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Physical Properties of a Material and Electronic Structure Methods

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1. Introduction

To calculate many of the physical properties of a material exactly, many body problems are faced. The forces acting between the particles are electromagnetic. On the microscopic level the description of matter is provided by the quantum mechanics laws. The equation that governs the particles is the Dirac equation [1,2], which solutions are many-body spin wave functions. It incorporates relativistic effects and predicts the intrinsic spin angular momentum of the particles. In the non-relativistic limit, the Dirac equation reduces to the Schrodinger equation [3]. The spin prediction and description are lost and has to be reintroduced by the following separate postulate. In a region of space where several identical particles may be found simultaneously, it is impossible to distinguish between them. If the particles also are fermions, for example electrons and protons, only one particle can occupy a given individual quantum state. This requires that the total wave function must be antisymmetric under interchange of the space and spin coordinates of two identical fermions. This is known as the Pauli exclusion principle [4]. The existence of spin, which is intimately connected with relativity, is however fully compatible with the description of the system in terms of the Schrodinger equation.

2. Relaxation of the Nuclear Configuration

Dealing with time-dependent system is in general a delicate task. The exact solutions of the time-dependent Schrodinger equation are usually impossible to find, though there are systems that can be solved approximately. If the Hamiltonian varies very slowly with time, the adiabatic theorem is applicable. It assumes that the instant (time-independent) solution, a non-degenerate discrete state and its energy, evolves to the corresponding state and energy at a later time without making any transition. If the adiabatic approximation is applied to molecules the slow time dependence of the Hamiltonian corresponds to the motion of the nuclei relative to the electrons. The charged particles are moving in the Coulomb potential of each other, but the nuclei are considerable heavier than the electrons so their speed is much lower. Therefore, the electrons manage to relax at any instant nuclear configuration and the Schrodinger equation becomes separable into an electronic and a nuclear part. For each nuclear configuration the electronic ground state is given by the time-independent electronic Schrodinger equation. In the nuclear part of the Schrodinger equation the electronic ground state energy appears as a potential energy. According to the Hellmann-Feynman theorem [5,6] gradient of this potential energy is interpreted as a generalized force that vanish is the equilibrium configuration. This is the essence of the Bohr-Oppenheimer approximation [7].

3. Electronic Structure Methods

The electronic structure is determined by the Hamiltonian in the time-independent Schrodinger equation. The Hamiltonian consists of an external coulomb potential, the kinetic energy operators and particle-particle coulomb interactions. Within the Born-Oppenheimer approximation, the nucleus-nucleus interaction appears as energy parameters and the electron-nucleus interaction is treated as an external potential. It is the remaining electron-electron interaction that defines a many-body problem.

4. Non-Interacting Electrons

Ignoring in electron-electron interaction, the separation of variables technique makes the Schrodinger equation exactly solvable. The eigenfunctions, called Hartree products, are thus products of occupied one-electron wave functions. From their classical counterpart these single particle wave functions are named spatial orbitals. They are infinite to the number and can be chosen to form an orthonormal [8] set. Each orbital is associated with an energy eigenvalue and the total energy is simply the sum of the occupied orbital energies. At the non-relativistic level of theory, spin-orbitals $\phi_i(r_i, \sigma_j)$ are formed as products of a spin function and a spatial orbital. To fulfil the Pauli exclusion principle for fermions, which the Hartree product does not, these singly occupied spin-orbitals have to be arranged in, what is known as a Slater determinant, in order to get an anti-symmetric wave function.

$$\Phi = \sqrt{\frac{1}{N!}}\begin{vmatrix} \phi_1(r_1,\sigma_1) & \phi_1(r_2,\sigma_2) & \ldots & \phi_1(r_N,\sigma_N) \\ \phi_2(r_2,\sigma_2) & \phi_2(r_2,\sigma_2) & \ldots & \phi_2(r_N,\sigma_N) \\ \vdots & \vdots & & \vdots \\ \phi_N(r_N,\sigma_N) & \phi_N(r_N,\sigma_N) & \ldots & \phi_N(r_N,\sigma_N) \end{vmatrix} \quad (2.1)$$

A Slater determinant is usually referred to as an uncorrelated wave function with function with respect to the motion of the electrons. Nevertheless, even the Pauli exclusion principle introduces correlation. Although, the Slater determinant only is an exact solution of a fictitious system it plays an important role in most of the more accurate methods for electronic structure calculations.

When the coulomb electron-electron interaction is added, numerical methods have to be applied. For many purposes it is sufficient to find the ground state solution. A powerful and straight forward method for doing this, is based on the variational principle. It is applied to the energy functional for the expectation value of the Hamiltonian H with a trial wave function ϕ.

