362121
0.002638499 0.991348277 0.995362121
0.993986775 0.993986775 0.000000000
```

(AuAg₆Cu)_{Phase3}

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag6-au-cu',
  outdir='./out-ag6-au-cu'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 8,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Au 0.000000000 0.000000000 0.000000000
Ag 0.496728918 0.000000000 0.496728918
Ag 0.000000000 0.496728918 0.496728918
Ag 0.496728918 0.496728918 0.000000000
Ag 0.496728918 0.993457837 0.496728918
Ag 0.993457837 0.496728918 0.496728918
Ag 0.496728918 0.496728918 0.993457837
Cu 0.993457837 0.993457837 0.993457837
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.993457837 0.000000000 0.993457837
0.000000000 0.993457837 0.993457837
0.993457837 0.993457837 0.000000000
```

(AuAg₆Cu)_{Phase4}

```
&control
  calculation= 'nscf',
  restart_mode= 'from_scratch',
  verbosity='high',
  wf_collect=.TRUE. ,
  prefix='ag-au-cu6',
  outdir='./out-ag-au-cu6'
  etot_conv_thr= 1.00-7,
  forc_conv_thr= 1.00-6,
/
&system
 ibrav= 0,
  cellldm(1)= 7.872598468,
  nat= 8,
  ntyp= 3,
  nosym=.TRUE.,
  ecutwfc= 50,
  occupations='smearing',
  smearing= 'mv',
  degauss= 0.007349862,
  nbnd=100,
/
&electrons
/
ATOMIC_SPECIES
Ag 1.0 Ag_PBE.upf
Au 1.0 Au_PBE.upf
Cu 1.0 Cu_PBE.upf
ATOMIC_POSITIONS
Cu 0.000000000 0.000000000 0.000000000
Cu 0.465349627 0.005454761 0.453675386
Cu 0.005454761 0.465349627 0.453675386
Cu 0.470803788 0.470803788 0.000000000
Cu 0.476258550 0.936152815 0.453675386
Cu 0.936152815 0.476258550 0.453675386
Au 0.470803788 0.470803788 0.907350773
Ag 0.941607577 0.941607577 0.907350773
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
0.930698054 0.010909523 0.907350773
0.010909523 0.930698054 0.907350773
0.941607577 0.941607577 0.000000000
```

(AuAgCu₆)_{Phase1}

A.2 The input files used for NSCF of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ using QE

<pre> &control calculation= 'nscf', restart_mode= 'from_scratch', verbosity='high', wf_collect=.TRUE., prefix='ag-au-cu6', outdir='./out-ag-au-cu6', etot_conv_thr= 1.0D-7, forc_conv_thr= 1.0D-6, / &system ibrav= 0, celldm(1)= 7.872598468, nat= 8, ntyp= 3, nosym=.TRUE., ecutwfc= 50, occupations='smearing', smearing= 'mv', degauss= 0.007349862, nbnd=100, / &electrons / ATOMIC_SPECIES Ag 1.0 Ag_PBE.upf Au 1.0 Au_PBE.upf Cu 1.0 Cu_PBE.upf ATOMIC_POSITIONS Cu 0.000000000 0.000000000 0.000000000 Cu 0.470798783 0.000000000 0.470798783 Cu 0.005451852 0.453661854 0.465346932 Cu 0.465346932 0.453661854 0.005451852 Au 0.470798783 0.907323708 0.470798783 Cu 0.936145715 0.453661854 0.476250635 Cu 0.476250635 0.453661854 0.936145715 Ag 0.941597567 0.907323708 0.941597567 K_POINTS (automatic) 8 8 8 0 0 0 CELL_PARAMETERS 0.941597567 0.000000000 0.941597567 0.010903703 0.907323708 0.930693864 0.930693864 0.907323708 0.010903703 </pre>	<pre> &control calculation= 'nscf', restart_mode= 'from_scratch', verbosity='high', wf_collect=.TRUE., prefix='ag-au-cu6', pseudo_dir = '/home/users/orhano/pseudopots/yambo', outdir='./out-ag-au-cu6', etot_conv_thr= 1.0D-7, forc_conv_thr= 1.0D-6, / &system ibrav= 0, celldm(1)= 7.872598468, nat= 8, ntyp= 3, nosym=.TRUE., ecutwfc= 50, occupations='smearing', smearing= 'mv', degauss= 0.007349862, nbnd=100, / &electrons / ATOMIC_SPECIES Ag 1.0 Ag_DAVID.upf Au 1.0 Au_DAVID.upf Cu 1.0 Cu_DAVID.upf ATOMIC_POSITIONS Cu 0.000000000 0.000000000 0.000000000 Cu 0.465350512 -0.005451601 0.453672826 Cu -0.005451601 0.465350512 0.453672826 Au 0.459898911 0.459898911 0.000000000 Cu 0.454447310 0.925249423 0.453672826 Cu 0.925249423 0.454447310 0.453672826 Cu 0.459898911 0.459898911 0.907345652 Ag 0.919797822 0.919797822 0.907345652 K_POINTS (automatic) 8 8 8 0 0 0 CELL_PARAMETERS 0.930701024 -0.010903202 0.907345652 -0.010903202 0.930701024 0.907345652 0.919797822 0.919797822 0.000000000 </pre>
--	--

(AuAgCu₆)Phase2

(AuAgCu₆)Phase3

<pre> &control calculation= 'nscf', restart_mode= 'from_scratch', verbosity='high', wf_collect=.TRUE., prefix='ag-au-cu6', outdir='./out-ag-au-cu6', etot_conv_thr= 1.0D-7, forc_conv_thr= 1.0D-6, / &system ibrav= 0, celldm(1)= 7.872598468, nat= 8, ntyp= 3, nosym=.TRUE., ecutwfc= 50, occupations='smearing', smearing= 'mv', degauss= 0.007349862, nbnd=100, / &electrons / ATOMIC_SPECIES Ag 1.0 Ag_PBE.upf Au 1.0 Au_PBE.upf Cu 1.0 Cu_PBE.upf ATOMIC_POSITIONS Au 0.000000000 0.000000000 0.000000000 Cu 0.460234695 0.000000000 0.460234695 Cu 0.000000000 0.460234695 0.460234695 Cu 0.460234695 0.460234695 0.000000000 Cu 0.460234695 0.920469389 0.460234695 Cu 0.920469389 0.460234695 0.460234695 Cu 0.460234695 0.460234695 0.920469389 Ag 0.920469389 0.920469389 0.920469389 K_POINTS (automatic) 8 8 8 0 0 0 CELL_PARAMETERS 0.920469389 0.000000000 0.920469389 0.000000000 0.920469389 0.920469389 0.920469389 0.920469389 0.000000000 </pre>
--

(AuAgCu₆)Phase4

Figure A.2: Input files for QE, NSCF levels of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ showing the final geometries.

A.3 The ONETEP input files

```

----- INPUT FILE -----
task      : SINGLEPOINT / COND / LR_TDDFT

lr_dddft_num_states : 50
lr_dddft_rpa : F
lr_dddft_restart : T
lr_dddft_restart_from_tda : F
lr_dddft_reset_cg : 10
lr_dddft_maxit_cg : 150
lr_dddft_maxit_pen : 50
lr_dddft_write_densities : T
lr_dddft_write_kernels : T
lr_dddft_init_random : F
lr_dddft_homo_num : 24
lr_dddft_lumo_num : 10

spin_polarized : F
spin : 0
xc_functional : PBE
charge : 0

pbe_correction_cutoff : 7.0

do_properties : T
initial_dens_realspace : T

write_denskernel : T
write_tightbox_ngwfs : T
read_denskernel : T
read_tightbox_ngwfs : T

ngwf_threshold_orig : 2.0e-7
elec_energy_tol : 1.0e-6

%block hubbard
Ni 2 10.0 0.0 -1.0 0.0 0.0
%endblock hubbard

cutoff_energy : 1200 eV

%block species_ngwf_plot
Ni
C
O
%endblock species_ngwf_plot

%block species
bohr
Ni Ni 28 9 12.00
C C 6 4 12.00
N N 7 4 12.00
%endblock species

%block species_cond
bohr
Ni Ni 28 18 12.00
C C 6 8 12.00
N N 7 8 12.00
%endblock species_cond

%block species_atomic_set
Ni "SOLVE"
C "SOLVE"
N "SOLVE"
%endblock species_atomic_set

%block species_pot
Ni "Ni_PBE.recpot"
C "C_PBE.recpot"

```

Input files of $\text{Ni}(\text{CN})_4^{-2}$ for single-point, conduction (extra lines highlighted with blue), and TDA (extra lines highlighted with red) calculations.


```

----- INPUT FILE -----
task      : SINGLEPOINT / COND / LR_TDDFT

lr_tddft_num_states : 50
lr_tddft_rpa : F
lr_tddft_restart : T
lr_tddft_restart_from_tda : F
lr_tddft_reset_cg : 10
lr_tddft_maxit_cg : 150
lr_tddft_maxit_pen : 50
lr_tddft_write_densities : T
lr_tddft_write_kernels : T
lr_tddft_init_random : F
lr_tddft_homo_num : 25
lr_tddft_lumo_num : 10

spin_polarized : F
spin : 0
xc_functional : PBE
charge : 0

pbc_correction_cutoff : 7.0

do_properties : T
initial_dens_realspace : T

write_dens_kern : T
write_tightbox_ngwfs : T
read_dens_kern : T
read_tightbox_ngwfs : T

ngwf_threshold_orig : 2.0e-7
elec_energy_tol : 1.0e-6

%block hubbard
Ni 2 10.0 0.0 -1.0 0.0 0.0
%endblock hubbard

cutoff_energy : 1200 eV

%block species_ngwf_plot
Ni
C
O
%endblock species_ngwf_plot

%block species
bohr
Ni Ni 28 9 12.00
C C 6 4 12.00
O O 8 4 12.00
%endblock species

%block species_cond
bohr
Ni Ni 28 18 12.00
C C 6 8 12.00
O O 8 8 12.00
%endblock species_cond

%block species_atomic_set
Ni "SOLVE"
C "SOLVE"
O "SOLVE"

```

Input files of Ni(CO)₄ for single-point, conduction (extra lines highlighted with blue), and TDA (extra lines highlighted with red) calculations.

A. Representative input files

```

----- INPUT FILE -----
task      : SINGLEPOINT / COND / LR_TDDFT

lr_tddft_num_states : 20
lr_tddft_rpa : F
lr_tddft_restart : T
lr_tddft_restart_from_tda : F
lr_tddft_maxit_cg : 150
lr_tddft_maxit_pen : 50
lr_tddft_write_densities : T
lr_tddft_write_kernels : T

spin_polarized : T
spin : 3
xc_functional : PBE
charge : 0

pbc_correction_cutoff : 7.0

do_properties : T
initial_dens_realspace : T

write_denskem : T
write_tightbox_ngwfs : T
read_denskem : T
read_tightbox_ngwfs : T

ngwf_threshold_orig : 2.0e-7
elec_energy_tol : 1.0e-6

%block hubbard
Co 2 3 79781 0.0 -20.0 0.0 0.0
%endblock hubbard

cutoff_energy : 1200 eV

%block species_ngwf_plot
Co
Cl
N
C
H
%endblock species_ngwf_plot

%block species
bohr
Co Co 27 9 12.00
Cl Cl 17 4 12.00
N N 7 4 12.00
C C 6 4 12.00
H H 1 1 12.00
%endblock species

%block species_cond
bohr
Co Co 27 18 12.00
Cl Cl 17 13 12.00
N N 7 8 12.00
C C 6 8 12.00
H H 1 2 12.00
%endblock species_cond

cond_num_states : 11
cond_num_extra_states : 11
cond_num_extra_its : 10
cond_maxit_lnv : 100
cond_minit_lnv : 5

%block species_atomic_set
Co "SOLVE conf=4s0 3d7 4d0 4fX 5s0 5p0 INIT SPIN=+3
CHARGE=0"
Cl "SOLVE"
N "SOLVE"
C "SOLVE"
H "SOLVE"
%endblock species_atomic_set

%block species_pot
Co "Co_PBE_2PLUS.recpot"
Cl "Cl_PBE.recpot"
N "N_PBE.recpot"
C "C_PBE.recpot"
H "H_PBE.recpot"
%endblock species_pot

%block lattice_cart
bohr
67.05477 0.00 0.00
0.00 67.23636 0.00
0.00 0.00 83.20274
%endblock lattice_cart

%block positions_abs
bohr
Co 33.52738000000000 33.6181800000000 41.60136500000000
Cl 36.7483782640047 35.8415560096178 40.0032879817863
Cl 30.3063817359953 35.8415560096178 43.1994420182137
C 36.2467467207727 32.3348236171724 46.3868333952300
C 35.6433458741291 28.8641075123512 48.8684196742588
C 34.1094817450216 27.7649446113974 47.0798129229302
C 33.6530033145708 29.1320460911536 44.9389291219102
C 30.8080132792273 32.3348236171724 36.8158966047700
C 33.4017566854292 29.1320460911536 38.2638027678158
C 32.9452782549784 27.7649446113974 36.1229189667958
C 31.4114141258709 28.8641075123512 34.3343103257412
N 34.6888792921530 31.4300700567889 44.5478578873906
N 37.2946319070150 34.5904780364083 46.0799211076306
N 36.7124318962420 31.1147768344282 48.5696407673160
N 32.3658788181210 31.4300700567889 38.6548740023354
N 30.3423262140320 31.1147768344282 34.6330892326840
N 29.7601280929850 34.5904780364083 37.1228107820954
H 35.9491337747651 28.0553123479632 50.4020494773437
H 32.4902794799769 28.4665639663193 43.5723681037869
H 33.5185644282613 26.2233741797068 35.9073598129565
H 31.1056262252349 28.0553123479632 32.8006824123823
H 28.7636906967932 35.2086017382322 35.9699286404523
H 29.7910383409871 35.3955353227901 38.5478758271122
H 38.2910693032068 35.2086017382322 47.2328032492737
H 37.2637197692870 35.3955353227901 44.6548541728878
H 33.5361936820127 26.2233741797068 47.2953720767695
H 34.5644805200231 28.4665639663193 39.6303637859391
%endblock positions_abs

```

Input files of CoL_2Cl_2 for single-point, conduction (extra lines highlighted with blue), and TDA (extra lines highlighted with red) calculations.

Appendix B

Supplementary information on $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys

B.1 Stretching operators

System	s_c	s_v	System	s_c	s_v
Au	0.825253	1.419797	Au_7Ag	0.967842	1.218996
Ag	0.846172	1.376302	Au_7Cu	0.959605	1.277749
Cu	0.809883	1.735804	AuAg_7	0.972795	1.072632
AuAg	0.942895	1.245925	AuCu_7	0.937301	1.459205
AuCu	0.921209	1.451945	Ag_7Cu	0.966574	1.138571
AgCu	0.921900	1.382942	AgCu_7	0.932309	1.414183
Au_3Ag	0.945233	1.197529	Au_6AgCu (p1)	0.961430	1.272030
Au_3Cu	0.936102	1.329064	Au_6AgCu (p2)	0.961097	1.26530
AuAg_3	0.951899	1.105431	Au_6AgCu (p3)	0.961277	1.266095
AuCu_3	0.922466	1.454606	Au_6AgCu (p4)	0.959646	1.268756
Ag_3Cu	0.945817	1.215392	AuAg_6Cu (p1)	0.965500	1.168711
AgCu_3	0.935669	1.382684	AuAg_6Cu (p2)	0.965551	1.177290
Au_2AgCu (p1)	0.936355	1.302908	AuAg_6Cu (p3)	0.974523	1.185852
Au_2AgCu (p2)	0.931013	1.311556	AuAg_6Cu (p4)	0.965523	1.174112
Au_2AgCu (p3)	0.930925	1.311619	AuAgCu_6 (p1)	0.936233	1.404183
AuAg_2Cu (p1)	0.938311	1.272339	AuAgCu_6 (p2)	0.943095	1.399728
AuAg_2Cu (p2)	0.934446	1.261742	AuAgCu_6 (p3)	0.936821	1.403408
AuAg_2Cu (p3)	0.934076	1.261342	AuAgCu_6 (p4)	0.943707	1.407826
AuAgCu_2 (p1)	0.933284	1.382637			
AuAgCu_2 (p2)	0.936700	1.371520			
AuAgCu_2 (p3)	0.936793	1.372440			

Table B.1: First-principles G_0W_0 stretching operators for conduction and valence bands of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$.

