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Colegio de Ciencias e Ingenierías

A Review on Density Functional Theory and GW
Approximation

Proyecto de Investigación

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**A Review on Density Functional Theory and GW
Approximation**

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La teoría del funcional de densidad y la aproximación GW son métodos computacionales utilizados para obtener propiedades de sólidos sin la necesidad de resolver la ecuación de Schrödinger. A pesar de que intentos para obtener la energía de átomos con la función de densidad fueron propuestos en 1927, la formalización de la teoría llegaría en los años 60 con los teoremas de Hohenberg-Kohn, que darían paso a los funcionales LDA, GGA y Meta-GGA. Los funcionales híbridos fueron creados posteriormente para mejorar la eficiencia de DFT por medio de ajustes empíricos. El modelo de cuasipartícula permitió el desarrollo de la aproximación GW, que se basa en la solución iterativa y autoconsistente de cinco ecuaciones. Si bien la aproximación completa aún no es factible, algunas simplificaciones han sido formuladas, y se desempeñan mejor que la mayoría de funcionales DFT. Este trabajo explica los conceptos teóricos fundamentales de estos modelos, así como algunas de las aproximaciones más comúnmente utilizadas. Finalmente, se presentan varios resultados numéricos para recalcar la utilidad y precisión de estos métodos, así como sus limitaciones.

Palabras Clave: Ab-initio, Aproximación GW, DFT, LDA, GGA, Meta-GGA, Teoría del Funcional de Densidad.

ABSTRACT

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Density functional theory and the GW approximation are computational methods used to obtain properties of solids without the need of solving Schrödinger's equation. While attempts to obtain the energy of atoms with the density function were proposed in 1927, the formalization of the theory came in the 60s with the Hohenberg-Kohn theorems, which gave way to LDA, GGA and Meta-GGA functionals. Hybrid functionals then attempted to improve the efficiency of DFT through empirical fitting. The quasiparticle model permitted the development of the GW approximation, which relies on the iterative, self-consistent solution of five equations. Even though the full scheme is still not practical, some simplifications have been formulated, and perform better than most DFT functionals. This review explains the theoretical concepts underlying these models, as well as some of the most commonly used approximations. Finally, multiple numerical results are presented to underline the utility and precision of these methods, as well as their limitations.

Keywords: Ab-initio, Density Functional Theory, DFT, GGA, GW Approximation, LDA, Meta-GGA.

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INTRODUCTION

The calculation of properties and behavior of many-body solids has become of great importance in the field of Solid-State Physics. The ability to predict the properties of new materials without the need of empiric tests permits to develop new semiconductors, better adapted for their designed use. Density Functional Theory, or DFT, and the GW approximation have become the methods of choice in chemistry, physics, and materials science to calculate structural and electronic properties of many-body solids.

The importance of these methods relies on the fact that the material properties are given by the electronic structure of the system (Hasnip et al., 2014). The equation published by Erwin Schrödinger in 1926 showed that all information about a system was contained in the wave function. As such, solving the Schrödinger equation became a fundamental step to obtain the properties of solids. However, for large many-body systems the equation becomes too complex, and practically impossible to solve (Kohn, 1999). As early as in 1927, the notion of expressing the energy of a system in terms of its electronic density instead of the wave function appeared (Laird, Ross, & Ziegler, 1996). Models formulated by Enrico Fermi and Llewellyn Thomas, and later by Paul Dirac and John Slater would expand on this idea. In 1964, Pierre Hohenberg and Walter Kohn presented a set of theorems that proved that the ground state energy of a system could be uniquely defined by the density, thus giving this notion a formal background.

Density Functional Theory and the GW approximation are techniques based on these theorems that generate models to calculate and predict the properties of many-body solids. These models are particularly useful for the development of semiconductor materials (Fraga, Prócel, Trojman, & Torres, 2013), which have applications in various domains such as photovoltaics (Even et al., 2014), vibrational spectroscopy (Baroni, de Gironcoli, Dal Corso, & Giannozzi, 2001), among others. Developing new tools for solving problems of many-electron systems through these techniques has become the focus of research for many Mathematicians, Physicists, Chemists and Computer Scientists (Bach & Delle, 2014)

Both Density Functional Theory and the GW approximation are methods that have been extensively in development for over 50 years. Even though their bases are well established, new approaches to these methods are constantly being published to reduce computational cost or provide a better fit. As a result, the volume of information on the topic required to understand the theory can be overwhelming. The present work aims to review Density Functional Theory and GW Approximation, both theoretically and with a comparison of numerical results. With that in mind, chapter 3 presents the background necessary to understand both methods. In chapters 4 and 5, the theoretical principles of the models created by DFT and the GW Approximation are described, and some of the most popular approximations based on each of these models are presented. Finally, we gather some numerical results from bibliography to provide context to the applicability of the methods, which depends on the requirements of the experiment.

THEORETICAL BACKGROUND

3.1 Schrödinger's Equation

Density functional theory is a method widely used to find a solution to the Schrödinger's equation for many-body solids. Schrödinger's equation describes the changes of a many-body system over time, taking quantum effects in consideration.

3.1.1 The Equation

The general time dependent form of Schrödinger's equation determines the existence of stationary states, or orbitals, and is expressed as

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi \quad (3.1)$$

where \hat{H} is the Hamiltonian operator of the system, and Ψ is the wave-function of all the bodies in the system, giving the description of the quantum state of the system. If the Hamiltonian operator does not depend on time, then the stationary state can be described by the time independent Schrödinger's equation

$$\hat{H} \Psi = E \Psi \quad (3.2)$$

which is an eigenvalue equation in which the constant E is the total energy of the orbital. This form of the equation is particularly useful to find the ground-state of the system (Griffiths, 1995).

3.1.2 Hamiltonian Operator

The Hamiltonian operator of the system is the sum of all kinetic and potential energies in the system. That is,

$$\hat{H} = \hat{T} + \hat{V} \quad (3.3)$$

where \hat{T} is the kinetic energy, and \hat{V} represents the potential energy. For a system composed of M nuclei and n electrons, the kinetic energy equals the sum of the kinetic energies of all bodies,

$$\hat{T} = - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^n \frac{1}{2} \nabla_i^2, \quad (3.4)$$

where M_A is the mass of nuclei A , ∇_A^2 is the Laplace operator for the nuclei A , ∇_i^2 is the Laplace operator for the electron i , and we use Hartree atomic units¹, such that $\hbar = m_e = e = 4\pi\epsilon_0 = 1$. The potential energy \hat{V} is the sum of the interactions between all nuclei and electrons,

$$\hat{V} = \hat{V}_{Ne} + \hat{V}_N + \hat{V}_e = - \sum_{A=1}^M \sum_{i=1}^n \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|} - \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_{i=1}^n \sum_{j>i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (3.5)$$

where \hat{V}_{Ne} is the potential energy due to interactions between electrons and nuclei, \hat{V}_N is the potential energy due to nuclei interactions, \hat{V}_e is the potential energy due to electron-electron interactions, \mathbf{R}_A is the position vector of nuclei A , \mathbf{r}_i is the position vector of electron i , and Z_A is the charge of nuclei A .

¹Throughout this thesis, Hartree atomic units are used.

