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AB-INTIO ELECTRONIC STRUCTURE CALCULATIONS - I

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Electronic Structure

The systems we want to deal with are made up by electrons and ions, and we want to describe their properties from the microscopic point of view starting from fundamental principles.

"At the present status of human knowledge, quantum mechanics can be regarded as the fundamental theory of atomic phenomena"
[L.I. Schiff, Quantum mechanics, 1955]

The Hamiltonian for molecules and solids reads:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{e^2}{|r_i - r_j|} \qquad \text{(electronic part)}$$

$$- \sum_{i=1}^{N} \sum_{\nu=1}^{n} \frac{Z_\nu e^2}{|R_\nu - r_i|} \qquad \text{(el-ion interaction)}$$

$$+ \sum_{\nu=1}^{n} \frac{P_\nu^2}{2M_\nu} + \frac{1}{2} \sum_{\substack{\nu,\mu=1 \\ \nu \neq \mu}}^{n} \frac{Z_\nu Z_\mu e^2}{|R_\nu - R_\mu|} \qquad \text{(ionic part)}$$

where
n = # of atoms (2-100 in molecules, $n=\infty$ in solids)
N = # of electrons
$Z_1, Z_2, \dots, Z_n$ = atomic numbers (charges)
$M_1, M_2, \dots, M_n$ = atomic masses ; m = electron mass
$\vec{R}_\nu, \vec{P}_\nu$ $\nu = 1, \dots, n$ ionic variables
$\vec{r}_i, \vec{p}_i$ $i = 1, \dots, N$ electron variables

in a shorter notation

$$H = T_e(\vec{p}) + V_{ee}(\vec{r}) + V_{en}(\vec{r},\vec{R}) + T_n(\vec{P}) + V_{nn}(\vec{R})$$

$\vec{r}$ = the vector of 3N electronic positions
$\vec{p}$ = the vector of 3N electronic momenta
$\vec{R}$ = the vector of 3n ionic positions
$\vec{P}$ = the vector of 3n ionic momenta

The two phases (ions and electrons) interact. Electrons are Fermion (the wavefunction must be antisymmetric for interchange of any two electrons), while nuclei are Fermions, Bosons or distinct particles according to the particular situation under examination.

The only stabilizing term in the Hamiltonian is the interaction between electrons and nuclei; all other interactions are repulsive.

All the ingredients entering the Hamiltonian are perfectly known and all properties can be derived by solving the Schroedinger equation

$$H(\vec{r},\vec{p},\vec{R},\vec{P})\,\Psi_i(\vec{r},\vec{R}) = E_i\,\Psi_i(\vec{r},\vec{R})$$

A number of approximations are necessery before this can be achieved in practice.

Adiabatic Approximation

The large mass difference between the two interacting "phases" and the fact that atoms in materials preserve their identity (we are not dealing with "plasma" physics) allow to simplify the problem separating the ionic and the electronic motion with the Adiabatic (Born-Oppenheimer) Approximation.

The root of Adiabatic Approximation is that the tipical excitation energy for the nuclei ($\hbar\omega_{nuc} \sim 10 meV$) is a few order of magnitude smaller than the one for electronic excitations ($\hbar\omega_{el} \sim 1 eV$), or in other words the time-scale of ionic motion is a few order of magnitude longer than the time-scale of electronic motion. So, on the time scale electrons need to readjust themsolves, ions essentielly don't move.

Let's "separate" the ionic and electronic motion in the wavefunction

$$\psi(\vec{r},\vec{R}) = \chi(R)\,\varphi(r;R)$$

This can allways be done; is not yet an approximation. The approximation is in the assumption that the electronic motion (φ) does not depend on the velocity of the nuclei but only on their position.

