Computational Nanoscience
NSE C242 & Phys C203
Spring, 2008

Lecture 18:

Density Functional Theory :

What it Does and Doesn't Do

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Updates

Homework Assignment: Hartree-Fock and DFT on molecules via GAMESS. Will be posted by Friday morning. Due: April 3rd
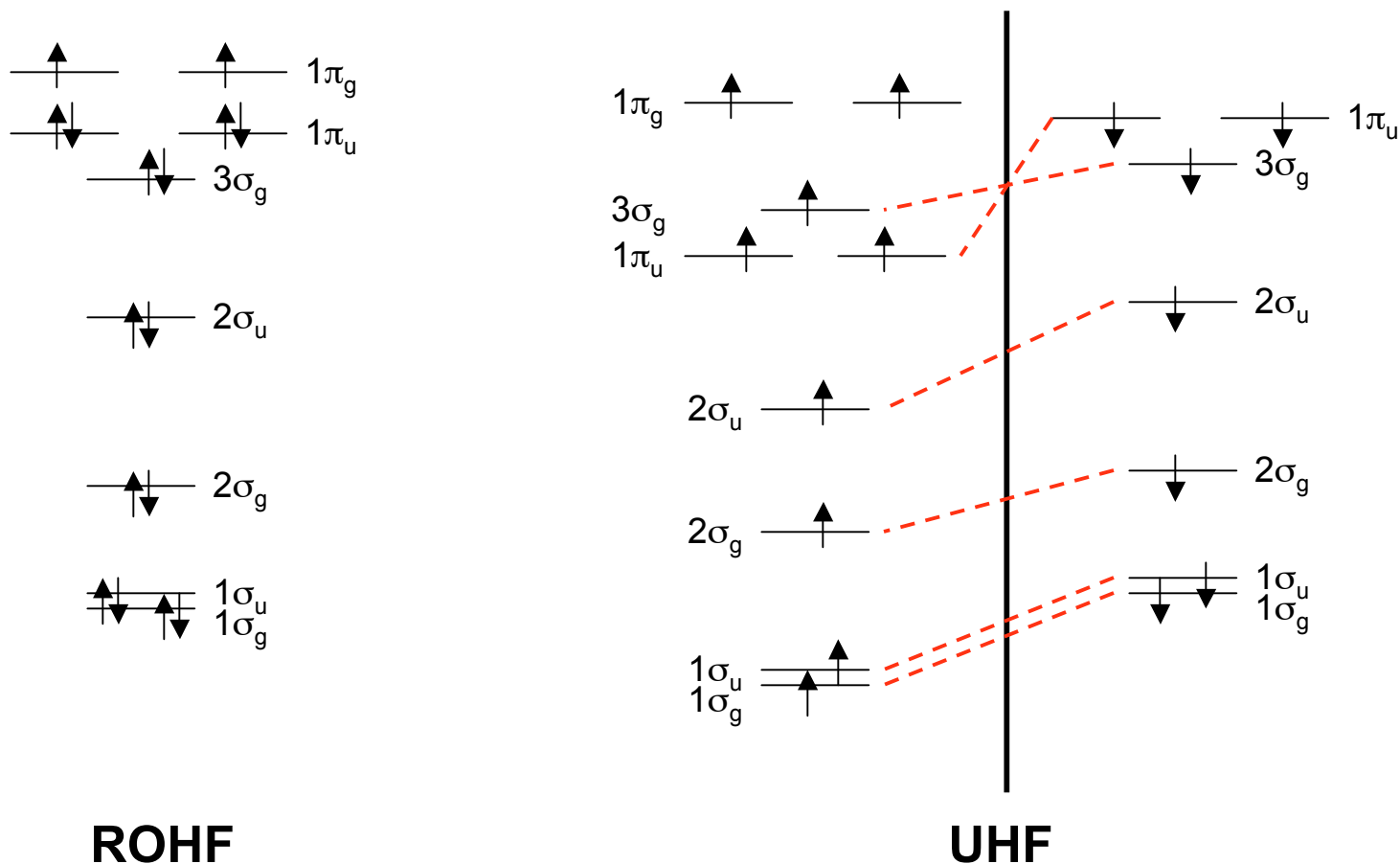
Class Projects: Abstract/Proposal for your class project is due on April 10th. (one or two paragraphs)

Bring your laptop for in-class simulation on Tuesday, April 1st.

REMEMBER : There is no class next week (so don't come!)

Errors, Lies, and Mistruths

Unrestricted vs. Restricted Open Shell Hartree-Fock for O_2

ROHF

UHF

For open shell systems, UHF is better. The enhanced exchange interaction in the α channel electrons "pushes down" the eigenvalues relative to the β channels. Energy of unrestricted calculation is always lower than or equal to that of restricted.

Scaling

After Foulkes, Mitas, Needs, and Rajagopal, pg 33.
Rev Mod Phys 73 (2001).