Thus, the complete Hamiltonian operator is

$$\hat{H} = - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^n \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \sum_{i=1}^n \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|} - \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_{i=1}^n \sum_{j>i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (3.6)$$

3.1.3 Expectation Value and Variational Principle

From equation (3.2) we see that the expectation value is

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (3.7)$$

where

$$\langle \Psi | H | \Psi \rangle = \int \Psi^* H \Psi dr, \quad \langle \Psi | \Psi \rangle = \int |\Psi|^2 dr.$$

The variational principle states that the energy calculated with a trial wave function Ψ is always greater or equal than the ground-state energy. This can be proved as follows.

Proof. Suppose that Ψ_n and E_n are the true quantum states and corresponding eigenvalues of the system, for $n \in \mathbf{N}$.

Let

$$E_0 < E_1 < E_2 < \dots,$$

such that Ψ_0 is the ground-state. If the wave function is normalized, we can write

$$\Psi = \sum_i c_i \psi_i \quad (3.8)$$

where

$$\sum_i |c_i|^2 = 1 \quad (3.9)$$

and all ψ_i are orthonormal.

Calculating the energy with our trial wave function, we obtain

$$E = \langle \Psi | H | \Psi \rangle = \left\langle \sum_i c_i \psi_i \left| H \right| \sum_j c_j \psi_j \right\rangle. \quad (3.10)$$

This is,

$$\begin{aligned} &= \int \left(\sum_i c_i \psi_i \right)^* H \left(\sum_j c_j \psi_j \right) dr \\ &= \int \left(\sum_i c_i^* \psi_i^* \right) \left(\sum_j c_j H \psi_j \right) dr \end{aligned} \quad (3.11)$$

Applying equation (3.2),

$$\begin{aligned}
&= \int \left(\sum_i c_i^* \psi_i^* \right) \left(\sum_j c_j E_j \psi_j \right) d\mathbf{r} \\
&= \sum_i \sum_j \int (c_i^* \psi_i^*) (c_j E_j \psi_j) d\mathbf{r} \\
&= \sum_i \sum_j c_i^* c_j E_j \int \psi_i \psi_j d\mathbf{r}
\end{aligned} \tag{3.12}$$

Because ψ_i and ψ_j are orthonormal,

$$\int \psi_i \psi_j d\mathbf{r} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases}$$

and (3.12) results in,

$$\sum_i |c_i|^2 E_i \tag{3.13}$$

$$= |c_0|^2 E_0 + \sum_{i>0} |c_i|^2 E_i \tag{3.14}$$

We can rewrite equation (3.9) as

$$|c_0|^2 = 1 - \sum_{i>0} |c_i|^2 \tag{3.15}$$

Applying this equation into equation (3.14), we finally obtain that

$$E = E_0 + \sum_{i>0} |c_i|^2 (E_i - E_0) \tag{3.16}$$

Since we started from the fact that $E_i > E_0 \forall i > 0$, we obtain that

$$E = \langle \Psi | H | \Psi \rangle \geq 0 \tag{3.17}$$

and that $E = E_0 \Leftrightarrow \Psi$ is the true ground-state wave function Ψ_0

■

3.2 Born-Oppenheimer Approximation

Schrödinger's equation becomes exceedingly difficult to solve in large systems, as for an n -body system, Ψ depends on $3n$ variables. To solve this problem, we can consider that under typical conditions, the speed of nuclei is insignificant compared to that of electrons. Thus, we can simplify the Hamiltonian operator for practical purposes disregarding the nuclei's motion in space. This simplification leads to

$$-\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 = 0 \tag{3.18} \quad \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} = \text{constant} \tag{3.19}$$

reducing the Hamiltonian operator to

$$\hat{H}_{elec} = - \sum_{i=1}^n \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \sum_{i=1}^n \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|} - \sum_{i=1}^n \sum_{j>i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (3.20)$$

which calculates only the energy of the electrons. With this approximation, we can solve the *electronic* Schrödinger equation,

$$\hat{H}_{elec} \Psi_{elec} = E_{elec} \Psi_{elec} \quad (3.21)$$

to obtain the pure electronic energy E_{elec} . Finally, to obtain the total energy of the system, the potential energy due to nuclear interactions, as described in equation (3.19), is added:

$$E = E_{elec} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}. \quad (3.22)$$

This simplification, called the Born-Oppenheimer approximation, is widely used to reduce the number of variables involved and the size of calculations performed.

3.3 Using Density Functionals

3.3.1 Functionals

A functional is a mapping from a vector space \mathbf{V} into its scalar field \mathbf{F} . The functionals used in DFT are mappings from the space of functions to \mathbb{R} , this means, a functional F is a map

$$F : f \rightarrow \mathbb{R}$$

$$f(x) \mapsto F[f(x)].$$

Here, x is a parameter.

These functionals are also often described as a function of a function (Eberhard & Dreizler, 2011).

3.3.2 Thomas-Fermi model

In 1927, Llewellyn Thomas and Enrico Fermi proposed, independently, an approximation using a functional of the electron density function instead of the wave function to estimate the kinetic and potential energy of a many-body system (Thomas, 1927) (Fermi, 1927). In order to estimate the electronic density, the model assumes that electrons are distributed uniformly in the volume occupied by the atom,

$$\rho = \frac{n}{V} \quad (3.23)$$

where ρ is the electron density, and V is the volume. This assumption is known as the *uniform electron gas model*, and immediately simplifies the calculation of the potential energy. The interaction between the uniform electron gas and the nuclei can be calculated with the expression

$$V_{Ne} = \sum_{A=1}^M \int \frac{Z_A \cdot \rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_A|} d\mathbf{r}, \quad (3.24)$$

and the potential energy of the uniform electron gas is

$$V_e = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (3.25)$$

To obtain the kinetic energy, we begin by calculating the maximum possible momentum for the electrons, p_F , within the volume occupied by the solid in phase space. This can be done with equation (3.26), where h^3 is the volume in phase space occupied by two electrons of opposite spin. By applying equation (3.23) here, we obtain the expression (3.27) for the maximum momentum in terms of ρ .

$$\frac{4\pi}{3} p_F^3 \cdot V \cdot \frac{2}{h^3} = n \quad (3.26)$$

$$p_F = \left[\frac{3h^3}{8\pi} \rho \right]^{1/3} \quad (3.27)$$

Since the kinetic energy at a specific point can be calculated as

$$t(\mathbf{r}) = \int_0^{p_F} \frac{p^2}{2m_e} \rho(\mathbf{r}) \frac{4\pi p^2}{\frac{4}{3}\pi p_F^3} dp \quad (3.28)$$

$$t(\mathbf{r}) = \frac{3\rho}{2p_F^3} \int_0^{p_F} p^4 dp$$

$$t(\mathbf{r}) = \frac{3\rho}{2p_F^3} \left[\frac{p^5}{5} \right]_0^{p_F}$$

$$t(\mathbf{r}) = \frac{3\rho}{10} p_F^2. \quad (3.29)$$

Applying equation (3.27) on equation (3.29), we obtain an expression for the kinetic energy t at a point \mathbf{r} in terms of ρ .

$$t(\mathbf{r}) = \frac{3\rho(\mathbf{r})}{10} \left(\frac{3h^3}{8\pi} \rho(\mathbf{r}) \right)^{\frac{2}{3}} \quad (3.30)$$

Finally, to obtain the general kinetic energy, \hat{T} , we integrate the expression (3.30) over the volume occupied by the system,

$$\hat{T} = \int_V t(\mathbf{r}) = \frac{3h^2}{10} \left(\frac{3}{8\pi} \right)^{\frac{2}{3}} \int [\rho(\mathbf{r})]^{\frac{5}{3}} d^3\mathbf{r} \quad (3.31)$$

The Thomas-Fermi model was the first attempt to solve Schrödinger's equation by using the electronic density instead of the wave function, but is very inaccurate. The kinetic energy is only approximated, and the potential energy does not consider correlation between electrons.

