Chapter 2: Theoretical background

2.1 Theoretical foundations of Density functional theory (DFT)

2.1.1 Quantum many-body problem: pre DFT era

The quantum mechanical description of matter, formalized by Schrödinger in 1926, provides the foundational framework for understanding electronic systems from first principles [1]. For a system of N interacting electrons, the time-independent Schrödinger equation becomes a many-body eigenvalue problem, where the full wavefunction $\Psi(r_1, r_2, \ldots r_N)$ depends on 3N spatial coordinates. This high dimensionality makes direct solutions computationally prohibitive for systems containing more than a few electrons. When the adiabatic or Born-Oppenheimer approximation is invoked, allowing the separation of electronic and ionic motions, the electronic Schrödinger equation describing electrons in the presence of fixed nuclei takes the form

$$\left[\sum_i \left(-\frac{\hbar^2}{2m}\nabla_i^2\right) + \frac{1}{2}\sum_i \sum_{j\neq i} U_{ee}(|r_i - r_j|) + \sum_i \sum_\alpha U_{ei}(|R_\alpha - r_i|)\right]\Psi_{el} = E_{el}\Psi_{el}$$

…(2.1)

or more compactly,

$$[T + U_{ee} + U_{ei}]\Psi_{el} = E_{el}\Psi_{el}$$

…(2.2)

where T is the kinetic energy operator, U_{ee} represents the electron-electron interaction, and U_{ei} the electron-ion interaction. The principal difficulty arises from the electron-electron term, which introduces complex correlations by coupling the motion of every electron to one another.

To manage this complexity, approximate methods such as the Hartree and Hartree-Fock (HF) approaches were developed [2,3]. In the Hartree approximation, the N-electron wavefunction is expressed as a simple product of single-electron orbitals [2] :

$$\Psi_{el}(r_1 r_2 \ldots r_N) = \prod_i \Psi_i(r_i) = \Psi_1(r_1)\Psi_2(r_2)\ldots\Psi_N(r_N)$$

…(2.3)

leading to an expression for the total electronic energy as a sum over one-electron energies:

$$\begin{aligned} E_{el} &= \sum_i E_i = \langle \Psi_{el} | H | \Psi_{el} \rangle \\ &= \int \ldots \int \Psi_1^* (r_1) \ldots \Psi_N^* (r_N) [T + U_{ei}] \Psi_1 (r_1) \ldots \Psi_N (r_N) dr_1 \ldots dr_N \\ &+ \frac{1}{2} \sum_i \sum_{j \neq i} \int \ldots \int \Psi_i^* (r_i) \Psi_j^* (r_j) \left[\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \right] \Psi_i (r_i) \Psi_j (r_j) dr_i dr_j \end{aligned}$$

…(2.4)

The Coulomb interaction contributes a classical term involving pairwise electron repulsion, often expressed using the Hartree potential. By assuming wavefunction normalization, the Coulomb energy can be simplified and represented via the Hartree potential as

$$W^H(r_i) = \frac{1}{2} \sum_{j \neq i} \int \frac{e^2}{4\pi\varepsilon_0} \frac{|\Psi_j(r_j)|^2}{r_{ij}} dr_j$$

…(2.5)

This transforms the many-electron Schrödinger equation into a set of decoupled one-electron equations of the form

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + \sum_\alpha U_{ei}(|R_\alpha - r_i|) + W^H(r_i) \right] \Psi_i = E_i \Psi_i$$

…(2.6)

However, the Hartree approach does not satisfy the antisymmetry requirement of fermionic wavefunctions. The HF method resolves this by constructing the wavefunction as a Slater determinant, a linear combination of anti-symmetrized products of single-particle orbitals [4]:

$$\Psi_{el}(r_1 r_2 \ldots r_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P_{\Psi_1}(r_1) \Psi_2(r_2) \ldots \Psi_N(r_N),$$

…(2.7)

and the electronic energy can be written as,

$$E_{el} = \langle \Psi_{el} | H | \Psi_{el} \rangle = \int [T + U_{ee} + U_{ei}] n(r) dr$$

…(2.8)

where, P is the permutation operator over electron indices, and $(-1)^P$ ensures antisymmetry under exchange. The term $n(r)dr$ represents the elemental probability of finding any electron in the volume element dr. Despite their significant improvements, both Hartree and HF theories still rely on the full many-electron wavefunction and inherently neglect dynamic electron correlation, which limits their predictive accuracy for many systems.

