Computational Nanoscience

NSE C242 & Phys C203

Spring, 2008

Lecture 17:

Tight-Binding &

Moving Towards Density Functional Theory

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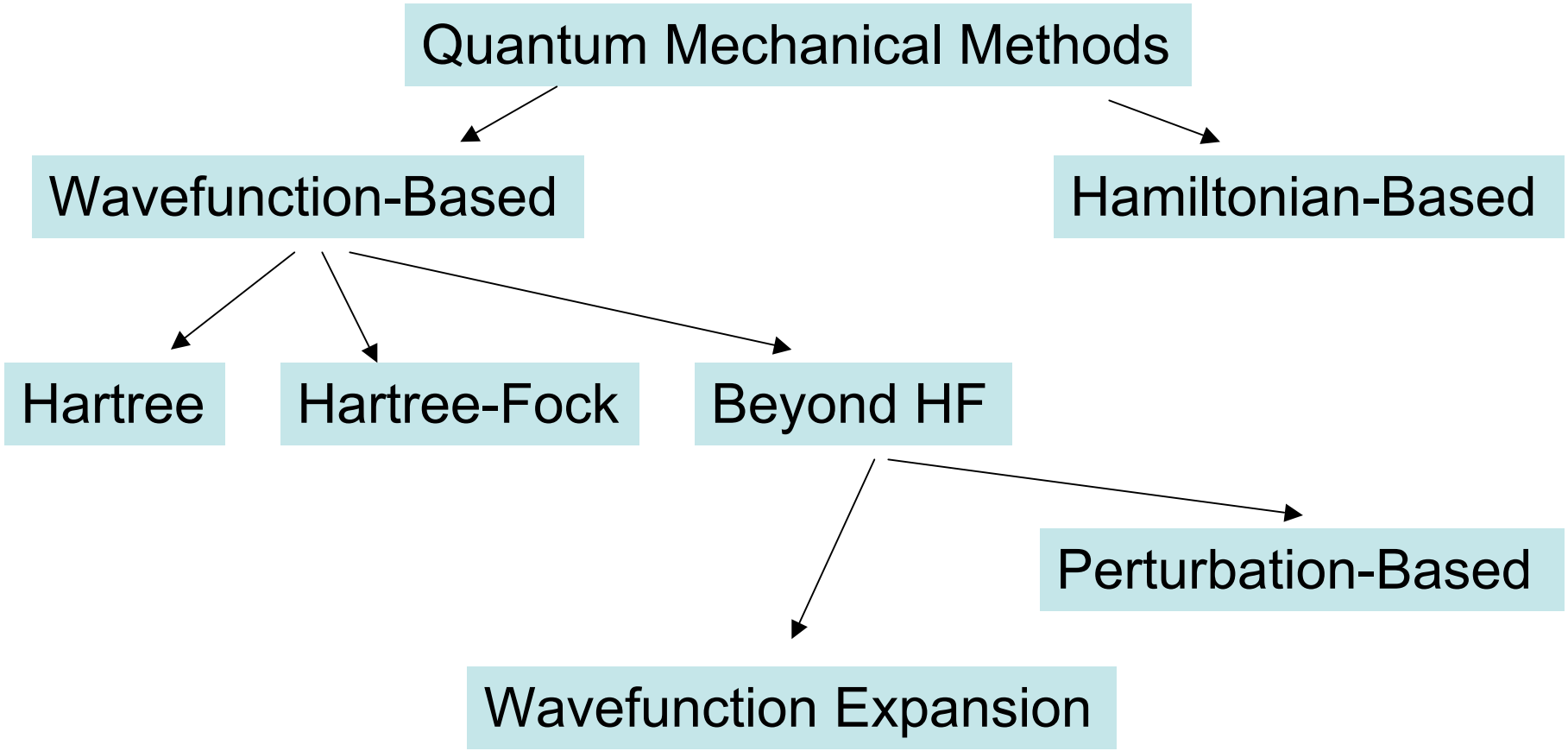
Review


Quantum Mechanical Methods
Wavefunction-Based
Hamiltonian-Based
Hartree
Hartree-Fock
Beyond HF
Perturbation-Based
Wavefunction Expansion

Empirical Tight Binding

The Tight Binding (TB) model was initially developed for solids (band structures) but currently is widely used for both solids and molecules.

TB is based on a description of electronic states starting from the limit of isolated atomic orbitals.

It is a simple model that gives good quantitative results for bands derived from strongly localized atomic orbitals, which decay to essentially zero on a radius much smaller than the next neighbor half-distance in the solid.

For the conduction bands (or “extended states”), the results of tight-binding are usually in rather poor agreement with experiment.

Tight binding can be systematically improved by including additional levels/bands, so that the accuracy of the calculated bands increases, at the expense of the simplicity and transparency of the model.