3.3.3 Electronic Density Function

The Thomas-Fermi model used equation (3.23) to find the electronic density, and apply it to the kinetic energy functional. For Density Functional Theory, however, we formalize the idea of the electronic density as a probability density function derived from the wave function.

The electronic density function, ρ , measures the probability of an electron being present in a unit of volume during a given state Ψ . It is defined as

$$\rho(\mathbf{r}) = \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_n)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_n \quad (3.32)$$

and depends only on 3 spatial variables.

Integrating the density function over all space, we obtain the number of electrons within the system. Approaching $\mathbf{r} = 0$, the density function approaches 0 as well.

DENSITY FUNCTIONAL THEORY

4.1 Founding results of DFT

The Thomas-Fermi model showed the possibility of calculating the energy of a system by using an electronic density function instead of the more complicated wave function. However, the formalism required for Density Functional Theory would come years later through the Hohenberg-Kohn theorems, and the Kohn-Sham equations.

4.1.1 Hohenberg-Kohn Theorems

In 1964, Pierre Hohenberg and Walter Kohn published proof for a variational principle where the density function was the variable. The two theorems published in this paper are presented below.

Theorem 4.1.1. *A given ground-state density $\rho_0(\mathbf{r})$ determines the ground-state wave function, Ψ_0 , as well as the external potential V_{ext} and all properties of the system.*

This theorem states, in other words, that the energy of the system is a unique functional of the density (Toffoli, 2009a).

Proof. Assume that there exist two potentials V_{ext} and V'_{ext} , which differ by more than a constant and result in the same ground-state density $\rho_0(\mathbf{r})$. Since the two potentials are different, they belong to different Hamiltonians H and H' and different wave functions Ψ and Ψ' .

Because of the variational principle,

$$E_0 < \Psi' H \Psi' = \Psi'^* H' \Psi' - \Psi'^* (H - H') \Psi' = E'_0 + \int \rho(\mathbf{r}) [V_{ext}(\mathbf{r}) - V'_{ext}(\mathbf{r})] d\mathbf{r} \quad (4.1)$$

and

$$E'_0 < \langle \Psi | H' | \Psi \rangle = \langle \Psi | H | \Psi \rangle - \langle \Psi | H' - H | \Psi \rangle = E_0 + \int \rho(\mathbf{r}) [V'_{ext}(\mathbf{r}) - V_{ext}(\mathbf{r})] d\mathbf{r} \quad (4.2)$$

Adding both sides we obtain that

$$E_0 + E'_0 < E'_0 + E_0 \quad (4.3)$$

which is a contradiction. ■

For this reason, we can write the energy functional as

$$E[\rho] = \int \rho(\mathbf{r}) V_{Ne}(\mathbf{r}) d\mathbf{r} + F[\rho] \quad (4.4)$$

where $F[\rho]$ is a functional corresponding to $T[\rho] + V_e[\rho]$, in which

$$V_e[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + F_e[\mathbf{r}] \quad (4.5)$$

where $F_e[\mathbf{r}]$ is the self-interaction correction, exchange and Coulomb correlation of the electron-electron interaction.

Theorem 4.1.2. *The density functional resulting in the ground-state energy will have a global minimum value only at the true ground-state density.*

$$E[\rho_0] \leq E[\rho] = T[\rho] + E_{Ne}[\rho] + E_e[\rho] \quad (4.6)$$

$$E[\rho_0] = E[\rho] \Leftrightarrow \rho = \rho_0 \quad (4.7)$$

Proof. The ground-state density returns the ground-state energy

$$E[\rho_0] = E_0 = \langle \Psi_0 | H | \Psi_0 \rangle \quad (4.8)$$

By theorem 1 and the variational principle, we know that a different density will return a different wave function and a greater energy

$$E[\rho'] = \langle \Psi' | H | \Psi' \rangle > \langle \Psi_0 | H | \Psi_0 \rangle = E_0 \quad (4.9)$$

■

4.1.2 Kohn-Sham equations

In 1965, Walter Kohn and Lu Jeu Sham created a model for solving the Schrödinger equation using the density function, using the Hohenberg-Kohn theorems to solve the problems that made the Thomas-Fermi method inaccurate (Kohn & Sham, 1965). The model proposes calculating the kinetic energy of a non-interacting system such that the electronic density is the same as that of the real, interacting one.

In order to calculate the ground-state energy of such a system, we need to obtain the wave function that describe the bodies in it. For this purpose, we set

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 = \rho_0(\mathbf{r}) \quad (4.10)$$

where ψ_i is the orbital corresponding to the i -th body. Next, we use the Slater determinant

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \cdots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \cdots & \psi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix} \quad (4.11)$$

to approximate the general wave function.

We can now calculate the kinetic energy using the new approximation of the wave function

$$T_{KS} = -\frac{1}{2} \sum_{i=1}^N (\psi_i^* \nabla^2 \psi_i) \quad (4.12)$$

Equation (4.4) then becomes

$$E[\rho] = T_{KS} + \int \rho(\mathbf{r}) V_{Ne}(\mathbf{r}) d\mathbf{r} + E_{XC} \quad (4.13)$$

where E_{XC} is the *exchange-correlation energy*, defined as

$$E_{XC} = (T[\rho] - T_{KS}) + F_e[\rho]. \quad (4.14)$$

The orbitals used must satisfy the Hohenberg-Kohn theorems, and they can be obtained by solving the following equations:

$$\left(-\frac{1}{2}\nabla^2 + \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 + \sum_{A=1}^M \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} + V_{XC} \right) \psi_i(\mathbf{r}) = \varepsilon \psi_i(\mathbf{r}) \quad (4.15)$$

$$V_{XC} = \frac{\partial E_{XC}}{\partial \rho} \quad (4.16)$$

Equations (4.15) and (4.16) are known as the Kohn-Sham equations.

To obtain the total energy using the Kohn-Sham equations, we need to approximate the unknown exchange-correlation potential functional, $V_{XC}[\rho]$.

