6.730 Physics for Solid State Applications

Lecture 1: Molecules – the Simple Solid

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Syllabus

- **Molecules**
  - Approximate models for molecular bonding
  - Vibrational and rotational modes

- **Continuum Models of Solids**
  - Elasticity   Phonons
  - Free electron gas   Electron

- **Lattice ('Atomic') Models of Solids**
  - Crystal structure
  - Phonons (lattice waves) on discrete lattice
  - Bloch electrons

- **Single Electron Transport**
  - 'Electrons' and 'holes'
  - Chemical potential and band bending

- **Electron Scattering**
  - Electron-phonon scattering; mobility
  - Electron-photon scattering; absorption and gain

- **Statistical Theory of Electron Transport**
  - Boltzmann transport
  - Drift-diffusion; hot electron effects

General Course Information

Required Text :
Fundamentals of Carrier Transport, Second Edition, by Mark Lundstrom, Cambridge University Press, 2000
Notes will be handed out to cover the first two-thirds of the class. This required text be used for the last third of the class.

Suggested Text :
Solid State Physics , N.W. Aschroft and M.D. Mermin, Saunders College Publishing, 1976.
This text is not required, but if you wish to purchase a textbook that covers some of the material in the first two-thirds of the class I would suggest this text because it is the one used in 6.732.

Problem Sets :
All homework sets are due at the begining of class on the assigned due date. You may work together on the problem sets but you are required to write up your own solution and code. Students will make oral presentations on the homework.

FINAL :
There will be a final examination for the class.

GRADES:
40% Group Project (30% written report and 10% presentation)
40% Problem Sets (25% written and 15% presentation)
20% Final Examination

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Band Formation in 1-D Solid

◆ Simple model for a solid: the one-dimensional solid, which consists of a single, infinitely long line of atoms, each one having one s orbital available for forming molecular orbitals (MOs).
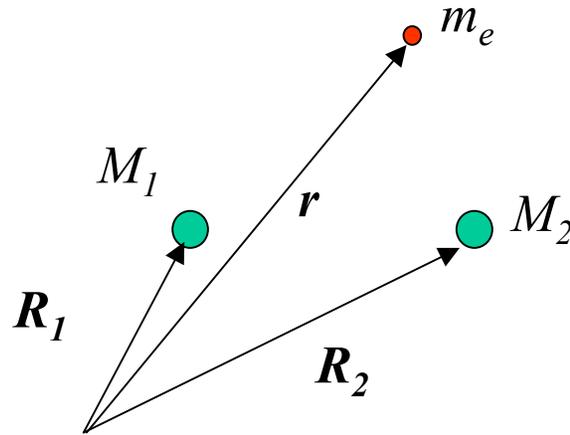
When the chain is extended:

➔ The *range of energies* covered by the MOs is *spread*

➔ This range of energies is filled in with *more and more orbitals*

➔ The *width of the* range of energies of the MOs is *finite*, while the number of molecular orbitals is *infinite*: This is called a *band* .

Band Formation in 1-D Solid with s & p orbitals

Before we can build models for the solid, we need to understand a simple diatomic molecule.

The Simplest Molecule: H$_2$

$\psi(\mathbf{r}, \mathbf{R_1}, \mathbf{R_2})$, the wavefunction for the entire system of nuclei and electrons

$$\widehat{\mathcal{H}}\psi(\mathbf{r}, \mathbf{R_1}, \mathbf{R_2}) = \mathbf{E}\psi(\mathbf{r}, \mathbf{R_1}, \mathbf{R_2})$$

$$\widehat{\mathcal{H}} = \frac{|\mathbf{P_1}|^2}{2M_1} + \frac{|\mathbf{P_2}|^2}{2M_2} + \frac{|\mathbf{p}|^2}{2m_e} - \frac{e^2}{4\pi\epsilon_o|\mathbf{r} - \mathbf{R_1}|} - \frac{e^2}{4\pi\epsilon_o|\mathbf{r} - \mathbf{R_2}|} + \frac{e^2}{4\pi\epsilon_o|\mathbf{R_1} - \mathbf{R_2}|}.$$

Approximate Models: Simplifying H_2

Born-Oppenheimer Approximation

◆ The electrons are much lighter than the nuclei ($m_e/m_H \cong 1/1836$), their motion is much faster than the vibrational and rotational motions of the nuclei within the molecule.

