Solid State Physics: Final Exam Review

December 8, 2018

1 LCAO and Tight Binding

1.1 Gentle Introduction: Covalent Bonding of Hydrogen Atoms

Imagine a system in which two Hydrogen atoms are held with fixed-position nuclei ("Born-Oppenheimer Approximation") and a shared electron between them. Goal: calculate the eigenenergies of the system as a funtion of the distance from the fixed nuclei.

The Hamiltonian of the system is given by

$$H = K + V_1 + V_2$$

where

$$K = \frac{\mathbf{p}^2}{2m}$$

and the coulombic potential due to the nucleus fixed at position $\mathbf{R}_i$ is given by

$$V_i = \frac{e^2}{4\pi\epsilon_0|\mathbf{r} - \mathbf{R}_i|}$$

We can write down a trial solution of the form

$$|\psi\rangle = \phi_1 |1\rangle + \phi_2 |2\rangle$$

where $|i\rangle$ are the atomic orbitals (or "tight-binding orbitals") representing the ground state solution for that particular isolated nucleus. That explicitly means the following

$$(K + V_1)|1\rangle = \epsilon_0 |1\rangle$$

$$(K + V_2)|2\rangle = \epsilon_0 |2\rangle$$

where ϵ_0 is the ground state energy of a single Hydrogen atom.

In the LCAO/tight-binding method, we make the following approximation: **the atomic orbitals $|i\rangle$ are orthogonal** such that

$$\langle i|j\rangle = \delta_{ij}$$

The Schrodinger equation can be written as

$$H \ket{\psi} = E \ket{\psi}$$

or, alternatively, in the $\ket{i}$ basis:

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} = E \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix}$$

By using a variational method where

$$E = \frac{\bra{\psi} H \ket{\psi}}{\braket{\psi|\psi}}$$

and

$$\frac{\partial E}{\partial \phi_i} = \frac{\partial E}{\partial \phi_i *} = 0$$

We obtain an eigenvalue equation

$$\sum_j H_{ij} \phi_j = E \phi_i$$

where $H_{ij} = \bra{i} H \ket{j}$. The components of H can be written explicitly as

$$H_{11} = \bra{1} H \ket{1} = \bra{1} K + V_1 \ket{1} + \bra{1} V_2 \ket{1} = \epsilon_0 + V_{cross}$$

$$H_{22} = \bra{2} H \ket{2} = \bra{2} K + V_2 \ket{2} + \bra{2} V_1 \ket{2} = \epsilon_0 + V_{cross}$$

$$H_{12} = \bra{1} H \ket{2} = \bra{1} K + V_2 \ket{2} + \bra{1} V_1 \ket{2} = -t$$

$$H_{21} = \bra{2} H \ket{1} = \bra{2} K + V_1 \ket{1} + \bra{2} V_2 \ket{1} = -t^*$$

We make the following observations:

- The on-site energy is given by

$$\bra{i} K + V_i \ket{i} = \epsilon_0$$

- The coulombic potential due to site j on site i is given by

$$\bra{i} V_j \ket{i} = V_{cross}$$

- The *hopping term* is defined by

$$\bra{j} V_j \ket{i} = \bra{i} V_i \ket{j}^* = -t$$

The eigenvalue equation then takes on the form of a 2×2 matrix equation

$$\begin{bmatrix} \epsilon_0 + V_{cross} & -t \\ -t^* & \epsilon_0 + V_{cross} \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} = E \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix}$$

Diagonalization yields the eigenenergies

$$E_\pm = \epsilon_0 + V_{cross} \pm |t|$$

1.2 Tight-Binding Chain

In this section, we seek to observe that all waves in periodic environments behave similarly. Here we consider electron waves, but we should consider the similarities to vibrational waves (phonons) as well.

The one-dimensional tight binding has the following description.

- There is a single orbital on atom n, denoted $|n\rangle$.

- Periodic boundary conditions are imposed such that $|N\rangle = |0\rangle$.

- Atomic orbital states are orthogonal.

$$\langle n|m\rangle = \delta_{nm}$$

- The general trial wavefunction has the form

$$|\Psi\rangle = \sum_n \phi_n |n\rangle$$

- The effective Schrodinger equation is

$$\sum_m H_{nm}\phi_m = E\phi_n$$

where $H_{nm} = \langle n| H |m\rangle$