B.2 Drude parameters

System	ω_p	η	ε_∞	System	ω_p	η	ε_∞
Au	8.947	0.02266	1.601	Au ₇ Ag	8.793	0.01992	1.073
Ag	8.925	0.01918	-2.624	Au ₇ Cu	8.708	0.01991	1.414
Cu	9.313	0.02426	0.1039	AuAg ₇	8.735	0.01748	-2.096
AuAg	10.36	0.02392	-0.5116	AuCu ₇	8.61	0.02041	0.291
AuCu	10.91	0.0252	0.8523	Ag ₇ Cu	8.918	0.01835	-2.283
AgCu	10.32	0.02466	-1.26	AgCu ₇	8.896	0.02108	-0.2371
Au ₃ Ag	12.8	0.0278	0.5446	Au ₆ AgCu (p1)	8.666	0.01969	0.8855
Au ₃ Cu	12.99	0.03062	1.227	Au ₆ AgCu (p2)	8.655	0.01963	0.8855
AuAg ₃	12.45	0.02519	-1.568	Au ₆ AgCu (p3)	8.634	0.01952	0.8855
AuCu ₃	12.41	0.02934	0.4781	Au ₆ AgCu (p4)	8.087	0.01788	0.8855
Ag ₃ Cu	12.58	0.02697	-1.942	AuAg ₆ Cu (p1)	8.571	0.01822	-1.755
AgCu ₃	12.51	0.02997	-0.5781	AuAg ₆ Cu (p2)	8.585	0.01828	-1.755
Au ₂ AgCu (p1)	12.64	0.02888	0.1703	AuAg ₆ Cu (p3)	8.614	0.01838	-1.755
Au ₂ AgCu (p2)	12.26	0.02872	0.1703	AuAg ₆ Cu (p4)	8.896	0.0184	-1.755
Au ₂ AgCu (p3)	12.26	0.02872	0.1703	AuAgCu ₆ (p1)	8.437	0.01975	-0.05001
AuAg ₂ Cu (p1)	11.97	0.02676	-0.8858	AuAgCu ₆ (p2)	8.445	0.01979	-0.05001
AuAg ₂ Cu (p2)	12.93	0.02774	-0.8858	AuAgCu ₆ (p3)	8.338	0.01949	-0.05001
AuAg ₂ Cu (p3)	12.92	0.02773	-0.8858	AuAgCu ₆ (p4)	8.246	0.01945	-0.05001
AuAgCu ₂ (p1)	12.84	0.02931	-0.2039				
AuAgCu ₂ (p2)	11.72	0.02738	-0.2039				
AuAgCu ₂ (p3)	11.73	0.02739	-0.2039				

Table B.2: Drude parameters for Au_xAg_yCu_{1-x-y}.

B.3 Dielectric functions of binary alloys

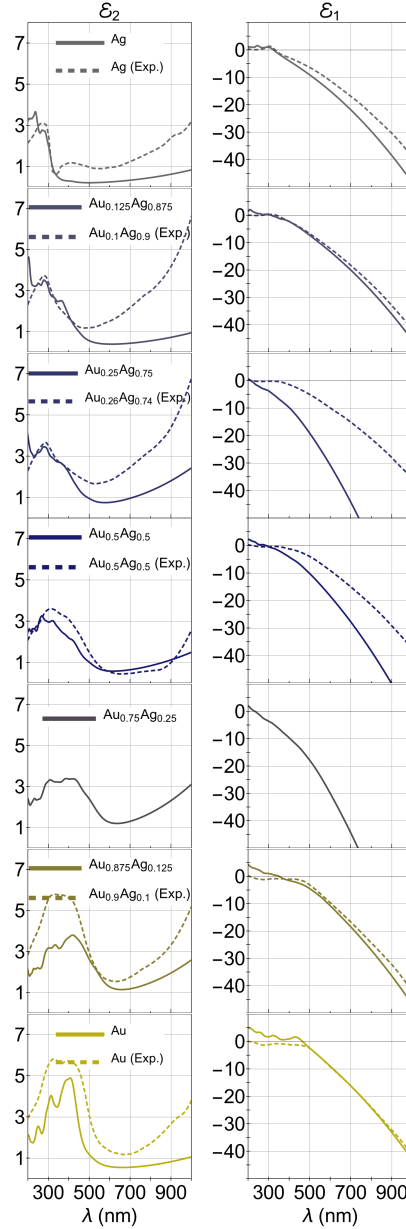


Figure B.1: Bulk ϵ_2 (first column), and ϵ_1 (second column) from first-principles bulk dielectric functions (solid lines) and experimental SPP measurements on thin-films (dashed lines) of Au-Ag binary alloys with similar stoichiometric ratios extracted from Ref. 1.

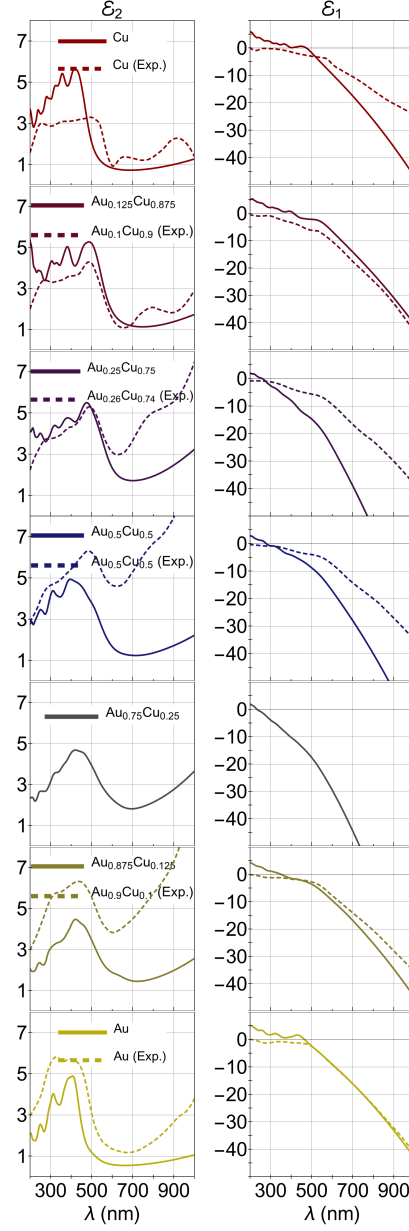


Figure B.2: Bulk ϵ_2 (first column), and ϵ_1 (second column) from first-principles bulk dielectric functions (solid lines) and experimental SPP measurements on thin-films (dashed lines) of Au-Cu binary alloys with similar stoichiometric ratios extracted from Ref. 1.

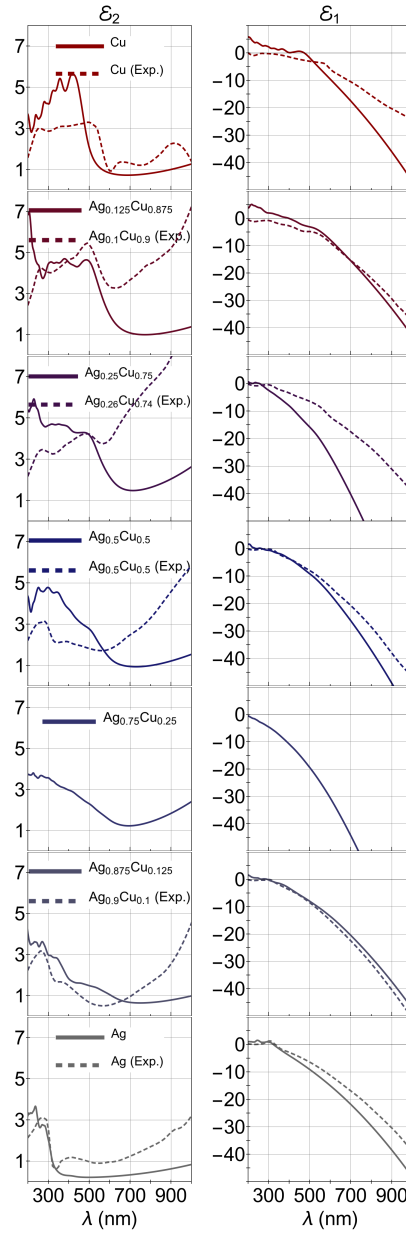
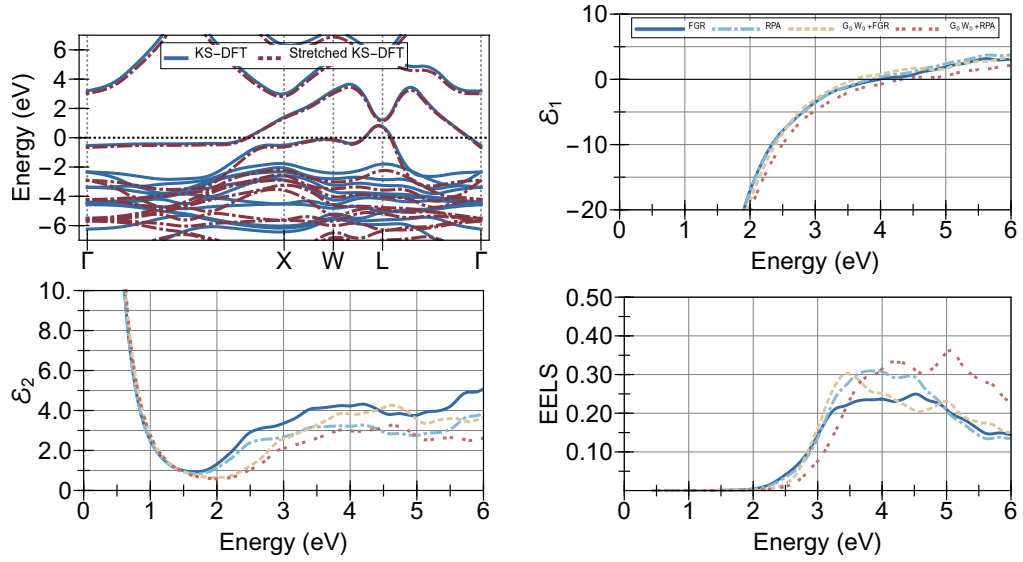
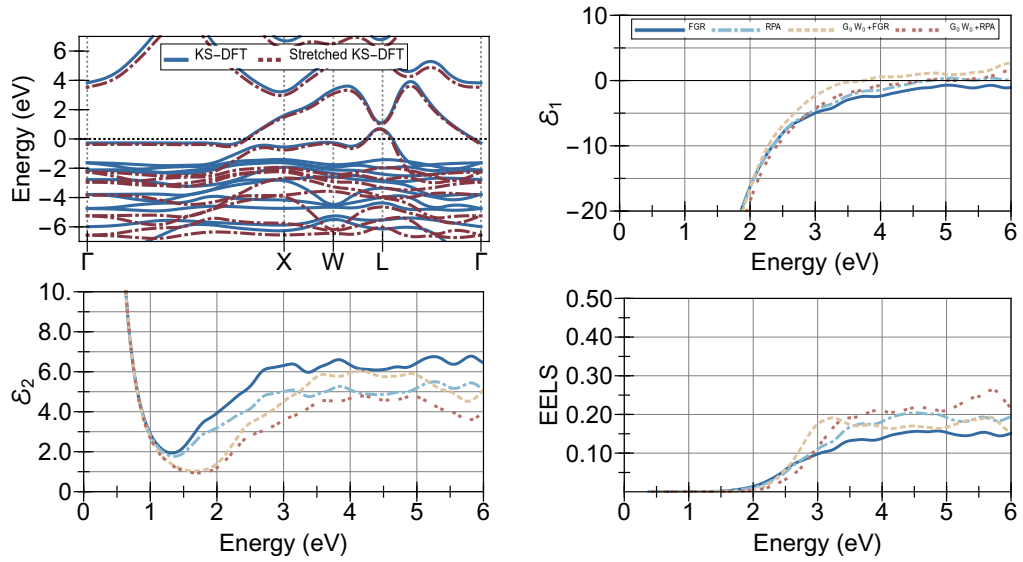


Figure B.3: Bulk ϵ_2 (first column), and ϵ_1 (second column) from first-principles bulk dielectric functions (solid lines) and experimental SPP measurements on thin-films (dashed lines) of Ag-Cu binary alloys with similar stoichiometric ratios extracted from Ref. 1.

B.4 Band-structure and spectra of alloys

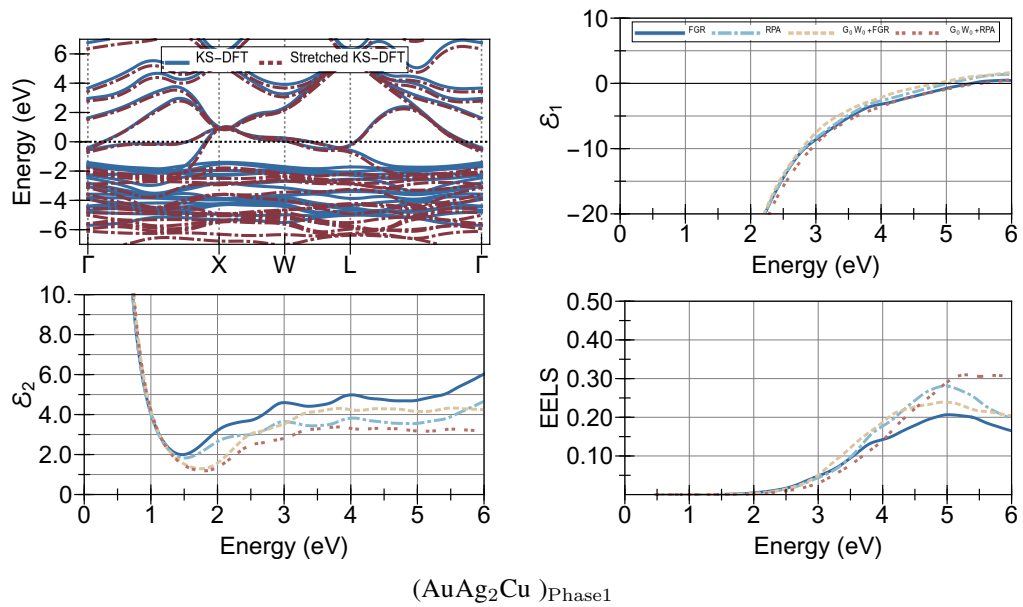
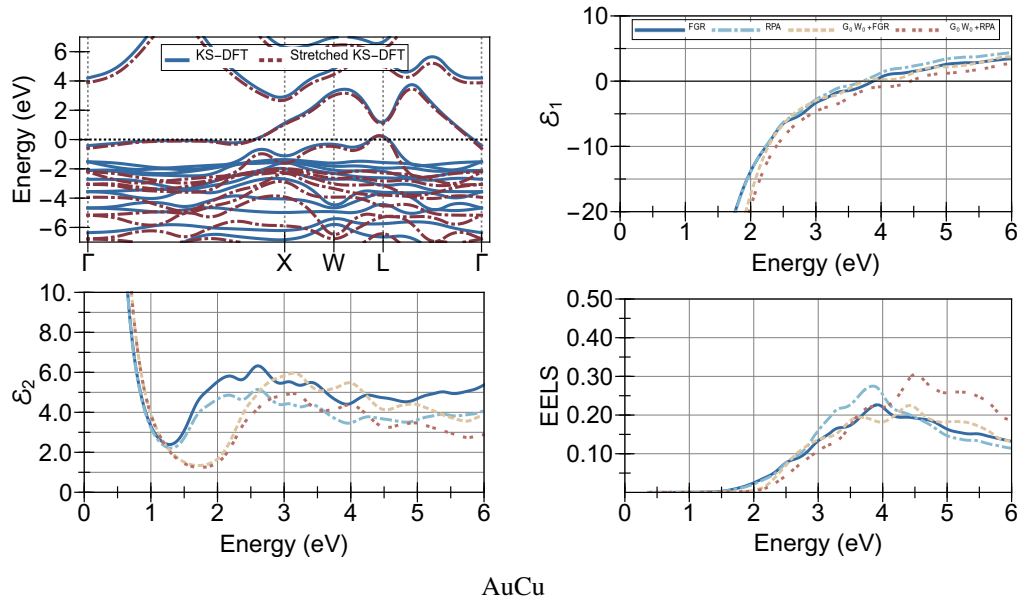


