P507A - Solid State Physics: I

Website: www.phys.unr.edu/chesnav/Teaching/P507A/Phys507A.html


Grading release: 50% of the grade based on 5 assignments, posted online.
(All are already in, due Sept. 25!)

50% final exam presentation: Based on either (1) Recent paper; (2) Classic paper defining well established effect; (3) Review paper on a topic.

Lecture #1

Ch. 1: Electrons in Crystals

<table>
<thead>
<tr>
<th>Particle Type</th>
<th># of Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen atom</td>
<td>1e + 1 proton = 2</td>
</tr>
<tr>
<td>Ammonia molecule (NH₃)</td>
<td>10 protons + 7 neutrons + 10 electrons = 27</td>
</tr>
<tr>
<td>Uranium atom</td>
<td>92 protons + 196 neutrons + 92 electrons = 330</td>
</tr>
</tbody>
</table>

1 cm³ of diamond ~ 10²³ Carbon atoms ~ 10²³ x (6 protons + 6 neutrons + 6 electrons)

N ~ 10²³ is similar to N = ∞! Various new effects arise when we are studying a system with an infinite number of particles. We call these "emergent phenomena," because we cannot guess them based on calculations of atoms or molecules.

⇒ Today we will discuss the simplest of these "emergent phenomena": energy bands in crystals.

⇒ The concept of energy bands explains why most solids with an odd number of valence electrons are metals.
1) Atom vs. molecules: energy splitting due to wavefunction overlap

\[ V(x) = \begin{cases} 0 & \text{for } |x| < a \\ \infty & \text{otherwise} \end{cases} \]

Quantum particle in a 1D square well:

\[ \frac{-h^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x) \psi(x) = E \psi(x) \quad (\text{2.1} \quad \hat{H} |\psi> = E |\psi> ) \]

\[ \hat{H} = -\frac{h^2}{2m} \frac{d^2}{dx^2} + V(x) \]

\[ \Rightarrow \quad \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x) \]

\[ \begin{align*}
\psi(x = 0) &= 0 \\
\psi(x = a) &= 0 
\end{align*} \quad (\text{Boundary conditions: particle cannot penetrate } |x > a \text{ region})
\]

\[ \Rightarrow \quad \psi_N(x) = \sqrt{\frac{2}{a}} \sin \left( \frac{n \pi x}{a} \right) \text{, with } k_N a = n \pi, \quad n = 1, 2, 3, \ldots \\
\Rightarrow \quad \frac{\hbar^2}{2m} k_N^2 = E_N \Rightarrow E_N = \frac{\hbar^2}{2m} \left( \frac{n \pi}{a} \right)^2 N^2 
\]

Now suppose we have two wells next to each other with a potential barrier separating them:

- For more than one barrier penetrate the barrier, each energy level
- \( E_{2L} = E_{2R} \)
- \( E_{1L} = E_{1R} \)
Let us now lower the barrier so that particles can "tunnel" through it.

A PM tells us that we can't solve two different Schrödinger

\[ \psi_L(x) \neq \psi_R(x) \]

for the whole system. The resulting ground state is:

\[ \psi_0(x) \approx \frac{1}{\sqrt{2}} \left[ \psi_{1L}(x) + \psi_{1R}(x) \right] \] ("symmetric" or "leading")

\[ \psi_{1A}(x) \approx \frac{1}{\sqrt{2}} \left[ \psi_{1L}(x) - \psi_{1R}(x) \right] \] ("antisymmetric" or "anti-lead")

The two degenerate states, \( E_{1L} \) and \( E_{1R} \), now split into two non-degenerate levels.

\[ E_A - E_S \approx 2 \langle \psi_{1L} | H | \psi_{1R} \rangle = 2 \int dx \psi_{1L}^*(x) H \psi_{1R}(x) \]

Why is the antisymmetric state with higher energy?

The \( \psi_{1A}(x) \) has a node at \( x=0 \), because \( \psi_{1A}(-x) = -\psi_{1A}(x) \). The fact that it has

\[ \psi_{1A}(x) \neq \psi_{1A}(x) \]

a node implies that it changes appreciably over small length scale; in other words, it has short wavelength components.

If we write \( \psi \) in Fourier representation:

\[ \psi_S(x) = \frac{1}{\sqrt{2\pi}} \int dq \ e^{iqx} \tilde{\psi}_S(q) \]

\[ \tilde{\psi}_S(q) = \frac{1}{\sqrt{2\pi}} \int dx \ e^{-iqx} \psi_S(x) \]

\[ \psi_A(x) = \frac{1}{\sqrt{2\pi}} \int dq \ e^{iqx} \tilde{\psi}_A(q) \]

\[ \tilde{\psi}_A(q) = \frac{1}{\sqrt{2\pi}} \int dx \ e^{-iqx} \psi_A(x) \]
\[
\begin{align*}
\psi_s(x) & \approx \frac{1}{\sqrt{\alpha}} \sin(k_1 x) \quad \Rightarrow \quad \tilde{\psi}_s(q) = \sqrt{\frac{2}{\pi \alpha}} \left( \frac{\sin[(q-k_1)\alpha]}{k_1+q} + \frac{\sin[(q+k_1)\alpha]}{k_1-q} \right) \\
\end{align*}
\]

\[
\begin{align*}
\psi_A(x) & \approx \frac{1}{\sqrt{\alpha}} \sin(k_1 x) \quad \Rightarrow \quad \tilde{\psi}_A(q) = \frac{i}{\sqrt{\pi \alpha}} \left( \frac{\sin[(q-k_1)\alpha]}{k_1+q} + \frac{\sin[(q+k_1)\alpha]}{k_1-q} \right) \\
\end{align*}
\]

\[
\tilde{\psi}_s(q) \text{ is peaked at } q = 0 \\
\tilde{\psi}_A(q) \text{ is peaked at } q = \pm k_1 = \pm \frac{\pi}{\alpha}
\]

