

# Chapter 1

## Density Functional Theory

As seen previously, Hartree-Fock theory does not succeed in explaining the physical properties of metallic systems, unless much more involved calculations such as RPA or CI are performed. Another approach to treat the electronic properties of a system was proposed in 1964 by Hohenberg and Kohn (HK)[1]. In this theory, the ground state total energy is a functional of the ground state density only, and all ground state properties can be expressed as a functional of this density.  $E[\rho] = \int V_{ext}(r)\rho(r) + F[\rho]$  where the functional  $F$  includes the kinetic energy of the electrons and the Coulomb interaction between them. At first sight, it would seem that many ground state wave functions could yield the same density, and therefore this statement seems unrealistic. But it can be shown that for a given ground state density  $\rho$ , there is a *unique* external potential  $V_{ext}$  that can produce the density  $\rho$  as its ground state. Therefore there is a unique one to one correspondence between the potential  $V_{ext}$ , the many-body ground state  $\Psi(r_1, \dots, r_N)$ , and the ground state charge density  $\rho$ .

$$\begin{aligned} \text{Standard : } V_{ext}(r) &\Rightarrow \Psi(r_1, \dots, r_N) \Rightarrow \rho(r) \\ \text{HK Theorem : } \rho(r) &\Rightarrow \Psi(r_1, \dots, r_N) \Rightarrow V_{ext}(r) \end{aligned} \tag{1.1}$$

The original proof of HK assumed that the ground state was non-degenerate. The **HK theorem** states this *one to one correspondence and the fact that the total energy  $E[\rho]$  is variational with respect to the density and it is minimum for the ground state density*. The functional  $F[\rho]$ , which includes all internal energies (kinetic and potential) of the interacting electron system, can be

shown to be universal, i.e. independent of the external potential  $V_{\text{ext}}(r)$ . It was defined by Levy and Lieb, as:

$$F[\rho] = \text{Min}_{\Psi \rightarrow \rho(r)} [\langle \Psi | T | \Psi \rangle + \langle \Psi | V_{ee} | \Psi \rangle] \quad (1.2)$$

and can be interpreted as the minimum of the sum of kinetic and interaction potential of the electrons, for all possible wavefunctions having the given density  $\rho$ . In searching the ground state, one minimizes the total energy with respect to the trial state  $\Psi$ . This minimization can be done in two steps. a minimization over all possible densities such that  $\int \rho(r) dr = \mathcal{N}$ , followed by a minimization over all states  $\Psi$  corresponding to a given density  $\rho(r)$ . In this process, the functional  $F$  appears naturally .

The functional  $F$  is usually written as:

$$F[\rho] = T_o[\rho] + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + E_{xc}[\rho] \quad (1.3)$$

$T_o$  is the kinetic energy of the non-interacting electron gas, and this relation can be taken as the definition of the exchange-correlation energy  $E_{xc}$ .

## 1.1 Kohn-Sham theory

Without any loss of generality, one can write the ground state density as:  $\rho(r) = \sum_{\lambda\sigma} f_{\lambda\sigma} |\psi_{\lambda\sigma}(r)|^2$  where the set  $\psi_{\lambda\sigma}(r)$  is an orthonormal set, and as before,  $f_{\lambda\sigma}$  is the occupation factor ( $f_{\lambda\sigma} = 0, 1$ ). The kinetic energy of the non-interacting system is then defined as:

$$T_o[\rho] = \sum_{\lambda\sigma} f_{\lambda\sigma} \int \psi_{\lambda\sigma}^*(r) \left( -\frac{\hbar^2 \nabla^2}{2m} \right) \psi_{\lambda\sigma}(r) dr \quad (1.4)$$

These ideas were put forth by Kohn and Sham[2]. They wanted to construct a “fictitious” one-particle Hamiltonian with eigenfunctions  $\psi_{\lambda\sigma}$  which would reproduce the exact ground-state density  $\rho$  of the interacting system<sup>1</sup>. This *effective* Hamiltonian is usually referred to as the Kohn-Sham Hamiltonian. The potential coming into it is not a physical one, nor are its eigenvalues