Substituting in the Schroedinger eq. and neglecting term like $\nabla_{\vec{R}}\varphi(r;R)$ we get

$$H\,\Psi(r,R) = H\,\chi(R)\,\varphi(r;R) \approx$$

$$\chi(R)\left[T_e+V_{ee}+V_{en}+V_{nn}\right]\varphi(r;R) + \varphi(r;R)\,T_n\,\chi(R) = E\,\chi(R)\,\varphi(r;R)$$

dividing by $\Psi(r,R)$ this becomes

$$\frac{\left[T_e+V_{ee}+V_{en}+V_{nn}\right]\varphi(r;R)}{\varphi(r;R)} + \frac{T_n\,\chi(R)}{\chi(R)} = E$$

The first term must not depend on the electronic variables (because the second one obviously does not!) Calling it $E(R)$, the equation of motion for the combined system reads as follows

$$\begin{cases}\left[T_e+V_{ee}+V_{en}+V_{nn}\right]\varphi(r;R) = E(R)\,\varphi(r;R)\\ \left[T_n+E(R)\right]\chi(R) = E\,\chi(R)\end{cases}$$

The interpretation is that during the ionic motion, for every set of atomic positions, electrons stay in an eigenfunction, usually the Ground State, of the electronic Hamiltonian. And ions move according to a potential energy that is not just their direct Coulomb repulsion but contains the screening effect of the electronic glue

There're situations in which this approximation is not adequate but are more the exception than the rule. In metals, for instance, one could argue that Adiabatic Approximation should break-down since electronic excitations of vanishing energy are possible. It happens however that these excitations are confined in a narrow energy region around the Fermi energy and most properties are not affected by neglecting the non-adiabatic contribution coming from these few electrons. Those which are, for instance transport properties, are treated starting from the adiabatic solution and introducing non-adiabatic terms (electron-phonon interactions) later.

The separation of ionic and electronic degrees of freedom, obtained with the AA, is very useful also because, while electrons must necessarily be treated quantum-mechanically, ionic degrees of freedom can, in most of the cases, be treated classically.

Molecular dynamics peoples do this every day evolving ions according to Newton's equation, using some model form for $E(R)$.
Ab-initio Molecular Dynamics (Car-Parrinello and variants) peoples do the same getting $E(R)$ from ab-initio calculations.

More on Adiabatic Approximation

A.A. Maradudin in "Dynamical Properties of Solids" vol I
G.K. Horton and A.A. Maradudin Eds p. 3-12

E.G. Brovman and Y.M. Kagan ibid p. 197-201

J.M. Ziman "Principles of Theory of Solids" p. 200 –

L.J. Sham and J.M. Ziman in Solid State Physics vol 15 p. 233-236

G.V. Chester, Advances in Physics (Phyl. Mag. Suppl) <u>10</u>, 357 (1961)

Electronic Ground State Properties

The knowledge of the Electronic Ground State energy of a system as a function of ionic positions gives access to many properties

- relative stability of different structures
- equilibrium structural information
- mechanical stability and elastic properties
- phase transitions between different structures (w.r.t pressure or temperature)
- dielectric properties
- lattice vibrations
- diffusion, melting

All (!?) we need is to be able to solve for the Ground State energy of a system of interacting electrons in a general external potential give by the ions

Self-Consistent Field

The problem of solving the Many-Body Schroedinger equation for the electrons at fixed atomic positions is a very difficult one and has been accomplished in a limited number of cases

In general for complex systems, involving many atoms and electrons, this is not done either because too complex or because, in most cases, simpler treatments based on some kind of mean field approach (in which electrons move "independently" in an "effective" potential generated by the ions and the others electrons) are accurate enough to give the correct answer.

A formal justification of this approach comes from Density Functional Theory, as we will see shortly, but for the moment, let me try to introduce the use of a Mean Field by some handwaving arguments, and to see how it should look like.