Method	E_{corr}	E_{coh} % error	Scaling with # electrons	Total time for C_{10}
HF	0	50%	N^4	14
DFT-LDA	N/A	15-25%	N^3	1
CC	75%	10-15%	N^7	1500
VMC	85%	2-10%	$N^3+\varepsilon N^4$	16
DMC	95%	1-4%	$N^3+\varepsilon N^4$	300

Density Functional Theory

- Completely rigorous approach to any interacting problem in which we can map, exactly, the interacting problem to a non-interacting one.
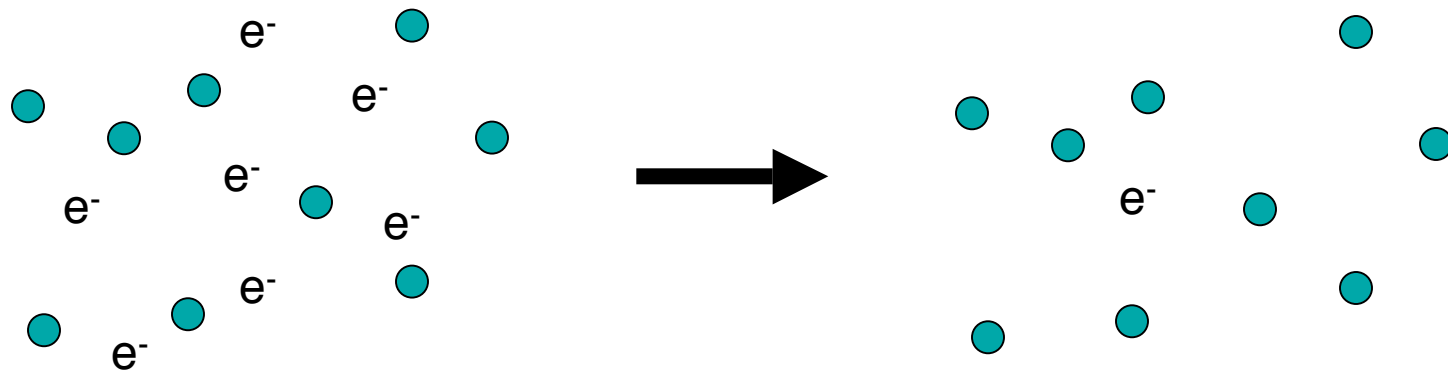
$$\widehat{H} = \frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\frac{Z_iZ_je^2}{|R_i - R_j|} - \sum_{j=1}^{N}\sum_{i=1}^{n}\frac{Z_je^2}{|r_i - R_j|} + \sum_{j=1}^{n}\left(-\frac{\hbar^2}{2m}\right)\nabla^2_{r_j} + \frac{1}{2}\sum_{j=1}^{n}\sum_{i=1}^{n}\frac{e^2}{|r_i - r_j|}$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad}_{V_{ext}(r_i)} \quad \underbrace{\quad}_{T} \quad \underbrace{\quad}_{V_{int}}$$

interacting particles in a real external potential

$$\widehat{H} = \left(-\frac{\hbar^2}{2m}\right)\nabla^2_r + V_{eff}(r)$$

Kohn-Sham system: a set of non-interacting electrons (with the same density as the interacting system) in some effective potential

Ingredients to Density Functional Theory

- Ingredients:
    - Note that what differs from one electronic system to another is the external potential of the ions
    - Hohenberg-Kohn I: one to one correpondence between the external potential and a ground state density
    - Hohenberg-Kohn II: Existence of a universal functional such that the ground state energy is minimized at the true ground state density

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

UNIVERSAL!

- The universality is important. This functional is exactly the same for any electron problem. If I evaluate F for a given trial orbital, it will always be the same for that orbital - regardless of the system of particles.
    - Kohn-Sham: a way to approximate the functional F

Euler-Lagrange System

The Hohenberg-Kohn theorems give us a variational statement about the ground state density:

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

"the exact density makes the functional derivative of F exactly equal to the negative of the external potential (to within a constant)"

If we knew how to evaluate F, we could solve all Coulombic problems exactly.

However, we do not know how to do this. We must, instead, approximate this functional. This is where Kohn-Sham comes in.

Kohn-Sham Approach

Kohn and Sham said:

$$F\big[\rho(\mathbf{r})\big] = E_{KE}\big[\rho(\mathbf{r})\big] + E_H\big[\rho(\mathbf{r})\big] + E_{XC}\big[\rho(\mathbf{r})\big]$$

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.

Kohn-Sham Approach

The next step to solving for the energy is to introduce a set of one-electron orthonormal orbitals.