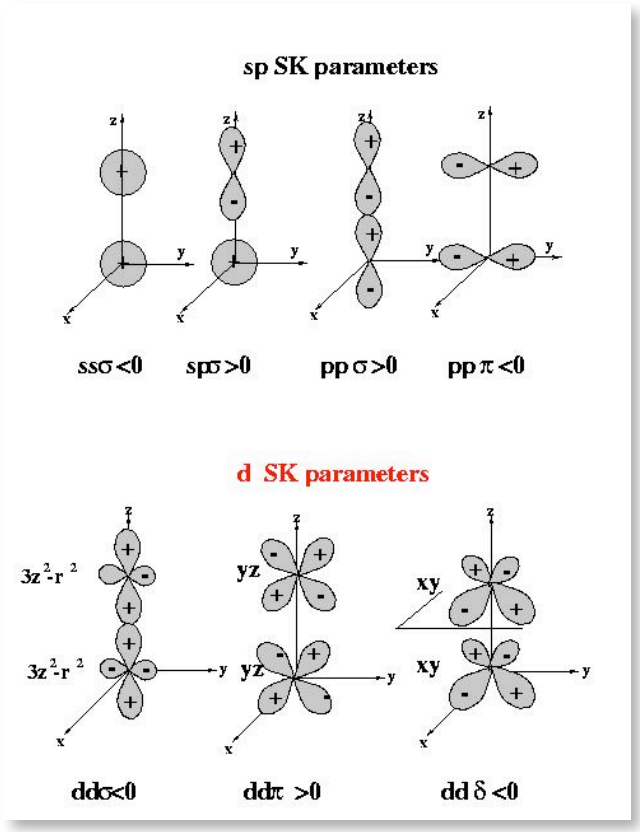
Tight Binding

The approximation of the TB method is to assume that phase space is spanned by atomic-like orbitals and that this is sufficient to describe the wave function solution of the Schrodinger equation.

TB is also referred to as LCAO - linear combination of atomic orbitals.

Such an atomic-like basis provides a natural, physically motivated description of electronic states in matter.

In practice there are many versions of TB, depending on the degree of "ab-initio". Some methods use true atomic-like orbitals and others are semi-empirical using fitted parameters.



Tight Binding - An Example

$$H|\psi\rangle = \varepsilon|\psi\rangle$$

LCAO expansion of wavefunction: $|\psi\rangle = c_A|s_A\rangle + c_B|s_B\rangle$

We wish to determine the coefficients in the expansion

In TB, this amounts to setting up a matrix eigenvalue problem

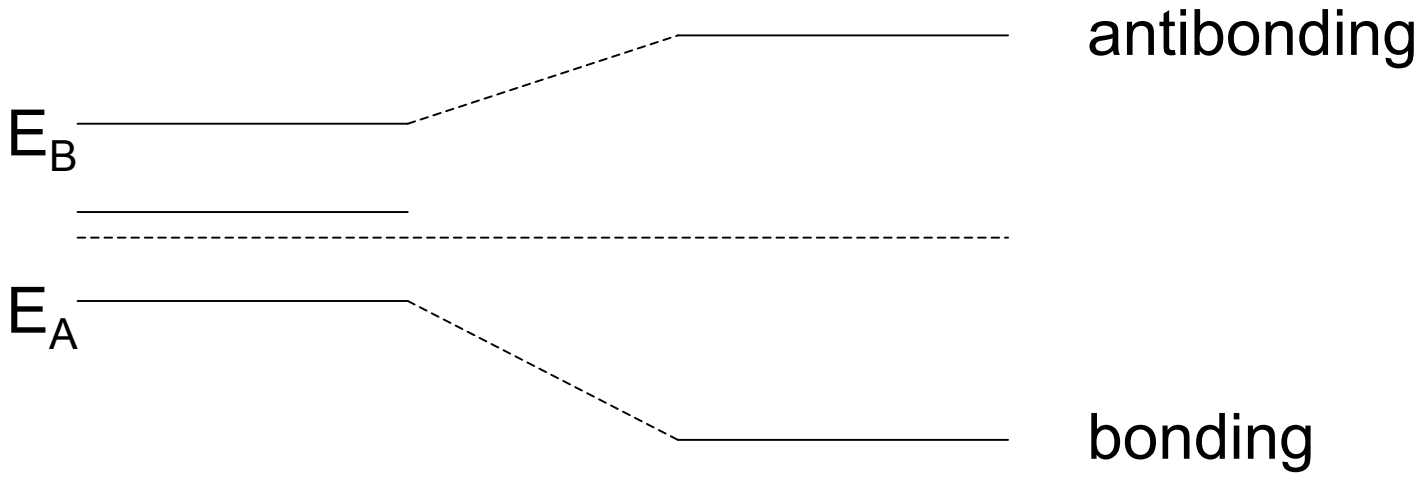
$$\begin{pmatrix} \langle s_A|H|s_A\rangle - \varepsilon & \langle s_A|H|s_B\rangle \\ \langle s_B|H|s_A\rangle & \langle s_B|H|s_B\rangle - \varepsilon \end{pmatrix} \begin{Bmatrix} c_A \\ c_B \end{Bmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

