

Theoretical background

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1 What problem are we trying to solve?

We want to calculate the electronic structure of real materials, and their physical properties by *ab-initio* method. Electrons are microscopic particle, hence their dynamics is governed by the laws of quantum mechanics. Quantum particles are described by the wave function.

$$\lambda \cdot p = h$$

where h is the Plank constant. Wavefunction of an electron in a potential filed (V) is calculated by solving the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) + V(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

Fortunately, in most practical purposes, the potential field is not a function of time (t), or even if it is a function of time, they changes relatively slowly compared to the dynamics we are interested in. For example, the electrons inside a material are subjected to the Coulomb filed of the nucleus. The nucleus is heavy and their motion is much slower than the motion of the electrons. In such situation, we can separate out the spacial and temporal parts of the wave function:

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})f(t)$$

That reduces our task to solving only time independent Schrödinger equation:

$$\left[-\frac{\hbar^2\nabla^2}{2m} + v(\mathbf{r})\right]\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r})$$

Once we have the wavefunction, we can calculate the observables by taking the expectation values.

$$\psi_i|\psi_j = \delta_{ij}$$

$$\psi_i|\hat{H}|\psi_i = \epsilon_i$$

However, the challenge is to solve the Schrödinger equation as a real physical system is consists of large number of atoms. The Schrödinger equation becomes coupled many-body equation.

$$\left[-\frac{\hbar^2}{2m}\sum_{i=1}^N\nabla_i^2 + \sum_{i=1}^NV(\mathbf{r}_i) + \sum_{i=1}^N\sum_{j<i}^NU(\mathbf{r}_i,\mathbf{r}_j)\right]\psi(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N)$$

$$= E\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

With today's available computing power, it is far from feasible to solve the actual electronic wavefunction of a condensed matter system, where N is of the order of 10^{23} .

2 Hartree-Fock Theory

Hartree-Fock theory is foundational to many electronic structure theory. It is an independent particle model or mean field theory. Consider we have two non-interacting electrons. In that case, the Hamiltonian would be separable, and the total wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ would be product of the individual wave function. Now if we consider two electrons are forming a single system, then there are two issues. (1) We can no longer ignore the electron-electron interaction. (2) The wavefunction describing fermions must be antisymmetric with respect to the interchange of any set of space-spin coordinates. A simple **Hartree product** fails to satisfy that condition:

$$\Psi_{HP}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N)$$

In order to satisfy the antisymmetry condition, for our two electron system we can formulate a total wavefunction of the form:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_2) - \chi_1(\mathbf{r}_2)\chi_2(\mathbf{r}_1)]$$

Slater determinant The above equation can be written as:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_1)\chi_1(\mathbf{r}_2)\chi_2(\mathbf{r}_2)$$

Now what happens if we have more than two electrons? We can generalize the above determinant form to N electrons:

$$\Psi = \frac{1}{\sqrt{N!}}\chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_1) \cdots \chi_N(\mathbf{r}_1)\chi_1(\mathbf{r}_2)\chi_2(\mathbf{r}_2) \cdots \chi_N(\mathbf{r}_2) \cdots \chi_1(\mathbf{r}_N)\chi_2(\mathbf{r}_N) \cdots \chi_N(\mathbf{r}_N)$$

The above antisymmetrized product can describe electrons that move independently of each other while they experience an average (mean-field) Coulomb force.

Resources - <http://vergil.chemistry.gatech.edu/notes/hf-intro/hf-intro.html>;

3 Introduction to Density Functional Theory

Density functional theory (DFT) approaches the many-body problem by focusing on the electronic density which is a function of three spatial coordinates instead of finding the wave functions. DFT tries to minimize the energy of a system (ground state) in a self-consistent way, and it is very successful in calculating the electronic structure of solid state systems.

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A functional is a function whose argument is itself a function. $f(x)$ is a function of the variable x while $F[f]$ is a functional of the function f .

$$y = f(x)$$

f is a function, it takes a number x as input and output y is also a number.

$$y = F[f(x)]$$

F is a functional it takes function $f(x)$ as input and output y is a number.

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3.1 Hohenberg-Kohn Theorem 1

The ground state density

$$n(\mathbf{r})$$

determines the external potential energy

$$v(\mathbf{r})$$

to within a trivial additive constant.

So what Hohenberg-Kohn theorem says, may not sound very trivial. Schrödinger equation says how we can get the wavefunction from a given potential. Then there is the Schrödinger equation, if we can solve it (which could be difficult), we know how to get the density. Now Hohenberg and Kohn says the opposite is also true. For a given density, the potential can be uniquely determined. For non-degenerate ground states, two different Hamiltonian cannot have the same ground-state electron density. It is possible to define the ground-state energy as a function of electronic density.