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \left| \varphi_i(\mathbf{r}) \right|^2$$

Now the variational condition can be applied, and one obtains the one-electron Kohn-Sham equations.

$$\left\{ -\frac{\nabla_1^A}{2} - \left(\sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} dr_2 + V_{XC}\left[\rho(\mathbf{r})_1 \right] \right\} \varphi_i(\mathbf{r}_1) = \varepsilon_i \varphi_i(\mathbf{r}_1)$$

Where V_{XC} is the exchange correlation functional, related to the xc energy as:

$$V_{XC}[\mathbf{r}] = \left(\frac{\delta E_{XC}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \right)$$

Comparison with Hartree-Fock

$$\left\{ -\frac{\nabla_1^A}{2} - \left(\sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} + V_{XC}[\mathbf{r}_1] \right\} \varphi_i(\mathbf{r}_1) = \varepsilon_i \varphi_i(\mathbf{r}_1)$$

Naturally, you're remembering the Hartree-Fock equations and realizing that this equation is in fact quite similar:

$$\left[-\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + V_{ion}(\mathbf{r}_i) + e^2 \sum_{j \neq i} \left\langle \varphi_j \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \varphi_j \right\rangle \right] \varphi_i(\mathbf{r}_i) - e^2 \sum_{j \neq i} \left\langle \varphi_j \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \varphi_i \right\rangle \varphi_j(\mathbf{r}_i) = \varepsilon_i \varphi_i(\mathbf{r}_i)$$

So, just as with Hartree-Fock, the approach to solving the Kohn-Sham equations is a self-consistent approach.

That is, an initial guess of the density is fed into the equation, from which a set of orbitals can be derived. These orbitals lead to an improved value for the density, which is then taken in the next iteration to recompute better orbitals. And so on.

Kohn-Sham System

To solve the Kohn-Sham equations, a number of different methods exist.

These tend to differ first and foremost in the choice of basis set for expanding the Kohn-Sham orbitals.

As in Hartree-Fock, for molecular systems a typical choice can be some type of atom-centered basis such as sums of Gaussians.

In extended (e.g., solid, liquid) systems, planewaves are a much more suitable choice of basis.

One important difference between DFT and Hartree-Fock, in general, is that the Kohn-Sham orbitals used in DFT are a set of non-interacting orbitals designed to give the correct density and have no physical meaning beyond that.

This is in contrast to the orbitals in Hartree-Fock theory, which directly represent electrons and are designed to give the correct wavefunction as opposed to just the density.

The Exchange-Correlation Functional

The exchange-correlation functional is clearly the key to success of DFT.

One of the great appealing aspects of DFT is that even relatively simple approximations to V_{XC} can give quite accurate results.

The local density approximation (LDA) is by far the simplest and most widely used functional.

The LDA approach is based on a model known as the uniform electron gas where the electron density is constant throughout all space.

In LDA, we approximate the exchange-correlation energy at each point in space by the exact exchange-correlation energy of the homogeneous electron gas.

The exchange-correlation energy per electron of the uniform electron gas is known accurately for all densities of practical interest from various approaches such as quantum Monte Carlo.

Ceperley and Alder* have perhaps the most commonly used QMC calculations for the electron gas, which are then expressed in some analytic or parametrized form (e.g., Perdew-Zunger) that makes them amenable to calculation in LDA.

Local Density Approximation

In the original Kohn-Sham paper, the authors themselves cast doubt on its accuracy for many properties. "We do not expect an accurate description of chemical bonding."

And yet, not until at least 10 years later (the 70's), time and time again it was shown that LDA provided remarkably accurate results.

LDA was shown to give excellent agreement with experiment for, e.g., lattice constants, bulk moduli, vibrational spectra, structure factors, and much more.

One of the reasons for its huge success is that, in the end, only a very small part of the energy is approximated.

For example, here are various energy contributions for a Mn atom:
• Hartree (E_{CV}, E_{VV})
• Kinetic ($T_{0,V}$)
• Exchange (E_X)
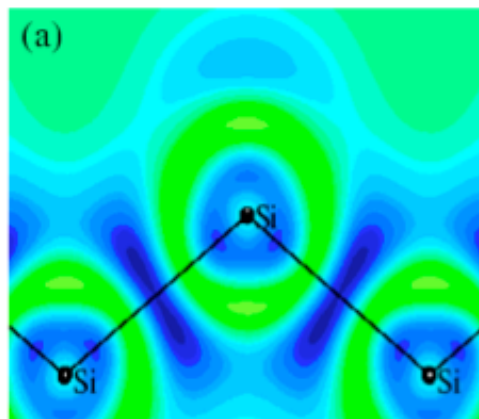• Correlation energy is about $E_C \sim 0.1 E_X$
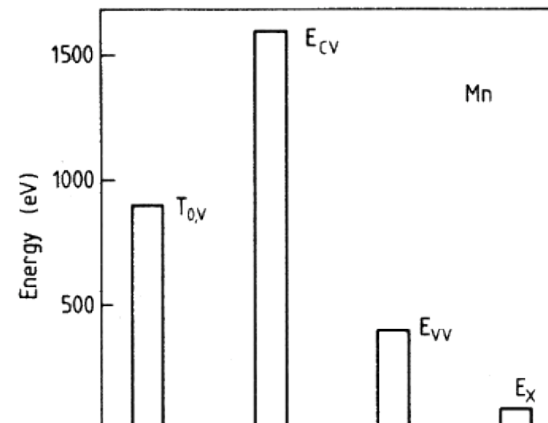
Local Density Approximation