4.2 Local Density Approximation

The Local Density Approximation (LDA) calculates the exchange-correlation energy by assuming that the system is a uniform electron gas (Kohn & Sham, 1965). It introduces an energy density functional $\varepsilon_{XC}[\rho]$, as seen in equation (4.17). This term corresponds to the exchange-correlation energy per particle.

$$E_{XC} = \int \rho(\mathbf{r}) \varepsilon_{XC}[\mathbf{r}] d\mathbf{r}. \quad (4.17)$$

The energy density functional can be divided into its exchange and correlation contributions, $\varepsilon_{XC} = \varepsilon_X + \varepsilon_C$. The exchange contribution is the same as that derived by Paul Dirac in 1930,

$$\varepsilon_X = -\frac{3}{4} \left(\frac{3\rho(\mathbf{r})}{\pi} \right)^{\frac{1}{3}}. \quad (4.18)$$

The correlation contribution was neglected initially, and Monte Carlo simulations were generally used to calculate it. Many alternative functionals for the correlation energy density have been developed since (Perdew & Wang, 1992) (Vosko, Wilk, & Nusair, 1980). However, because of the uniform electron gas model used, LDA tends to overestimate the exchange energy, and underestimate the correlation energy (Tofoli, 2009b).

4.3 Generalized Gradient Approximation

To improve the accuracy of LDA, Generalized Gradient Approximations introduced the gradient of the density into the exchange and correlation functional, which takes the general form

$$E_{XC}^{GGA}[\rho \uparrow, \rho \downarrow] = \int \rho(\mathbf{r}) \varepsilon_{XC}[\rho] F_{XC}[s] \quad (4.19)$$

where $\rho \uparrow$ and $\rho \downarrow$ are the spin densities such that $\rho = \rho \uparrow + \rho \downarrow$, F_{XC} is the GGA correction factor, and $s = |\nabla\rho| / \left(2 [3\pi\rho(\mathbf{r})]^{\frac{1}{3}} \rho \right)$.

The correction factor, F_{XC} depends on the approximation used. Some functionals are made to satisfy physical restrictions, such as PBE and PW91; whereas others are obtained by fitting to empirical data, like B88.

PBE Functional

One of the most used GGA approximations is the PBE functional (Swart, Bickelhaupt, & Duran, 2016). This functional is built to only satisfy physical conditions that are energetically significant (Perdew, Burke, & Ernzerhof, 1996). To do so, Perdew, et al. began with the correlation functional

$$E_C^{PBE}[\rho \uparrow, \rho \downarrow] = \int \rho(\mathbf{r}) [\varepsilon_C^{LDA} + H(r_S, \zeta, t)], \quad (4.20)$$

where $r_S = (3/(4\pi\rho))^{1/3}$ is the Seitz radius, $\zeta = (\rho \uparrow - \rho \downarrow)/\rho$ is the relative spin polarization, and $t = |\nabla\rho|/(2gk_s\rho)$ is a density gradient correction factor, where $g = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}]/2$ is a spin scaling factor and $k_s = \left(\left(4[3\pi^2\rho]^{(1/3)}\right)/\pi\right)^{(1/2)}$ is the Thomas-Fermi screening wave number 1996.

The correlation correction functional $H(r_S, \zeta, t)$ was defined so that:

1. In the slowly varying limit, when the density gradient tends to 0, H is given by

$$\lim_{t \rightarrow 0} H = \beta g^3 t^2, \quad (4.21)$$

where $\beta \approx 0.066725$ is the high density limit of the gradient coefficient for the correlation energy.

2. In the rapidly varying limit, correlation vanishes, so

$$\lim_{t \rightarrow \infty} H = -\varepsilon_C^{LDA}. \quad (4.22)$$

3. Under uniform scaling, $\rho(\mathbf{r}) = \lambda^3 \rho(\lambda\mathbf{r})$, the correlation energy must scale to a constant.

The functional H was then defined by the ansatz

$$H^{PBE} = \gamma g^3 \ln \left[1 + \frac{\beta}{\gamma} \left(\frac{t^2 + At^4}{1 + At^2 + A^2 t^4} \right) \right] \quad (4.23)$$

where $\gamma = (1 + \ln 2)/\pi^2$ and

$$A = \frac{\beta}{\gamma} \left[\exp \left(-\frac{\varepsilon_C^{LDA}}{\gamma g^3} \right) - 1 \right]^{-1}. \quad (4.24)$$

This functional satisfies all three conditions.

The exchange functional for PBE must also satisfy the following restrictions:

1. Under uniform scaling, $F_X(0) = 1$
2. The exchange energy obeys the relationship

$$E_X[\rho \uparrow, \rho \downarrow] = \frac{E_X[2\rho \uparrow] + E_X[2\rho \downarrow]}{2} \quad (4.25)$$

3. The functional recovers the linear response of LDA, so

$$\lim_{s \rightarrow 0} F_X(s) = 1 + \mu s^2, \quad (4.26)$$

where $\mu = \beta(\pi^2/3)$

4. The functional must satisfy the Lieb-Oxford bound,

$$E_X [\rho \uparrow, \rho \downarrow] \geq E_{XC} [\rho \uparrow, \rho \downarrow] \geq -1.679e^2 \int \rho(\mathbf{r}) d\mathbf{r}, \quad (4.27)$$

which provides a lower bound for the exchange correlation energy.

The exchange correction functional $F_X(s)$ that Perdew, et al. chose is

$$F_X^{PBE}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}, \quad (4.28)$$

which satisfies all restrictions.

This functional was built upon the PW91 functional, which satisfied more theoretical restrictions but did not recover the linear response that LDA has (Perdew et al., 1992) (Perdew et al., 1996).

B88 functional

The B88 exchange functional was developed by Axel Becke in 1988. The functional was developed such that the real asymptotic behavior of the exchange energy as r tends to ∞ is generated. The B88 functional has the form

$$E_X^B = E_X^{LDA} - \beta \int \frac{|\nabla\rho|}{1 + 6\beta \frac{|\nabla\rho|}{\rho^{4/3}} \sinh^{-1}\left(\frac{|\nabla\rho|}{\rho^{4/3}}\right)}, \quad (4.29)$$

where $\beta = 0.0042$. This is considered a semi-empiric functional, as β was obtained through a least-squares fit using the exact exchange energies of the first six noble gases. The functional was obtained by adapting previous empirical non-universal functionals (Becke, 1988).

While LDA and GGA show good agreement with experimental results for the calculation of exchange and correlation energies, it has been shown that the errors obtained by these approximations come from self-correlation in the case of energy (Seidl, Perdew, & Levy, 1999), and the Kohn-Sham scheme in the case of band gaps (Perdew, 1985), since Kohn-Sham band gaps are always smaller than the fundamental band gap.

4.4 Meta-GGA

To improve the accuracy of GGA functionals even further, some functionals also include the kinetic energy density obtained from the Kohn-Sham orbitals,

$$\tau = \sum_i \frac{1}{2} |\nabla\psi_i(\mathbf{r})|^2. \quad (4.30)$$

The kinetic energy density can be written in terms of the electronic density. A commonly used functional for τ is the Weizsäcker functional

$$\tau_W = -\frac{1}{8} \frac{|\nabla\rho|^2}{\rho}, \quad (4.31)$$

obtained in 1935 by Carl Friedrich von Weizsäcker.