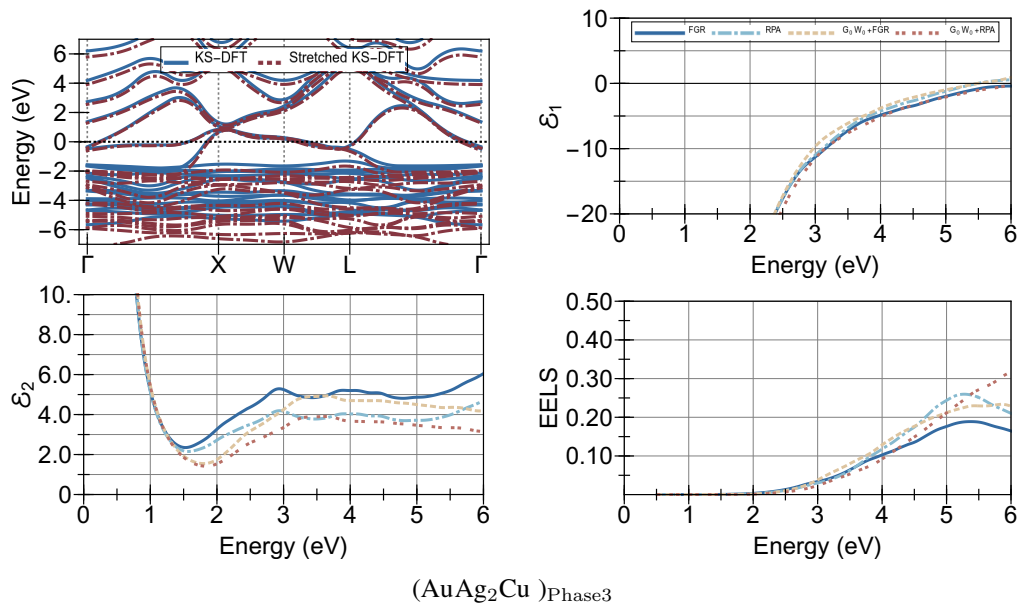
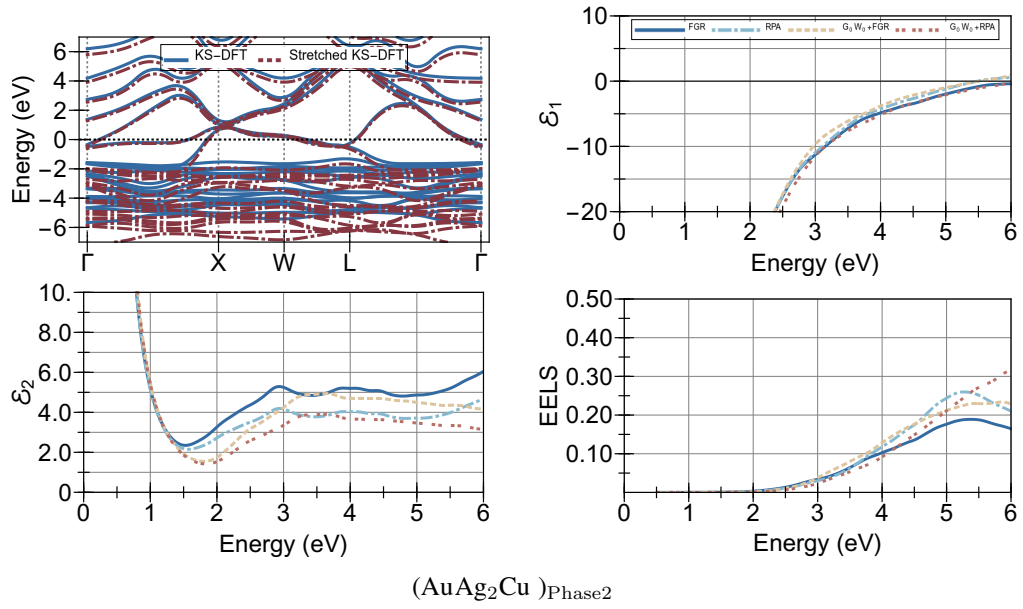
AuAg



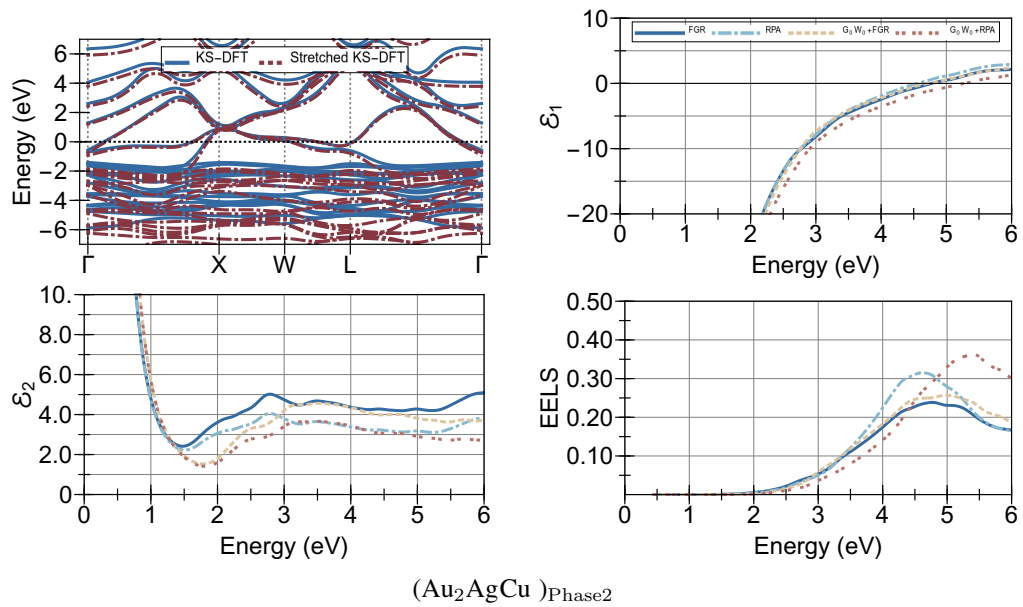
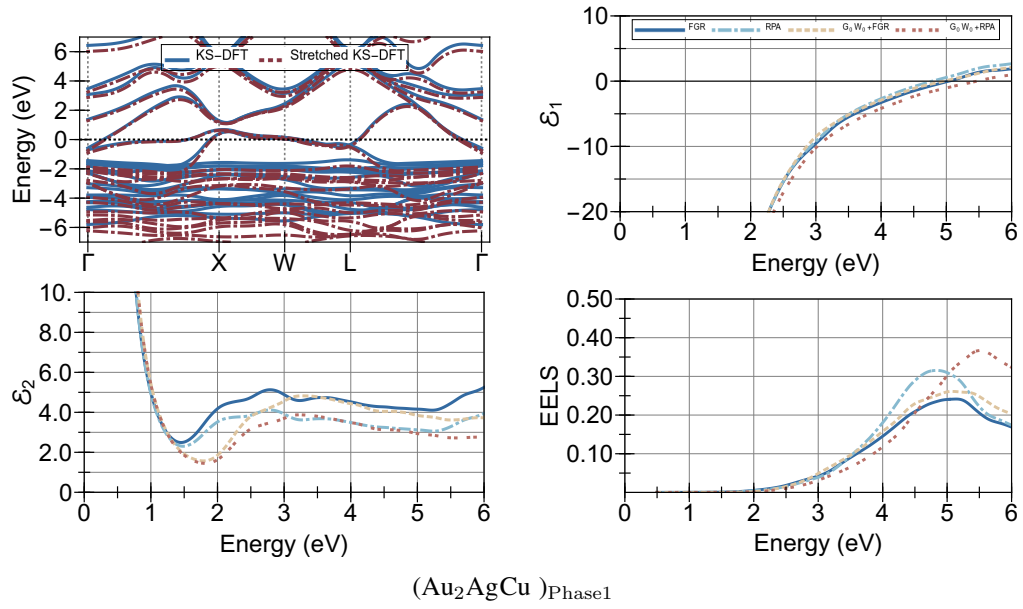
AgCu

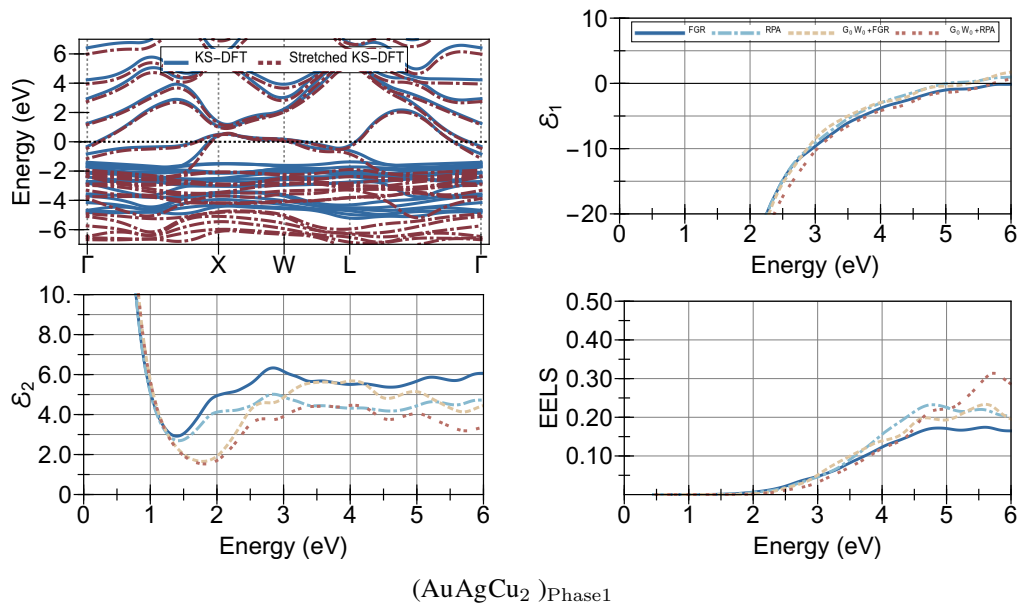
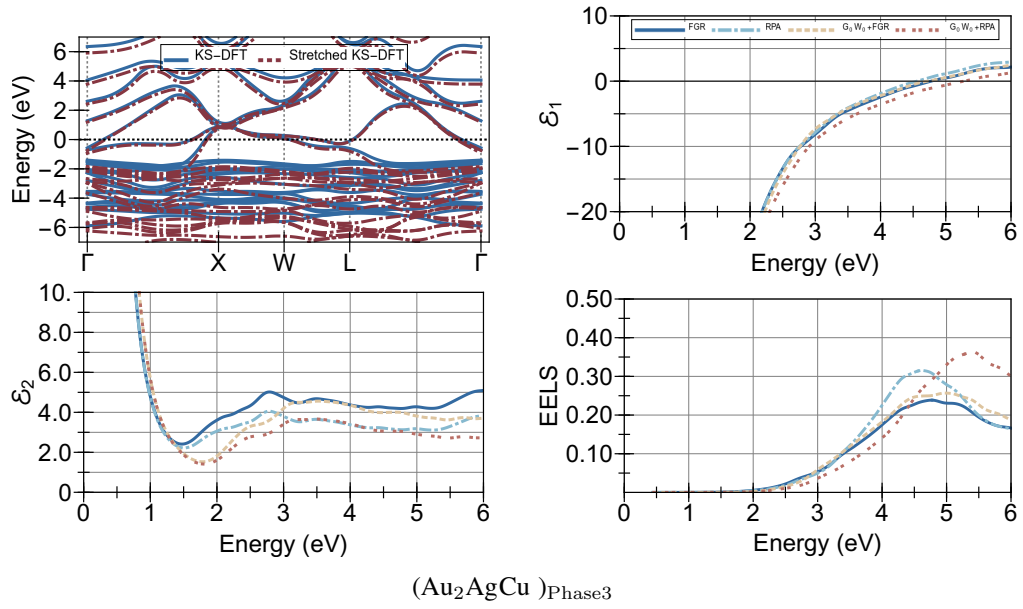
B. Supplementary information on $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys



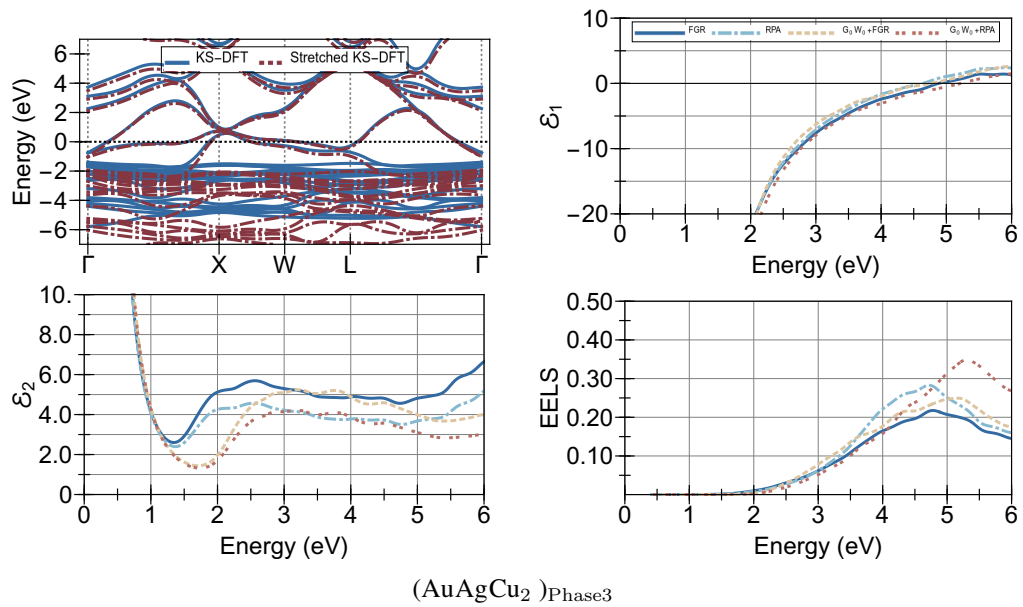
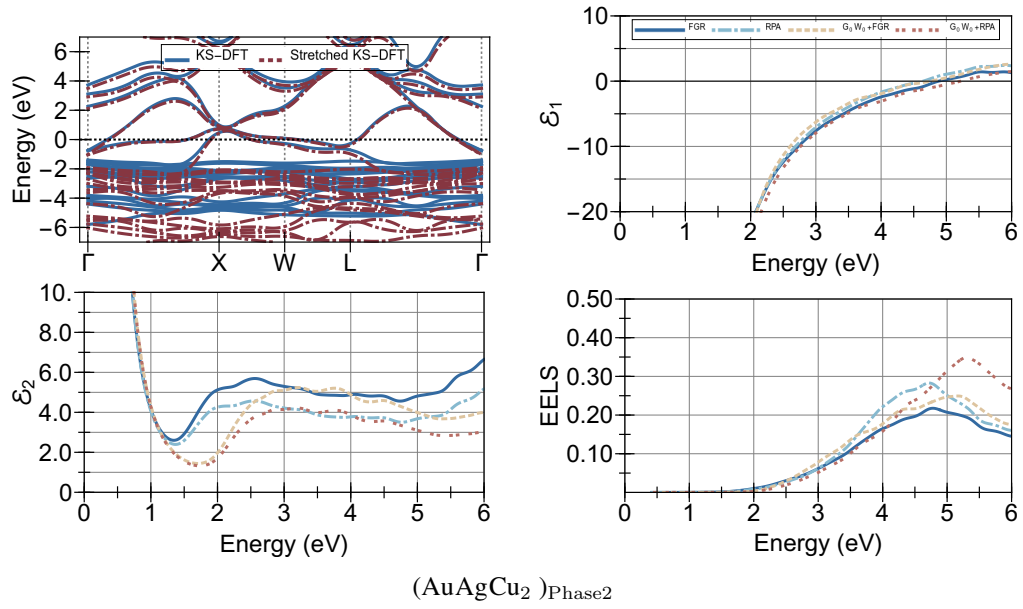