LDA also works well because errors in the approximation of exchange and correlation tend to cancel.
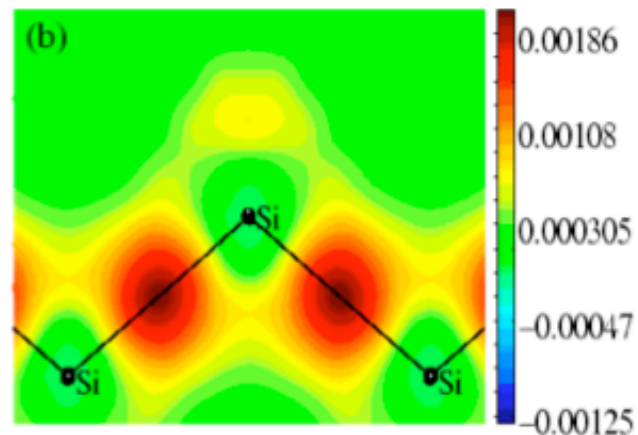
For example, in a typical LDA atom, there's a ~10% underestimate in the exchange energy.

This error in exchange is compensated by a ~100-200% overestimate of the correlation energy.

Hood et al PRB **57** 8972 (1998)

Local Density Approximation

In theory, the LDA method should work best for systems with slowly varying densities (i.e., as close to a homogeneous electron gas as possible).
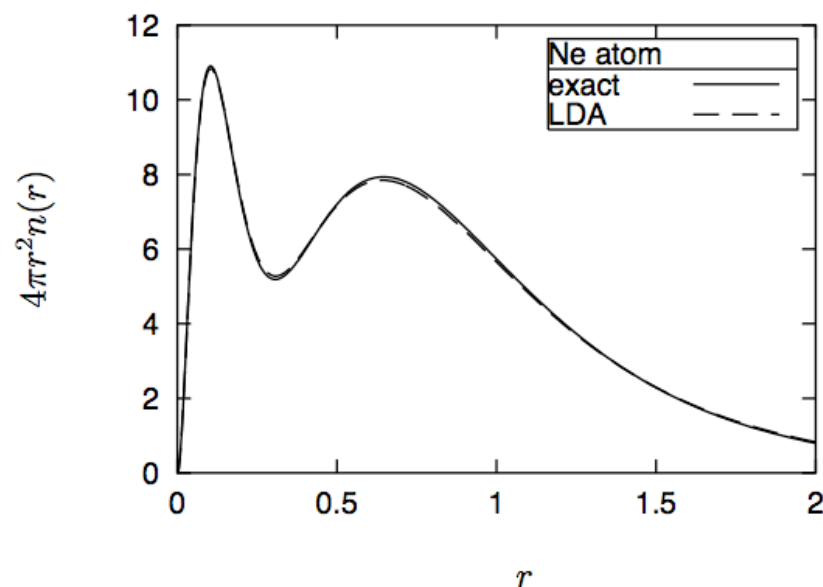
However, it is interesting that even for many systems where the density varies considerably, the LDA approach performs well!
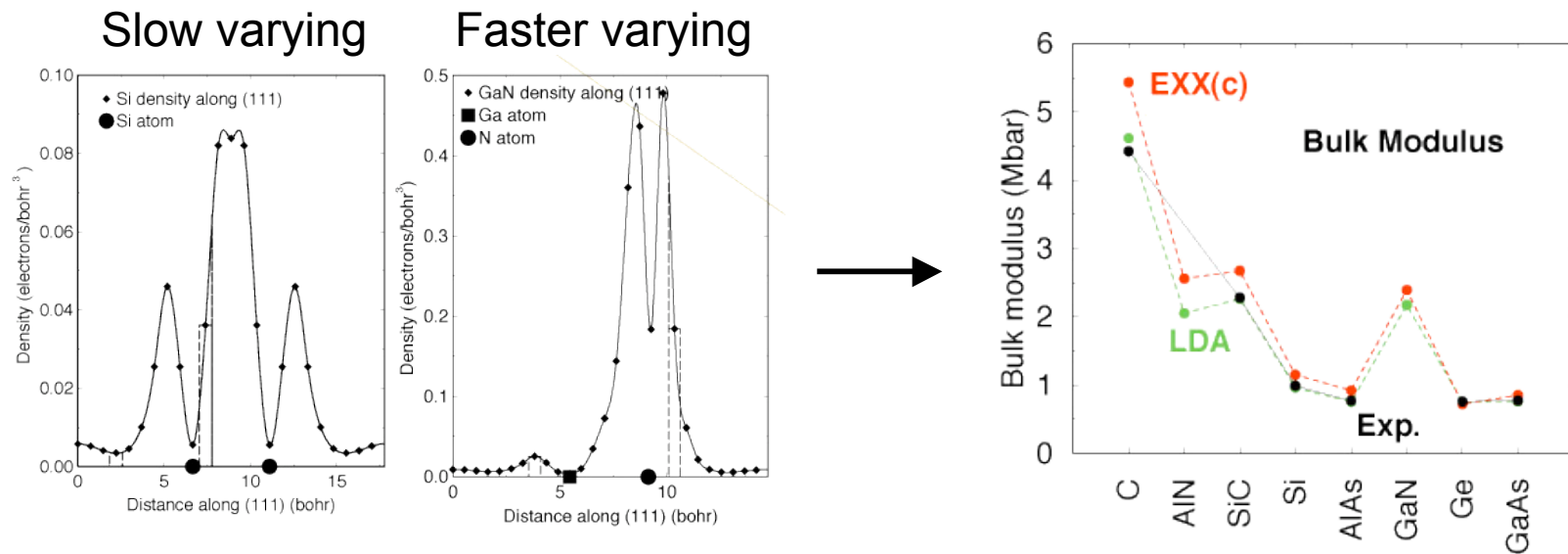
Good & Bad - Local Density Approximation

Total energies

Ground state densities well-represented

Cohesive energies are pretty good; LDA tends to overbind a system (whereas HF tends to underbind)

Bond lengths are good, tend to be underestimated by 1-2%

Good for geometries, vibrations, etc.