Let us consider a system of electrons and ions and ask what is the potential energy that acts upon a static point-like test charge of infinitesimal charge q

Obviously it depends on the location of the test charge and is:

$$E_{q\text{-test}}(r) = q\left[\sum_{\nu} \frac{Z_\nu e}{|R_\nu - r|} + \int \frac{(-e)\,n(r')}{|r'-r|}\,d^3r'\right]$$

where $n(r)$ is the electronic (number) density of the system. This is true if q is infinitesimal and the test-charge does not perturb the system. If we take the test-charge to be finite (say $q = -e$) the interaction with the system is instead:

$$E(r) = -\sum_{\nu} \frac{Z_\nu e^2}{|R_\nu - r|} + e^2\int \frac{n(r') + \delta n(r')}{|r'-r|}\,d^3r'$$

where the $\delta n(r)$ describe the response of the system to the external perturbation. It is an attractive term coming from the local readjustment (static screening) of the electronic cloud around the impurity.
The screening lenght is usually short (in metals 1-3 Å)
The dominant terms are the first two (both of order N = # of electrons), the last one is of order 1.

If our test particle was a negative muon ($m_\mu = 207\, m_e$ so adiabatic approximation still applies) its motion would be ruled by the following Schroedinger equation

$$\left[-\frac{\hbar^2}{2m_\mu}\nabla^2 + V_{ion}(r) + e^2\int\frac{n(r')}{|r'-r|}\,d^3r' + v_{screen}(r)\right]\varphi_\mu(r) = \varepsilon_\mu\, \varphi_\mu(r)$$

We are obviously interested instead in the case in which our "test-charge" is just an electron among the others and we can still think that the same Schroedinger equation will apply with some modifications.

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{ion}(r) + e^2\int\frac{n(r')}{|r-r'|}\,d^3r' + v_{xc}(r)\right]\varphi_i(r) = \varepsilon_i\,\varphi_i(r)$$

1) Electrons are Fermions and satisfy Pauli principle, so different electrons must occupy different states. In the independent particles scheme, we are considering, the N-body wfc is just a Slater determinant made up by the N independent and orthogonal single-particle wfc's

$$\psi(r_1,\dots,r_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\varphi_1(r_1) & \cdots & \varphi_1(r_N)\\ \vdots & & \vdots\\ \varphi_N(r_1) & \cdots & \varphi_N(r_N)\end{vmatrix}$$

and the charge density entering the potential is determined self-consistently from it as

$$n(r) = \sum_{i=1}^{N}|\varphi_i(r)|^2.$$

2) The screening term contains in general contributions due to the statistics (exchange) and not only static but also dynamical correlations.

It remains to be statet to which extent this procedure is justified and to give a practical recipe for v_{xc}

Hartree Fock approximation

In the Hartree-Fock approximation v_{xc} is defined by looking for the best variational wavefunction of the Slater determinant type.

The expectation value of the energy

$$E[\psi_{HF}] = \langle \psi_{HF} | H_{el} | \psi_{HF} \rangle \quad ; \quad \psi_{HF} = \text{Slater det.}$$

is minimized with respect to the set of N orthogonal single-particle wavefunctions.

$$E[\psi_{HF}] = \sum_{i=1}^{N} \langle \varphi_i | -\frac{\hbar^2}{2m}\nabla^2 + V_{ion}(r) | \varphi_i \rangle + \frac{1}{2}\sum_{ij}\int |\varphi_i(r)|^2 \frac{e^2}{|r-r'|} |\varphi_j(r)|^2 d^3r\, d^3r'$$

$$-\frac{1}{2}\sum_{ij}\int \varphi_i^*(r)\varphi_j(r) \frac{e^2}{|r-r'|} \varphi_j^*(r')\varphi_i(r')\, d^3r\, d^3r'$$

orthogonality conditions → $-\sum_{ij} \lambda_{ij} \left(\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right)$

Functional minimization leads to HF eqs.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ion}(r) + \int \frac{e^2}{|r'-r|} \sum_j |\varphi_j(r)|^2 \right] \varphi_i(r) - \sum_j \int \varphi_j(r) \frac{e^2}{|r-r'|} \varphi_j^*(r')\varphi_i(r')\, d^3r' = \varepsilon_i \varphi_i(r)$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ion}(r) + e^2\int \frac{n(r')}{|r-r'|} + \hat{V}_x \right] \varphi_i(r) = \varepsilon_i \varphi_i(r)$$

In HF the exchange potential is a non local operator.

