PHY 752 Solid State Physics
11-11:50 AM MWF Olin 103

Plan for Lecture 3:

Reading: Chapter 1.4 & 1.6 in GGGPP – tight binding model & electron dynamics

1. Atom
2. Molecule
3. Solid
4. Linear combination of atomic orbital (LCAO) or tight binding method
5. Electron dynamics

PHY 752 Solid State Physics

MWF 11 AM-11:50 PM | OPL 103 | http://www.wfu.edu/~natalie/f15phy752/

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Course schedule

(Preliminary schedule -- subject to frequent adjustment.)

	Date	F&W Reading	Topic	Assignment
1	Wed, 8/26/2015	Chap. 1.1-1.2	Electrons in a periodic one-dimensional potential	#1
2	Fri, 8/28/2015	Chap. 1.3	Electrons in a periodic one-dimensional potential	#2
3	Mon, 8/31/2015	Chap. 1.4	Tight binding models	#3
4	Wed, 9/02/2015			
5	Fri, 9/04/2015			
6	Mon, 9/07/2015			
7	Wed, 9/09/2015			
8	Fri, 9/11/2015			

Electronic structure of an atom

For simplicity we will first consider a single electron system; a H-like ion with atomic charge *Ze*

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

E_{100}=-13. 60569253 Z² eV
a_0 = 0. 52917721092 Å

$$H\Psi_{nlm}(r,\theta,\phi) = E_{nlm}\Psi_{nlm}(r,\theta,\phi)$$

$$E_{nlm} = -\frac{Z^2e^2}{4\pi\epsilon_0 a_0}\frac{1}{2n^2} \equiv \frac{E_{100}}{n^2} \qquad a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

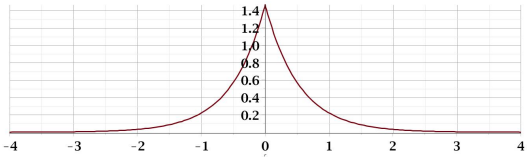
$$\Psi_{100}(r,\theta,\phi) = \sqrt{\frac{Z^3}{\pi a_0^3}}e^{-Zr/a_0} \qquad E_{100} = E_{100}$$

$$\Psi_{200}(r,\theta,\phi) = \sqrt{\frac{Z^3}{32\pi a_0^3}}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0} \qquad E_{200} = \frac{E_{100}}{4}$$

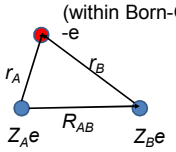
$$\Psi_{210}(r,\theta,\phi) = \sqrt{\frac{Z^3}{32\pi a_0^3}}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta \qquad E_{210} = \frac{E_{100}}{4}$$

$$\Psi_{21\pm1}(r,\theta,\phi) = \mp\sqrt{\frac{Z^3}{64\pi a_0^3}}\frac{Zr}{a_0}e^{-Zr/2a_0}\sin\theta\, e^{\pm i\phi} \qquad E_{21\pm1} = \frac{E_{100}}{4}$$

$$\Psi_{100}(r,\theta,\phi) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0}$$



Electronic structure of H-like molecular ion (within Born-Oppenheimer approximation)



$r_A = |\mathbf{r} - \mathbf{R}_A|$ $\quad r_B = |\mathbf{r} - \mathbf{R}_B|$

$R_{AB} = |\mathbf{R}_B - \mathbf{R}_A|$

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Z_A e^2}{4\pi\epsilon_0 r_A} - \frac{Z_B e^2}{4\pi\epsilon_0 r_B} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}$$

Approximate wavefunction:

$\Psi(\mathbf{r},\mathbf{R}_A,\mathbf{R}_B) = X_A\Psi_{100}(\mathbf{r}-\mathbf{R}_A) + X_B\Psi_{100}(\mathbf{r}-\mathbf{R}_B)$

X_A and X_B can be determined variationally by optimizing

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

Electronic structure of H-like molecular ion – continued

Ref. Pauling and Wilson, *Introduction to Quantum Mechanics* (1935) (now published by Dover)

Necessary integrals:

$$\Delta \equiv \int d^3r \Psi_{100}^*(\mathbf{r}-\mathbf{R}_A)\Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

$$H_{AA} \equiv \int d^3r \Psi_{100}^*(\mathbf{r}-\mathbf{R}_A)H\Psi_{100}(\mathbf{r}-\mathbf{R}_A) = H_{BB}$$

$$H_{AB} \equiv \int d^3r \Psi_{100}^*(\mathbf{r}-\mathbf{R}_A)H\Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

Generalized eigenvalue problem for energy E in the variational approximation:

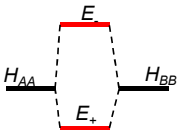
$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}\begin{pmatrix} X_A \\ X_B \end{pmatrix} = E\begin{pmatrix} 1 & \Delta \\ \Delta & 1 \end{pmatrix}\begin{pmatrix} X_A \\ X_B \end{pmatrix}$$

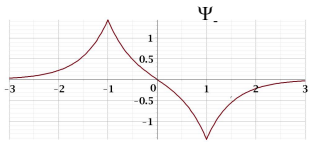
Eigenstates:

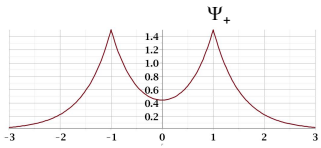
$$\begin{pmatrix} X_A \\ X_B \end{pmatrix}_+ = \frac{1}{\sqrt{2(1+\Delta)}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad E_+ = \frac{H_{AA}+H_{AB}}{1+\Delta}$$

$$\begin{pmatrix} X_A \\ X_B \end{pmatrix}_- = \frac{1}{\sqrt{2(1-\Delta)}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad E_+ = \frac{H_{AA}-H_{AB}}{1-\Delta}$$

Electronic structure of H-like molecular ion – continued







Extension of approximate "linear combination of atomic orbital" idea to larger systems

Idealized model Hamiltonian with only nearest neighbor interactions:

$$\begin{pmatrix} \alpha & \beta & \cdots & 0 \\ \beta & \alpha & \cdots & 0 \\ \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & \cdots & \alpha \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix} = E \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix}$$

Extension of approximate "linear combination of atomic orbital" idea to larger systems – some details

$N = 2$ case:
$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} = E \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} \qquad E = \begin{cases} \alpha + \beta \\ \alpha - \beta \end{cases}$$

$N = 4$ case:
$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \end{pmatrix} = E \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \end{pmatrix} \qquad E = \begin{cases} \alpha + 1.618\beta \\ \alpha + 0.618\beta \\ \alpha - 0.618\beta \\ \alpha - 1.618\beta \end{cases}$$

Using ideas from PHY 711, we can show that for N sites, there are N eigenvalues given by

$$E_\nu = \alpha + 2\beta \cos\left(\frac{\pi\nu}{N+1}\right) \quad \text{where} \quad \nu = 1, 2, \ldots N$$

Digression –
eigenvalues/eigenvectors of a tridiagonal matrix

$$\begin{pmatrix} \alpha & \beta & \cdots & 0 \\ \beta & \alpha & \cdots & 0 \\ \vdots & \vdots & \cdots & \beta \\ 0 & 0 & \cdots & \alpha \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix} = E \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix}$$

General form of equations:

$\beta x_{j+1} + \alpha x_j + \beta x_{j-1} = E x_j$ with $x_0 = 0 = x_{N+1}$

Try: $x_j = \Re\left(A e^{iqaj}\right)$

$\left(\alpha + \beta\left(e^{iqa} + e^{-iqa}\right)\right) A e^{iqaj} = EA e^{iqaj}$

$\Rightarrow E = \alpha + 2\beta\cos(qa)$ determines E in terms of q

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Impose boundary condition: $x_0 = 0 = x_{N+1}$

with $x_j = \Re\left(A e^{iqaj}\right)$

$\Rightarrow x_0 = \Re(A) = 0$ and $x_{N+1} = \Re\left(A e^{iqa(N+1)}\right) = 0$

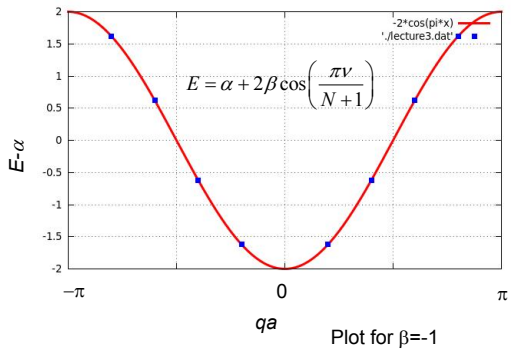
$\Rightarrow A = iC$ where C is a real constant

$\Rightarrow C\sin\left(qa(N+1)\right) = 0 \qquad qa(N+1) = \pi\nu$

$$E = \alpha + 2\beta\cos\left(\frac{\pi\nu}{N+1}\right)$$

Distinct values of ν :

$\nu = 1, 2, 3 \ldots . N$



Plot for β=-1

Extension of approximate "linear combination of atomic orbital" idea to larger systems – more details