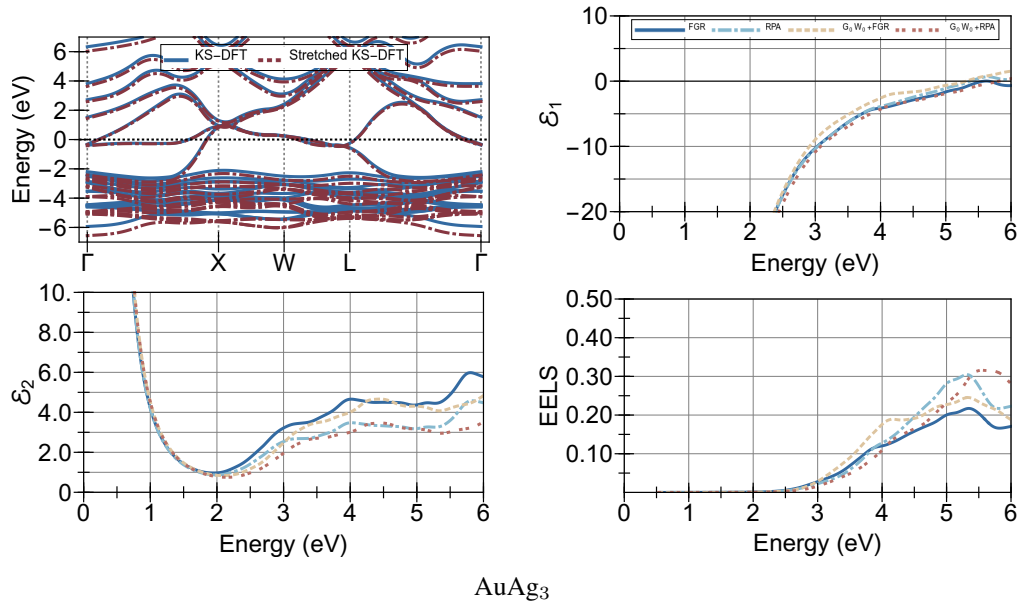
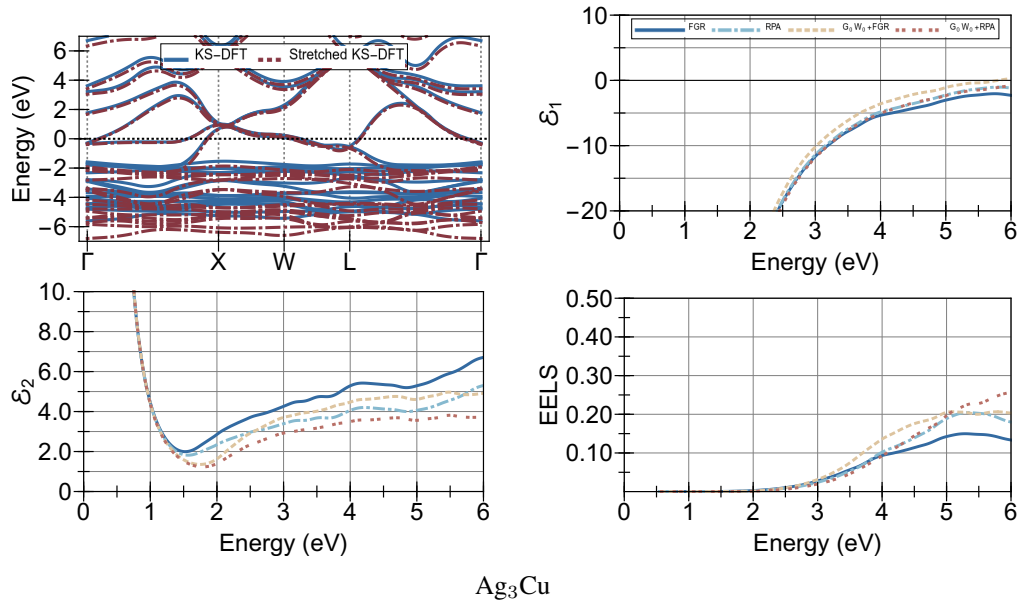
B. Supplementary information on $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys



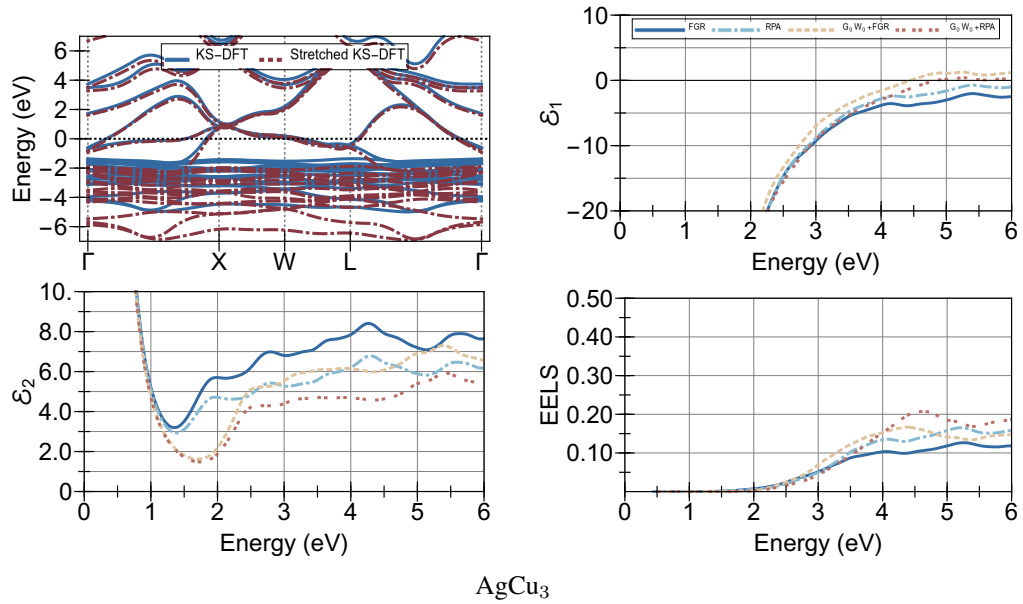
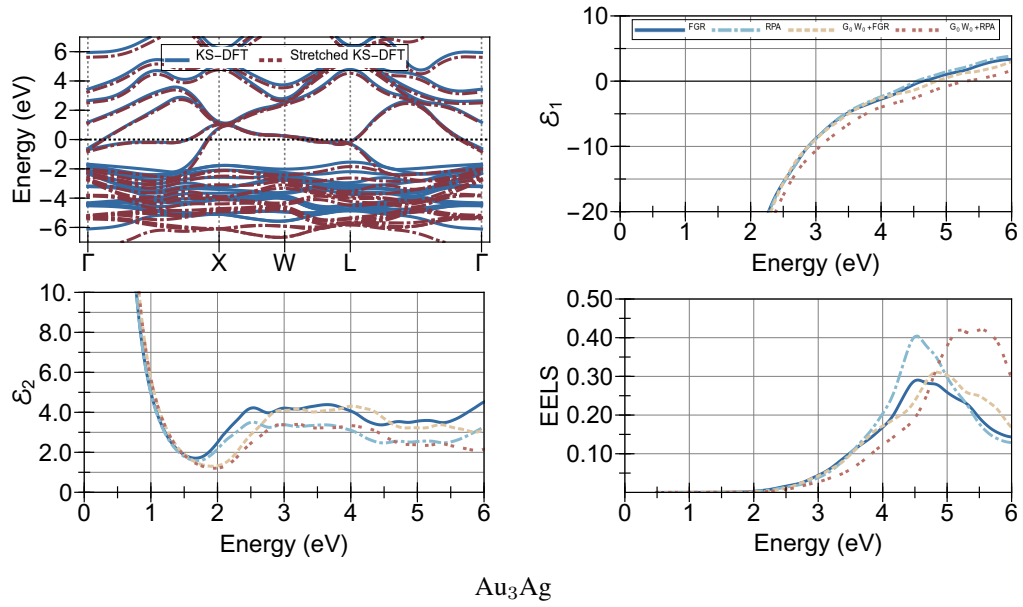


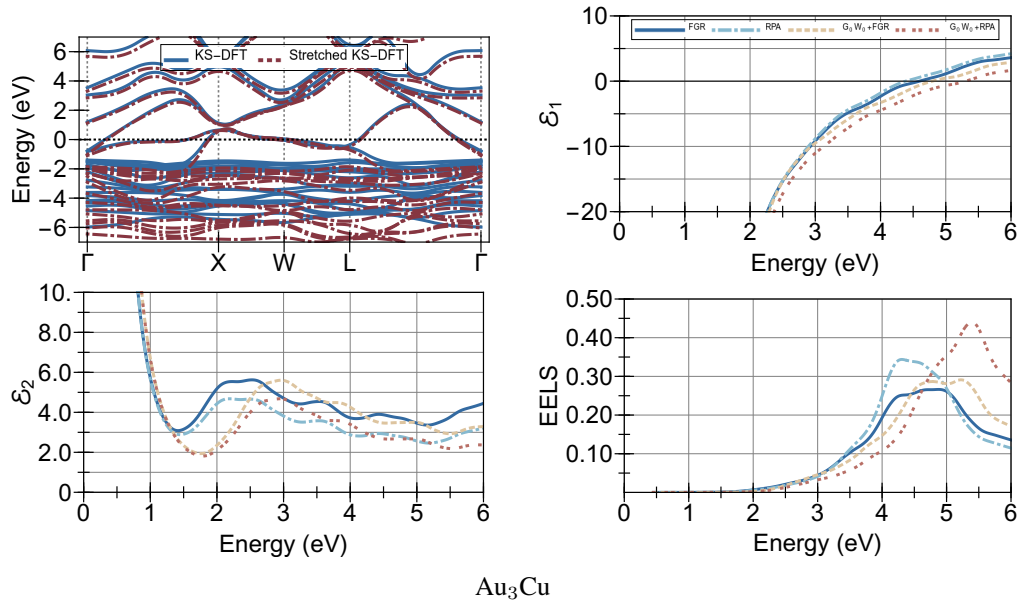
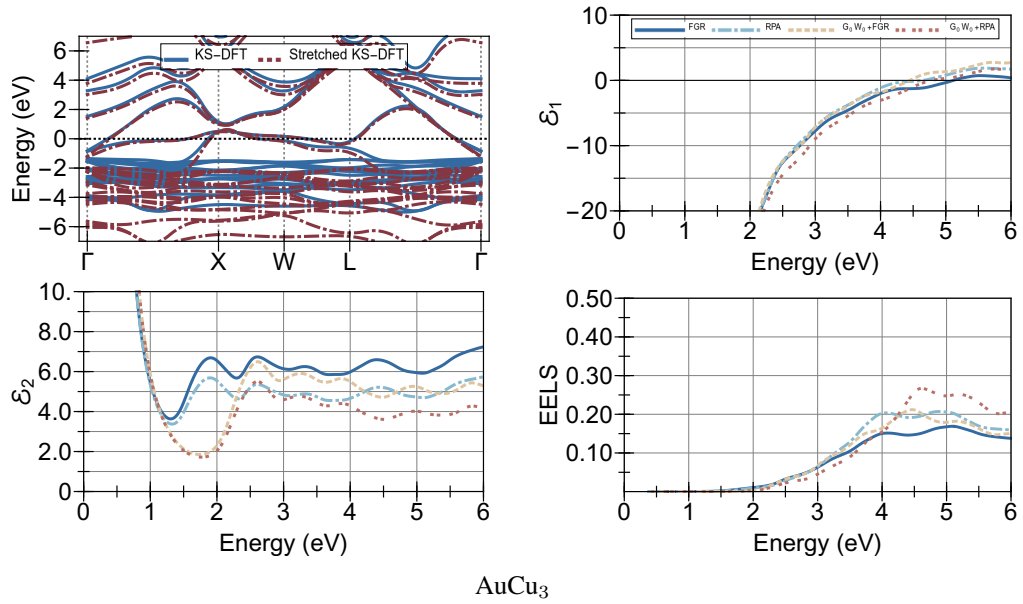
B. Supplementary information on $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys



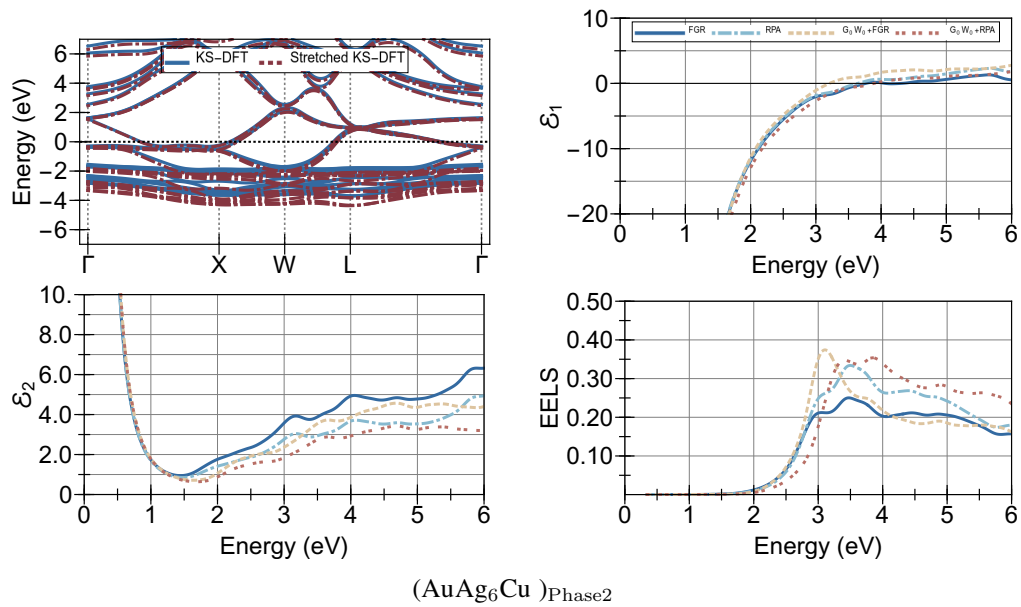
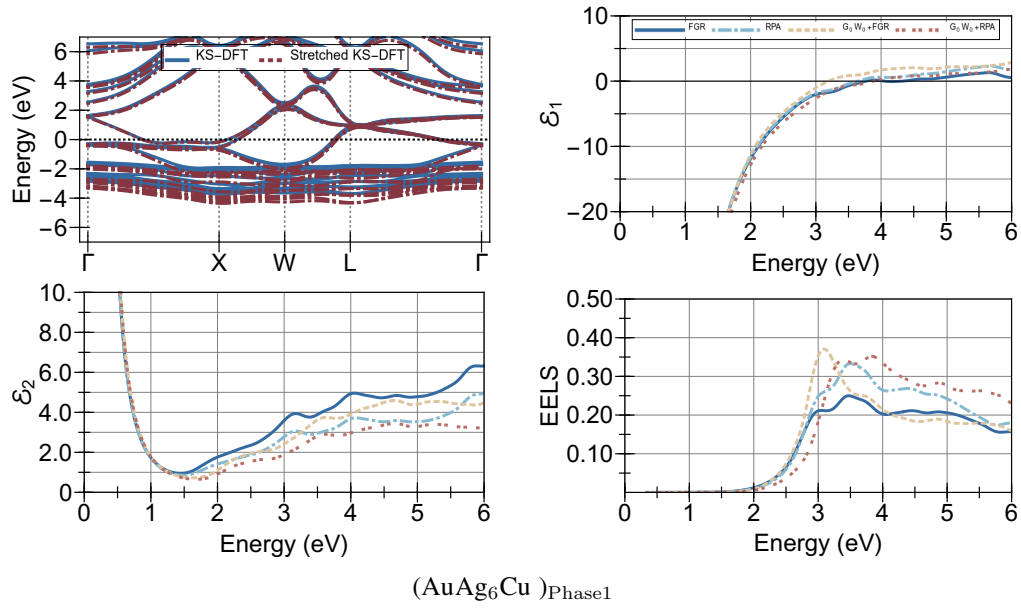