---

<sup>1</sup>Here, Kohn and Sham have assumed that the ground state density of any interacting system can be represented by a sum of squares of eigenstates of a non-interacting Hamiltonian

and eigenfunctions, but from its  $N$  lowest eigenfunctions, one can form the ground state density of the real physical system, from which one can calculate the total energy, and the forces on the atoms if needed. Minimizing the total energy  $F[\rho] + \int V_{ext}\rho$  with respect to  $\psi_{\lambda\sigma}$  including the constraint of orthonormality, one finds that the functions  $\psi_{\lambda\sigma}$  must be eigenstates of a single particle Hamiltonian called the Kohn-Sham Hamiltonian:

$$H_{KS} = -\frac{\hbar^2\nabla^2}{2m} + V_{ext}(r) + V_{Coulomb}(r) + v_{xc}(r) \quad (1.5)$$

where  $V_{Coulomb}(r) = \int \rho(r')/|r-r'|dr'$  is the electrostatic interaction between the electrons, and  $v_{xc}[\rho](r) = \delta E_{xc}/\delta\rho(r)$  is called the exchange-correlation potential. In this Hamiltonian, the Coulomb and exchange-correlation potentials depend on the charge density which is itself calculated from the eigenfunctions. This non-linear problem must therefore be solved self-consistently similar to the HF case.

To conclude, all properties of an interacting many-body system, can, in principle, be obtained from the solution of a non-interacting (but self-consistent) one-body problem defined by the Kohn-Sham Hamiltonian.

## 1.2 Finite temperature generalization

Mermin generalized in 1965 after the proof of HK, the DF theory to finite temperatures[3]. In this case, one needs to find the energy of the equilibrium state, which is not one state, but a statistical average. The equilibrium density, in this case, is obtained by minimizing the functional:

$$\Omega[\varrho] = \text{Tr} \varrho[(\mathcal{H} - \mu\mathcal{N}) + k_B T \ln \varrho] \quad (1.6)$$

whose minimum is the equilibrium grand potential

$$\Omega[\varrho_o] = E - TS - \mu\mathcal{N} = -k_B T \ln \text{Tr} e^{-\beta(\mathcal{H}-\mu\mathcal{N})}$$

with the density matrix

$$\varrho_o = e^{-\beta(\mathcal{H}-\mu\mathcal{N})} / \text{Tr} e^{-\beta(\mathcal{H}-\mu\mathcal{N})}$$

(not to be confused with the ground state density  $\rho$ ).

Thus one can also define the entropy and other thermodynamic properties of the interacting electron system, in addition to its ground state properties. Using this functional, one finds that the entropy is given by:

$$S = -k_B \sum_{\lambda} [f_{\lambda} \ln f_{\lambda} + (1 - f_{\lambda}) \ln(1 - f_{\lambda})] \quad (1.7)$$

where again  $\lambda$  refers to the eigenstates of the Kohn-Sham Hamiltonian, and  $f_{\lambda}$  is the occupation of that state and is given by the Fermi-Dirac distribution function. While the total energy increases quadratically as a function of the temperature, the free energy has a quadratic decrease, so that  $(E + F)/2$  is a better estimate of the zero-temperature ground state energy, if one does a finite temperature calculation. The latter has the advantage that properties converge better at high temperatures.

### 1.3 The Local Density Approximation (LDA)

The whole problem of many-body interactions is now recasted into proposing a good exchange-correlation functional. The Local Density Approximation consists in writing:

$$E_{xc}^{\text{LDA}}[\rho] = \int f[\rho(r)]dr = \int \rho(r)e_{xc}[\rho(r)]dr \quad (1.8)$$

where  $e_{xc}$  is called the exchange-correlation energy density. It is related to the XC potential through:  $v_{xc} = \delta E_{xc}/\delta\rho = e_{xc} + \rho\partial e_{xc}/\partial\rho$ . This approximation is “local” since the potential at  $r$  depends on the density at  $r$  only. In the special case of the uniform electron gas, it has been possible to calculate the XC energy analytically by many-body techniques or by accurate quantum Monte Carlo simulations. Fits to these results were used to devise an XC potential[4]. This form has been adopted even for a non-uniform density. On the other hand, a simple local approximation to the exchange was also independently proposed by Slater[5]. In this approximation,  $v_{xc}(r) = -\alpha(3e^2/2\pi)[3\pi^2\rho(r)]^{1/3}$  with  $\alpha$  being a numerical factor between 2/3 and 1. This potential has been very successful to predict electronic properties of atoms and molecules. It is local, and therefore much easier to compute numerically than the non-local exchange potential in the HF theory. It can also predict properties of metallic systems correctly. Generally, since the density in a metal is almost uniform, one expects the LDA to

work well, especially if the parametrization of Perdew and Zunger[4] is used for the XC potential.