3.2 Hohenberg-Kohn Theorem 2

Total energy of the system $E(n)$ is minimal when $n(\mathbf{r})$ is the actual ground-state density, among all possible electron densities.

The ground state energy can therefore be found by minimizing $E(n)$ instead of solving for the many-electron wavefunction. However, note that HK theorems do not tell us how the energy depends on the electron density. In reality, apart from some special cases, the exact $E(n)$ is unknown and only approximate functionals are used.

3.3 Kohn-Sham hypothesis

For any system of N interacting electrons in a given external potential $v_{ext}(\mathbf{r})$, there is a virtual system of N non-interacting electrons with exactly the same density as the interacting one. The non-interacting electrons subjected to a different external (single particle) potential.

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + e^2 \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}; [n])$$

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

where f_i is the occupation factor of electrons ($0 \leq f_i \leq 2$). The KS equation looks like single particle Schrödinger equation, however $e^2 \int d^3r' \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$ and $v_{xc}(\mathbf{r}; [n])$ terms depend on $n(\mathbf{r})$ i.e., on ψ_i which in turn depends on v_{ext} . Therefore the problem is non-linear. It is usually solved computationally by starting from a trial potential and iterate to self-consistency. Also note that we have not included the kinetic energy term for the nucleus. This is because the nuclear mass is about three orders of magnitude heavier than the electronic mass ($M \gg m$), so essentially electronic dynamics is much faster than the nuclear dynamics (see Born-Oppenheimer approximation).

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   $v_{ext}(\mathbf{r})$  includes the potential energy due to nuclear field, and external electric and magnetic fields if present.
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3.4 Algorithmic implementation

We can write our Schrödinger in Dirac Bra-Ket notation:

$$\hat{H}\psi = E\psi$$

We start with an initial guess for the electron density $n(\mathbf{r})$, and construct a pseudo potential for the nuclear potential. In turn, we have the Hamiltonian. Solve for $\psi_i(\mathbf{r})$, subsequently $n(\mathbf{r})$, and iterate until self consistency is achieved.

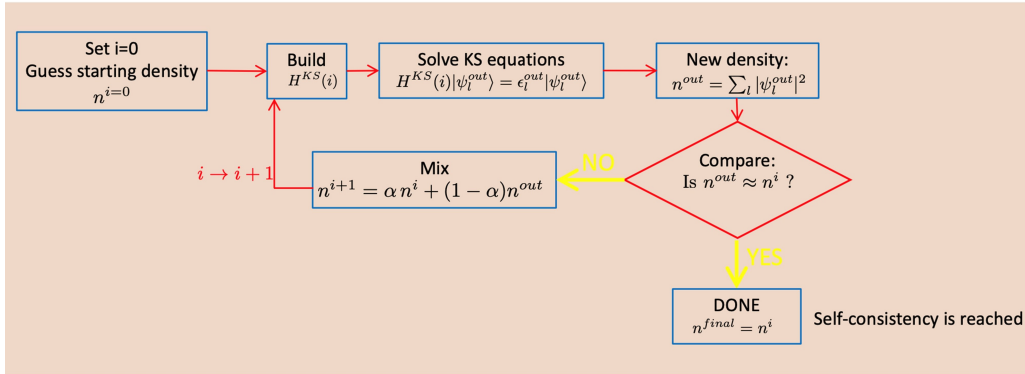


Figure 1: Self consistency loop in DFT calculation. The above screenshot was taken from lecture slide of Professor Ralph Gevauer from ICTP MAX School 2021.

The potential due to the ions is replaced by the pseudo potentials which removes the oscillations near the atomic core (reducing number of required plane wave basis vectors) and simulates the exact behavior elsewhere. The pseudo potential is also different for different exchange correlation functional, and it is specified in the pseudo potential file. If a system had more than one type of atom, always choose the pseudo potentials with same exchange correlation (e.g., PBE).

It is important to note that DFT calculations are not exact solutions to the real systems because the exact functional (v_{xc}) we need to solve the Kohn-Sham equation is not known. Therefore, we have to compare the results with experimental observations.

3.5 Plane-wave expansion

The wavefunctions are expanded in terms of a basis set. In quantum espresso, the basis function is plane waves. There exist other DFT codes that use localized basis functions as well. Plane waves are simpler but generally require a much larger number of them compared to other localized basis sets.

$$\psi_i(\mathbf{r}) = \sum_{\alpha=1}^{N_b} c_{i\alpha} f_{\alpha}(\mathbf{r})$$

Where N_b is the size of the basis set. Then the eigenvalue equation becomes:

$$\sum_{\beta} H_{\alpha\beta} c_{i\beta} = \epsilon_i c_{i\alpha}$$

$$\Rightarrow (H)_{11} \dots H_{1b} \dots H_{b1} \dots H_{bb} (c)_1 \dots c_b = \epsilon_i (c)_1 \dots c_b$$

This is a linear algebra problem, solving the above involves diagonalization of $(N_b \times N_b)$ matrix which gives us corresponding eigenvalue and eigenfunction.