Would the true GS wfc be a Slater determinant this procedure would lead to it. Unfortunately this is usually not the case and in general HF only gives an upper bound to the true energy.

Moreover in HF the effect of exchanging "independent" particles is dealt with exactly but the effects of locally correlated motion are completely absent

Density Functional Theory

Density Functional Theory allows to recast, in a formally exact way, the Many-Body problem, as far as GS is concerned, in terms of single particles Schroedinger eqs, of the mean field type, for an auxiliary system of non interacting particles.

DFT states that, if one is interested in GS properties, the electronic density (a function of 3 real variables) can be used as the basic object (instead of the N-body w/f with its 3N variables) and it is possible to define a unique functional of the density F[n] such that it exists a variational principle for the GS energy with respect to variation of the density.

The energy functional (for an external potential $V(r)$) is

$$E[n] = F[n] + \int V(r)\,n(r)\,d^3r$$

it is minimum for the GS density and the minimum value is the GS energy of the system.

The functional F[n] contains the kinetic and the el-el interaction parts of the energy while the second term describes the interaction with the external potential

All this has been demonstrated by Hohenberg and Kohn in 1964 in a seminal paper [Phys Rev <u>136</u>, B864 (1964)] in the case of non degenerate GS. The result has been generalized later to general systems

More precisely they have demonstrated that not only, through the Schroedinger eqs., the GS density is determined

by the external potential, but also the converse is true and a GS density uniquely identifies its external potential. (up to a trivial additive constant).
Since the wfc is determined, in turn, by the potential this results that the GS wfc, and all properties that can be derived from it, is a functional of the density

$$\left.\begin{array}{ll} \text{QM}: & V(r) \rightarrow H \rightarrow \psi_{GS} \rightarrow n_{GS} \\ \text{HK}: & n_{GS} \rightarrow V(r) \end{array}\right\} \rightarrow \psi_{GS}[n] \text{ is a functional of } n$$

In particular $F[n] = \langle \psi_{GS}[n] | T_e + V_{ee} | \psi_{GS}[n] \rangle$
so the total energy functional is

$$E[n] = F[n] + \int V_{ext}(r)\, n(r)\, d^3r = \langle \psi_{GS}[n] | T_e + V_{ee} + V_{ext} | \psi_{GS}[n] \rangle$$

which is obviously minimum when n (and therefore $\psi_{GS}[n]$) is the correct GS density (wfc).

<u>PROOF</u> by reduction to contraddiction.
Suppose $n(r)$ does not determine $V(r)$, that is we can find two potentials $V(r)$, $V'(r)$ that differ by more than a constant and have the same GS density:

$$\begin{array}{lll} V(r) \rightarrow \psi \rightarrow n(r) & \text{with} & \psi \neq \psi' \text{ because } V(r) \neq V'(r) + \text{const} \\ V'(r) \rightarrow \psi' \rightarrow n'(r) & \text{but} & n(r) = n'(r) \end{array}$$

This would imply

$$E_{GS} = \langle \psi | T_e + V_{ee} + V | \psi \rangle < \langle \psi' | T_e + V_{ee} + V | \psi' \rangle = \langle \psi' | (T_e + V_{ee} + V') + (V - V') | \psi' \rangle$$

therefore $\quad E_{GS} < E'_{GS} + \int (V(r) - V'(r))\, n'(r)\, d^3r$

similarly $\quad E'_{GS} < E_{GS} + \int (V'(r) - V(r))\, n(r)\, d^3r$

adding the two inequalities and assuming $n(r) = n'(r)$

$$E_{GS} + E'_{GS} < E_{GS} + E'_{GS}$$

which is clearly false!
Therefore if $V(r) \neq V'(r) + c$ we must have $n(r) \neq n'(r)$. QED