LYP Functional

The LYP functional was developed by Chengteh Lee, Weitao Yang and Robert Parr. It was built upon the Colle-Salvetti correlation formula which used the second order density matrix. By applying the Weizsäcker kinetic energy density, Lee, et al. turned this formula into the functional shown in equation (4.32).

$$E_C^{LYP} = -a \int \frac{1}{1 + d\rho^{-\frac{1}{3}}} \left\{ \rho + b\rho^{-\frac{2}{3}} \left[\frac{3}{10} (3\pi^2)^{\frac{2}{3}} \rho^{\frac{5}{3}} - \frac{17}{72} \left(\frac{|\nabla\rho|^2}{\rho} - \nabla^2\rho \right) + \frac{1}{18} \nabla^2\rho \right] e^{-c\rho^{-\frac{1}{3}}} \right\} dr, \quad (4.32)$$

where $a = 0.04918$, $b = 0.132$, $c = 0.2533$, $d = 0.349$ are the coefficients obtained by Colle-Salvetti (Lee, Yang, & Parr, 1988).

Other examples of Meta-GGA functionals are PKZB and M06L.

4.5 Hybrid Functionals

A fourth kind of functionals mixes previously developed GGA functionals with the Hartree-Fock exchange energy,

$$E_X^{HF} = \frac{1}{2} \sum_{i=0}^n \sum_{j>i}^n \int \int \psi_i^*(r_1) \psi_j^*(r_2) \frac{1}{|r_1 - r_2|} \psi_i(r_2) \psi_j(r_1) dr_1 dr_2, \quad (4.33)$$

usually taking the general form

$$E_{XC}[\rho] = \alpha E_X^{HF} + (1 - \alpha) E_{XC}^{GGA} + E_C^{GGA}. \quad (4.34)$$

where α is a parameter usually obtained through fitting. Functionals of this form are called hybrid functionals.

Among the most used hybrid functionals are B3LYP, HSE and PBE0.

B3LYP Functional

The B3LYP functional has the form

$$E_{XC}^{B3LYP} = E_X^{LDA} + a_0 (E_X^{HF} - E_X^{LDA}) + a_x (E_X^B - E_X^{LDA}) + E_C^{VWN} + a_c (E_C^{LYP} - E_C^{VWN}) \quad (4.35)$$

where $a_0 = 0.2$, $a_x = 0.72$, $a_c = 0.81$ are weights obtained from experimental data (Stephens, Devlin, Chabalowski, & Frisch, 1994), E_X^{B88} is the B88 exchange functional, and E_C^{VWN} is the semi-empiric VWN correlation functional for LDA developed by S. H. Vosko, L. Wilk and M. Nusair (1980).

HSE and PBE0 Functionals

The HSE hybrid functionals published by Jochen Heyd, Gustavo Scuseria, and Matthias Ernzerhof separate the exchange functional into a short range term and a long range term, taking the form

$$E_{XC}^{HSE} = a E_X^{HF,SR} + (1 - a) E_X^{PBE,SR} + E_X^{PBE,LR} + E_C^{PBE} \quad (4.36)$$

where $a = 1/4$ is the mixing coefficient, SR represents that the functional is applied to the short range, and LR represents a long range application. The PBE exchange and correlation functionals are used. The

separation between short and long range is performed by dividing the Coulomb operator as it appears in equation (4.33) in the following manner:

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{\text{erfc}(\omega |\mathbf{r}_i - \mathbf{r}_j|)}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{\text{erf}(\omega |\mathbf{r}_i - \mathbf{r}_j|)}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (4.37)$$

where erf is the error function, and $\text{erfc} = 1 - \text{erf}$. ω is the parameter that controls the effective radius of the short range functional. The PBE functionals $E_X^{PBE,SR}$ and $E_X^{PBE,LR}$ are modified by multiplying the correction factor with the error function (Heyd, Scuseria, & Ernzerhof, 2003). The value of *omega* varies depending on the approximation used. For HSE03, $\omega = 0.3$; for HSE06, $\omega = 0.2$; and finally, if $\omega = 0$ we obtain the PBE0 functional (Heyd et al. 2003, 2006).

The use of short and long range functionals, along with the Hartree-Fock exchange energy helps solve the band gap problem that arises from the Kohn-Sham scheme, as HF band gaps are generally larger than those of KS (Crawford, Furche, & Burke, 2009).

GW APPROXIMATION

In 1965, Lars Hedin proposed an alternative method to obtain the energy of a system. This method utilizes the quasiparticle model to maintain a system with independent particles.

5.1 Quasiparticle model

In a solid, an electron repels other electrons due to the Coulomb potential, and forms a positively charged polarization cloud around it, which we call electron hole. The electron and electron hole pair forms a quasiparticle which only interacts weakly with other quasiparticles via a screened Coulomb potential (Aulbur, Jönsson, & Wilkins, 2000). This weak interaction allows us to consider a non-interacting system. The exchange and correlation energies of the bare electron are considered as the self-energy Σ of the quasiparticle.

The energy of a system formed by independent quasiparticles is calculated in a similar manner to that of the Kohn-Sham model. Each quasiparticle responds to the equation

$$\left[\frac{1}{2} \nabla^2 + \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 + V_{Ne} \right] \psi_i(\mathbf{r}_1) + \int \Sigma(\mathbf{r}_1, \mathbf{r}_2) \psi_i(\mathbf{r}_2) d\mathbf{r}_2 = E_i \psi(\mathbf{r}_1) \quad (5.1)$$

where ψ_i is the wave function of the quasiparticle, and E_i is the total energy of the quasiparticle.

5.1.1 Green Function

For a linear differential operator \mathcal{L} , a Green function G corresponding to \mathcal{L} is a function that satisfies the equation

$$\mathcal{L}G(x, x_1) = \delta(x - x_1) \quad (5.2)$$

where δ is Dirac's delta function

$$\delta(x) = \begin{cases} \infty & x = 0 \\ 0 & x \neq 0 \end{cases} . \quad (5.3)$$

The Green function is defined this way to find the solution to the differential equation

$$\mathcal{L}u(x) = f(x) . \quad (5.4)$$

Here, the function $u(x)$ takes the integral form

$$u(x) = \int G(x, x_1) f(x_1) dx_1 . \quad (5.5)$$

(Stover, n.d.)

For equation (5.1), the corresponding Green function satisfies the equation

$$[\omega - h(1)]G(1, 2) + \int \Sigma(\mathbf{r}_1, \mathbf{r}_2) G(1, 2) d\mathbf{r}_2 = \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (5.6)$$

where the numerals 1, 2, ... represent the space and time pair (\mathbf{r}_1, t_1) , and h is the one body hamiltonian. The Green function G describes the effects of the propagation of an electron or electron hole in the system. Thus, in order to obtain G , we first define the propagation functions as follows:

Let E_N be the energy of the $|N, 0\rangle$ ground state of the N -body system, $E_{N+1,a}$ the energy of the a -th state $|N+1, a\rangle$ of the $N+1$ -body system, $E_{N-1,i}$ the energy of the i -th state $|N-1, i\rangle$ of the $N-1$ -body system, $\hat{\psi}^\dagger(\mathbf{r})$ the electron creation operator and $\hat{\psi}(\mathbf{r})$ the electron annihilation operator.

$$\left\langle N, 0 \left| \left[\hat{\psi}(\mathbf{r}_1, t_1) \hat{\psi}^\dagger(\mathbf{r}_2, t_2) \right] \right| N, 0 \right\rangle = iG_e(1, 2) \quad (5.7)$$

represents the propagation of an electron from 2 to 1.

$$\left\langle N, 0 \left| \left[\hat{\psi}^\dagger(\mathbf{r}_2, t_2) \hat{\psi}(\mathbf{r}_1, t_1) \right] \right| N, 0 \right\rangle = iG_h(1, 2) \quad (5.8)$$

represents the propagation of an electron hole from 1 to 2.