These limitations motivated the development of alternative theoretical frameworks that would avoid the need for the many-body wavefunction altogether. One such approach focused on the electron density $n(r)$, a function of only three spatial variables, regardless of the number of electrons. This shift was motivated by the empirical observation that ground-state properties of matter, such as total energy and molecular geometry, correlate more directly with the spatial distribution of charge than with the full quantum state. The idea of describing the many-body system entirely through its electron density laid the conceptual groundwork for the advent of density-based theories.

2.1.2 Thomas-Fermi model

In response to the formidable challenges posed by the full many-body Schrödinger equation, the Thomas-Fermi (TF) model emerged in the late 1920s as the first theoretical framework to describe electronic systems solely in terms of the electron density $\rho(r)$ [5,6]. Independently proposed by L.H. Thomas and E. Fermi in 1927 and 1928, respectively, the TF model represented a fundamental shift from wavefunction-based methods to a density-based perspective. The central idea was to express the total energy of an atom as a functional of the spatially varying electron density, thereby reducing the dimensionality of the system. The TF energy functional comprised three main contributions: the kinetic energy of a homogeneous electron gas (approximated locally), the interaction of electrons with the external potential (typically the nuclear Coulomb attraction), and the classical electrostatic repulsion between the continuous electron charge distributions. Assuming uncorrelated electron motion, Thomas and Fermi approximated the kinetic energy using a local expression derived from the free-electron gas, known as the Thomas-Fermi kinetic energy functional, $T_{\mathrm{TF}}[n]$.

In 1930, Dirac extended this model by introducing an additional term to account for exchange effects, based on the exchange energy density of a homogeneous electron gas [7]. He showed that even in inhomogeneous systems, such approximations could yield reasonably accurate results. Despite these early successes, the Thomas-Fermi model had significant limitations. It lacked essential quantum mechanical features such as shell structure, failed to include proper exchange and correlation effects beyond Dirac's correction, and provided only a crude representation of the kinetic energy. Consequently, it could not reliably predict many of the properties of atoms and molecules, particularly those sensitive to the detailed electronic structure. Nevertheless, the TF model introduced a transformative concept: that the electron density, not the many-electron wavefunction, could serve as the fundamental variable in the theoretical description of electronic systems. This conceptual innovation established the groundwork for the development of density functional theory (DFT), in which more sophisticated functionals aim to systematically improve upon the Thomas-Fermi approximation while retaining its essential density-based formulation.

2.1.3 Theorems of Hohenberg and Kohn

The modern theoretical foundation of DFT was laid in 1964 by Pierre Hohenberg and Walter Kohn, who formalized the groundbreaking idea that all ground-state properties of an interacting electronic system are uniquely determined by its electron density $n(r)$ [8]. Their work culminated in two seminal theorems that extended and generalized the early density-based approaches proposed by Thomas, Fermi, and Dirac [5–7], establishing electron density as the fundamental variable in electronic structure theory.

For practical and general applications, the electron-ion interaction term U_{ei} in the many-body Hamiltonian [Equation (2.2)], is replaced with a more general external potential V_{ext}, which includes the Coulomb potential of point nuclei or any other external field. The electronic Schrödinger equation is then rewritten as:

$$[T + U_{ee} + V_{ext}]\Psi_{el} = E_{el}\Psi_{el}$$

…(2.9)

The first Hohenberg-Kohn theorem asserts that, for a system of interacting electrons in a non-degenerate ground state, the external potential $V_{ext}(r)$ is uniquely determined, up to a constant, by the ground-state electron density $n(r)$. This implies that the full Hamiltonian, wavefunction, and all observable quantities of the system are uniquely defined by the ground-state density alone. Hence, the complex many-electron wavefunction can, in principle, be replaced by the much simpler three-dimensional function $n(r)$, without loss of physical information.