➔ A good approximation is to neglect the coupling terms between the motion of the electrons and the nuclei: this is the **Born-Oppenheimer approximation**. The Schrödinger equation can then be divided into two equations:

$$\Psi(\mathbf{r}, \mathbf{R_1}, \mathbf{R_2}) \approx \Phi(\mathbf{R_1}, \mathbf{R_2})\psi(\mathbf{r}; \mathbf{R_1}, \mathbf{R_2}).$$

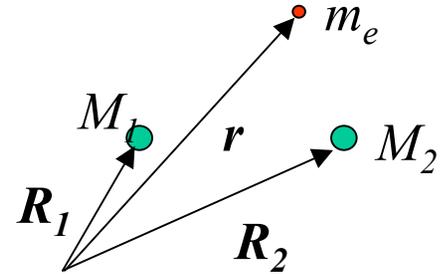## Linear Combination of Atomic Orbitals (LCAO)

Even the electron part of the problem is too hard to solve exactly
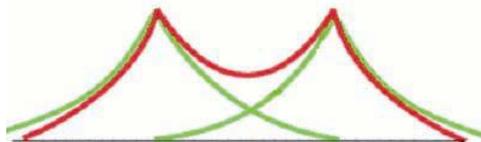
$$\psi(\mathbf{r}; \mathbf{R_1}, \mathbf{R_2}) = \mathbf{C}\left[\phi_{1s}(\mathbf{r} - \mathbf{R_1}) + \phi_{1s}(\mathbf{r} - \mathbf{R_2})\right]$$

Born-Oppenheimer Approximation

$$\Psi(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2) \approx \Phi(\mathbf{R}_1, \mathbf{R}_2)\psi(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2)$$

Electronic Part: $\psi(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) \longrightarrow \psi(\mathbf{r})$

$$E_e(\mathbf{R}_1, \mathbf{R}_2)\psi(\mathbf{r}) = \underbrace{\left[-\frac{\hbar^2\nabla^2}{2m_e} - \frac{e^2}{4\pi\epsilon_o|\mathbf{r} - \mathbf{R}_1|} - \frac{e^2}{4\pi\epsilon_o|\mathbf{r} - \mathbf{R}_2|} \right]}_{\hat{\mathcal{H}}_e}\psi(\mathbf{r})$$
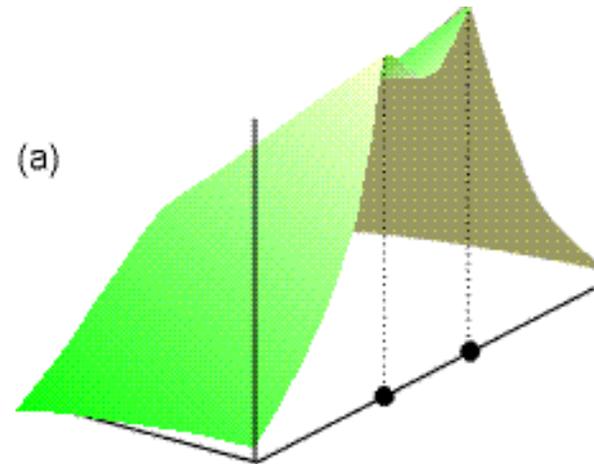
Nuclear Part:

$$E\Phi(\mathbf{R}_1, \mathbf{R}_2) = \left[-\frac{\hbar^2\nabla_1^2}{2M_1} - \frac{\hbar^2\nabla_2^2}{2M_2} + \underbrace{E_e(\mathbf{R}_1, \mathbf{R}_2) + \frac{e^2}{4\pi\epsilon_o|\mathbf{R}_1 - \mathbf{R}_2|}}_{V_{\text{eff}}} \right]\Phi(\mathbf{R}_1, \mathbf{R}_2)$$

where *E* is the energy of the <u>entire</u> molecule

Electronic Part: LCAO

$$E_e(R)\psi(\mathbf{r}) = \left[-\frac{\hbar^2 \nabla^2}{2\mathbf{m_e}} - \frac{\mathbf{e^2}}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{R_1}|} - \frac{\mathbf{e^2}}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{R_2}|} \right] \psi(\mathbf{r}) \, .$$

$$\psi(\mathbf{r}) = \mathbf{C} \left[\phi(\mathbf{r} - \mathbf{R_1}) + \phi(\mathbf{r} - \mathbf{R_2}) \right]$$

