Course Overview
Discuss Syllabus
Introduction to Basic Quantum Mechanics
Energy States in Periodic Crystals
Quick Review of Quantum Mechanics

Conservation of Energy
(Hamilton-Jacobi; 1834):

\[ E = PE + KE = U + \frac{p^2}{2m} \]

Planck (1901), Einstein (1905):

\[ E = hf = \hbar \omega \]

Wave-like properties of matter

de Broglie (1923):

\[ p = \frac{\hbar}{\lambda} = \frac{\hbar}{\frac{2\pi}{\lambda}} = \hbar k \]

Hamilton believed that mechanics was the zero-wavelength limit of wave propagation, so why not represent matter by a wave?

Schrödinger introduces a matter-wave \( \Psi \), but what is the appropriate wave equation?

Schrödinger's ansatz (complex wave function!!!) in 1D:

\[ \Psi = Ae^{(ik_xx - \omega t)} \]
\[
\begin{align*}
\frac{\partial}{\partial t} \Psi &= -i \omega \Psi \\
\frac{\partial}{\partial x} \Psi &= i k_x \Psi \\
\frac{\partial^2}{\partial x^2} \Psi &= -k_x^2 \Psi
\end{align*}
\]

\[
i\hbar \frac{\partial}{\partial t} \Psi = \left[ U(x) - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right] \Psi
\]

\[
E \Psi = \left[ U(x) + \frac{\hbar^2 k_x^2}{2m} \right] \Psi
\]

\[
E \Psi = \left[ U(x) + \frac{p_x^2}{2m} \right] \Psi
\]

When applied to the hydrogen atom:

\[
U(x) \rightarrow U(r) = \frac{1}{4\pi\varepsilon_o} \frac{e^2}{r}
\]

The calculated values of \(E\) exactly matched Bohr’s results from 1911!

What is physical interpretation of \(\Psi\)? Max Born (1926):

\[
P = \text{Probabilty that particle is in volume } dV = \left| \Psi \right|^2 dV
\]

\(\Psi\) is probability amplitude and \(\Psi \Psi^*\) (or \(|\Psi|^2\)) is probability density
Noble Prizes in Physics:

• 1918 Planck
• 1921 Einstein
• 1922 Bohr
• 1929 de Broglie
• 1933 Schrödinger
• 1954 Born
Quick Review of Quantum Mechanics

• Focus on energies, not equation of motion
• Wave-Particle duality - de Broglie matter-waves
• Emphasize particle (electron) wavefunction, \( \Psi(x,y,z) \)
• Wavefunction \( \Psi \) is complex
• \( |\Psi(x,y,z)\Psi^*(x,y,z)| \) gives probability of finding particle at \((x,y,z)\)
• 3D Schrödinger's time dependent equation (1926):

\[
-\frac{\hbar^2}{2m_e}\nabla^2 \Psi(\vec{r}, t) + U(\vec{r})\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi}{\partial t}(\vec{r}, t) = E\Psi
\]
The Hydrogen Atom

We now know that
\[ a_0 \approx 0.0529 \text{ nm} \]
(52.9 pm)
\[ (5.29 \times 10^{-11} \text{ m}) \]

<table>
<thead>
<tr>
<th></th>
<th>neutron</th>
<th>proton</th>
<th>electron</th>
</tr>
</thead>
<tbody>
<tr>
<td>symbol</td>
<td>n</td>
<td>P</td>
<td>e^-</td>
</tr>
<tr>
<td>charge</td>
<td>0 (zero)</td>
<td>+1.6 x 10^{-19} C</td>
<td>-1.6 x 10^{-19} C</td>
</tr>
<tr>
<td>mass</td>
<td>1.675 x 10^{-27} kg</td>
<td>1.673 x 10^{-27} kg</td>
<td>9.11 x 10^{-31} kg</td>
</tr>
</tbody>
</table>

Note: 1 C = 1 Coulomb

Electrically Neutral H Atom

Attractive Force via Coulomb's Law
Understanding atomic electron states

What are the allowed energies of an electron in this confining potential?

\[ U(r) = \frac{1}{4\pi\varepsilon_0} \frac{Ze(-e)}{r} = -\frac{Ze}{4\pi\varepsilon_0} \frac{e^2}{r} \]

\[ \Phi(r) = \frac{1}{4\pi\varepsilon_0} \frac{(Ze)}{r} \]

\[ E_n = -\frac{Z^2e^4m}{32\pi^2\varepsilon_0\hbar^2} \frac{1}{n^2} = -2.18 \times 10^{-18} \frac{Z^2}{n^2} \]
Define a Hamiltonian Operator, $H$

\[ H \equiv -\frac{\hbar^2}{2m_e} \nabla^2 + U(\vec{r}) \]

Then solve for $\Psi$

\[ H\Psi = E\Psi \]

Probability of finding electron at position $r$ is given by

\[ \text{Probability} = \Psi(\vec{r})\Psi^*(\vec{r}) \]
The consequences: Atomic Physics – all confined electron energies are quantized.

\[ U(r) = -\frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r} \]
Radial (3D) Schrödinger Equation

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \varphi} \frac{\partial}{\partial \varphi} \left( \sin \varphi \frac{\partial \psi}{\partial \varphi} \right) + \frac{1}{r^2 \sin^2 \varphi} \frac{\partial^2 \psi}{\partial \theta^2} + \frac{8\pi^2 n (E + V)}{\hbar^2} \psi = 0
\]