The resulting Green function for the quasiparticle system is

$$G(1, 2) = -i\theta(t_1 - t_2) \left\langle N, 0 \left| \hat{\psi}(\mathbf{r}_1, t_1) \hat{\psi}^\dagger(\mathbf{r}_2, t_2) \right| \psi \right\rangle + i\theta(t_2 - t_1) \left\langle N, 0 \left| \hat{\psi}^\dagger(\mathbf{r}_2, t_2) \hat{\psi}(\mathbf{r}_1, t_1) \right| \psi \right\rangle \quad (5.9)$$

where θ is the Heaviside step function.

Through the Fourier transformation $t_1 - t_2 \rightarrow \omega$, we obtain the Lehmann form for the Green function,

$$G(\mathbf{r}_1, \mathbf{r}_2; \omega) = \lim_{\eta \rightarrow 0} \left(\frac{f_a(\mathbf{r}_1) f_a^*(\mathbf{r}_2)}{\omega - E_a + i\eta} + \frac{f_i(\mathbf{r}_1) f_i^*(\mathbf{r}_2)}{\omega - E_i - i\eta} \right) \quad (5.10)$$

where $f_a(x) = \langle N, 0 | \hat{\psi}(x) | N+1, a \rangle$, $f_i(x) = \langle N-1, i | \hat{\psi}(x) | N, 0 \rangle$ are the quasiparticle wave functions, and $E_a = E_{N+1,a} - E_N$ and $E_i = E_N - E_{N-1,i}$ are the quasiparticle energies (Toulouse, 2015).

5.2 Hedin Equations

In order to obtain the total energy of the system under this model, we need the self-energy of the quasiparticles. We can calculate the self-energy by solving a set of five equations self-consistently (Aulbur et al., 2000).

5.2.1 Dyson Equation

We now consider the non-interacting Green function, G_0 , which corresponds to a one body system and follows the equation

$$[\omega - h_0] G_0(1, 2) = \delta(1 - 2), \quad (5.11)$$

From equations (5.6) and (5.11), we obtain the Dyson equation,

$$G(1, 2) = G_0(1, 2) + \int \int G_0(1, 3) \Sigma(3, 4) G(4, 2) d3d4 \quad (5.12)$$

which calculates the Green function.

5.2.2 Vertex Function

We introduce now a fictional effective potential, V_{eff} , which we will use for the following derivations, and define the vertex function Γ as the variation of the inverse of the Green function with respect to the effective potential,

$$\Gamma(1; 2, 3) = \frac{\partial G^{-1}(2, 3)}{\partial V_{eff}(1)} \quad (5.13)$$

To obtain a closed set of equations, we find the expression for G^{-1} , defined as

$$\int G^{-1}(1, 3) G(3, 2) d3 = \delta(1, 2). \quad (5.14)$$

From equation (5.11) we get that

$$G_0^{-1}(1, 2) = (\omega - h(1)) \delta(1 - 2). \quad (5.15)$$

From equation (5.6) we also get

$$G^{-1}(1, 2) = (\omega - h(1)) \delta(1 - 2) + \Sigma(1, 2), \quad (5.16)$$

and because of equation (5.15),

$$G^{-1}(1, 2) = G_0^{-1}(1, 2) + \Sigma(1, 2). \quad (5.17)$$

We can now express Γ in terms of G and Σ ,

$$\Gamma(1; 2, 3) = \frac{\partial G_0^{-1}(2, 3)}{\partial V_{eff}(1)} + \frac{\partial \Sigma(2, 3)}{\partial V_{eff}(1)} \quad (5.18)$$

which becomes

$$\begin{aligned} \Gamma(1; 2, 3) &= \delta(1 - 2) \delta(1 - 3) + \frac{\partial \Sigma(2, 3)}{\partial V_{eff}(1)} \\ &= \delta(1 - 2) \delta(2 - 3) + \int \int \frac{\partial \Sigma(2, 3)}{\partial G(4, 5)} \frac{G(4, 5)}{\partial V_{eff}(1)} d4d5 \\ &= \delta(1 - 2) \delta(2 - 3) + \int \int \frac{\partial \Sigma(2, 3)}{\partial G(4, 5)} \int \int G(4, 6) \frac{G^{-1}(6, 7)}{\partial V_{eff}(1)} G(7, 5) d6d7d4d5. \end{aligned}$$

Finally, because of equation (5.13), we obtain the final form of the vertex function

$$\Gamma(1; 2, 3) = \delta(1 - 2) \delta(2 - 3) + \int \int \frac{\partial \Sigma(2, 3)}{\partial G(4, 5)} \int \int G(4, 6) \Gamma(1; 6, 7) G(7, 5) d6d7d4d5. \quad (5.19)$$

5.2.3 Polarization

The polarization function is defined as

$$P(1, 2) = -i \frac{\partial G(2, 2^+)}{\partial V_{eff}(1)} \quad (5.20)$$

where 1^+ represents an infinitesimal change in t_1 .

Applying equation (5.14),

$$P(1, 2) = -i \int G(2, 3) \frac{G^{-1}(3, 4)}{V_{eff}(1)} G(4, 2)$$

To obtain the final form of the polarization function, we apply equation (5.13),

$$P(1, 2) = -i \int G(2, 3) \Gamma(1; 3, 4) G(4, 2). \quad (5.21)$$

5.2.4 Screened Coulomb Potential

To calculate the effective interaction between quasiparticles, we use a screened Coulomb potential. This is the effect of the Coulomb potential on the quasiparticles as if it were an external field (Pavlyukh, 2003). The screened Coulomb potential has the form

$$W(1, 2) = V_e(1, 2) + \int W(1, 3) P(3, 4) V_e(4, 2) d3d4 \quad (5.22)$$

where V_e is the bare Coulomb potential.

5.2.5 Self-Energy

The self-energy of the quasiparticles is defined by the equation

$$\Sigma(1, 2) = i \int G(1, 4) W(1^+, 3) \Gamma(3; 4, 2) d3d4 \quad (5.23)$$

This expression gives the GW approximation its name.

The equations

$$G(1, 2) = G_0(1, 2) + \int \int G_0(1, 3) \Sigma(3, 4) G(4, 2) d3d4 \quad (5.12 \text{ revisited})$$

$$\Gamma(1; 2, 3) = \delta(1-2) \delta(2-3) + \int \int \frac{\partial \Sigma(2, 3)}{\partial G(4, 5)} \int \int G(4, 6) \Gamma(1; 6, 7) G(7, 5) d6d7d4d5. \quad (5.19 \text{ rev.})$$

$$P(1, 2) = -i \int G(2, 3) \Gamma(1; 3, 4) G(4, 2). \quad (5.21 \text{ rev.})$$

$$W(1, 2) = V_e(1, 2) + \int W(1, 3) P(3, 4) V_e(4, 2) d3d4 \quad (5.22 \text{ rev.})$$

$$\Sigma(1, 2) = i \int G(1, 4) W(1^+, 3) \Gamma(3; 4, 2) d3d4 \quad (5.23 \text{ rev.})$$

are called the Hedin equations. These equations form a recursive set of five equations that, when solved iteratively, return the self-energy and all properties of the quasiparticles. The complete iterative cycle can be appreciated in figure 5.1. However, the process of solving the complete system of equations is still too computationally heavy for practical purposes. For this reason, simplified GW approximations are used.