The second Hohenberg-Kohn theorem establishes a variational principle for the energy as a functional of the electron density. It states that there exists a universal functional $F[n]$ such that the ground-state energy of any interacting electron system is obtained by minimizing this functional with respect to $n(r)$, subject to the constraint that the total number of electrons is conserved:

$$E_{el} = \langle \Psi_{el} | H | \Psi_{el} \rangle = F[n] + \int V_{ext} n(r) dr, \qquad \dots(2.10)$$

here, $F[n]$ is a universal functional, independent of the external potential, encompassing the kinetic energy and electron-electron interaction:

$$F[n] = \langle \Psi_{el} | T | \Psi_{el} \rangle + \langle \Psi_{el} | U_{ee} | \Psi_{el} \rangle = T[n] + U_{ee}[n] \qquad \dots(2.11)$$

Although the Hohenberg-Kohn theorems rigorously establish the existence and variational minimization of such a functional, they do not provide an explicit form for $F[n]$, limiting the immediate practical utility of the theory. Nevertheless, this foundational framework revolutionized the way electronic structure problems are conceptualized, shifting the focus from the prohibitively complex many-body wavefunction to the much more manageable electron density. This paradigm shift set the stage for the subsequent development of practical and accurate density-functional methods.

2.1.4 Kohn-Sham equation

To render density functional theory computationally tractable while preserving accuracy, Walter Kohn and Lu Jeu Sham proposed a reformulation in 1965 that introduced an auxiliary system of non-interacting electrons yielding the same ground-state density as the real, interacting system [9]. This approach, known as the Kohn-Sham (KS) scheme, enabled the exact treatment of the kinetic energy of non-interacting electrons and isolated the unknown many-body contributions into a single term: the exchange-correlation energy functional.

The total electronic energy in KS DFT is expressed as:

$$E_{el}[n] = T_0[n] + E_{xc}[n] + W^H[n] + \int V_{ext} n(r) dr$$

…(2.12)

here, $T_0[n]$ is the kinetic energy of the non-interacting reference system, $W^H[n]$ is the classical electrostatic (Hartree) energy, $E_{xc}[n]$ is the exchange-correlation energy capturing all many-body quantum effects beyond the Hartree approximation.

Applying the variational principle to this functional, subject to particle number conservation, yields a set of single-particle Schrödinger-like equations known as the KS equations:

$$\left(-\frac{\hbar^2}{2m}\nabla_i^2 + v_{KS}(r)\right)\Psi_i(r) = E_i\Psi_i(r)$$

…(2.13)

where the effective KS potential $v_{KS}(r)$ is given by:

$$v_{KS}(r) = V_{ext}(r) + V^H(r) + V_{xc}(r)$$

…(2.14)

and the exchange-correlation potential is defined as the functional derivative:

$$V_{xc}(r) = \frac{\delta E_{xc}(n)}{\delta n(r)}$$

…(2.15)

The KS equations are solved self-consistently: starting with an initial guess for the electron density, the KS potential is constructed, the equations are solved for the orbitals $\Psi_i(r)$, and a new density is computed. This procedure is iterated until convergence is achieved, known as the self-consistent field (SCF) method.

The KS formulation transformed DFT into a quantitatively reliable and computationally efficient method. By allowing systematic approximations for $E_{xc}(n)$, such as the local density approximation (LDA) and generalized gradient approximation (GGA), the KS framework has become the most widely used approach in electronic structure calculations across condensed matter physics, quantum chemistry, and materials science.

2.2 The concept of pseudopotential

In practical electronic structure calculations, solving the KS equations directly for all electrons in an atom, including both core and valence electrons, poses significant computational challenges. Core states are localized in the vicinity of the nucleus, where valence states oscillate in order to maintain orthogonality with the core functions. This results in a large kinetic energy (kinetic energy pressure) for the valence electrons in the core region, which roughly cancels the large potential energy from the Coulomb interaction (this can nicely be seen in the work by Schwarz *et al.* [10]). The core electrons, which are tightly bound and localized close to the nucleus, exhibit rapid oscillations in their wavefunctions due to the strong Coulomb potential. These oscillations necessitate the use of very fine spatial grids or large plane-wave basis sets to accurately describe the wavefunction, significantly increasing the computational cost.