 AuAg_3

 Ag_3Cu

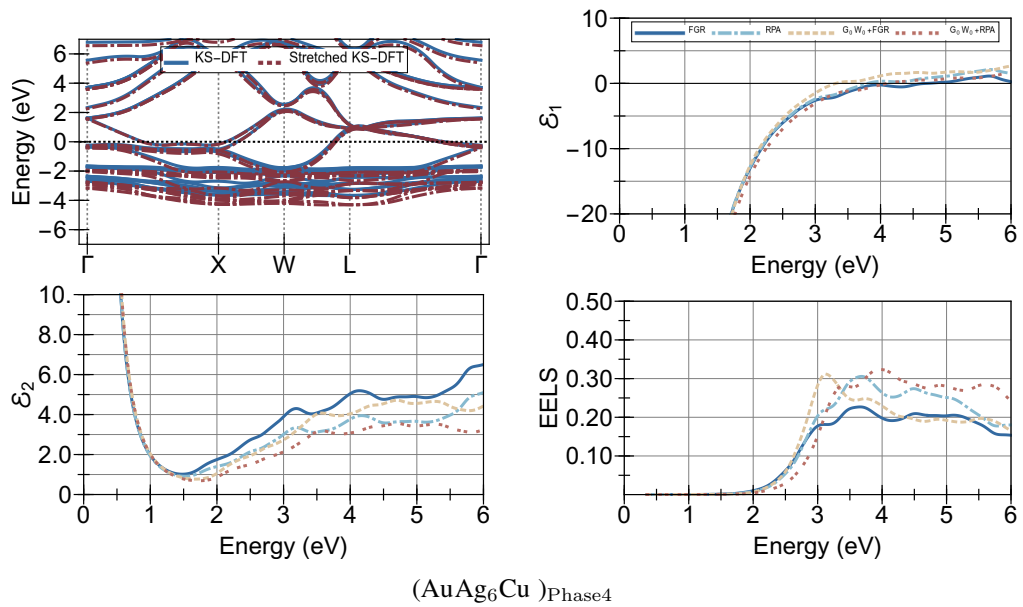
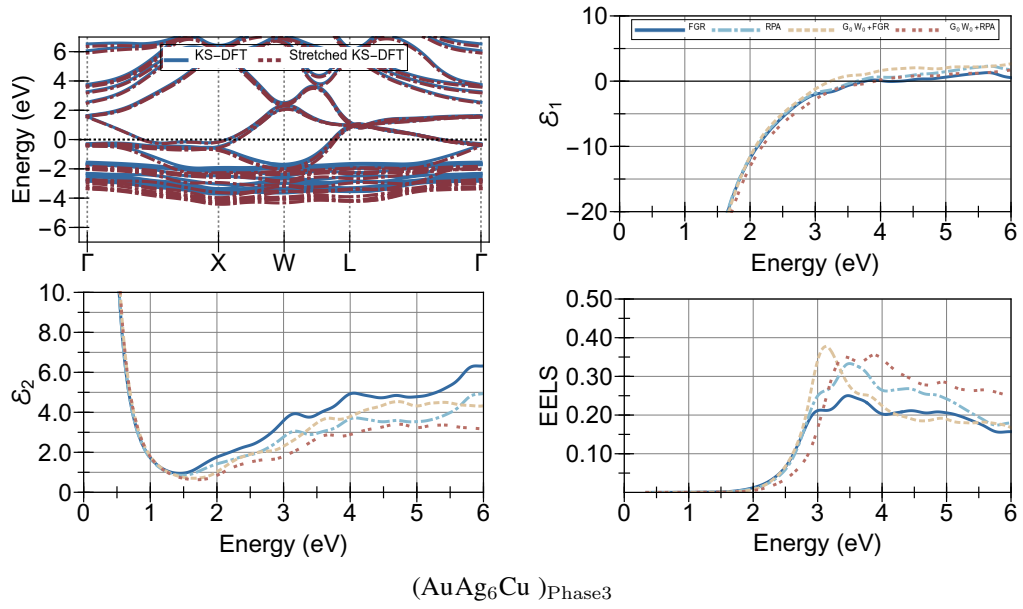
B. Supplementary information on $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys



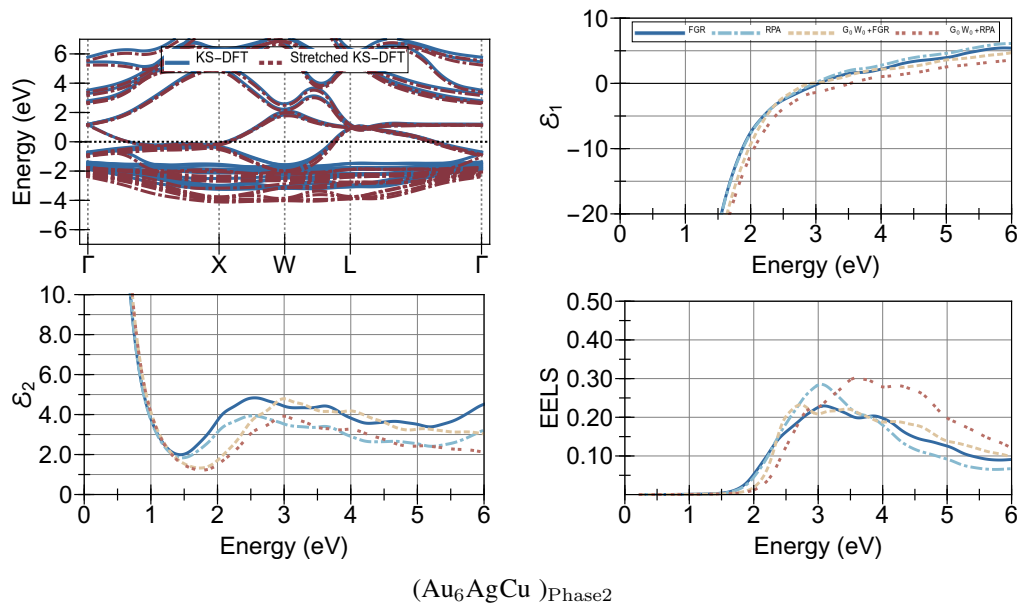
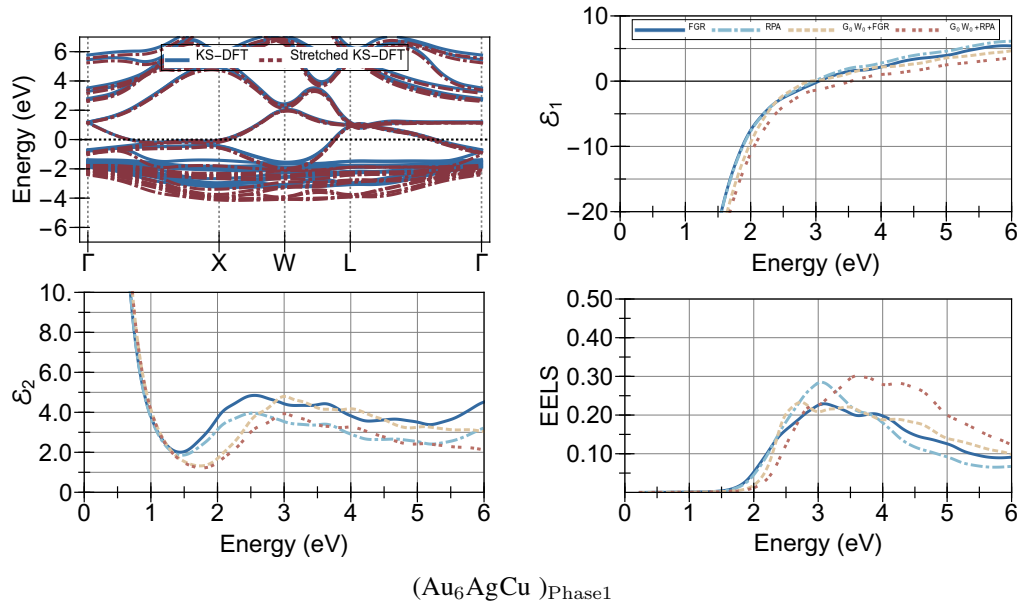

 Au_3Cu

 AuCu_3

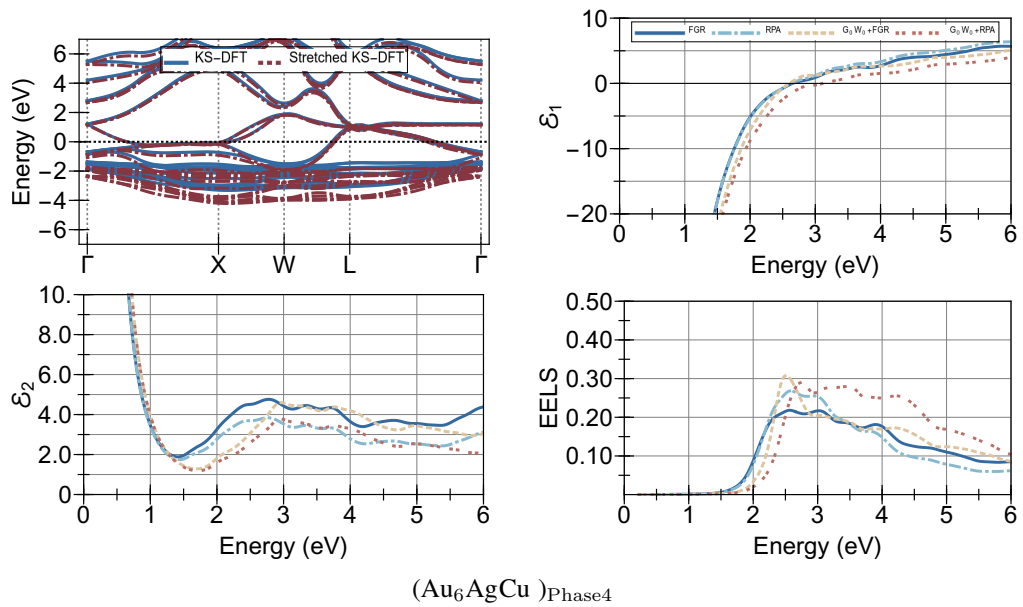
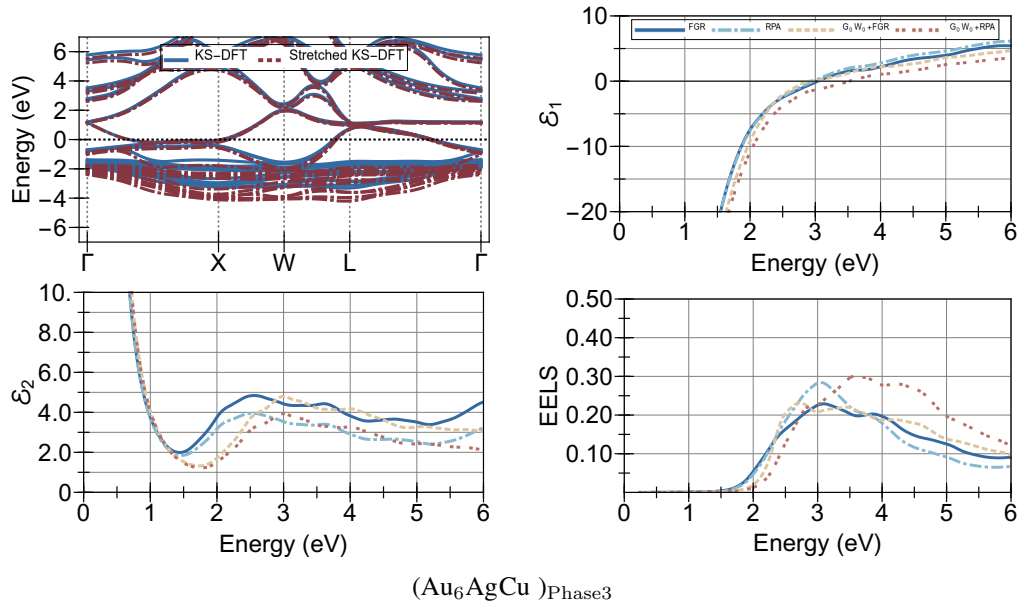
B. Supplementary information on $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys



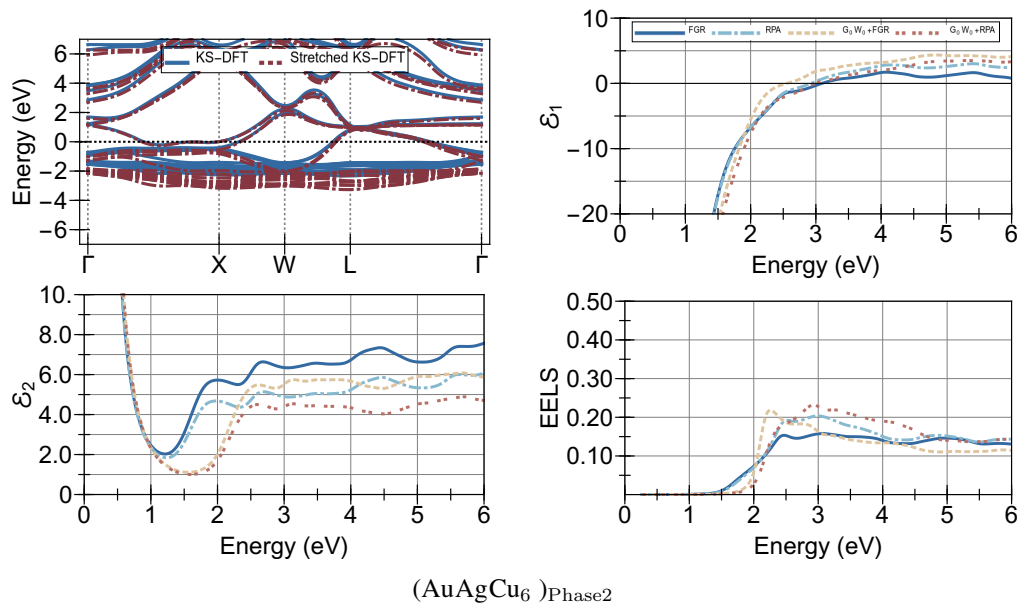
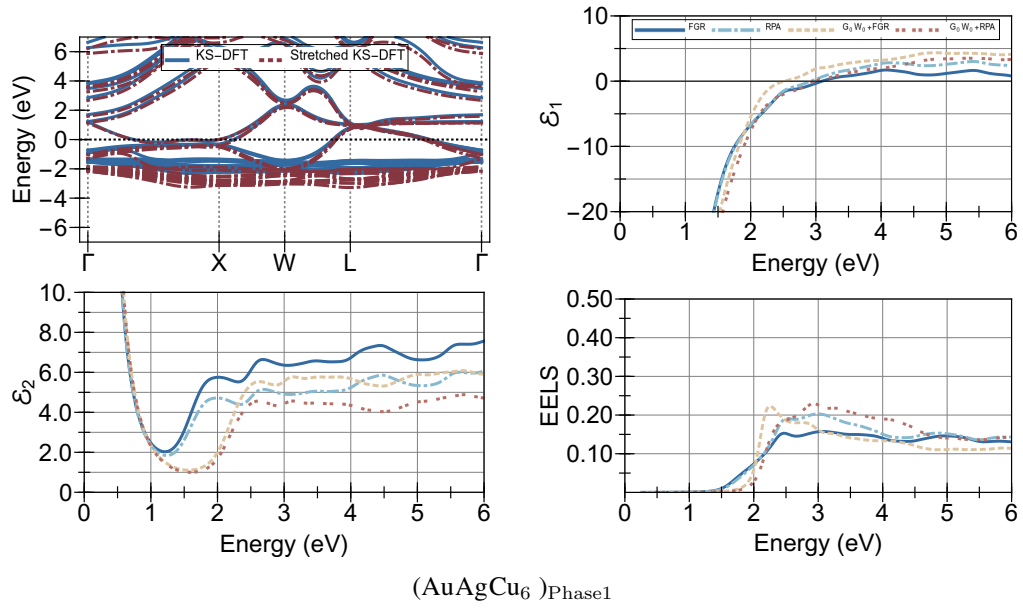