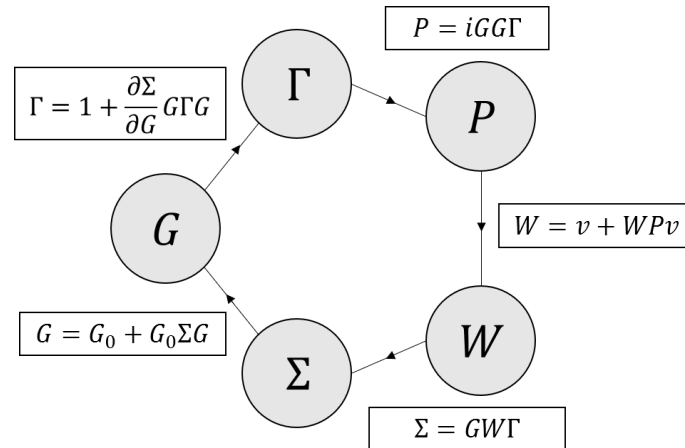


Figure 5.1: Representation of the complete GW approximation iterative cycle

5.3 Simplifications of the GW model

Different types of GW approximations can be performed, with various levels of complexity. The three most widely used are explained below.

5.3.1 G_0W_0 Approximation

The GW approximation begins by obtaining the initial quasiparticle wave functions through a DFT method, and then setting the initial value of the self-energy $\Sigma = 0$, which also leads to $G(1, 2) = G_0(1, 2)$. The calculation then proceeds through each equation.

Stopping the process after the first iteration, one obtains values for W and Σ approximated by using only non-interacting quasiparticles. This approach is called the G_0W_0 approximation. This approximation does not have a high computational cost and shows improvement over LDA (van Schilfgaarde, Kotani, & Faleev, 2006), but because the solution was not obtained self-consistently, it heavily depends on the DFT method used initially to calculate G_0 . Another downside of this approximation is that the G_0W_0 approximation does not obey conservation laws for "particle number, momentum, angular momentum and energy" (Stan, Dahlen, & van Leeuwen, 2009), which in turn has negative effects on spectral and conductive properties.

5.3.2 GW_0 Approximation

The GW_0 approximation is a partially self-consistent approach that obeys particle number conservation, and its solution does not depend on the DFT method used. The method begins with a complete iteration of the Hedin equations. It then solves the Dyson equation and updates the self-energy iteratively, effectively reducing the system of equations to only equations (5.12) and (5.24), as shown in figure 5.2.

$$\Sigma(1, 2) = iG(1, 2)W_0(1, 2) \quad (5.24)$$

This approximation is not moment or energy conserving, as W is not solved self-consistently. However, the computational cost is not severely increased (Stan et al., 2009)

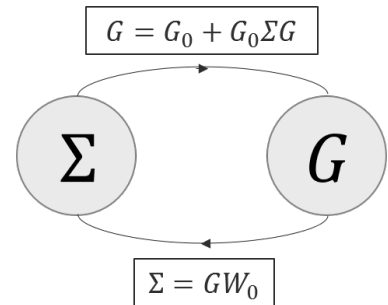


Figure 5.2: Representation of the iterative cycle using the GW_0 approximation

5.3.3 scGW Approximation

A simple self-consistent and practical approximation of the Hedin equations is performed by setting the vertex function $\Gamma = 1$. With this change, the four remaining equations are the Dyson equation (5.12), and (5.21), (5.22) and (5.23) without vertex corrections. With these changes the system of equations that must be solved iteratively is as follows:

$$G(1, 2) = G_0(1, 2) + \int \int G_0(1, 3)\Sigma(3, 4)G(4, 2)d3d4$$

$$P(1, 2) = -iG(1, 2)G(2, 1) \quad (5.25)$$

$$W(1, 2) = V_e(1, 2) + \int W(1, 3)P(3, 4)V_e(4, 2)d3d4 \quad (5.26)$$

$$\Sigma(1, 2) = iG(1, 2)W(1, 2) \quad (5.27)$$

This approximation obeys all conservation laws, and is independent of the DFT method used to calculate G_0 , but is much more computationally expensive (Aulbur et al., 2000). Furthermore, the scGW approximation results in a more accurate total energy, but overestimates the band gaps (Hafner, 2008) due to ignoring vertex corrections.

The iterative scheme of the scGW approximation is shown in figure 5.3.

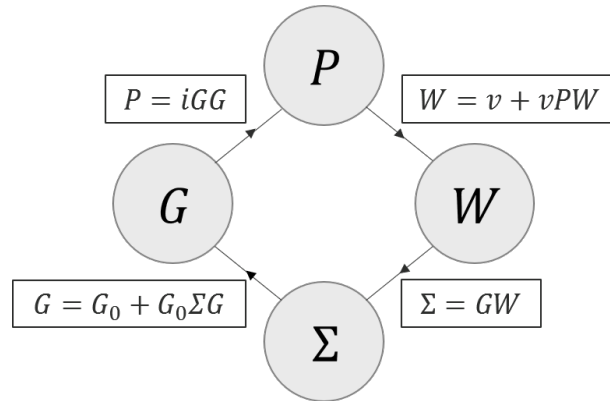


Figure 5.3: Representation of the iterative cycle using the scGW approximation

5.3.4 Vertex corrections

Currently, some studies prove that the inclusion of a simplified vertex function can reduce the error in band gap calculations, but the computational cost is as prohibitive as that of the scGW approximation (Schmidt, Patrick, & Thygesen, 2017) (Chen & Pasquarello, 2015).

EXPERIMENTAL RESULTS

Chapters 4 and 5 present some of the approximations that have been developed under the DFT and quasiparticle models. The importance of each of these approximations relies on their applicability. The different functionals used in DFT take different approaches to obtain the exchange and correlation energies, and therefore each approximation may prove more suitable to calculate specific parameters for different solids. The difference in accuracy to calculate atomization energies of molecules shows this, as can be seen in table 6.1, where ΔE is the experimental exchange and correlation energy.

Table 6.1: Exchange and correlation atomization energies (in kcal/mol) of 6 small molecules

Molecule	$\Delta E^{(1)}$	$\Delta E^{LDA(1)}$	$\Delta E^{PBE(1)}$	$\Delta E^{PKZB(1)}$	$\Delta E^{HSE(2)}$
H ₂	109.5	113.2	104.6	114.5	104.4
CH ₄	419.3	462.3	419.8	421.1	418.0
LiF	138.9	156.1	138.6	128.0	131.2
HCN	311.9	361.0	326.1	311.8	311.6
CO	259.3	299.1	268.8	256.0	255.7
N ₂	228.5	267.4	243.2	229.2	225.86

⁽¹⁾ Values published by Kurth, Perdew, and Blaha (1999)

⁽²⁾ Values published by Schimka, Harl, and Kresse (2011).