Since \( \psi_s(x) \) is made of longer wavelengths (low \( q \)) waves, while \( \psi_A(x) \) is made of waves peaked at \( \pm \frac{\pi}{\alpha} \) (because it has a node at \( x = 0 \)).

Since \( E = \int dq \left( \frac{\tilde{\psi}_A(q)^2}{2m} \right) \) for lower kinetic energy!
What happens when we have 3 wells?

\[ \psi(x) = a_L \psi_L(x) + a_M \psi_M(x) + a_R \psi_R(x) \]

\[
\begin{array}{cccc}
q_L & q_M & q_R \\
+ & + & + \\
+ & + & - \quad \text{or} \quad - & - & + \\
+ & - & + \\
- & + & + \\
\end{array}
\]

Determined by "global phase" $e^{i \beta}$

Actually \((+++)= (++-) + (+-+) + (-++)\), so only three states are linearly independent!

$m$ wells $\Rightarrow$ $m$ states for each "orbital quantum number" $N$

One well Two wells Three wells Infinite wells

"atom" "Molecule" "Crystal"
2) The Linear Combination of Atomic Orbitals (LCAO) method

There is nothing special about the choice of square well potentials made in the previous section. We can obtain the same results using atoms; however in this case there is no exact solution.

A useful approximation is to "cut" the Hilbert space. Consider for example two hydrogen atoms in H₂ molecule

\[ |1+L\rangle \]

The two linearly related excitations of the H₂ molecule can be found assuming

a two state Hilbert space spanned by \( |1+L\rangle, |1+R\rangle \). As an approximation, we make \( \langle 1+L | 1+R \rangle \approx 0 \). The Schrödinger equation becomes:

\[
\begin{bmatrix}
& (c_1 | 1+L\rangle + c_2 | 1+R\rangle) \\
(1+L) \\
1+R
\end{bmatrix} = E
\begin{bmatrix}
(1+L) \\
1+R
\end{bmatrix}
\]

We get two eqns by multiplying by \( |1+L\rangle \) and \( |1+R\rangle \), respectively:

\[
\begin{align*}
& c_1 \langle 1+L | 1+L \rangle + c_2 \langle 1+L | 1+R \rangle = c_1 E \\
& c_1 \langle 1+R | 1+L \rangle + c_2 \langle 1+R | 1+R \rangle = c_2 E
\end{align*}
\]

\[
\begin{align*}
& \Rightarrow (E_0 - V) (c_1) = E (c_1) \\
& (E_0 - V) (c_2) = E (c_2)
\end{align*}
\]

Use the transformation

\[
\begin{pmatrix}
E_0 - V \\
V
\end{pmatrix} = 1 \begin{pmatrix}
1 & 1 \\
1 & -1
\end{pmatrix} \quad \text{diagonal: } C \cdot \hat{E} = 1
\]

\[
\begin{pmatrix}
E_0 + V \\
V
\end{pmatrix} = 1 \begin{pmatrix}
1 & 1 \\
1 & -1
\end{pmatrix} \begin{pmatrix}
E_0 + V \\
V
\end{pmatrix} = E (E_0 + V)
\]

=1
\[ \psi_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \text{with energy} \quad (E_0 - V) \]

\[ \psi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{with energy} \quad (E_0 + V). \]

**Note:** Energy splitting is given by

\[ 2V = -2 \langle \tau_L | H | \tau_R \rangle = -2 \int \tau_L(\mathbf{r}) \cdot \tau_R(\mathbf{r}) \, d\mathbf{r} > 0 \]

\[ V \approx -\frac{V}{\lambda} b^2 : \]

\[ 2V = -\frac{\lambda}{m^2} \int \tau_L(\mathbf{r}) \cdot \tau_R(\mathbf{r}) \, d\mathbf{r} = -\frac{\lambda}{m^2} \int \left( \int \left( \tau_L(\mathbf{r}) \cdot D \tau_R(\mathbf{r}) \right) \, d\mathbf{r} \right) > 0 \]

in the overlap region, derivatives have opposite sign!

What happens in 3d?

In 1d, they move. In 3d, band overlap can happen.

![Graph showing energy bands](image)
5 lectures on energy bands:

1) Multiple wells, LCAD
2) Kossig - Reiner, Bloch's theorem, Bravais lattice
3) Crystals, Bravais lattice, x-ray Laue theory, General prop. of crystals and their defects
4) Finite crystals, X-ray diffraction, Neutron diffraction, Nearly free electron approach
5) K. P. theory, molecular bonds, crystal symmetry