3.6 Variational Principle

Finding the ground state:

$$E[\Phi] = \frac{\Phi | \hat{H} | \Phi}{\Phi | \Phi}$$

$$E[\Phi] \geq E_0$$

Bloch theorem

$$\psi_k(r) = e^{i\mathbf{k} \cdot \mathbf{r}} u_k(\mathbf{r})$$

$$u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{R})$$

\mathbf{R}

is lattice vector.

Fourier expansion:

$$u_k(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} c_{\mathbf{k}, \mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}$$

\mathbf{G}

is reciprocal lattice vector.

$$\psi_k(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}$$

Contribution from higher Fourier components are small, we can limit the sum at finite $|\mathbf{k} + \mathbf{G}|$

$$\frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m} \leq E_{cutoff}$$

The charge density can be obtained from:

$$n(\mathbf{r}) = \sum_k \psi_k^*(\mathbf{r}) \psi_k(\mathbf{r})$$

We need two set of basis vectors: one to store the wavefunctions, and another for the charge density.

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We need about 4 times the cutoff for the charge density compared to the cutoff for the wavefunction. In case of ultrasoft pseudo potentials, we require lower cutoff for energy, therefore ‘ecutrho’ might require 8 or 12 times higher than the ‘ecutwfc’.

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3.7 Resources

[MIT Course](<https://ocw.mit.edu/courses/materials-science-and-engineering/3-320-atomic-computer-modeling-of-materials-sma-5107-spring-2005/video-lectures/>)

[Quantum Espresso Tutorials](<https://www.quantum-espresso.org/resources/tutorials>)

[http://compmatphys.epotentialia.com](<http://compmatphys.epotentialia.com/>)

4 Pseudo potentials

In Quantum Espresso, pseudopotential replaces the actual electron-ion interaction. The pseudopotential describes the atomic nucleus and all the electrons except the outermost valence shell. The rapidly changing potential field near the atomic core is replaced by a smoother function that simulates the potential field far from the core very well. By doing so, it requires less number plane wave basis for wavefunction expansion.

We can choose from various pseudopotential libraries. Choice of pseudopotential depends on the problem we are investigating, e.g., if there is a heavy element present in our system and we are interested in the spin-orbit coupling effects, we should choose a full relativistic pseudo potential. We need to be careful whether our chosen pseudo potential correctly reproduces physical properties. Various pseudopotential libraries:

<https://www.quantum-espresso.org/pseudopotentials> (<https://www.quantum-espresso.org/pseudopotentials>)

<https://www.materialscloud.org/discover/sssp/table/efficiency>
(<https://www.materialscloud.org/discover/sssp/table/efficiency>)

<http://www.pseudo-doj.org> (<http://www.pseudo-doj.org>)

<https://www.physics.rutgers.edu/gbrv/> (<https://www.physics.rutgers.edu/gbrv/>)

Ultra soft pseudo potentials are computationally efficient than the norm conserving pseudo potentials. You will find the recommended ‘ecutwfc’ in the header of each pseudo potential file. If you choose an ultra-soft pseudo potential, you will need ‘ecutrho’ about 8 times the value of ‘ecutwfc’. The default ‘ecutrho’ is 4 times ‘ecutwfc’ in Quantum Espresso code, which is a good choice for norm conserving pseudo potentials. You should check energy convergence against ‘ecutwfc’ for your system.

By using pseudo potential, we want to get rid of the core electrons that do not participate in the chemical properties of material. This is known also as rigid core approximation. Instead of accounting the nucleus and core electrons separately, we want to have a pseudo potential that interacts in a similar way with the valence electrons.

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We can mix different types of pseudo potentials (e.g., norm conserving, ultra-soft, or PAW), but we cannot mix different functional (e.g., PBE and LDA).

”sol” in PBE-sol stands for solid. For bulk systems PBE-sol should be used, while PBE is appropriate for molecules. In case of 2D materials generally PBE is chosen, but one can check PBE-sol.

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:::danger Common error

If you mix PBE with PBE-sol type, it results in Error: conflicting values for igcx. However, it is allowed to mix those two types of pseudo. We can set desired exchange functional via inputdft instead of reading from the pseudo potential file.

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4.1 Resources

Naming convention for PP files (<https://www.quantum-espresso.org/pseudopotentials/naming-convention>)