$E[\phi] = \langle\phi|H|\phi\rangle$ (2.2)

The wave function that minimizes the expectation value is the exact ground state solution and the ground state energy is the minima. This is the main concept for both Hartree-Fock [9] based methods and the density-functional theory [10] (DFT). In the DFT this energy functional is rewritten is terms of the electron density, which plays the central role rather than the many-body wave function. Though these two approaches are different they both end up with effective one electron Schrodinger equations, the Hartree-Fock equations and Kohn-Sham equations, respectively. However, the interpretation of the solution differs.

5. The Hartree-Fock Method

This is a variational method finding an upper limit to ground state energy using a Slater determinant with spin-orbitals as trial wave function. The inherent approximation comes from the restrictions on the total wave function resulting from a description-based Slater-determinant. By minimizing the total energy with respect to the spin orbitals a system of coupled equations, the Hartree-Fock equations are found. They are pseudo-eigenvalue equations with an effective one-electron operator, the Fock operator, that depends on all the occupied orbitals. Apart from the kinetic energy operator and the external potential, it is composed of the coulomb and exchange operators. Both of them origin from the expectation value of the Coulomb electron-electron interaction for a Slater determinant. Considering the probability density of occupied spin-orbitals as charge density, the Coulomb part represents the classical Coulomb repulsion. There is no classical analogy for the exchange part that arises from the anti-symmetry of the Slater determinant. The deficient description of correlated electronic motions in the Slater determinant leads to a situation in which that each electron influenced by the average positions of the other electrons. The effect of these other electrons can be expressed as a potential, named the Hartree-Fock potential (that depends on the electron density). Due to this mutual dependence of the orbital solutions, the Hartree-

Fock equations have to be solved self-consistently. Consequently, the Hartree-Fock method is often referred to as a self-consistent field method.

6. Density-Functional Theory

In this theory the basic entity is the particle position probability density n(r), often called particle density. If the normalized N-particle wave function is known the particle density is given by

$$n(\mathbf{r}) = \sum_{\sigma_1 \ldots \sigma_N} \int \; \ldots . \int N|\Psi\,(r_1\, \sigma_1, \,.\,.\,\ldots\, r_N,\, \sigma_N)|^2\, dr_2 \,.\,.\,.\, dr_N \qquad (2.3)$$

The major advantage of considering the particle density instead of the many particle wave functions is that the number of needed space coordinates is reduced to three, independently of the number of particles. For a classical continuous charge distribution n($\mathbf{r}$) the electrostatic energy is given by a density functional E_H [n] usually called the Hartree energy in quantum mechanical contexts.

$$E_H[n] = \int \frac{1}{2} \int \frac{n\,(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r'}\; n(\mathbf{r})\, d\mathbf{r} \; (2.4)$$

The potential energy for a classical and quantum mechanical charge density n(r) in an external potential $V_{ext}(\mathbf{r})$ is also given by a simple density functional

$$E_{ext}[n] = \int V_{ext}(\mathbf{r})\, n(\mathbf{r})\, d\mathbf{r}. \; (2.5)$$

7. The Thomas-Fermi-Dirac Approximation

The idea of using the electron density in electronic structure calculations were initiated by Thomas [11] and Fermi [12] in 1927. They introduced a local functional of the electron density $T^{LDA}[\mathbf{n}]$ as an approximation of kinetic energy.

$$T^{LDA}\,[n] = \int \frac{3}{10}\,(3\pi^2\, n(\mathbf{r}))^{2/3}\, n(\mathbf{r})\, d\mathbf{r} \; (2.6)$$

It is referred to as a local density approximation (LDA), since it assumes that the density locally can be considered as an homogeneous electron gas. Using the Hartree energy as an approximation for the electron-electron repulsion, an approximate total energy functional was obtained as a sum of the kinetic, Hartree and external potential energy functional.

$$E[n] = T^{LDA}\,[n] + E_H\,[n] + E_{ext}\,[n] (2.7)$$

An estimation of the ground state energy and the corresponding density is found by minimizing the total energy functional with the respect to the electron density, under the constraint that the number of particles is conserved.

$$N = \int n(\mathbf{r})\, d\mathbf{r} \; (2.8)$$

The variational principle in the form of the method of Lagrange multipliers results in an Euler-Lagrange equation that gives the density that minimizes the total energy with the Lagrange multiplier as the chemical potential.