The eigenvalues correspond to the energies, and the eigenvectors (the coefficients) to the states

Tight Binding - An Example

If we were to do this, we would find an expression for the eigenvalues that looks like:

$$\varepsilon_{\pm} = \frac{1}{2}(E_A + E_B) + \overline{V}s \pm \frac{1}{2}\left[4\overline{V}^2 + (\Delta\varepsilon)^2\right]^{1/2}$$



If atoms A and B are both H, is the system bound? What if they are both He?

Describe some similarities and differences between Tight-Binding and HF.

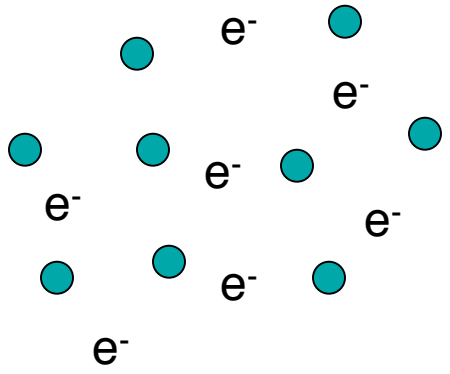
Multi-electron Atoms and Molecules

Let $R_1, \ldots, R_N$ = positions of the N nuclei

$eZ_1, \ldots, eZ_N$ = charge of the N nuclei

$M_1, \ldots, M_N$ = masses of the nuclei

$r_1, \ldots, r_n$ = positions of the n electrons



The electronic Hamiltonian looks like this:

$$\hat{H} = \underbrace{\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\frac{Z_i Z_j e^2}{|R_i - R_j|} - \sum_{j=1}^{N}\sum_{i=1}^{n}\frac{Z_j e^2}{|r_i - R_j|}}_{V_{ext}(r_i)} + \underbrace{\sum_{j=1}^{n}\left(-\frac{\hbar^2}{2m}\right)\nabla_{r_j}^2}_{T} + \underbrace{\frac{1}{2}\sum_{j=1}^{n}\sum_{i=1}^{n}\frac{e^2}{|r_i - r_j|}}_{V_{\text{int}}}$$

Note how the only part of the Hamiltonian that changes for different systems is the external potential.

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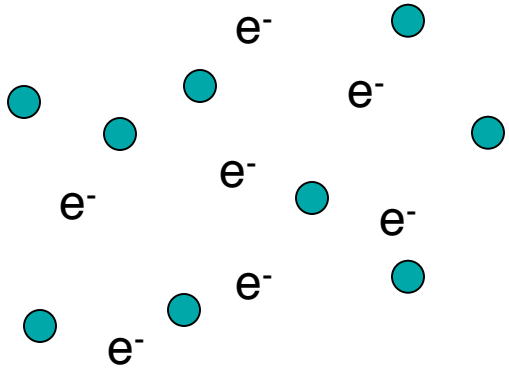

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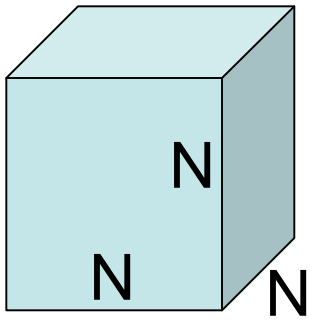
Note how the only part of the Hamiltonian that changes for different systems is the external potential.

And our eigenvalue problem looks like: $\hat{H}\Psi(r_1,\ldots,r_n) = \varepsilon\Psi(r_1,\ldots,r_n)$

Solving the Eigenvalue Equations

- We've talked about the Hartree, Hartree-Fock, and post-HF approaches. We've also seen that we get poor scaling when we want to include any correlation effects at all.
- An underlying issue here is that, no matter how you slice it, the wavefunction Ψ is a beast of an entity to have to deal with.
- For example, consider that we have n electrons populating a 3D space. Let's divide 3D space into NxNxN=2x2x2 grid points. To reconstruct Ψ, how many points must we keep track of?

$$\Psi = \Psi(r_1,\ldots,r_n) \qquad \#\ \text{of points} = N^{3n}$$



n = # electrons	Ψ (N^{3n})	ρ (N^3)
1	8	8
10	10^9	8
100	10^{90}	8
1000	10^{900}	8

- The electron density seems to be a more manageable quantity. Wouldn't it be nice if we could reformulate our problem in terms of the density, rather than the wavefunction?