Consider case where $N \to \infty$:

$$\begin{pmatrix} \alpha & \beta & \cdots & 0 \\ \beta & \alpha & \cdots & 0 \\ \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & \cdots & \alpha \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix} = E \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix}$$

$$\alpha X_n + \beta(X_{n-1} + X_{n+1}) = EX_n$$

Let $X_n = X_0 e^{ikna} \quad \Rightarrow X_0 e^{ikna}\left(\alpha + 2\beta\cos(ka)\right) = X_0 e^{ikna} E_k$

$$E_k = \alpha + 2\beta\cos(ka)$$

Comment on tight-binding Bloch states

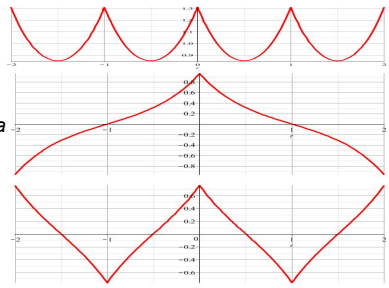
LCAO basis functions with Bloch symmetry:

$$\Phi_{\mathbf{k}}^{a\,nlm}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi_{nlm}^{a}\left(\mathbf{r} - \boldsymbol{\tau}^{a} - \mathbf{T}\right)$$

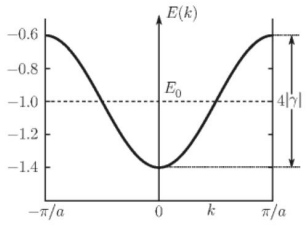
***k*=0**

***k*=π/2a**

***k*=π/a**



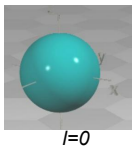
Energy spectrum tight-binding Bloch states



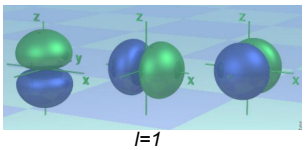
$$E(k) = \alpha + 2\beta\cos(ka)$$

LCAO methods -- continued – angular variation

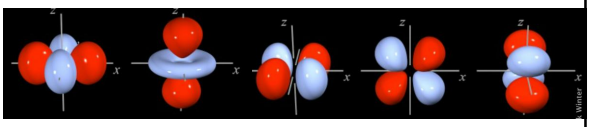
http://winter.group.shef.ac.uk/orbitron/



l=0



l=1



l=2

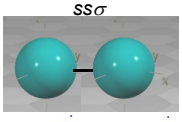
LCAO methods -- continued – angular variation

While, for atoms the "*z*" axis is an arbitrary direction, for diatomic molecules and for describing bonds, it is convenient to take the "*z*" axis as the bond direction.

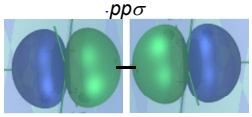
Atom			Bond		
		symbol			*symbol*
l=0	*m=0*	*s*	*l=0*	$\lambda=0$	σ
l=1	*m=0*	*p*	*l=1*	$\lambda=0$	σ
	m= ±1	*p*		$\lambda=1$	π
l=2	*m=0*	*d*	*l=2*	$\lambda=0$	σ
	m= ± 1	*d*		$\lambda=1$	π
	m= ± 2	*d*		$\lambda= 2$	δ

LCAO methods -- continued – bond types

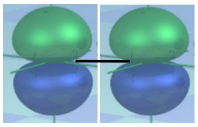
ssσ



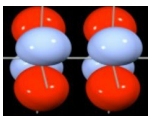
ppσ



ppπ



ddπ



More details of LCAO and tight-binding methods will be covered in Chapter 5 ….

Electron velocity:

$$v(k) = \langle \psi(k,x) | \frac{p}{m} | \psi(k,x) \rangle .$$

$$\langle \psi(k,x) | \frac{p^2}{2m} + V(x) | \psi(k,x) \rangle = E(k),$$

$$\boxed{v(k) = \langle \psi(k,x) | \frac{p}{m} | \psi(k,x) \rangle = \frac{1}{\hbar} \frac{dE(k)}{dk}} ;$$

➔Band dispersion is related to electron velocity

Electron effective mass from semi-classical analysis

$$\boxed{\frac{d(\hbar k)}{dt} = -eF} .$$ For applied force *F*

$$\frac{dv(k)}{dt} = \frac{d}{dt}\frac{1}{\hbar}\frac{dE(k)}{dk} = \frac{1}{\hbar}\frac{d^2E(k)}{dk^2}\frac{dk}{dt} = \left(\frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}\right)(-e)F.$$

1/m*

$$\boxed{\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}} .$$