Structures of highly correlated systems (transition metals, FeO, NiO, predicts the non-magnetic phase of iron to be ground state)
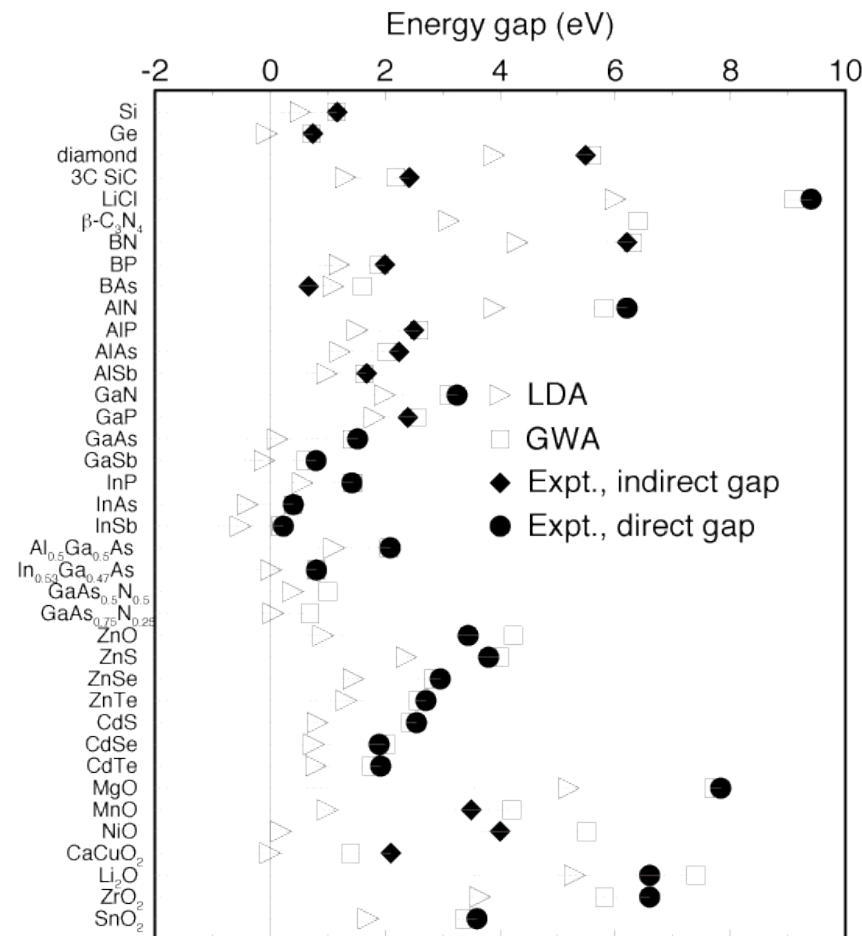
Doesn't describe weak interactions well.

Makes hydrogen bonds stronger than they should be.

Band gaps (shape and position is pretty good, but will underestimate gaps by roughly a factor of two; will predict metallic structure for some semiconductors)

Local Density Approximation

One place where LDA performs poorly is in the calculation of excited states.

Beyond LDA - GGA

The most common method for improving upon the simple LDA is to use gradient corrected "non-local" functionals.

These GGA functionals depend on both the value of the density at each point in space as well as the gradient of the density.

The two most popular GGA's are the PBE functional and the BLYP functional (the acronyms refer to the authors - Perdew and Becke being the primary ones).

In some GGA's, empirical-type fits are introduced, such as in BLYP where the one parameter is fit to the exact exchange Hartree-Fock energies for noble gas atoms.

Beyond LDA

Recently, so-called "hybrid" functionals have gained in popularity.

These functionals attempt to add correlation energy derived from DFT to the Hartree-Fock energy which has the exchange contribution exact.

However, a true "exact exchange" DFT is actually too hard to do (for the moment), so presently hybrid functionals do a kind of mixture of exact exchange.

In this way, the exchange-correlation functional is written as a sum of terms, some of which we had before, one of which is the "exact" exchange from a slater determinant of Kohn-Sham orbitals, and two more of which are fit to experimental data (precisely, fit to 56 binding energies, 42 ionization potentials, 8 proton affinities, and total atomic energies for the second-row elements).

This is the B3LYP functional and, even though it's kind of empirical, it is the best "ab initio" DFT method in terms of overall performance.