For example, if we consider 1s orbitals only…

$$\phi(\mathbf{r})_{1s} = \frac{1}{\pi^{1/2} \mathbf{a_o^{3/2}}} \mathbf{e^{-r/a_o}}$$

$$a_o = 4\pi\epsilon_o \hbar^2 / (m_e e^2)$$

$$\langle \phi | \phi \rangle = 1$$

(a)

Normalization of Electronic Part: LCAO cont.
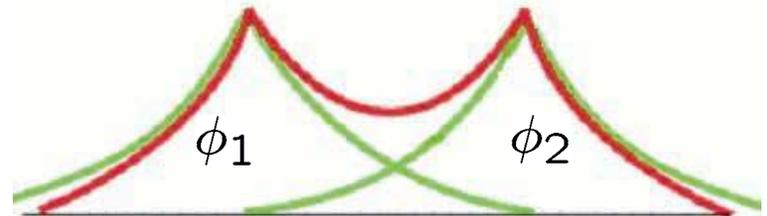
Normalize to guarantee the probability of finding an electron anywhere is still 1

$$\langle \psi | \psi \rangle = 1$$

$$\psi(\mathbf{r}) = \mathbf{C}\left[\phi(\mathbf{r} - \mathbf{R_1}) + \phi(\mathbf{r} - \mathbf{R_2})\right]$$

$$\langle \phi_1 + \phi_2 | \phi_1 + \phi_2 \rangle = 2\left(1 + S(1)\right)$$

$$C = \frac{1}{\sqrt{2 + 2S(1)}}$$

ϕ_1 ϕ_2

where

$$S(1) = \langle \phi_1 | \phi_2 \rangle = e^{-R/a_o}\left(1 + R/a_o + \frac{1}{3}(R/a_o)^2\right)$$

Approximate Electronic Energy

$$E_e(R) = \frac{\langle \psi(\mathbf{r})|\hat{H}_e|\psi(\mathbf{r})\rangle}{\langle \psi(\mathbf{r})|\psi(\mathbf{r})\rangle} \qquad \psi(\mathbf{r}) = \mathbf{C}\left[\phi(\mathbf{r} - \mathbf{R_1}) + \phi(\mathbf{r} - \mathbf{R_2})\right]$$

$$\langle \psi(\mathbf{r})|\hat{H}_e|\psi(\mathbf{r})\rangle = \left\langle \phi_1 + \phi_2 \left| \frac{p^2}{2m_e} + \underbrace{V(\mathbf{r_1} - \mathbf{R})}_{V_1} + \underbrace{V(\mathbf{r_2} - \mathbf{R})}_{V_2} \right| \phi_1 + \phi_2 \right\rangle$$

$$= \left\langle \phi_1 \left| \frac{p^2}{2m_e} + V_1 + V_2 \right| \phi_1 \right\rangle + \left\langle \phi_1 \left| \frac{p^2}{2m_e} + V_1 + V_2 \right| \phi_2 \right\rangle$$