However, the core electrons are chemically inert and do not participate directly in bonding or chemical reactivity. It is primarily the valence electrons that determine the electronic, structural, and chemical properties of materials. Capitalizing on this observation, the pseudopotential approximation was introduced by G. A. Hellmann as a means to remove the explicit treatment of core electrons while retaining their influence on the valence electrons [11]. Initially, he termed the pseudopotentials as '*Zusatzpotential*'.

The basic idea is to replace the all-electron potential (which includes the singular Coulomb potential near the nucleus) with a smoothed, effective potential, called the pseudopotential, that reproduces the correct valence electron behaviour outside a chosen core cutoff radius r_c (as depicted in Fig. 2.1). In this region, the pseudopotential is constructed such that the valence pseudo-wavefunction matches the true all-electron wavefunction in both value and derivative, ensuring norm conservation and transferability.

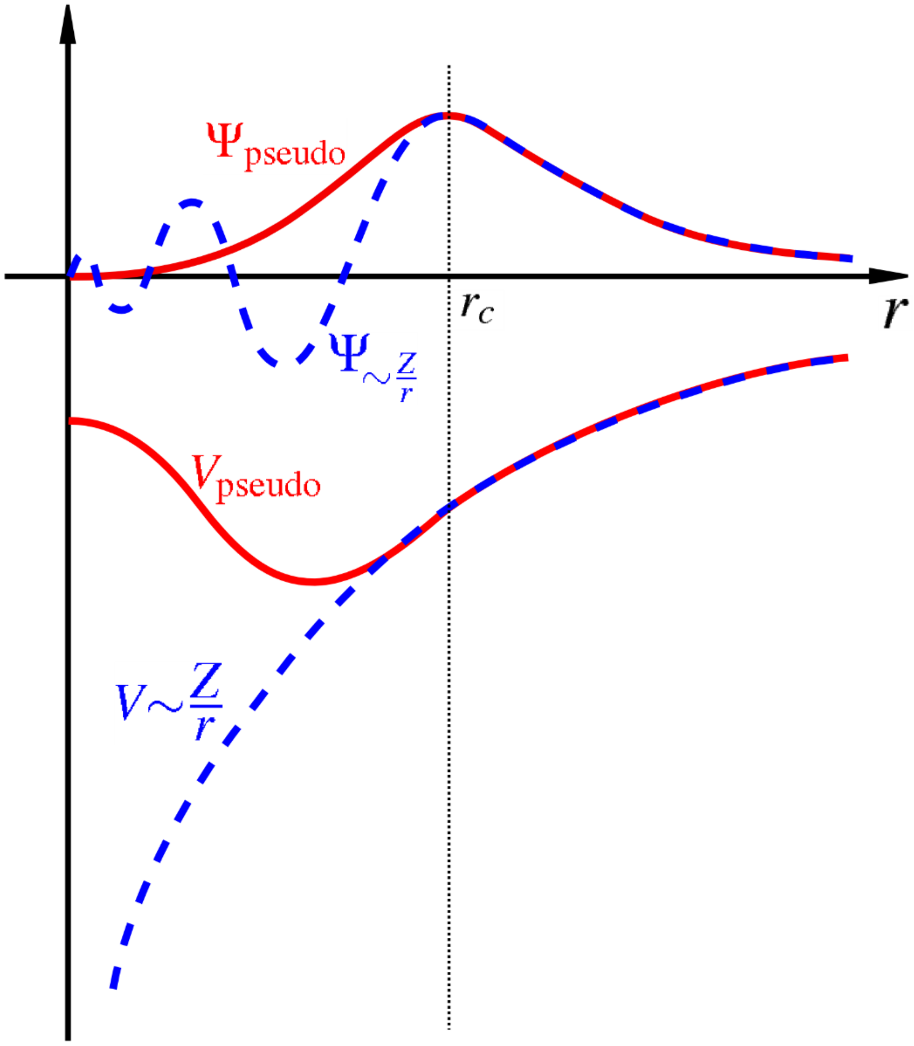

Figure 2.1: *Comparison between the wavefunction in the true Coulomb potential of the nucleus (blue) and that in the corresponding pseudopotential (red). Both the wavefunctions and the potentials coincide beyond a specific cutoff radius r_c. (Image taken from the Quantum Espresso Hands-on Tutorial file by N. T. Hung, A. R. T. Nugraha and R. Saito group from Tohoku University, Sendai, Japan; Image source: https://flex.phys.tohoku.ac.jp/QE/workshop_QE_2016/DFT-hands-on-nguyen.pdf).*

Mathematically, the KS equation for valence electrons in the pseudopotential approach is written as:

$$\left(-\frac{\hbar^2}{2m}\nabla_i^2 + V_{pseudo}(r) + V^H(r) + V_{xc}(r)\right)\Psi_i(r) = E_i\Psi_i(r)$$

…(2.16)

where $V_{pseudo}(r)$ replaces the bare nuclear Coulomb potential and the effects of the core electrons. It is usually non-local, meaning it depends not only on the position but also on the angular momentum of the valence electron.

There are various types of pseudopotentials used in practice:

- Norm-conserving pseudopotentials [12,13]: maintain the same norm (integrated charge) of the pseudo and all-electron wavefunctions inside the core.
- Ultrasoft pseudopotentials [14]: relax the norm-conservation condition, allowing for even softer potentials and lower plane-wave cutoffs.
- Projector Augmented-Wave (PAW) method [15,16]: combines the efficiency of pseudopotentials with the accuracy of all-electron methods by reconstructing the full wavefunction from a pseudo-wavefunction.