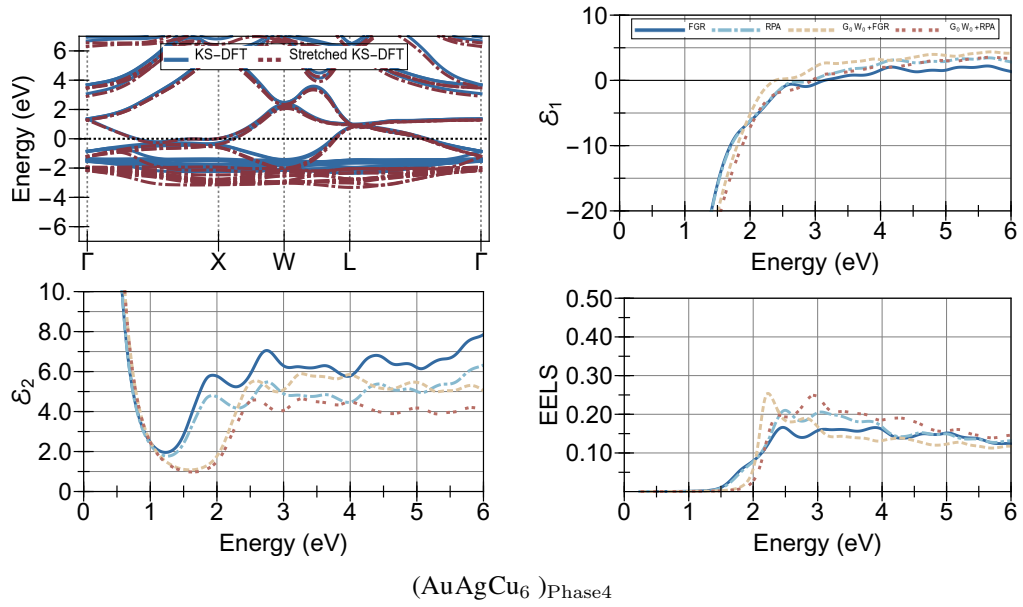
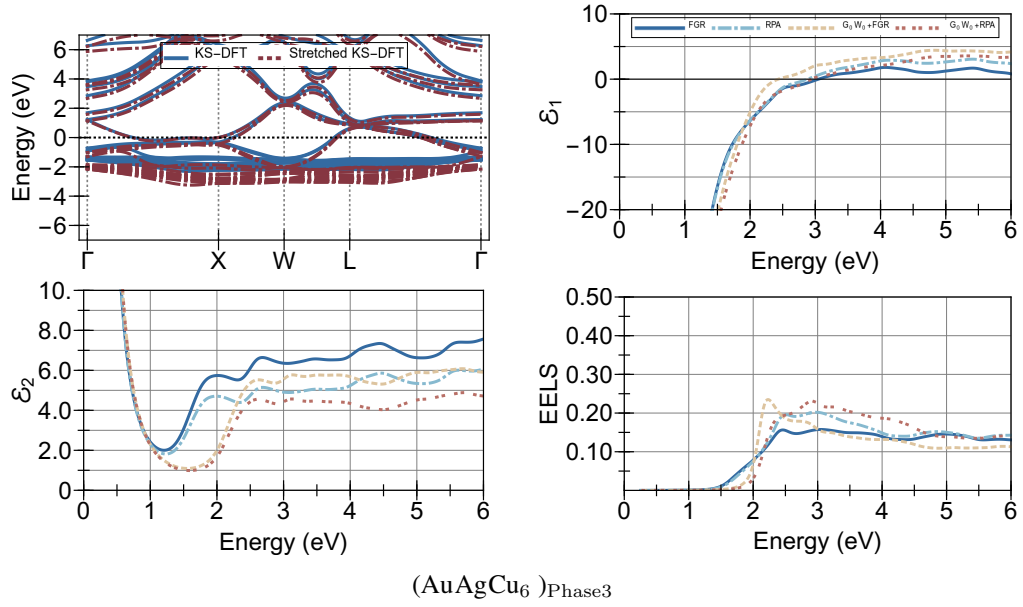
B. Supplementary information on $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys



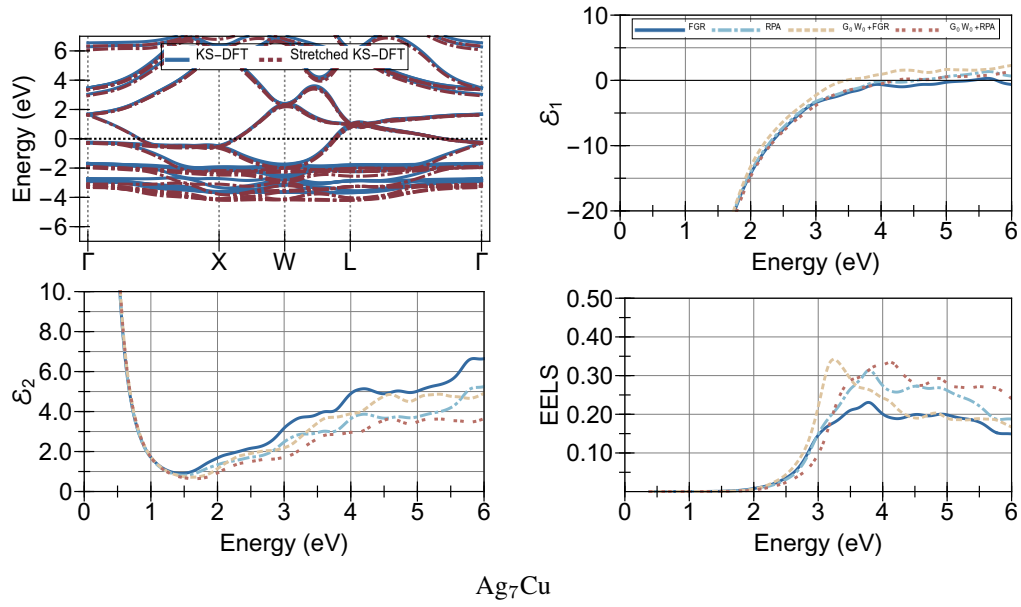
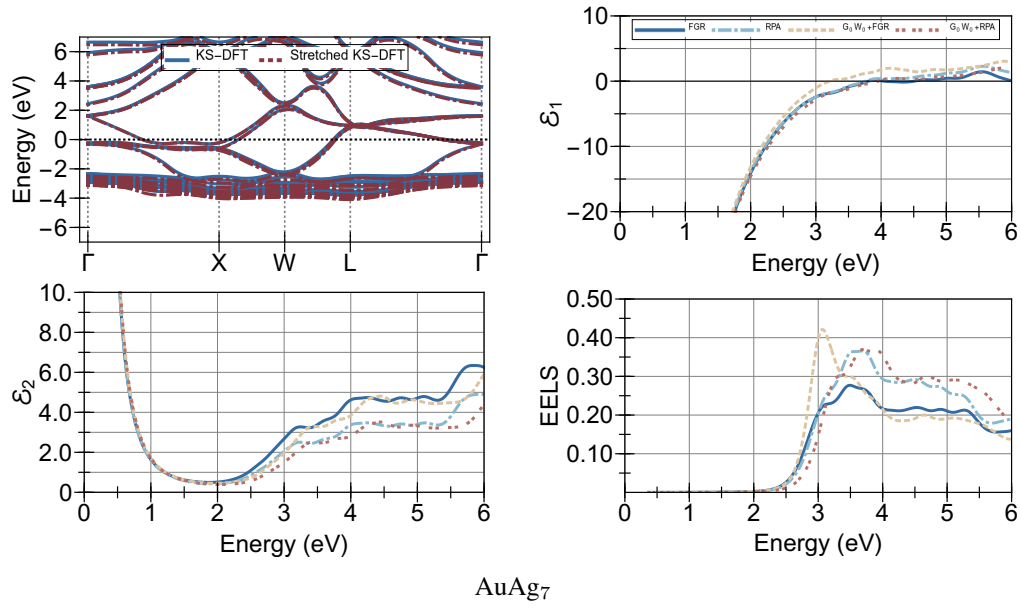


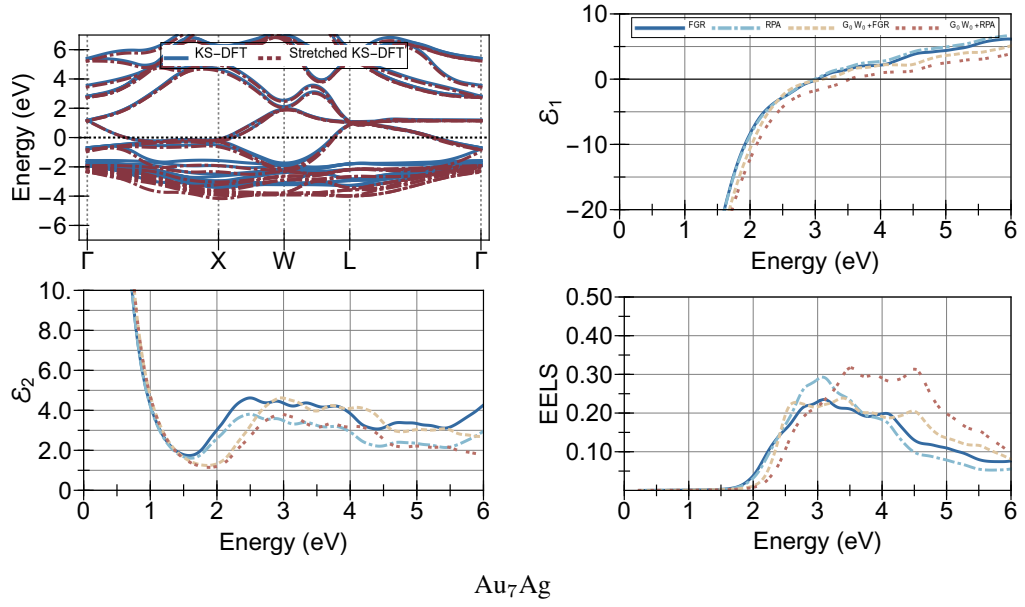
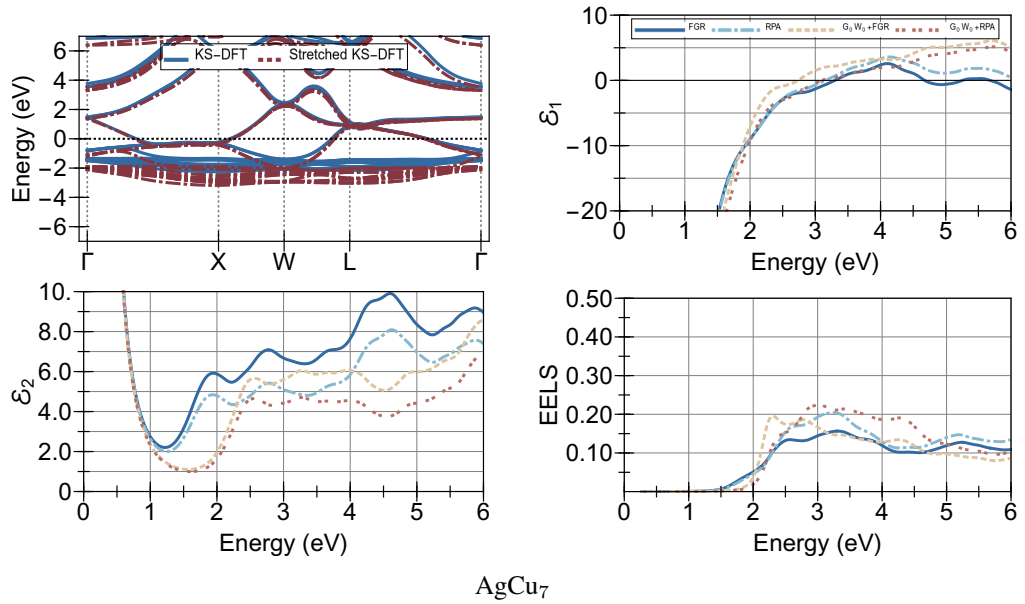
B. Supplementary information on $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys





B. Supplementary information on $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys




 Au_7Ag

 AgCu_7

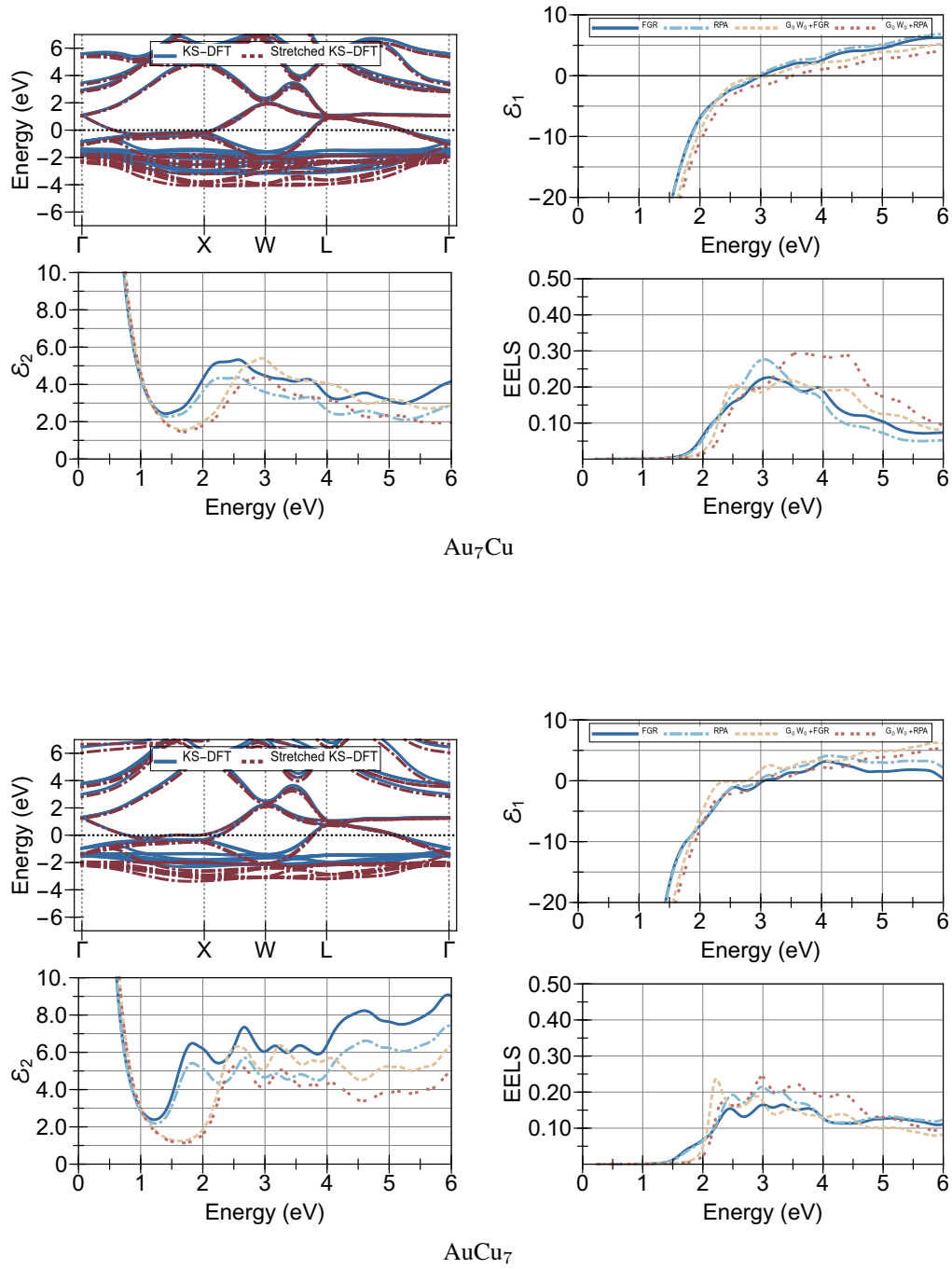


Figure B.4: Band structures and spectra of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$.

References

- [1] C. Gong and M. S. Leite, *ACS Photonics*, **3**(4), pp. 507–513 (2016), URL <http://dx.doi.org/10.1021/acsphotonics.5b00586>.