Remember these shapes

\[\psi_{n\ell m}(r, \theta, \varphi) = \frac{2}{(2\pi \hbar)^{3/2}} \left( \frac{n^2}{(n+\ell)!} \right)^{1/2} \omega_{n\ell} = \frac{m \pi n^2}{\hbar} \cdot Y_{\ell m}(\theta, \varphi)\]

A few links:
http://www.orbitals.com/orb/orbtable.htm
http://qsad.bu.edu/applets/qexp/atomicexplorer.html
s-electrons: http://hogan.chem.lsu.edu/matter/chap26/animate2/an26_019.mov
He: 1s^2, Ne: 1s^2 2s^2 2p^6, and Ar: 1s^2 2s^2 2p^6 3s^2 3p^6.
Transition to Crystalline Solids
Schematic $U(x)$ for a periodic 1D solid (exact):

Work function $\varphi$

surface

vacuum

metal
Schematic $U(x)$ for a periodic solid (approximate)

- Free electron model
- Nearly free electron model
- Kronig Penny model
1D Free Electron Model

Free electron model

U(x) = 0

\[ -\frac{\hbar^2}{2m_e} \nabla^2 \Psi(\vec{r}, t) + U(\vec{r}) \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi}{\partial t}(\vec{r}, t) = E \Psi(\vec{r}, t) \]

\[ -\frac{\hbar^2}{2m_e} \nabla^2 \Psi(x, t) = E \Psi(x, t) \]

let \( \Psi(x) = Ae^{ikx} \)

\[ \nabla^2 \Psi = A(-k^2)e^{ikx} = -k^2 \Psi \]

\[ \frac{\hbar^2 k^2}{2m_e} \Psi = E \Psi \Rightarrow E = \frac{\hbar^2 k^2}{2m_e} = \frac{p^2}{2m} \Rightarrow p = \hbar k \]

free-electron E(k)
The free electron model explains heat capacity, magnetic susceptibility, electronic resistivity, and the electrodynamics of many metals reasonably well.

The free electron model neglects electron-ion interactions and electron-electron interactions. It treats electrons as independent (uncharged) particles.

In the free electron model, there are no restrictions on the “allowed” energies for an electron. The momentum of an electron is $\hbar k$. 

The free electron model explains heat capacity, magnetic susceptibility, electronic resistivity, and the electrodynamics of many metals reasonably well.
Including the electron-ion core interaction: the nearly free electron model

Let \( U(x) = U_o \cos(Gx) \)

where \( G = \frac{2\pi}{a} \) with \( a = \) lattice constant

Note that \( U(x) = U(x + a) \)
In the nearly free electron model, something new happens - not all solutions to Schrödinger's Equation will propagate freely through a periodic lattice!
Consider what happens if waves reflected at \( x_1, x_2, x_3, \ldots \) constructively reinforce each other?

A full reflected wave will develop if the path difference (2a) between \((x_1, x_2); (x_2, x_3); \ldots \) is \( n\lambda \) where \( n \) is an integer

\[
2a = n\lambda;
\]

\( n=1,2,3,\ldots \)

\[
k \equiv \frac{2\pi}{\lambda} = \frac{n\pi}{a} = \frac{nG}{2}
\]

In what follows, let \( n=1 \)
In general, the 1D crystal will develop waves traveling in the forward and backward directions. When $\Psi$ has a $k$ value that satisfies the constructive interference condition ($n\lambda=2a$), $\Psi$ will no longer propagate through the lattice. The electron wavefunction will consist of two waves $\Psi_k$ and $\Psi_{-k}$. These waves can combine in two ways (pick $n=1$):

$$
\Psi_{\text{even}}(x) = Ae^{ikx} + Ae^{-ikx} = 2A \cos(kx) = 2A \cos\left(\frac{Gx}{2}\right)
$$

$$
\Psi_{\text{odd}}(x) = Ae^{ikx} - Ae^{-ikx} = i2A \sin(kx) = i2A \sin\left(\frac{Gx}{2}\right)
$$

specifies phase of wave
\[ \Psi_{\text{even}}(x)\Psi^*_{\text{even}}(x) \]

\[ \Psi_{\text{odd}}(x)\Psi^*_{\text{odd}}(x) \]

KE is same for both waves: \[ KE = \frac{(\hbar k)^2}{2m} \]

PE is different for each wave:

\[ \langle U_{\text{even}} \rangle = \int_0^L U_o \co (Gx) \left| \Psi_{\text{even}}(x)\Psi^*_{\text{even}}(x) \right| dx = \frac{U_o}{2} \]

\[ \langle U_{\text{odd}} \rangle = \int_0^L U_o \co (Gx) \left| \Psi_{\text{odd}}(x)\Psi^*_{\text{odd}}(x) \right| dx = -\frac{U_o}{2} \]
At \( k = \pm \frac{G}{2} = \pm \frac{\pi}{a} \), we have

\[
E_{\text{energy}} = E_e = \frac{(\hbar k)^2}{2m} + \frac{U_o}{2}
\]

\[
E_{\text{energy}} = E_o = \frac{(\hbar k)^2}{2m} - \frac{U_o}{2}
\]

\[
\Delta E = E_e - E_o = U_o
\]
In the nearly free electron model, including a simple sinusoidal model for the electron-ion interaction opens up “gaps” in the allowed energy states.

The nearly free electron model explains the difference between metals, insulators and semiconductors reasonably well.