2.3 Many-body perturbation theory (MBPT): an approach beyond DFT

DFT, particularly within the KS framework, has become an indispensable tool for electronic structure calculations, yielding high-quality results across a wide range of systems, from periodic crystals to isolated molecules and nanostructures [17]. However, standard DFT is fundamentally a ground-state theory, limiting its ability to accurately describe phenomena involving electronic excitations and excited states [18]. Although KS eigenvalues are often interpreted as approximate quasiparticle (QP) energies, this interpretation is not formally justified. This limitation is especially evident in the underestimation of band gaps in semiconductors and insulators, sometimes by several electron volts [19].

To overcome these limitations and access excited-state properties with greater accuracy, Many-Body Perturbation Theory (MBPT) provides a more rigorous theoretical framework. It does so by introducing the concept of quasiparticles, renormalized electronic excitations that account for many-body interactions. MBPT has proven capable of producing band structures and band gaps in good agreement with experimental data [19]. The first successful QP calculations were performed in the mid-1980s [20], while the incorporation of many-body effects in *ab initio* calculations to study the optical properties of semiconductors emerged in the 1990s [21,22].

2.3.1 Green’s function with screened Coulomb potential (GW) approach

MBPT builds upon the exact solution of the many-body Schrödinger equation by systematically treating electron-electron interactions as perturbations to a non-interacting reference system. The central mathematical object in this framework is the single-particle Green’s function, which encodes information about electronic excitations and can be used to calculate both quasiparticle and optical spectra. A thorough treatment of Green's function formalism and many-body techniques in condensed matter physics can be found in Refs. [23–25]. In practical implementations such as those used in the Yambo code, the starting point for MBPT is the non-interacting system derived from the KS DFT solution [26,27]. In this formalism, the single-particle states are labelled as $|nk\rangle$, where n is the band index and k is a point on the Brillouin Zone (BZ) sampling grid. The non-interacting Green's function $G^0_{nk}(\omega)$ is expressed as:

$$G^0_{nk}(\omega) = \frac{f_{nk}}{\omega - \varepsilon_{nk} - i0^+} + \frac{1 - f_{nk}}{\omega - \varepsilon_{nk} + i0^+}$$

…(2.17)

where f_{nk} is the occupation factor and ε_{nk} are the KS energies.