Appendix C

KS-DFT molecular orbitals of CoL_2Cl_2

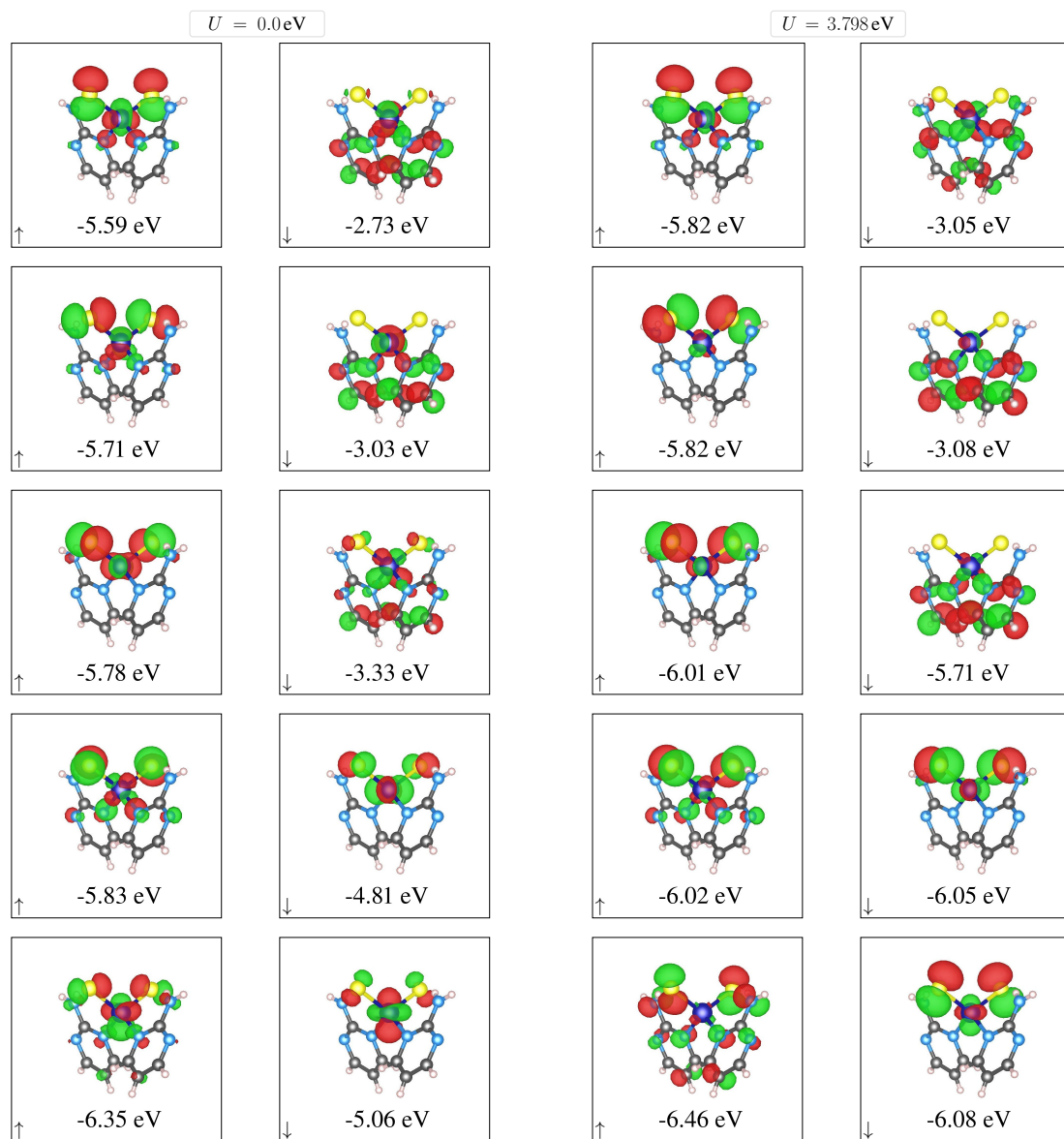


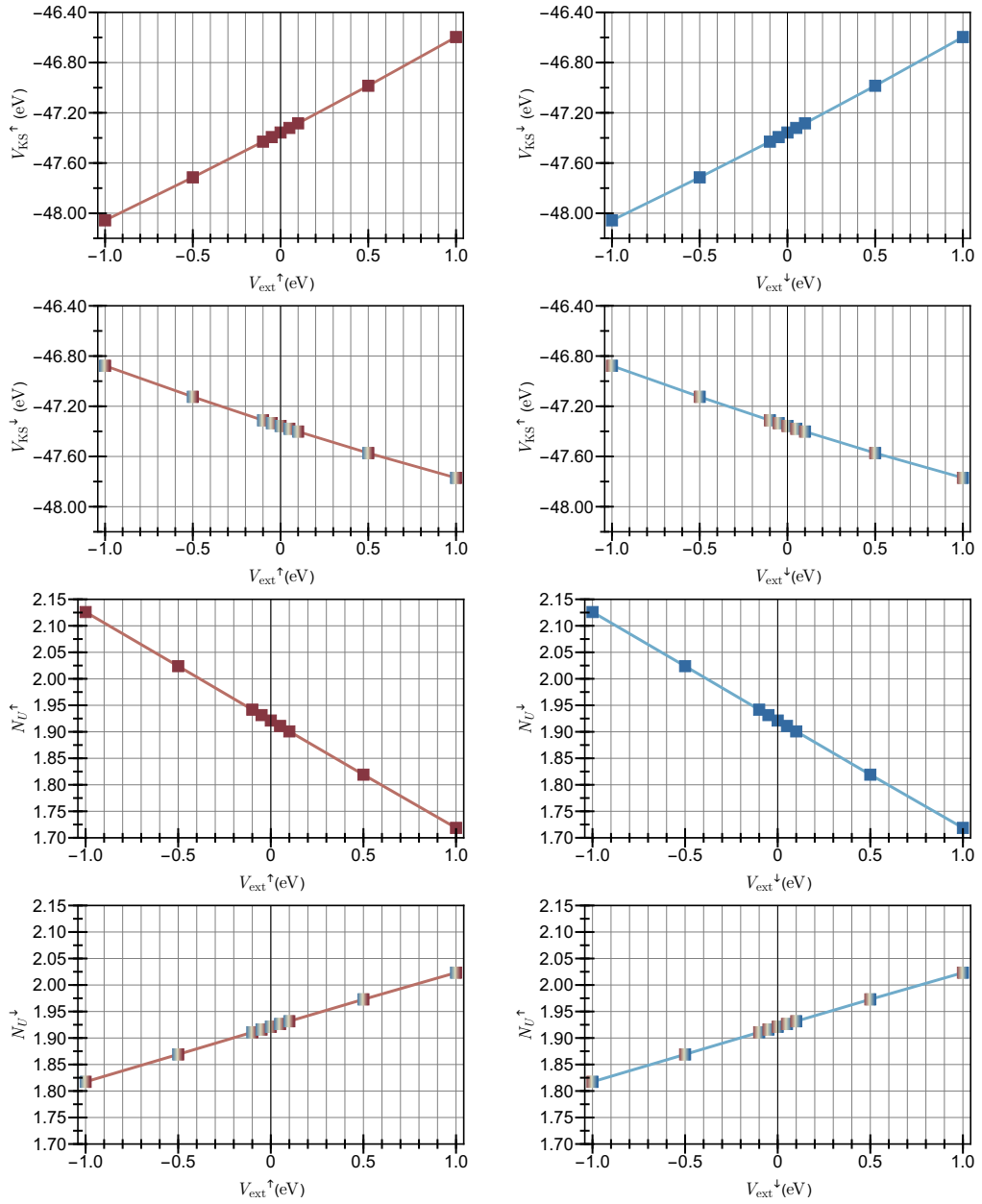
Figure C.1: KS-DFT molecular orbitals of CoL_2Cl_2 with partial $3d$ character due to ligand-field splitting, and their respective KS energies for $U = 0.0 \text{ eV}$ and $U = 3.798 \text{ eV}$. Isosurface values are set to $\pm 0.05 \text{ a}_0^{-3/2}$.

Appendix D

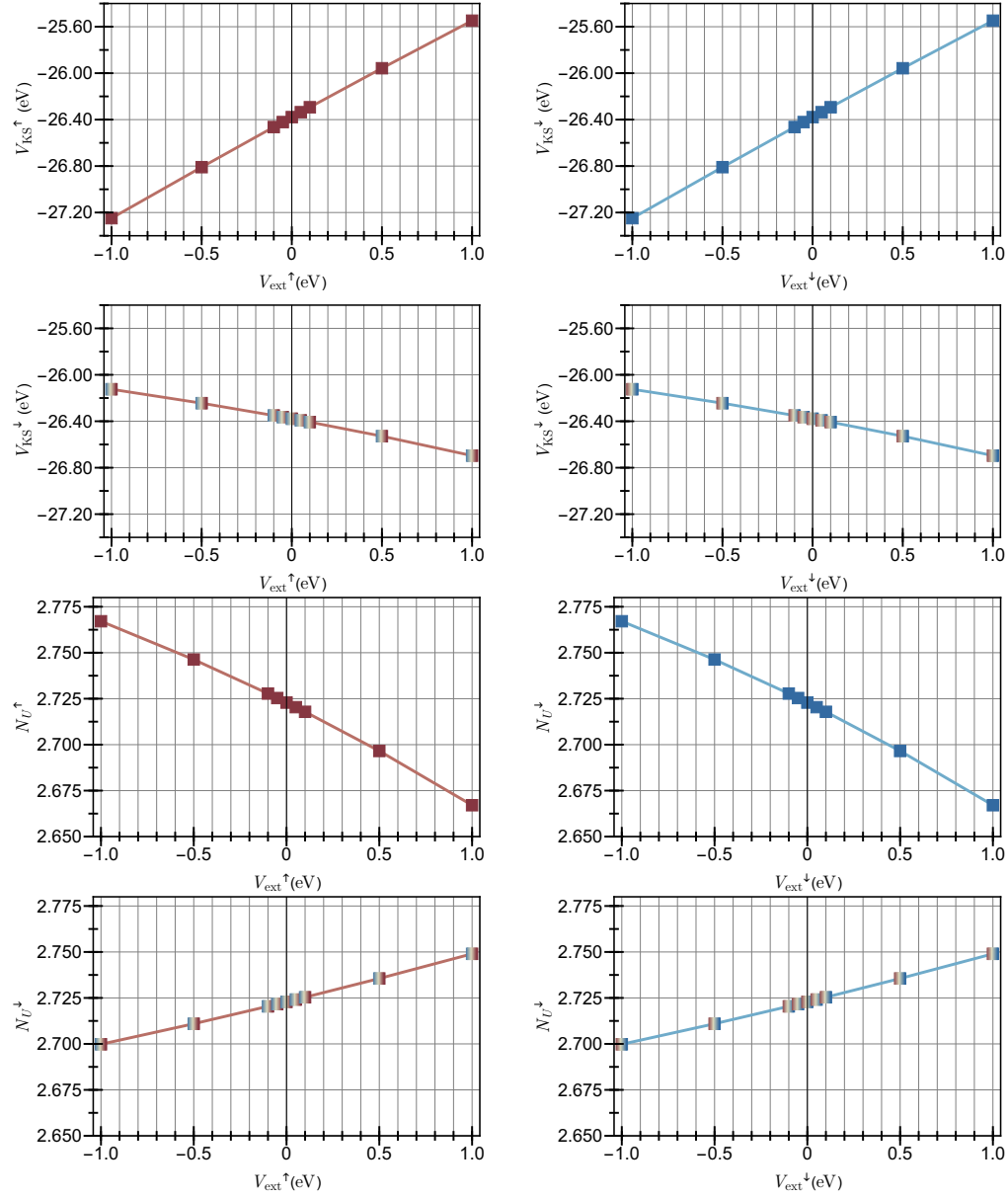
Supplementary information on TMOs

D.1 Linear fitting to V_{KS} and N_U versus V_{ext}

D.1.1 TiO_2 -rutile

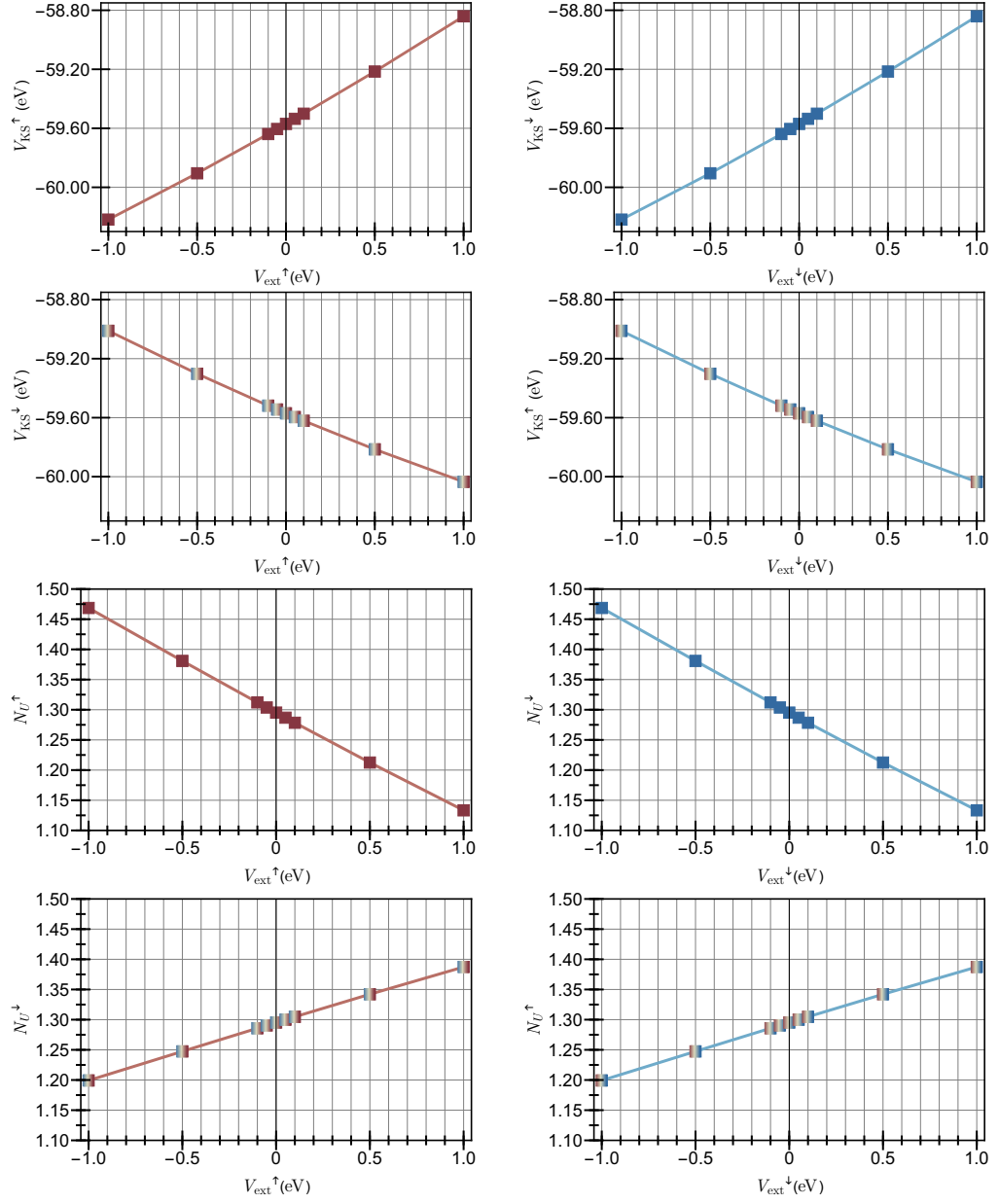


(a) Single Ti site



(b) Single O site

Figure D.1: The linear-response of up(down)-spin occupancies and the corresponding KS potentials of the 3d sub-shell of Ti and the 2p sub-shell of O atoms with neutral configurations in TiO₂-rutile used to calculate Hubbard U and Hund's J .