Thomas and Femi neglected correlation between electrons and what is called exchange integration n the Hartree-Fock method. When the expectation value of the Hamiltonian is calculated with a Slater-determinant, as it is in Hartree-Fock method, the correlated motion of the electrons the lower the total energy is missed. Therefore, both the kinetic and the electron repulsion energies only become approximations. Due to the anti-symmetric nature of the Slater determinant the expectation value of the electron repulsion consists of two terms. The first one is identified as the electrostatic potential of a classical continuous charge distribution, the Hartree energy. It includes the spurious self-interaction energies, that are negligible if the number of particles in the density is large, but are considerable with only a few particles present. These energies cancelled by the second term, the exchange energy. Besides that, this term is needed due to the Pauli exclusion principle. Therefore, a few years later Dirac added a LDA functional E_x^{LDA} [$\mathbf{n}$] for the exchange energy [2].

$$E_x^{LDA}\,[n] = \int -\frac{3}{4}\left(\frac{3n\,(\mathbf{r})}{\pi}\right)^{1/3}\, n(\mathbf{r})\, d\mathbf{r} \; (2.9)$$

These LDA functional for the kinetic and exchange energies are only exact for an non-interacting homogeneous electron gas. Furthermore, this local density functional for the exchange energy does not completely cancel the self-interaction in the Hartree-energy. However, in the Thomas-Fermi-Dirac approximation no neutral molecules are stable [13-15], which considerable reduces its applicability.

8. The Hohenberg-Kohn Theorems

In 1964 two important theorems concerning the electron density were presented and proofed by Hohenberg and Kohn [16]. It turns the approximate density-functional theory for the electronic ground state, developed by Thomas, Fermi and others, into an exact theory for interacting many-body systems, based on the density. The first theorem states that the ground state particle density $n_0(\mathbf{r})$ for system of interacting particles uniquely determines the external potential $V_{ext}(\mathbf{r})$ except for an additive constant. No restrictions to coulomb potentials are needed. Since the Hamiltonian is completely determined by the external potential, also the many-body wave functions for all states are determined. Hence, the ground state density $n_0(\mathbf{r})$completely determines all properties of the system. A consequence of this theorem is that there exist functionals of the density, though unknown and probably complex, for every observable quantity of such systems. This theorem also shows that assumptions in the Thomas-Fermi approximation, that the kinetic and electron-electron interaction can be described as density functionals, is in fact no approximation. Denoting these quantities T[n] and E_{ee} [n] the exact total energy is given by
$E[n] = T[n] + E_{ee}[n] + E_{ext}[n]$ (2.10)

The second theorem states that the exact total energy E(n) is always larger than or equal to the ground state energy for a V-representable trial density n(r). It is analogous to the energy variational principle for the wave functions used in Hartee-Fock method and justifies the use of this principle in the Thomas-Fermi approximations. The functional E(n) alone is sufficient to determine the ground state density and energy, exactly. If a density can be obtained from an anti-symmetric wave function, it is N-representable, while a V-representable density has to be N- representable and correspond to a density of a non-degenerate ground state in some external potential. However, there exist reasonable densities that are not V-representable. Levy and Lieb solved this dilemma with their constraint search formulation [17-19] in DFT, in which the density only has to satisfy the weaker condition of N-representability. The solution is to minimise the kinetic and electron-electron repulsion energies with respect to the wave function for each density first and then minimise the total energy with respect to the density.
$E[n] = \min_{\Psi \to n} < \Psi|\hat{T} + \hat{V}_{ee}|\Psi > + E_{ext}[n]$ (2.11)

With this two-step minimization procedure, the density only needs to be N-representable and the degenerate ground states can be handled by DFT. Mermin [20] has extended the theory to cover finite temperature canonical and grand canonical ensembles. His work shows that the free-energy functional of the density directly determines thermal equilibrium properties such as specific heat.

9. The Kohn-Sham Ansatz

Kohn and Sham's idea was to map the interacting electronic system to an auxiliary system of non-interacting electrons with the same ground state electron density $n_0(\mathbf{r})$ [21]. For this auxiliary system the total energy functional is composed of the kinetic energy of non-interacting particles T_s [n] and an effective potential energy functional $E_{eff}[n]$ including all potential and particle interaction energies,
$E[n] = T_s[n] + E_{eff}[n]$(2.12)

According to the Hartree-Fock and Thomas-Fermi-Dirac approximations the major electron-electron interaction energies are the Hartree and exchange energies, while the excluded remainder is the correlation energy. In the density-functional approach, only the functional of the Hartree energy is known explicitly. Kohn and Sham introduced a successful approximation of a combined exchange and correlation energy functional, that is very accurate for a homogeneous electron gas. Due to its local functional nature, it is called the local density approximation of the exchange-correlation energy $E_{xe}^{LDA}[n]$.

