10.675 LECTURE 14

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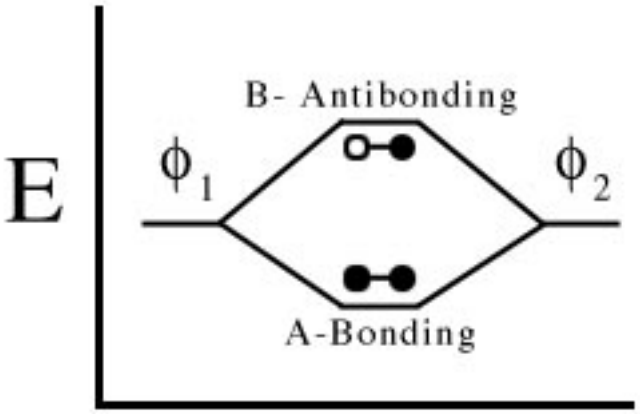
1. Today

Introduction to Plane Wave Pseudo Potential Methods
→ Electronic Structure of Extended Systems
→ Bloch's Thereom
→ Plane Wave Basis Set
→ Implementation of DFT Pseudo potentials

2. MOT

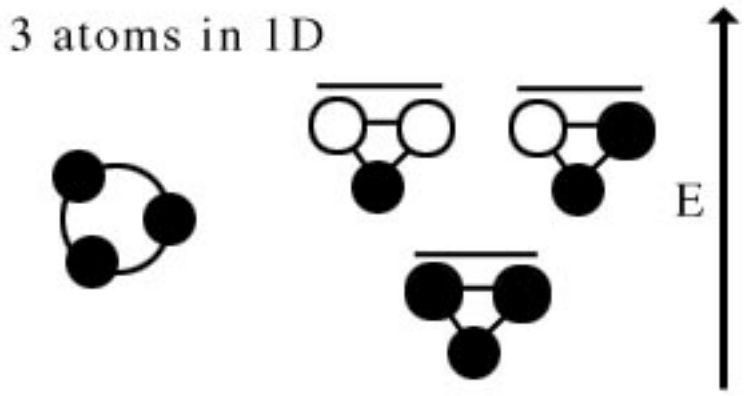
Molecular Orbital Theory
→ 1D configuration of H-atoms
Atoms 1 and 2
Φ_1 wave function centered around atom 1
Φ_2 wave function centered around atom 2
Bonding $\Phi_A = \Phi_1 + \Phi_2$
Anti-Bonding $\Phi_B = \Phi_1 - \Phi_2$



The bonding state is energetically favorable in the band splitting that occurs.
Move on to 3 atoms in a ring (1D line)
3 energy configurations (2 unique)
Lowest, $\Phi_1 + \Phi_2 + \Phi_3$
Highest $\Phi_1 + \Phi_2 - \Phi_3$ AND $\Phi_1 - \Phi_2 - \Phi_3$

Date: Fall 2004.

Every reverse of sign from neighboring atoms (1 links to 2, 2 links to 3, 3 links back to 1) is a node. Nodes are higher in energy from the band splitting.



N atoms, 1 huge ring.
Lowest energy is all wave functions of the same sign
Highest energy is an alternating arrangement of wave functions.
Each energy in between (combinations of + and -'s) creates a continuum of levels between the highest and lowest energy.
with $10^{20} \rightarrow$ is a virtual continuum of levels.

3. Notation

The wave functions Φ_k's are spaced "a" distance apart.
$\Phi_k = \sum_n e^{iknd}\phi_n$ which is the generalized phase relationship
$k \rightarrow$ is the index or "momentum" vector.
This results from the translational symmetry of the system.
Unique values of $|k| < +/- \frac{\pi}{a}$ are in the first "brillioun zone".
$E(k) - E(-k)$ from 0 to π/a and DOS (# of states between E and E + dE)

4. Physics approach.

Bloch's Thereom. Given the Hamiltonian H = R +V(r) where
V(r)=V(r+R)=V(r) for all R in a periodic lattice.
$\Psi_{nk}(r) = e^{ikr}u_{nk}(r)$ where $u_{nk}(r) = u_{nk}(r + R)$
k is the quantum # that characterized the translational symmetry of the system
Periodic lattice. $1cm^3$ 10^{22} atoms 10^{17} on the surface.
$10^{-5} - 10^{-6}$ surface/volume ratio.

5. reciprocal lattice

k space
The set of all wave vectors g that yield plane waves w/the periodicity of a given lattice is it's reciprocal lattice.
$e^{ig(r+R)} = e^{igr} \Rightarrow e^{igR} = 1$
Reciprocal lattice holds this equations
Expand $h_{nk}(r)$ in a "basis set" of plane waves w/periodicity of lattice
$e_{nk}(r) = \sum_g c_n(q)e^{igr} \Rightarrow \Psi_{nk}(r) = e^{ikr}\sum_q c_n^k(q)e^{igr}$

Where do we stop? Choose an energy criteria and set of k's $E_k = \frac{1}{2}(k+g)^2 < E_{cut}$

6. Advantages of method

Syntax easier, no *'s, +'s etc etc
Can methodically increase accuracy of your basis set
BSSE is not an issue

7. Disadvantages

Must treat empty space
Many plane waves needed (costly)
Amorphous systems need to be large enough such that there is no periodic interaction.

8. Misc

For insulators and semiconductors, on the k point is used. The "gamma" point.
Another problem $\Rightarrow$ plane waves don't describe huge variations in $\rho(r)$ well
Solution $\rightarrow$ introduce pseudo potentials
$\rho_o(r) = \sum_k w_k \sum_n |\Psi_{nk}(r)|^2$ where w is the weighting function
In metals, small #'s of k's are chose on a mesh that physicists have developed.
Metals $\rightarrow$ k points used.

9. Pseudopotentials

$\Rightarrow$ treat only valence electrons explicitly
$\Rightarrow$ can describe variations in ρ