Modeling Solids

A number of approaches are used for studying solid systems.

We'll discuss a couple of these here, for example, the band theory approach vs. the free-electron model.

Band Theory
- Atomic orbitals are combined to give the equivalent of molecular orbitals.
- Based on the assumption that the effect of orbital overlap is to modulate but not change completely the initial atomic levels.
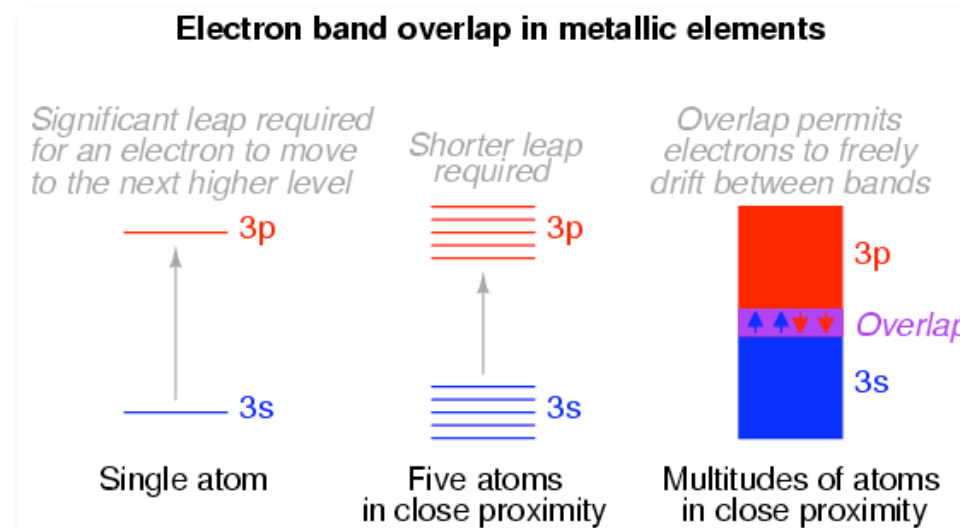- Good approach for insulators and transition metals

Nearly Free-Electron Theory
- Electrons are free particles whose motion is modulated by the presence of a lattice
- Good for metals where there is large overlap among valence orbitals

Band Theory

Band theory begins from an atomic orbital picture.

If we start from a single atom and then add more and more, the energy levels merge to give what is essentially a continuous band of energy levels.

Electron band overlap in metallic elements

Significant leap required for an electron to move to the next higher level — 3p

Shorter leap required — 3p

Overlap permits electrons to freely drift between bands — 3p, *Overlap*, 3s

3s

Single atom

Five atoms in close proximity

Multitudes of atoms in close proximity

http://www.allaboutcircuits.com/vol_3/chpt_2/3.html

An even simpler way to get a metal is to start with atom species that only have 1 valence electron, say Na. Then the band is by default half-filled and the electrons are very mobile (easy to excite, etc).

Metal, Semiconductor, Insulator

The energy gap E_g between the conduction band and the valence band (LUMO and HOMO in a molecule) determines whether the system is a metal, semiconductor, or insulator.

In metals, E_g is zero, and a significant amount of electrons are thermally excited into empty levels.

In semiconductors, E_g is small, typically on the order of $k_B T$, so that excitation between bands can take place at room temperature.

In insulators, E_g is large so exciting an electron from the valence to conduction band requires considerable energy.

http://www.chemistry.adelaide.edu.au/external/soc-rel/content/bands.htm
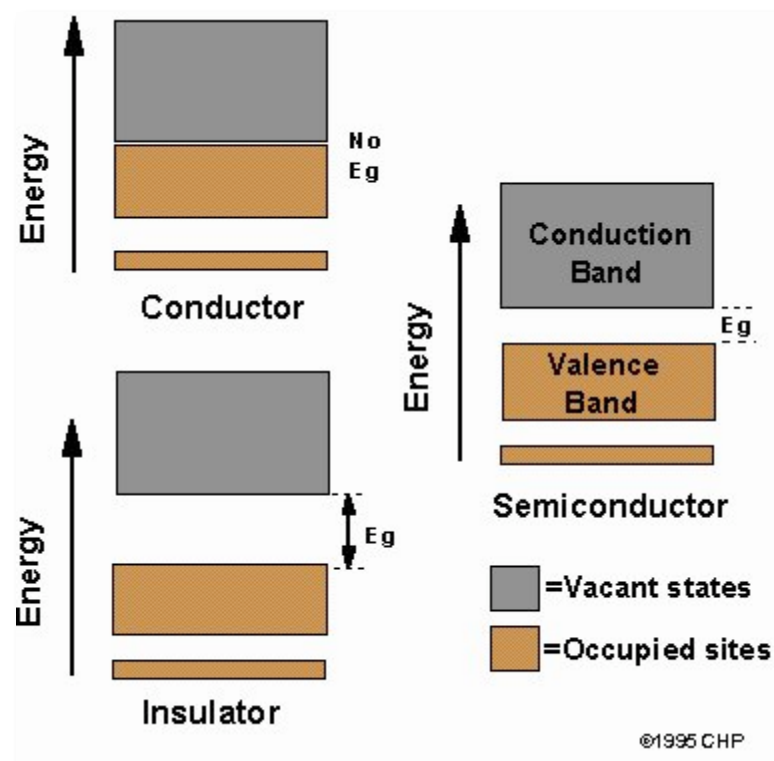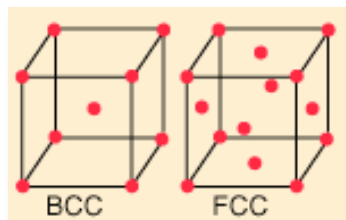
Aside - Reciprocal Lattice & Brillouin Zone

Associated with each real space lattice, there exists something we call a reciprocal lattice.