In principle this solve the problem without the need of introducing explicitely the Many-Body w/c. All you have to do is to minimize the energy functional $E[n] = F[n] + \int V_{ext}(r)\, n(r)\, d^3r$ with respect to variation of the density with the constraint of conservation of particles $\int n(r)\, d^3r = N$

$$\delta \left[E[n] - \mu \left(\int n(r)\, d^3r - N \right) \right] = 0$$

$$\frac{dF[n]}{\delta n(r)} + V_{ext}(r) - \mu = 0$$

Unfortunately $F[n]$ is a very non trivial functional of the density and simple approximation to it are not accurate enough for practical purposes.
The true step toward a practical implementation has been made by Kohn and Sham one year later [Phys. Rev. 140, A1133 (1965)] when they proposed to split $F[n]$ in three pieces <u>defining</u>

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n]$$

where $E_H[n] = \frac{e^2}{2} \int \frac{n(r)\, n(r')}{|r-r'|}\, d^3r\, d^3r'$ is the classical electrostatic energy of the electronic charge density,

$T_s[n]$ is the kinetic energy of an <u>auxiliary</u> system of non interacting electrons with GS density $n(r)$, and

$E_{xc}[n]$ is the reminder (the above equation is the definition of E_{xc} !) that describes xc effects.

$E_{xc}[n]$ IS NOT easier to calculate than $F[n]$ but is much smaller in magnitude and approximations on it have hopefully less important consequences. $T_s[n]$ and $E_H[n]$, together with

$\int V(r) n(r) d^3r$ dominate the energy of the system and determine to a large extent its properties.

In order to give an explicit definition for $T_s[n]$ let's note that it is the non-interacting analogue of $F[n]$

$$T_s[n] = \langle \Phi^{[n]}_{NIGS} | T_e | \Phi^{[n]}_{NIGS} \rangle = \sum_{i=1}^{N} \langle \varphi_i | -\frac{\hbar^2}{2m} \nabla^2 | \varphi_i \rangle$$

let V_{eff} be the potential that has $n(r)$ as its non-interacting GS density. We must have

$$\delta \left[T_s[n] + \int V_{eff}(r) n(r) d^3r - \mu \left(\int n(r) d^3r - N \right) \right] = 0$$

$$\frac{\delta T_s[n]}{\delta n(r)} + V_{eff}(r) - \mu = 0$$

for the interacting systems we knows that

$$\frac{\delta T_s[n]}{\delta n(r)} + e^2 \int \frac{n(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}[n]}{\delta n(r)} + V_{ext}(r) - \mu = 0$$

whence

(KS1) $$V_{eff}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

the GS of a non interacting system is just $\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(r_1) & \cdots & \varphi_1(r_N) \\ \vdots & & \vdots \\ \varphi_N(r_1) & \cdots & \varphi_N(r_N) \end{vmatrix}$

where

(KS2) $$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(r) \right] \varphi_i(r) = \varepsilon_i \varphi_i(r)$$

and the density is

(KS3) $$n(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2$$

The kinetic energy expression has been given previously.

Eqs KS1-3 are the Kohn-Sham self consistent eqs.

Formally everything is exact. $E_{xc}[n]$ is a well defined functional of the density, although definitely non trivial to calculate, and so its functional derivative v_{xc}

For DFT and KS equations to become of practical use we need to give an approximate practical recipe to calculate $E_{xc}[n]$

As we will see, there exist simple approximations to E_{xc} that give very satisfactory results

More on Density Functional Theory

P. Hohenberg and W. Kohn, Phys. Rev. <u>136</u>, B864 (1964)

W. Kohn and L. J. Sham, Phys. Rev. <u>140</u>, A1133 (1965)

R. G. Parr and W. Yang, "Density-Functional Theory of Atoms and Molecules"