$$+ \left\langle \phi_2 \left| \frac{p^2}{2m_e} + V_2 + V_1 \right| \phi_2 \right\rangle + \left\langle \phi_2 \left| \frac{p^2}{2m_e} + V_2 + V_1 \right| \phi_1 \right\rangle$$
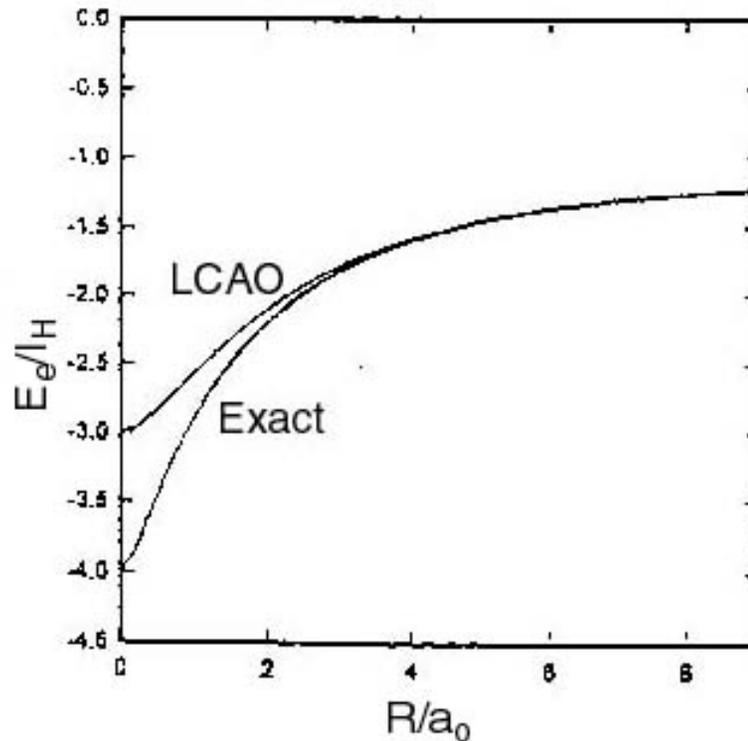
$$= E_s + V_{ss\sigma} + E_s + V_{ss\sigma}$$

$$\boxed{E_e(R) = \frac{E_s + V_{ss\sigma}}{1 + S(1)}}$$

Approximate Electronic Energy

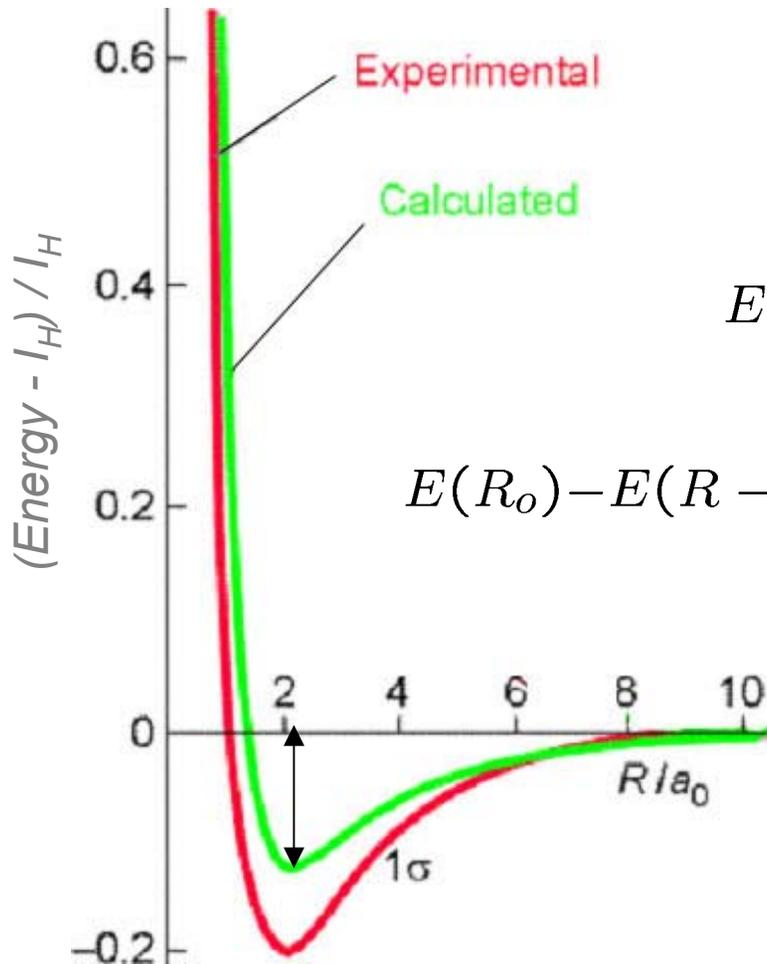$$E_e(R) = \frac{E_s + V_{ss\sigma}}{1 + S(1)}$$