In the case of spin polarized systems, the Local Spin Density Approximation (LSDA)[6] is often used. In the LSDA,  $E_{xc} = \int \rho(r) e_{xc}[\rho^\uparrow, \rho^\downarrow] dr$ , and the KS equations result in two Hamiltonians, one for spin up, and one for spin down:

$$H_{KS}^\sigma = t + V_{ext} + V_{Coulomb} + v_{xc}^\sigma[\rho^\uparrow, \rho^\downarrow]$$

where

$$v_{xc}^\sigma(r) = \frac{\delta E_{xc}[\rho^\uparrow, \rho^\downarrow]}{\delta \rho^\sigma(r)}$$

After initializing each Hamiltonian with some proper initial guess for the spin up and spin down charge densities, one should compute the XC potential and diagonalize the Hamiltonian for each spin. From the output eigenvalues and the given number of electrons, one then computes the Fermi energy and then the occupation of the spin up and down levels ( $f^{\lambda\sigma}$ ) from which it becomes possible to deduce the corresponding charge densities

$$\rho^\sigma(r) = \sum_\lambda f^{\lambda\sigma} |\psi^{\lambda\sigma}(r)|^2$$

These charge densities are then used in the KS Hamiltonians and the process repeated until self-consistent.

## 1.4 Improvements to the LDA

The LDA, even though successful in describing properties of many metals and semiconductors, has many shortcomings. One obvious one is the local approximation! Another one is the *imperfect cancellation* in the self-interaction. Therefore, improvements should include Self-Interaction Corrections (SIC)[4], and information about the charge density in the neighborhood of the considered point. The latter can be dealt with in two ways: One is called the Generalized Gradient Approximation (GGA) which is still local, but it is a functional of the density and its gradients at the considered point [7], and the other is the weighted density approximation (WDA) which uses a non-local form for the XC energy:  $E_{xc} = \int dr dr' w_{xc}(r, r') \rho(r) \rho(r')$ . Its calculation is maybe comparable to that of the exchange term in HF, and involves the calculation of a three-dimensional integral at each point  $r$ . The

functional form is usually determined from a fit to some exact calculation, and some sum rule constraints. GGA is not necessarily an improvement to LDA, especially when variations of the charge density have large amplitudes, since it is based on a perturbation expansion in powers of  $\nabla\rho$  and not derived variationally. In the case of metals, however, it has improved the total energies. For example, in the case of iron, in contradiction to the experimental results, LDA predicts that the FCC phase is more stable than BCC. GGA corrections reproduce, however, the experimental findings. This could be because in metals, gradients of the density are small and therefore the perturbation expansion is valid. Other than subtle spin effects, predictions of LDA are generally good for metals. For semiconductors and insulators however, there is always the underestimation of the gap. Tendencies in HF are opposite to LDA:

$$Gap^{\text{LDA}} < Gap^{\text{experiment}} < Gap^{\text{HF}}$$

$$E_{\text{binding}}^{\text{LDA}} > E_{\text{binding}}^{\text{experiment}} > E_{\text{binding}}^{\text{HF}}$$

More accurate treatments of the conduction bands in semiconductors is done by the GW method[8]. LDA, being a ground state theory, is not necessarily going to give correct answers for excited states. GW, on the other hand, treats subtle many-body correlation effects more accurately by replacing the XC potential by a non-local, energy-dependent self energy. But the price to pay is the CPU time and memory of the computer. GW calculations could typically be 50 times more time-consuming than a simple LDA calculation. More details about the DF theory, GW, and their applications can be found in the book by Fulde[9].

# Bibliography

- [1] P. C. Hohenberg and W. Kohn, Phys. Rev. B. **136**, 864 (1964).
- [2] W. Kohn and L. J. Sham, Phys. Rev. A. **140**, 1133 (1965).
- [3] N.D. Mermin, Phys. Rev. **137**, A1441 (1965).
- [4] Perdew and Zunger, P. R. B. **23**, 5048 (1981).
- [5] J. C. Slater, *The self-consistent field for molecules and solids*, Vol. 4 , Mc Graw Hill Pub. (1974).
- [6] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
- [7] J. P. Perdew et al., Phys. Rev. B. **46** , 6671 (1992).
- [8] M. Hybertsen and S. G. Louie P. R. B. **34**, 5390 (1986).
- [9] P. Fulde , *Electron correlations in molecules and solids* , 2<sup>nd</sup> Edition (1993), Springer Pub.