The exact Green’s function $G_{nk}(\omega)$ is related to $G^0_{nk}(\omega)$ via the Dyson equation:

$$G_{nk}(\omega) = \left[\left(G^0_{nk}(\omega)\right)^{-1} - \Sigma_{nk}(\omega) + V^{xc}_{nk}\right]^{-1}$$

…(2.18)

A key physical distinction between a bare particle and a quasiparticle lies in the screening of the particle by polarization of the surrounding electronic medium. To model this effect, Yambo employs the GW approximation for the electronic self-energy Σ, where the self-energy is computed using the non-interacting Green's function G^0 and the dynamically screened Coulomb interaction W, with $\in$ being the dielectric function.

The GW self-energy is typically decomposed into exchange (x) and correlation (c) parts:

$$\Sigma_{nk}(\omega) = \Sigma^x_{nk} + \Sigma^c_{nk}(\omega)$$

…(2.19)

The exchange part is simply the Fock term of the HF self-energy, and it can be rewritten as

$$\Sigma^{x}_{nk} = \langle nk|\Sigma^{x}(r_1,r_2)|nk\rangle = -\sum_{m}\int_{BZ}\frac{dq}{(2\pi)^3}\sum_{G} v(q+G)\,|\rho_{nm}(k,q,G)|^2\, f_{m(k-q)}$$

…(2.20)

where $\rho_{nm}(k,q,G)$ are the reciprocal lattice vectors, and $v(q+G) = \frac{4\pi}{|q+G|^2}$. The correlation part of the self-energy is given by

$$\begin{aligned}\Sigma^{c}_{nk}(\omega) &= \langle nk|\Sigma^{c}(r_1,r_2;\omega)|nk\rangle\\ &= -i\sum_{m}\int_{BZ}\frac{dq}{(2\pi)^3}\sum_{G,G'}\frac{4\pi}{|q+G|^2}\rho_{nm}(k,q,G)\,\rho_{nm}(k,q,G)\rho^{*}_{nm}(k,q,G')\\ &\times\int d\omega'\, G^{0}_{mk-q}(\omega-\omega')\,\in^{-1}_{GG'}(q,\omega')\end{aligned}$$

…(2.21)

The energy integral entering Equation (2.21) can be solved once the inverse dielectric function is known. The equation of motion for $\in^{-1}$ follows from that of the reducible response function χ [24,25]. The *GW* approximation for the self-energy is obtained when χ is calculated within the random phase approximation (RPA) [28].

The noninteracting response function is easily calculated in terms of the bare Green's function G_0:

$$\begin{aligned}\chi^{0}_{GG'}(q,\omega) &= 2\sum_{nn'}\frac{dk}{(2\pi)^3}\rho^{*}_{n'nk}(q,G)\rho_{n'nk}(q,G')f_{nk-q}(1-f_{n'k})\\ &\times\left[\frac{1}{\omega+\varepsilon_{nk-q}-\varepsilon_{n'k}+i0^{+}}-\frac{1}{\omega+\varepsilon_{n'k}-\varepsilon_{nk-q}-i0^{+}}\right]\end{aligned}$$

…(2.22)

As the direct numerical evaluation of $\in^{-1}$ over many frequency points is computationally expensive, Yambo implements the plasmon-pole approximation (PPA). In this scheme, $\in^{-1}$ is modelled as:

$$\epsilon^{-1}_{GG'}(q,\omega) \approx \delta_{GG'} + R_{GG'}(q)[(\omega - \Omega_{GG'}(q) + i0^+)^{-1} - (\omega + \Omega_{GG'}(q) - i0^+)^{-1}]$$

…(2.23)

The residues $R_{GG'}$ and plasmon frequencies $\Omega_{GG'}$ are determined by fitting the model to match the exact dielectric function at $\omega=0$ and $\omega = iE_{\mathrm{PPA}}$, with E_{PPA} being a user-defined parameter.

