Lecture 6

6. The Tight-Binding Approximation

... or from Bonds to Bands

Basic concepts in quantum chemistry - LCAO and molecular orbital theory

The tight binding model of solids - bands in 1, 2, and 3 dimensions

References:

- 1. Marder, Chapters 8, pp. 194-200
- 2. Kittel, Chapter 9, pp.244-265

- Ashcroft and Mermin, Chapter 8
 R. Hoffmann, "Solids and Surfaces: A chemists view of bonding in extended structures" VCH, 1988, pp 1-55, 65-78.
 P.A. Cox, "The Electronic Structure and Chemistry of Solids", Oxford, 1987, Chpts. 1, 2(skim), 3 (esp. 45-62), and 4 (esp. 79-88).





Two main approaches in electronic structure calculations:

- Build up from atom: atomic orbitals + ...
- Infinite solid down: plane waves + ...

Two methods used in quantum mechanics are $\ensuremath{\textit{variational}}$ and $\ensuremath{\textit{perturbation}}$ theory methods

Perturbation theory: $H = H^o + \lambda H^1 + \lambda^2 H^2 + \dots$ $H^{\circ}\Psi_{n}^{\circ} = E_{n}^{\circ}\Psi_{n}^{\circ}$ (often known)

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Variational Method

Variational Method Use matrix notations Ψ = | $\Psi\!\!>$ H| Ψ > = E| Ψ > (time indep. Sch. Eqn.) For stationary stats, if $\boldsymbol{\Psi}$ is normalized, well-behaved function, it can be shown that $<\Psi \ ^{\ast}|H \mid \Psi > = \ <\Psi \ ^{\ast}|E| \ \Psi > \ = E \ <\Psi \ ^{\ast}| \ \Psi > \quad \leftarrow (\text{variational integral})$ \Rightarrow Minimize variational integral to get ground state Ψs $E = \frac{\langle \Psi^* | H | \Psi \rangle}{\langle \Psi^* | \Psi \rangle} \quad \leftarrow \text{(overlap integral)}$ 4

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LCAO	
General problem is to minimize variational integral by finding coefficients c_n the make variational integral stationary: $\frac{\partial c_n}{\partial E} = 0!$ $H\Psi = E\Psi \Rightarrow$ $H\sum_n c_n \phi_n = E\sum_n c_n \phi_n$ $(H-E)\sum_n c_n (\phi_n = 0)$ $\sum_n c_n (H \phi_n - E\phi_n) = 0$ $\sum_n c_n (\int \phi_n^* H \phi_n^* dV - \int \phi_n^* E \phi_n^* dV) = 0$	at
$\sum_{n=1}^{n} c_n [H_{mn} - E\delta_{mn}] = 0 \text{ if } \phi_{mn} \text{ orthonormal, if not}$	
$\sum_{n} c_n [H_{mn} - ES_{mn}] = 0$	6

Most simple molecular system H₂⁺ (molecular ion with one electron)

• For trial functions choose 2 simple 1s atomic orbitals

$$\begin{split} \psi_{i} &= c_{Ai}\phi_{iSA} + c_{Bi}\phi_{iSB} \\ H_{AA} &= \left\langle \phi_{iSA}^{i} \mid H \mid \phi_{iSA} \right\rangle = H_{BB} \\ H_{AB} &= \left\langle \phi_{iSB}^{i} \mid H \mid \phi_{iSA} \right\rangle = H_{BA} \\ S_{AB} &= \left\langle \phi_{SB}^{i} \mid \phi_{iSA} \right\rangle = S_{BA} \\ S_{AA} &= 1 \\ \text{Lecture 6} \end{split}$$

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Correlation Diagrams			
Homonuclear diatomics	Heteronuclear diatomics		
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Some symmetry considerations	
 Strength of bond due to: overlap of wavefunctions in space inv. prop. to energy difference of non-interacting orbitals electron + core repulsions 	
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AES	Auger electron spectroscopy	Photon (electron) in, electron out, inner shells
EELS	Electron energy loss spectroscopy	Electron in/out; Conduction electrons
EXAFS	Extended x-ray absorption fine structure	Photon in; filled bands
IPS	Inverse Photoemission Spectroscopy	Electron in, photon out; Empty Levels
STM(S)	Scanning Tunneling Microscopy (Spectroscopy)	Electrons in, conduction and valence bands
Vis(UV) abs	Vis./ UV absorption	Photon in; band gap, defects
UPS	Ultraviolet photoelectron spectroscopy	Photon in, electron out, filled bands
XPS	X-ray photoelectron spectroscopy	Photon in, electron out, filled bands
XAS	X-ray absorption	Photon in, empty levels

















