(a) Single Ti site

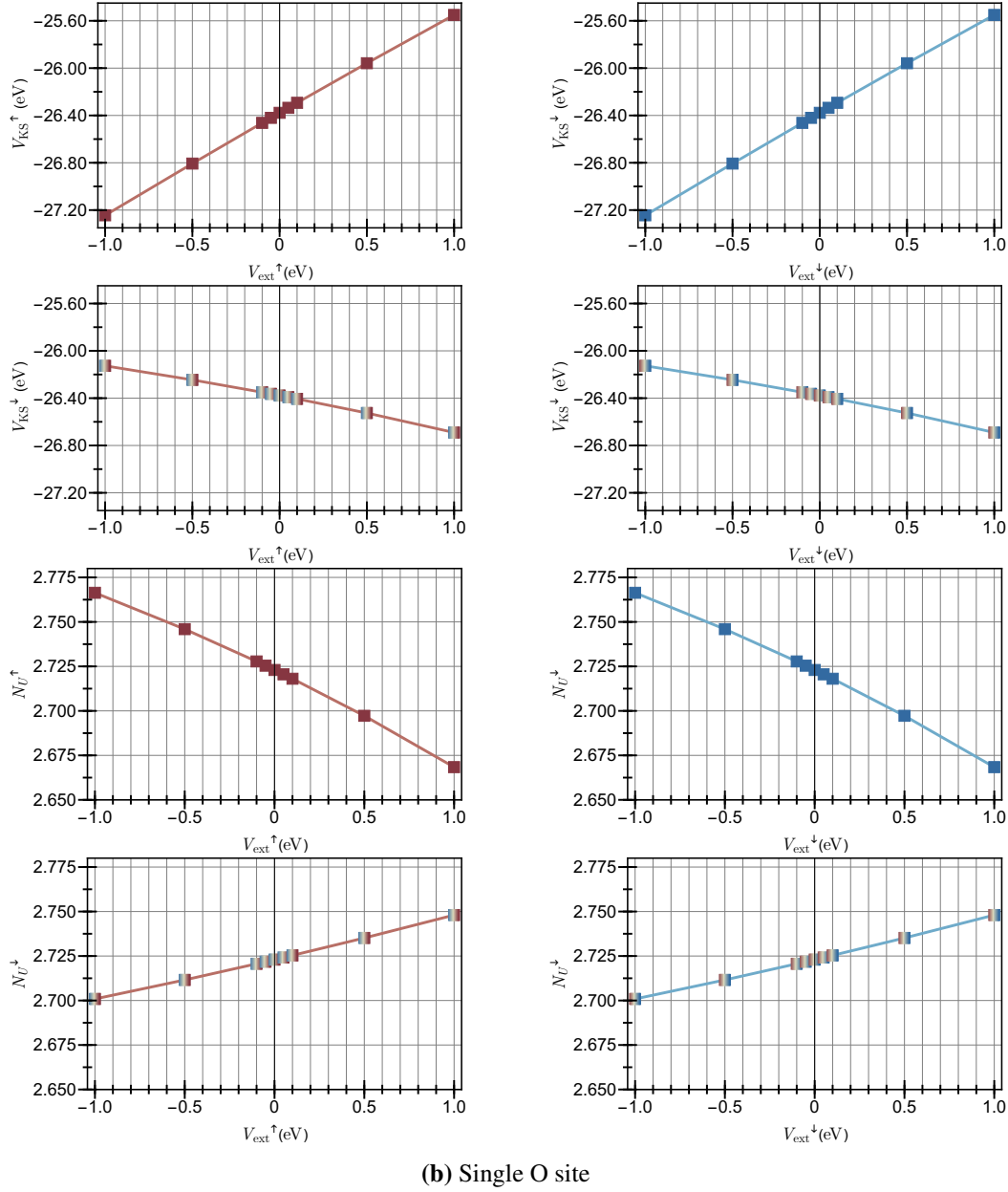
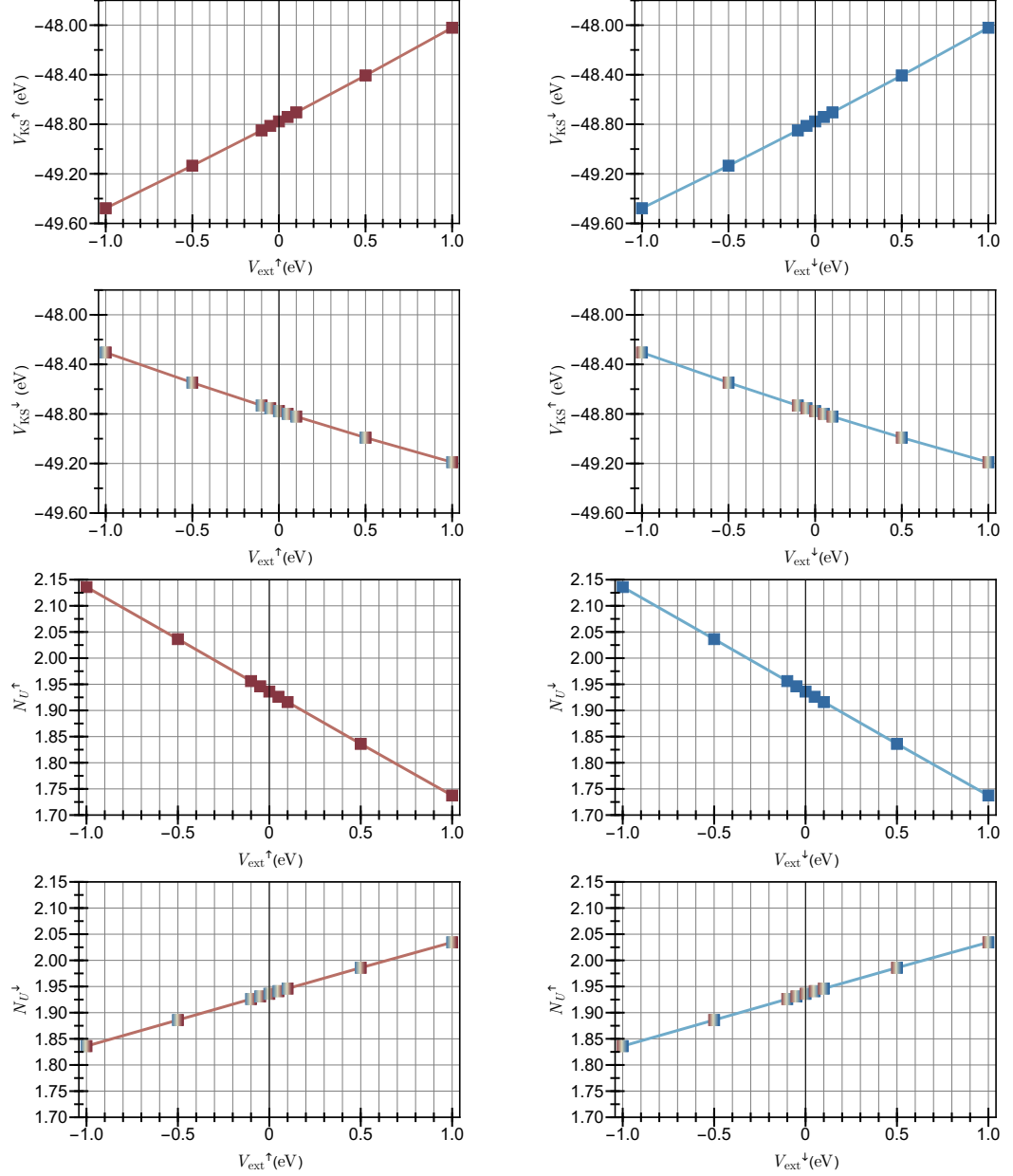
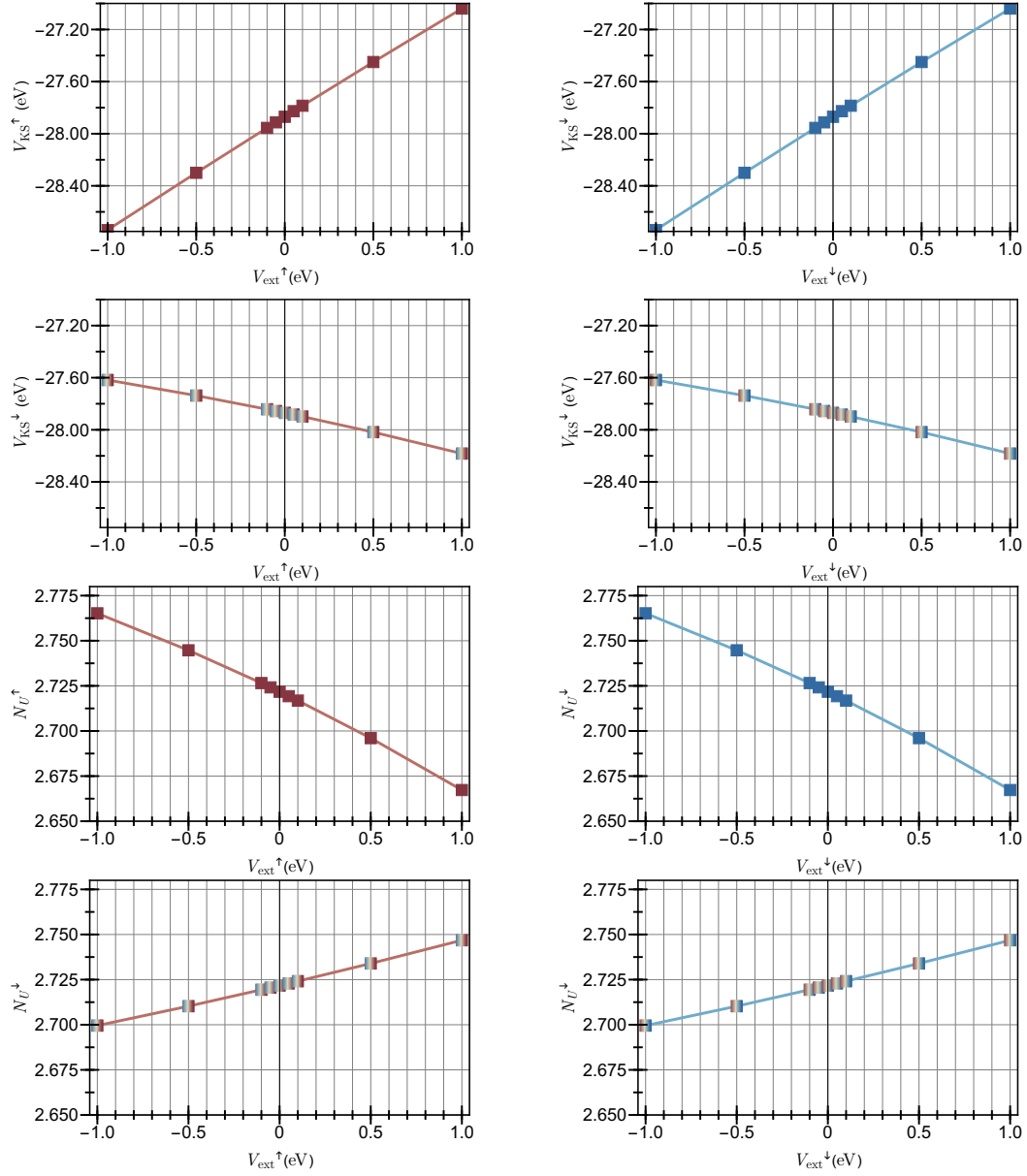


Figure D.2: The linear-response of up(down)-spin occupancies and the corresponding KS potentials of the $3d$ sub-shell of Ti and the $2p$ sub-shell of O atoms with $3+$ and neutral configurations, respectively, in TiO_2 -rutile used to calculate Hubbard U and Hund's J .

D.1.2 TiO_2 -anatase

(a) Single Ti site



(b) Single O site

Figure D.3: The linear-responses of up(down)-spin occupancies and the corresponding KS potentials of the $3d$ sub-shell of Ti and the $2p$ sub-shell of O atoms with neutral configurations in TiO_2 -anatase used to calculate Hubbard U and Hund's J .

D.2 DoS of TiO₂-rutile with V_O

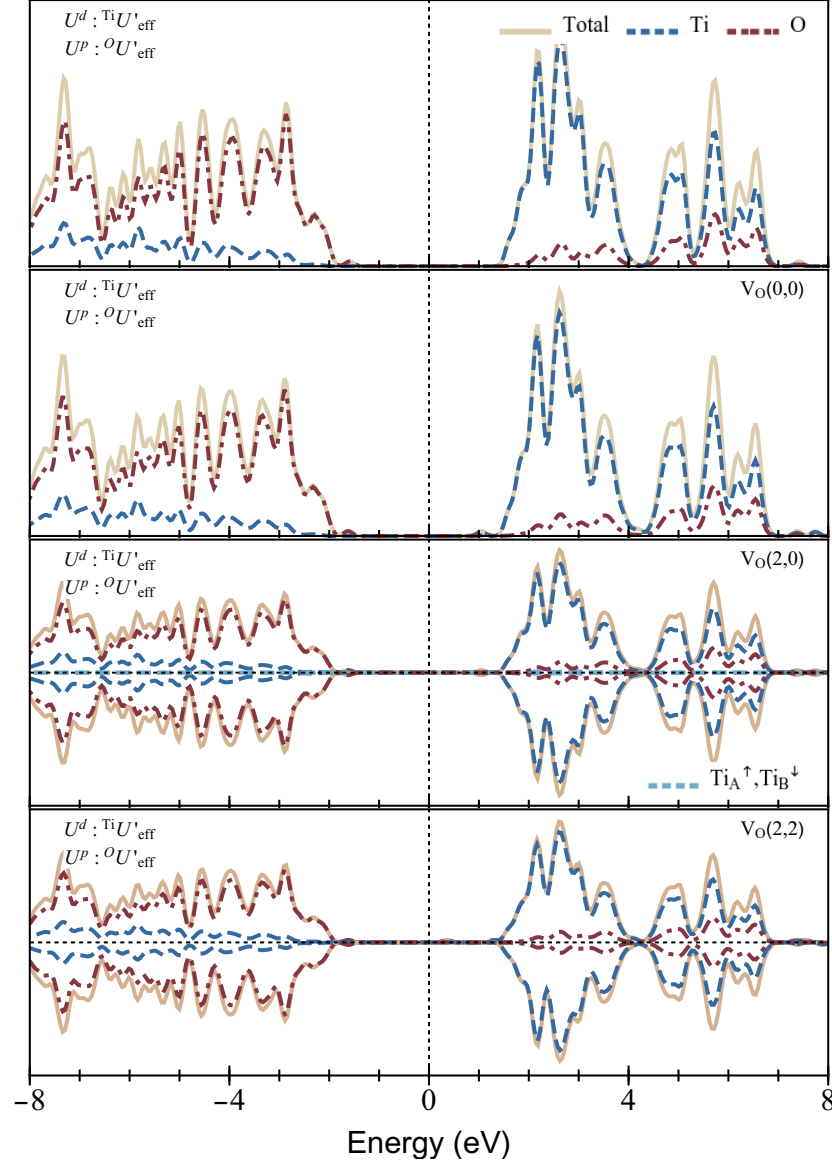


Figure D.4: DOS of (from top to bottom) pristine TiO₂-rutile, the V_O(0,0), the V_O(2,0), the V_O(2,2) vacancy in TiO₂-rutile with DFT+ U^d+U^p with the Hubbard U'_{eff} parameters for 3d-states of Ti ($U^d : {}^{\text{Ti}}U'_{\text{eff}}=2.982$ eV) and for 2p-states for O atom ($U^p : {}^{\text{O}}U'_{\text{eff}}=6.742$ eV), shown with a Gaussian broadening of 0.1 eV.

D.3 DoS of TiO₂-anatase with V_O

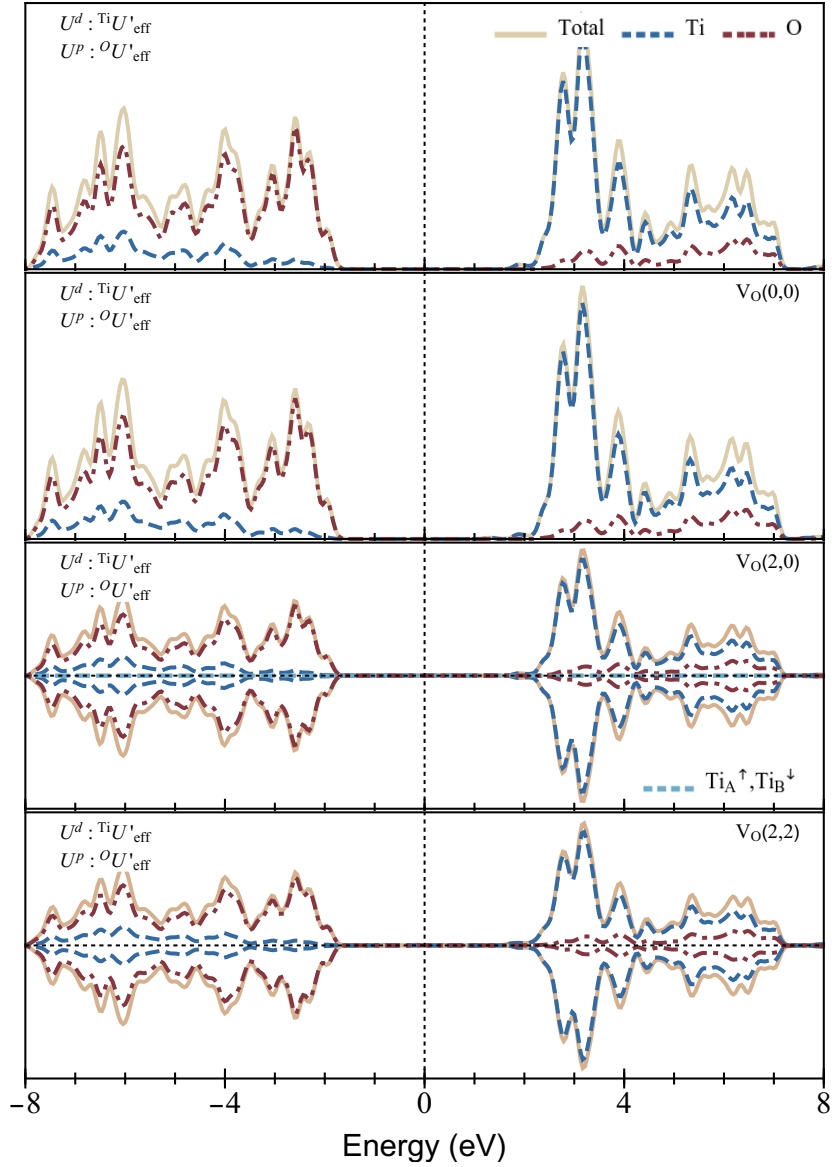


Figure D.5: DOS of (from top to bottom) pristine TiO₂-anatase, the V_O(0,0), the V_O(2,0), the V_O(2,2) vacancy in TiO₂-anatase with DFT+ U^d+U^p with the Hubbard U_{eff}^d parameters for 3d-states of Ti ($U^d : {}^{\text{Ti}}U_{\text{eff}}^d=2.996$ eV) and for 2p-states for O atom ($U^p : {}^{\text{O}}U_{\text{eff}}^p=6.746$ eV), shown with a Gaussian broadening of 0.1 eV.