Hohenberg-Kohn I

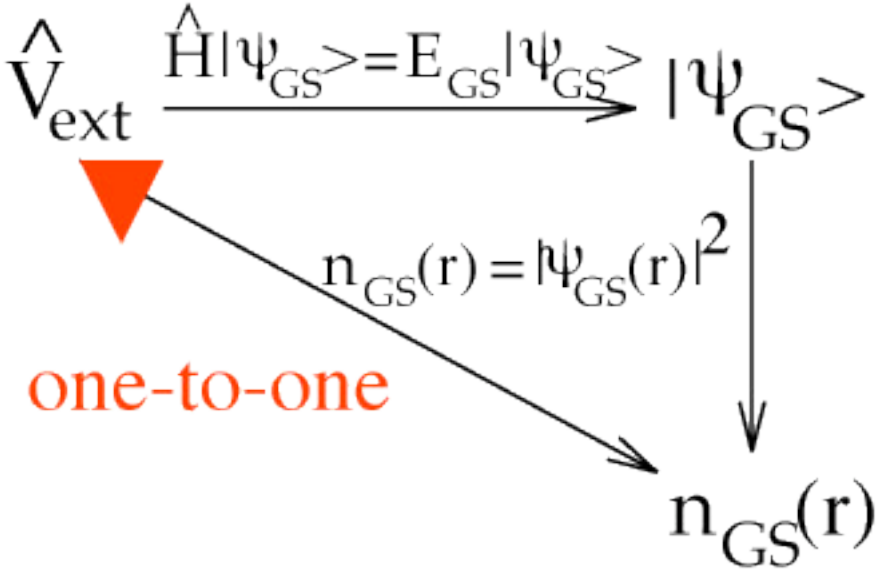
- As it turns out, we can - and this is the basis for DFT.
- In order to reformulate our problem in terms of the electronic density, we must first establish a few ground rules
- These are, namely, the two Hohenberg-Kohn theorems and the Kohn-Sham formalism

HOHENBERG-KOHN I

- The external potential corresponds to a unique ground state electron density.

- A given ground state electron density corresponds to a unique external potential

- In particular, there is a one to one correspondence between the external potential and the ground state electron density



Hohenberg-Kohn II

There exists a universal functional of the density F[ρ(r)] such that the ground state energy E

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

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is minimized at the true ground state density.

Note how very useful this is. We now have a variational theorem to obtain the ground state density (and, correspondingly, the energy)

By the way, what is a "functional"?

A functional is a mapping from a function (the electron density) to a number (the ground state energy).

The equation that we need to solve comes from taking a functional derivative

$$\frac{\delta}{\delta\rho}\left(E - \mu\int \rho(r)dr\right) = V_{ext} + \frac{\delta F}{\delta\rho} - \mu = 0$$

Hohenberg-Kohn II

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Note that a Lagrange multiplier has showed up. The constraint that we are accomodating is:

$$n=\int\rho(\mathbf{r})d\mathbf{r}$$

Hohenberg-Kohn II

But, back to the functional form of the Hohenberg-Kohn expression, which we will use to evaluate the energy.

$$E\left[\rho(\mathbf{r})\right] = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F\left[\rho(\mathbf{r})\right]$$

Aha - we have gone from the 3n dimensional integrals to the 3 dimensional integrals.

i.e., previously, we had to deal with:

$$E = \int \Psi^*(V_{ext} + T + V_{\text{int}})\Psi d^{3n}r$$

In principle - if you tell me the ground state electron density, I can plug into this integral expression and give you the GS energy.

But wait … what is the form of the universal functional F? We only said that it exists; we did not specify what it is.

This is, in fact, the origin of the ubiquitous statement that "In principle, DFT is exact. In practice, we must approximate."

What might F[ρ(r)] look like?

From simple inspection:

$$E = \int \Psi^* (V_{ext} + T + V_{\text{int}}) \Psi d^{3n} r$$

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

Naively, we might expect the functional to contain terms that resemble the kinetic energy of the electrons and the coulomb interaction of the electrons

Kohn-Sham Approach

Kohn and Sham said:

$$F\left[\rho(\mathbf{r})\right] = E_{KE}\left[\rho(\mathbf{r})\right] + E_{H}\left[\rho(\mathbf{r})\right] + E_{XC}\left[\rho(\mathbf{r})\right]$$

Where we have a separation of kinetic, Coulomb, and exchange/correlation terms.

Importantly, the kinetic part is defined as the kinetic energy of the system of non-interacting electrons at the same density.

The Coulomb term is simply the Hartree electrostatic energy - namely, a classical interaction between two charges summed over all possible pairwise interactions.

The equation above, in a sense, acts to define the last term, the exchange-correlation part, as simply everything else that should be there to make this approximation to *F* as accurate as possible.