$$E_s = -I_H = -m_e e^4/(32\pi^2 \epsilon_o^2 \hbar^2) = -13.6\,\text{eV}$$

Nuclear and Electronic Energy Together

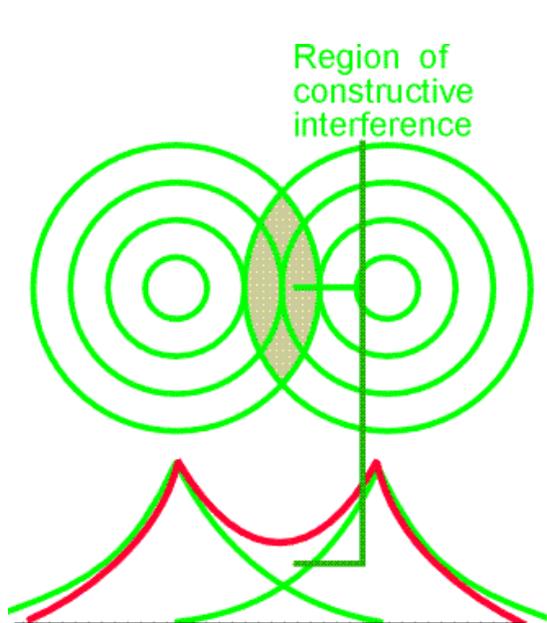$$V_{\mathsf{eff}} = E_e(R) + \frac{e^2}{4\pi\epsilon_o R}$$

$$E\Phi(\mathbf{R}_1, \mathbf{R}_2) = \left[-\frac{\hbar^2\nabla_1^2}{2M_1} - \frac{\hbar^2\nabla_2^2}{2M_2} + \underbrace{E_e(\mathbf{R}_1, \mathbf{R}_2) + \frac{e^2}{4\pi\epsilon_0|\mathbf{R}_1 - \mathbf{R}_2|}}_{V_{\mathsf{eff}}} \right] \Phi(\mathbf{R}_1, \mathbf{R}_2)$$
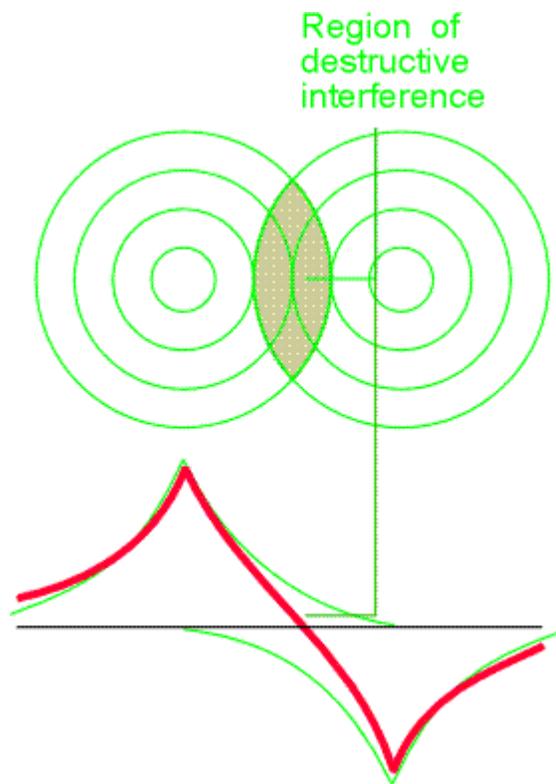

$$E(R_o) = V_{\mathsf{eff}}[LCAO](R_o) = -1.13\, I_H$$

$$E(R_o) - E(R \to \infty) = -0.1\, I_H = -1.4\,\mathsf{eV} \text{ per bond}$$

First Excited State Energy: Antibonding

$$\psi_{1\sigma g}(\mathbf{r}) = \mathbf{C}\left[\phi(\mathbf{r} - \mathbf{R_1}) + \phi(\mathbf{r} - \mathbf{R_2})\right]$$

$$\psi_{1\sigma u}(\mathbf{r}) = \mathbf{C}\left[\phi(\mathbf{r} - \mathbf{R_1}) - \phi(\mathbf{r} - \mathbf{R_2})\right]$$

$$E_{e,1\sigma g}(R) = \frac{E_s + V_{ss\sigma}}{1 + S(1)}$$

$$E_{e,1\sigma u}(R) = \frac{E_s - V_{ss\sigma}}{1 - S(1)}$$

First Excited State Energy: LCAO