In table 6.2 we can see that the calculation of the lattice constant through different DFT functionals shows similar results (Torres, Reytier, & Trojman, 2017). LDA performs well, underestimating the real value by less than 0.5%. PBE and B3LYP overestimate experimental values by around 2%. PBE0 and HSE06 perform similarly well, with errors under 1%.

Table 6.2: Lattice constant of 4 semiconductors

Solid	Exp.	LDA	PBE	PBE0	B3LYP	HSE06
Si	5.4307	5.4032	5.4696	5.4307	5.4859	5.4354
Ge	5.6575	5.6466	5.7823	5.6969	5.7962	5.7033
GaAs	5.65	5.6258	5.7622	5.6900	5.7825	5.6961
GaN	3.1889	3.1843	3.2462	3.2079	3.2346	3.2093

Tables 6.1 and 6.2 show that LDA and PBE work well to obtain structural properties of simple molecules, but fails for larger systems. Each hybrid functional was developed for a different purpose, which explains the consistency of HSE06 and PBE0, while B3LYP fails to estimate the lattice constant. Meta-GGA methods like PKZB have a higher accuracy than LDA or PBE for energy calculations of bigger molecules such as HCN or N₂ because it eliminates the self-correlation error, but overestimates the correlation energy for simpler molecules like H₂.

Hybrid functionals prove to be better at estimating the band gap than LDA or GGA functionals, as the latter tend to significantly underestimate the real value. However, since these functionals introduce empirical parameters, they are sensitive to the material. The data presented in table 6.3 shows, for example, that HSE06 provides the best approximation for Si, whereas B3LYP provides a better result for GaN, and GaAs is better approximated by PBE0. For this reason, the application of these functionals on new materials requires a previous study, in order to choose the most appropriate method.

Table 6.3: Band gaps for four semiconductors ⁽¹⁾

Solid	Exp.	LDA	PBE	PBE0	B3LYP	HSE06
Si	1.17	0.4416	0.6104	1.6396	1.7165	1.1684
Ge	0.74	0	0	1.1203	0.1325	0.5883
GaAs	1.52	0.5079	0.1751	1.6369	0.9508	1.2353
GaN	3.47	2.0284	1.6112	3.7853	3.2328	3.0941
MgO	7.83 ⁽²⁾	5.39 ⁽²⁾	4.91 ⁽²⁾	7.220 ⁽³⁾	7.3 ⁽⁴⁾	7.09 ⁽²⁾

⁽¹⁾ All values published by Torres et al. (2017) unless noted otherwise

⁽²⁾ Values published by Heyd and Scuseria (2004)

⁽³⁾ Values published by Fritsch, Morgan, and Walsh (2017)

⁽⁴⁾ Values published by Muscat, Wander, and Harrison (2001)

The GW approximations greatly improve the accuracy of the band gaps in comparison to DFT functionals. Table 6.4 shows the band gap estimation of the three GW approximation methods, where the G_0 function was obtained from PBE calculations. The data shows a very noticeable improvement from the PBE band gaps. G_0W_0 usually underestimates the values, and gives the best results for Si and MgO. GW_0 and scGW tend to overestimate the band gap. Nevertheless, for Ge, GaAs and GaN, a self-consistent method provides a better approximation, probably due to the particularly small gaps obtained by PBE (Shishkin & Kresse, 2007).

Table 6.4: Band gaps of four semiconductors (cont.)

Solid	Exp.	G_0W_0	GW_0	GW
Si ⁽¹⁾	1.17	1.12	1.20	1.28
Ge ⁽²⁾	0.66	0.50	0.72	0.96
GaAs ⁽¹⁾	1.52	1.30	1.42	1.52
GaN ⁽¹⁾	3.20	2.80	3.00	3.32
MgO ⁽¹⁾	7.25	7.72	8.47	7.83

⁽¹⁾ Values published by Shishkin and Kresse (2007).

⁽²⁾ Values published by Chen and Pasquarello (2015)

It is worth noting that the improvement in accuracy comes at a high computational cost. The GW_0 and scGW approximations take much longer than DFT methods or even the G_0W_0 approximation because of their iterative scheme.

CONCLUSIONS

Computational methods such as Density Functional Theory and the GW approximation provide a practical and efficient way of calculating electronic and material properties of solids, which could not be obtained by solving Schrödinger's equation due to its complexity. The accurate knowledge of the properties of different materials allows the development of new technologies. The approximations presented in this work are important, as they brought significant advancements to the fields of Chemistry, Electronics and Material sciences.

Several improvements have been made since Thomas and Fermi proposed the calculation of atomic energy using the electronic density. The formalization provided by the Hohenberg-Kohn theorems and the Kohn-Sham model allowed the development of more satisfying functionals based on the uniform gas model. Local density approximation was the first functional created, and it provides good results for the energy of many-body systems. The GGA functionals presented in this paper, PBE and B88, were built with energy approximations in mind. For this reason they are better than LDA at these calculations. The band gap problem encountered by LDA and GGA comes from the Kohn-Sham model itself, since Kohn-Sham band gaps are smaller than fundamental band gaps. Meta-GGA functionals reduce the errors associated with the uniform density model, and eliminate the self-correlation error from LDA and GGA. The hybrid functionals developed later introduced the Hartree-Fock potential and were tuned to perform well through empirical fitting.

The quasiparticle model allows for the GW approximation, which relies on an entirely theoretical method to obtain the energy of the system. The method consists in solving a set of five equations iteratively, and is too expensive computationally to be performed fully, but simplifications such as G_0W_0 , GW_0 , and scGW prove to be sufficient to outperform most DFT methods. Some problems, however, arise from these approaches. G_0W_0 does not obey conservation laws for particle number, momentum, or energy, and heavily depends on the method used to obtain the initial Green function. The other methods, GW_0 and scGW, do not have these downsides, but are still very computationally expensive compared to DFT. Furthermore, many studies suggest that the vertex function, omitted by these simplifications, has very important consequences in the results, which explains the reduction in band gap accuracy between G_0W_0 and scGW. GW_0 and scGW approximations tend to overestimate the band gap, depending on the material studied.

The numerical values presented in chapter 6 for atomization energies and lattice constants show the validity of DFT methods, yielding very similar results to those obtained empirically. Moreover, the data shows that no functional is strictly better than any other for these calculations, and that the precision of the approximation depends on the material. The hybrid functionals are generally better at estimating the band gap than LDA or GGA, but due to the empirical parameters introduced, the efficiency of each of these is sensitive to the material studied. The GW approximation drastically reduces the errors from the DFT functional. Self-consistent GW approximations tend to overestimate the band gap compared to G_0W_0 , as discussed previously.

The theoretical and experimental results of this study show that the GW approximation serves as a good method to refine DFT results. Self-consistent solutions are required to obtain correct structural and energetic properties; nonetheless, further research in this topic is required to solve the problems of high computational cost and overestimation found in iterative forms of GW. Nowadays, some studies seek to reduce the overestimation of self-consistent GW approximations without increasing the computational time significantly, and give great results. Vertex corrected schemes in GW are

promising new approaches to overcome the present difficulties associated with the current computational methodologies. Approximations that include the vertex function in some form open a new field of investigation that would increase the applicability of the already very effective method.

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