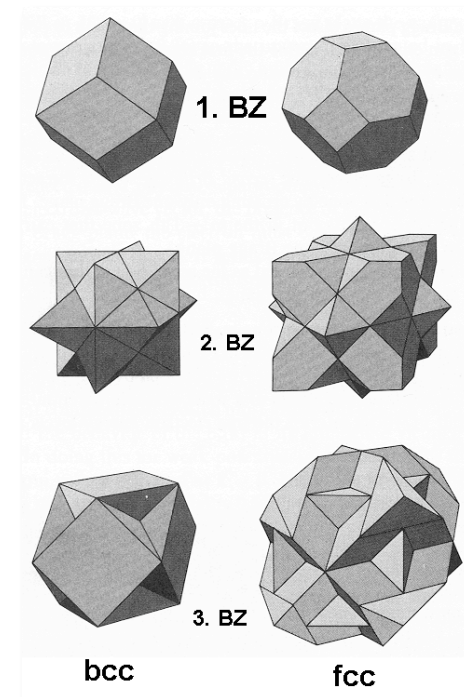The reciprocal lattice is the set of wavevectors which are commensurate with the real space lattice.

It is defined by a set of vectors **a*, b*,** and **c*** such that **a*** is perpendicular to **b** and **c** of the Bravais lattice, and the product **a* x a** is 1.

In particular, $\quad \mathbf{a}^* = \dfrac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$

BCC   FCC

1. BZ

2. BZ

3. BZ

bcc   fcc

Aside - Reciprocal Lattice & Brillouin Zone

Reciprocal lattice vectors have some special properties that are of particular value for solid-state electronic structure calculations.

Remember that we usually write the reciprocal lattice vector as:

$$\mathbf{G} = 2\pi n\mathbf{a}^* + 2\pi m\mathbf{c}^* + 2\pi o\mathbf{c}^*$$

We added the 2π simply for convenience, and the n, m, o, are integers.

Now consider the behavior of the function $\exp(i\mathbf{G}\cdot\mathbf{r})$:

$$\exp(i\mathbf{G}\cdot\mathbf{r}) = \exp\left[i(2\pi n\mathbf{a}^* + 2\pi m\mathbf{c}^* + 2\pi o\mathbf{c}^*)\cdot(\alpha\mathbf{a} + \beta\mathbf{b} + \gamma\mathbf{c})\right]$$

$$= \exp\left[i(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma)\right]$$

$$= \cos(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma) + i\sin(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma)$$

Aside - Reciprocal Lattice & Brillouin Zone

$$\exp(i\mathbf{G} \cdot \mathbf{r}) = \cos(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma) + i\sin(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma)$$

As **r** is varied, the coefficients of the lattice vectors (α, β, γ) change between 0 and 1 and the value of the function exp(i**G·r**) changes too.

However, since n, m, and o are integral, the function exp(i**G·r**) will always vary with the periodicity of the real-space lattice.

A couple of interesting observations of this function:

1) If we were to write a function as a Fourier series of terms from exp(i**G·r**) the resulting series will be periodic on the real lattice.

2) These are called planewaves.

3) Such exponential functions represent wavefunctions for a free particle.

Bloch Theorem

The periodicity of the lattice in a solid means that the values of a function (e.g., density) will be identical at equivalent points on the lattice.

The wavefunction, on the other hand, is periodic but only when multiplied by a phase factor.

This is known as Bloch's theorem. For a 1-D periodic system with a lattice constant of a, it reads:

$$\varphi^k(x + a) = e^{ika}\varphi^k(x)$$

The label k for the wavefunction can be considered an index. There are as many values of k as there are unit cells in the system.

Bloch Theorem

Any overall wavefunction we come up with for our solid should meet the Bloch requirement.

Suppose we have a certain type of orbital in our lattice, labeled χ_n where the nth orbital is located at position x=na.