$E_{\mathrm{eff}}\,[n] = E_H[n] + E_{xe}[n] + E_{ext}[n]$(2.13)
The major error in the Thomas-Fermi-Dirac approximation comes from the local density approximation of the kinetic energy. Therefore, the most ingenious proposal of Kohn and Sham was the kinetic energy functional

$T_s\,[n] = \min_{\Phi\to n} \, < \Phi|\hat{T}|\Phi >$ (2.14)

Where Φ is a Slater determinant, which is sufficient to describe the exact wave function of the non-interacting electrons. For a given electron density, the Slater determinant orbitals that minimize the kinetic energy are the so-called Kohn-Sham orbitals.

If the variational principle is applied to the total energy functional with the Kohn-Sham kinetic energy, a set of one-electron Schrodinger-like equations is obtained. These are the Kohn-Sham equations with the effective potential V_{eff} (r) that is the variation of the potential energy functional with respect to the density.

$V_{\mathrm{eff}}(\mathbf{r}) = \frac{\delta\, E_{\mathrm{eff}}\,[n]}{\delta n} = \int \frac{n\,(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \frac{\delta\, E_{xe}\,[n]}{\delta n} + V_{\mathrm{ext}}\,(\mathbf{r})$ (2.15)

Due to the density dependence in the effective potential, these Kohn-Sham equations have to be solved self-consistently.

10. Exchange-Correlation Functional

The major drawback of DFT is that a general exact exchange correlation functional is obviously not known. There is not even a systematic way to improve approximations. Kohn and Sham themselves proposed the first and so far the most used approximation, the local density approximation of the exchange-correlation functional E_{xe}^{LDA} [n] [21]. The idea behind it is that it is exact for a homogeneous electron gas and should be valid for other systems with a density slowly varying over the space.

Consider a homogeneous interacting electron gas, completely specified by its constant density **n**. The exact exchange energy is possible to derive, while an accurate correlation energy can be calculated numerically. A function of the density ϵ_{xe}^{hom} [n] is obtainably for the exchange-correlation energy per electron. Using this function for an homogeneous electron n(**r**) at each point r gives an approximation of the exchange-correlation energy according to:

$E_{xe}^{LDA}[n] = \int \epsilon_{xe}^{hom}(n\,(\mathbf{r}))\, n(\mathbf{r})\, d\mathbf{r}.$ (2.16)

The LDA has proved to be strikingly accurate in many electronic structure calculations in solid state physics. However, the use of LDA in quantum chemistry, dealing with molecules of even individual atoms that have densities with large gradients, has been limited. A functional with a gradient expansion approximation (GEA) were already proposed in the original paper of Kohn and Sham. These early attempts did not lead to consistent improvement over the LDA. The breakthrough came with generalized gradient approximation (GGA) that provides accuracy needed for molecular systems. Three widely used parametrizations of the functional are Becke [22], Perdew, Becke and Nederlof [23] Perdew and Wang [24-26].

$E_{xe}^{GGA}[n] = \int \epsilon_{xe}^{GGA}\,[n\,(\mathbf{r}), |\nabla n\,(\mathbf{r})|]\, d\mathbf{r}.$ (2.17)

Both the functions ϵ_{xe}^{hom} and ϵ_{xe}^{GGA} are parametrized analytic functions to facilitate numerical calculations.

11. Spin-Density Functionals

So far only spin unparsed densities have been considered, where the spin-up and spin-down densities are equal, $n_\uparrow(\mathbf{r}) = n_\downarrow(\mathbf{r}) = n(\mathbf{r})/2$. Even without magnetic fields, spin density functionals are needed to cope with unpaired electrons in atoms and decuples. Such functionals for spin polarized densities have thus been derived.

Both for the exact and the local density approximations of the kinetic and exchange energy functionals, the spin-scale relation $(F[2n_\uparrow] + F[2n_\downarrow])/2$ works, while the Hartree energy functional is simply $E[n_{\uparrow,}n_\downarrow] = E_H[n_\uparrow + n_\downarrow]$.The spin-scaling for correlation energy is not known, but the spin-scaling of the dominant exchange energy is used to construct the spin-polarized exchange-correlation energy functionals.