Starting from Equation (2.18), and assuming $f_{nk} = 0$ or 1, we obtain:

$$(\omega - \varepsilon_{nk})G_{nk}(\omega) = 1 + [\Sigma_{nk}(\omega) - V^{xc}_{nk}]G_{nk}(\omega)$$

…(2.24)

To proceed, a first-order Taylor expansion of the self-energy around ε_{nk} is performed:

$$G_{nk}(\omega) = Z_{nk}\left[\frac{f_{nk}}{\omega - E^{QP}_{nk} - i0^+} + \frac{1 - f_{nk}}{\omega - E^{QP}_{nk} + i0^+}\right]$$

…(2.25)

here, the quasiparticle energy E^{QP}_{nk} is given by:

$$E^{QP}_{nk} = \varepsilon_{nk} + Z_{nk}[\Sigma_{nk}(\varepsilon_{nk}) - V^{xc}_{nk}],$$

…(2.26)

and the renormalization factor Z_{nk} is:

$$Z_{nk} = \left[\left|1 - \frac{d\Sigma_{nk}(\omega)}{d\omega}\right|_{\omega=\varepsilon_{nk}}\right]^{-1}$$

…(2.27)

Equations (2.26) and (2.27) constitute the core of the quasiparticle approximation in the GW framework [28], allowing for the accurate prediction of band structures and electronic excitation energies that go significantly beyond standard DFT.

2.3.2 Bethe-Salpeter equation

While the GW approximation provides accurate quasiparticle energies by incorporating many-body effects beyond standard DFT, it does not account for interactions between excited electrons and the holes they leave behind. These electron-hole interactions are particularly important in optical absorption and emission processes, where they give rise to excitonic effects that significantly modify the spectrum. To accurately describe such phenomena, one must solve the Bethe-Salpeter Equation (BSE), which governs the dynamics of electron-hole pairs in an excited state [18,29]. The BSE is derived from the equation of motion for the two-particle Green's function, and it takes the form of an effective eigenvalue problem for the excitonic Hamiltonian. The BSE can be written as:

$$(E_{ck} - E_{vk})A^{S}_{vck} + \sum_{kv'c'} < vck|K^{eh}\,|v'c'k' > A^{S}_{v'c'k'} = \Omega^{s} A^{S}_{vck}$$

…(2.28)

where E_{ck} and E_{vk} are GW quasiparticle energies of conduction and valence bands, respectively. A^{S}_{vck} is the exciton amplitude, Ω^{s} is the exciton eigenvalue (excitation energy), and K^{eh} is the electron-hole interaction kernel, which includes both screened Coulomb attraction and exchange repulsion.

In equation (2.28), the first term represents the independent particle transition energy between valence (v) and conduction (c) bands at a given *k*-point, while the second term captures the effects of electron-hole interactions. The interaction kernel K^{eh} consists of two main contributions:

$$K^{eh} = K^{dir} + K^{exc}$$

…(2.29)

K^{dir} is the direct interaction, which describes the screened Coulomb attraction between the excited electron and the hole it leaves behind. K^{exc} is the exchange term, which accounts for the antisymmetry of the electron-hole wavefunction and is typically derived from the unscreened Coulomb interaction.

The solution of the BSE provides the exciton energies Ω^{s} and the corresponding amplitudes A^{S}_{vck}, which describes the composition of each excitonic state in terms of valence-to-conduction transitions across the BZ. These quantities can be used to construct the macroscopic dielectric function and compute the optical absorption spectrum.

2.4 List of software packages used

Quantum ESPRESSO: an integrated suite of open-source codes for electronic-structure calculations and materials modelling based on DFT, plane waves, and pseudopotentials [30,31].

YAMBO: a post-processing code for calculating excited-state properties of materials using MBPT, particularly within the GW and BSE frameworks [26,27].

VESTA: a 3D visualization and modelling software used to construct, analyse, and visualize crystal structures, volumetric data, and isosurfaces. It also enables the manipulation and assembly of complex layered structures, making it particularly useful for heterostructure modelling [32].

XCrySDen: a graphical program primarily used to display crystal structures and is particularly useful for visualizing the reciprocal lattice and BZ in electronic structure calculations [33].

Bader: a tool used to perform Bader charge analysis, enabling partitioning of charge density among atoms based on zero-flux surfaces in the electron density [34].

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