Then a linear combination of these orbitals that also satisfies Bloch's theorem would be:

$$\varphi^k = \sum_n e^{ikna} \chi_n$$

Periodicity and Bloch's Theorem

$$\varphi^k = \sum_n e^{ikna} \chi_n$$

At k=0, we would have:

$$\varphi^{k=0} = \sum_n \chi_n = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$$

At k=π/a, all the sine terms (imaginary ones) would be zero, and we'd have cosine terms that can be expressed as $(-1)^n$:
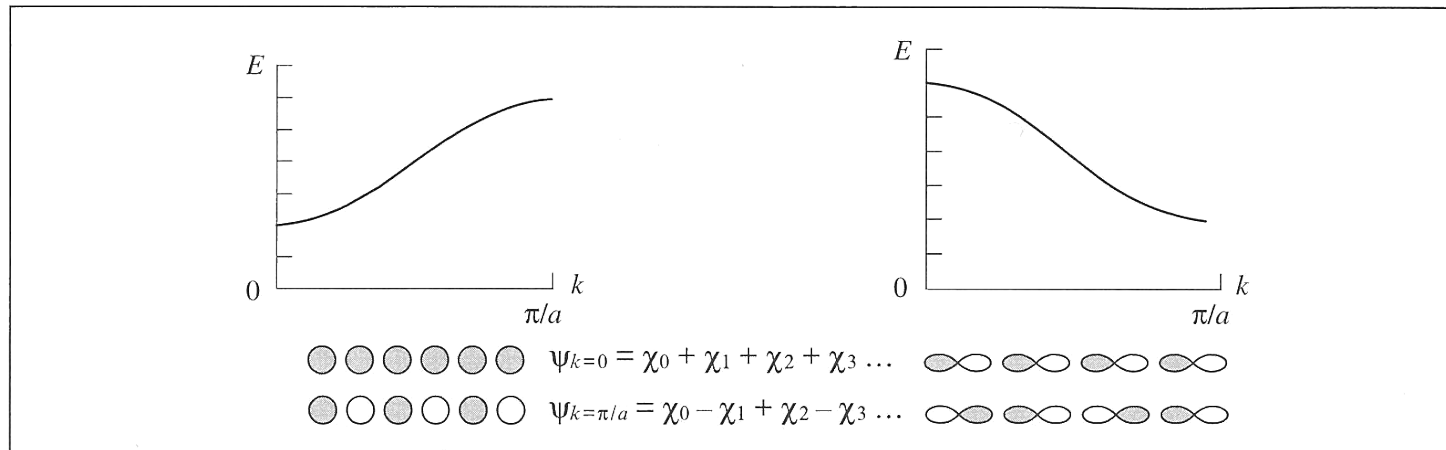
$$\varphi^{k=\pi/a} = \sum_n (-1)^n \chi_n = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$$

These limits - k= 0 and k=π/a - correspond to the lowest and highest-energy wavefunctions.

The energy varies in a cosine-like manner in between.

Band Structure

The graph of energy versus k is called the band structure.

This variation in energy depends on the type of orbital that was used to construct the wavefunction.

For a 1-D lattice, as in this example, the bandwidth (difference in energy between the highest and lowest levels in the band) is determined by the distance between the atoms.

Band Structure
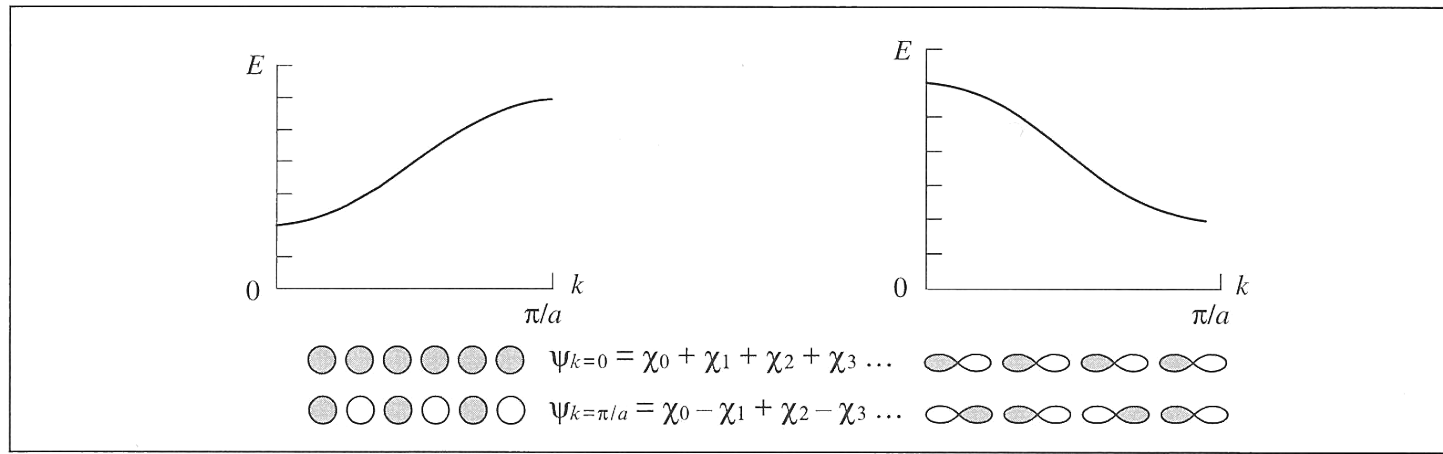
As we increase the number of dimensions, the band structure becomes more and more complex.

Note that for more than 1 dimension, **k** becomes a vector, known as the wavevector (having components k_x, k_y, for example in 2-D).