$E_{xe}^{LDA}[n_{\uparrow,}n_\downarrow] = \int \epsilon_{xe}^{hom}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}))\, n(\mathbf{r})\, d\mathbf{r}$ (2.18)

$E_{xe}^{GGA}[n_{\uparrow,}n_\downarrow] = \int \epsilon_{xe}^{GGA}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})||\nabla n_\uparrow(\mathbf{r})|, |\nabla n_\downarrow(\mathbf{r})|)\, n(\mathbf{r})\, d\mathbf{r}$(2.19)

12. The Vienna Ab-initio Simulation Package

In all the DFT calculations presented in this thesis the Vienna ab-initio simulation package code VASP [27-29] has been used. It offers periodic boundary conditions on supper cells. This package provides both LDA and GGA exchange correlation energy functionals. For the studied molecular crystals, the PW91 version of the GGA was chosen. The electronic valence wave functions were expanded in a plane-wave basis set, while the core states were described by frozen atomic wave functions. Only plane waves with a kinetic energy smaller than a chosen cut off energy were included in the basics set. In conjunction with the frozen core approximation, the Blochl's projector augmented-wave (PAW) method [30,31] was used to reduce the size of the basis set. The first Brillouin zone (BZ) was sampled with the Monkhorst–Pack [32] method, which subdivides the zone along the reciprocal lattice vectors. To reduce the number of points needed in BZ to get an accurate band-structure energy, partial occupancies for each wave function was used according to the Methfessel-Paxton smearing method. In this method the Fermi-Dirac step function is expanded in a complete orthonormal set of functions, where the first function in the expansion is the Gaussian function. Electronic relaxations were performed with a preconditioned conjugate-gradient (CG) method [33], the Davidson blocked iteration scheme [34], or preconditioned residual minimisation method-direct inversion in the iterative subspace (RMMDIIS) [35]. For the ionic relaxations both a preconditioned CG algorithm or a RMM-DIIS algorithm were employed, depending on the starting guess of the ionic structure. If the ionic structure was unreasonable the more reliable CG algorithm was used, while closer to a local minimum the RMM-DIIS algorithm usually was more efficient.

13. The Tight- Binding and the Huckel Approximation

The tight-binding method was developed by the Block [36] in 1928. This was probably the first theory of electrons in crystals. In his ansatz to solve the Schrodinger equation for crystals, he considered the crystal potential as a sun of atomic potentials plus a small perturbation term ΔV including all corrections to the atomic potentials. Without the perturbation, the exact solutions are the degenerated atomic energy eigenvalues $\epsilon_n^{(0)}$and a sum of the localized atomic wave functions. Using the atomic orbitals as an approximation of the atomic wave functions, the unperturbed crystal wave function can be written as a linear combination of atomic orbitals $\varphi_i^{(0)}(\mathbf{r})$ (Bloch himself only used a spherical symmetric function at each atom). The perturbation theory for degenerate energy levels gives the following generalized matrix eigenvalue equation for each energy eigenvalue

$(\Delta V - \epsilon_n^{(1)})\, c = 0$(2.20)

where the matrix elements are

$(\Delta V)_{i,j} = < \varphi_i |\Delta V |\varphi_j>$(2.21)

$(S)_{i,j} = < \varphi_i |\varphi_j >$(2.22)

Thus the energy eigenvalues up to the first order energy corrections and the corresponding wave functions, the are Bloch functions, are given by

$\epsilon_n = \epsilon_n^{(0)} + \epsilon_n^{(1)}$ (2.23)

$\Phi_n = \sum_i C_i\, \varphi_i^{(0)}$ (2.24)

The matrix element $(\Delta V)_{i,i}$, $(\Delta V)_{i,j\neq i}$ and $(S)_{i,j}$ are called Coulomb integrals, resonance integrals, and overlap integrals, respectively. In one element crystals the Coulomb integrals are equal, so Bloch introduced the parameter α for the their value. Due to the localized nature of the atomic orbitals, the values of the overlap integrals and the resonance integrals for nearest neighbours and next nearest neighbours (and more distant neighbours), respectively are small and neglected. Bloch also introduced the parameter β for the nearest neighbour resonance integrals and considered each atomic orbital to be normalised to unity. Depending on the crystal symmetry a few different β might be needed. For parametrisation of resonance integrals in crystals or molecules with varying inter-atomic distances the Mullikin approximation [37] is applicable. It estimates the resonance integral from the overlap integral $\beta_{i,j} = k(S)_{i,j}$, where the parameter k has to be determined empirically.

Three years after Bloch introduced the tight binding approximation. Huckel [38] applied this method on hydrocarbon molecules. He used the method for describing the π electrons of the carbon atoms. This early variant of Bloch's tight binding method has been known as the Huckel theory. Later Hoffman [39] generalised this approximation for the hydrocarbons to include all the atomic orbitals, and named it the extended Huckel theory.

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