

Sept 10, 2010 (1)

cle 0130

P507A - Solid State Physics: I

website: www.phys.uvic.ca/robertson/teaching/P507A/Phys507A.html

Textbook: D.W. Sucke, "Solid state physics: Essential concepts"

Grading scheme: 50% of the grade based on 5 assignments, posted online.
(A1 is already in, due Sept. 25!)

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

Lecture # 1

Ch. 1: Electrons in Crystals

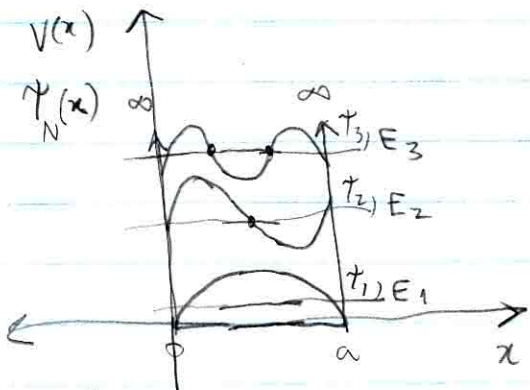
	# of (quantum) particles
<u>More independent</u> : Hydrogen atom	$1e + 1 \text{ proton} = 2$
Ammonia molecule (NH_3)	$10 \text{ protons} + 7 \text{ neutrons} + 10 \text{ electrons} = 27$
Uranium atom	$92 \text{ protons} + 146 \text{ neutrons} + 92 \text{ electrons} = 330$
⋮	⋮
1 cm^3 of diamond	$\sim 10^{23}$ Carbon atoms $\sim 10^{23} \times (6 \text{ protons} + 6 \text{ neutrons} + 6 \text{ elect.})$

$N \sim 10^{23}$ is similar to $N = \infty$! Various new effects arise when we are studying a system with an infinite number of particles. We call these "emergent phenomena", because we can not guess them based on calculations of atoms or molecules.

⇒ Today we will discuss the simplest of these "emergent phenomena", energy bands in a crystal.
→ The concept of energy bands explains why most solids with an odd number of valence electrons are metals, and

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1) Atoms vs. molecules : energy splitting due to wavefunction overlap



"Simplification":

Quantum particle in a 1d square well:

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

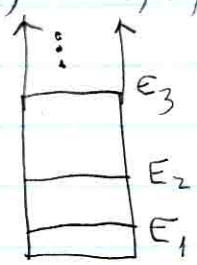
$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x) + V(x)\psi(x) = E \psi(x) \quad \left(\text{or } \hat{H}|\psi\rangle = E|\psi\rangle \right)$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x)$$

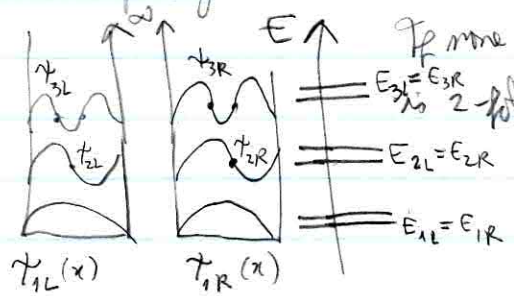
$$\Rightarrow \begin{cases} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x) \\ \psi(x=0) = 0 \\ \psi(x=a) = 0 \end{cases} \quad \left(\text{Boundary condition: part. can not penetrate } \begin{matrix} x > a \\ x < 0 \end{matrix} \text{ region} \right)$$

$$\Rightarrow \psi_N(x) = \sqrt{\frac{2}{a}} \sin(k_N x), \quad \text{with } k_N a = N\pi, \quad N = 1, 2, 3, \dots$$

$$\Rightarrow \frac{\hbar^2}{2m} k_N^2 = E_N \Rightarrow E_N = \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2 N^2$$

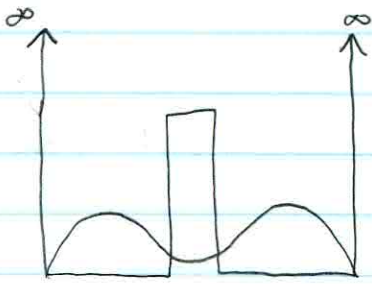


Now suppose we have two wells next to each other, with a potential barrier separating them:



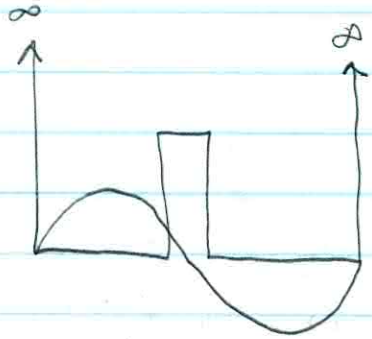
If none of the wavefunctions penetrate the barrier, each energy level is 2-fold degenerate.

Let's now lower the barrier so that particles can "tunnel" through it.



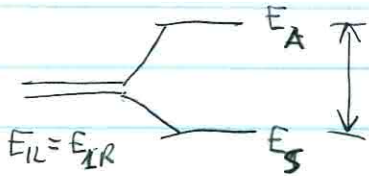
QM tells us that we can't solve two different Schrödinger eqns (for two wells) anymore. We need to solve a single Schrödinger eqn for the whole system. The resulting ground state is:

$$\Psi_S(x) \approx \frac{1}{\sqrt{2}} [\Psi_{1L}(x) + \Psi_{1R}(x)] \quad (\text{"Symmetric", or "bonding"})$$



$$\Psi_A(x) \approx \frac{1}{\sqrt{2}} [\Psi_{1L}(x) - \Psi_{1R}(x)] \quad (\text{Antisymmetric, or "antibonding"})$$

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



$$E_A - E_S \approx 2 \langle \Psi_{1L} | \hat{H} | \Psi_{1R} \rangle = 2 \int dx \Psi_{1L}^*(x) \hat{H} \Psi_{1R}(x)$$

Why is the antisymmetric state with higher energy?

The $\Psi_A(x)$ has a node at $x=0$, because $\Psi_A(-x) = -\Psi_A(x)$. The fact that it has a node implies that it changes appreciably over small length scales; in other words, it has shorter wavelength components.

If we write Ψ in Fourier representation:

$$\Psi_S(x) = \frac{1}{\sqrt{2\pi}} \int dq e^{iqx} \tilde{\Psi}_S(q)$$

$$\Psi_A(x) = \frac{1}{\sqrt{2\pi}} \int dq e^{iqx} \tilde{\Psi}_A(q)$$

$$\tilde{\Psi}_S(q) = \frac{1}{\sqrt{2\pi}} \int dx e^{-iqx} \Psi_S(x)$$

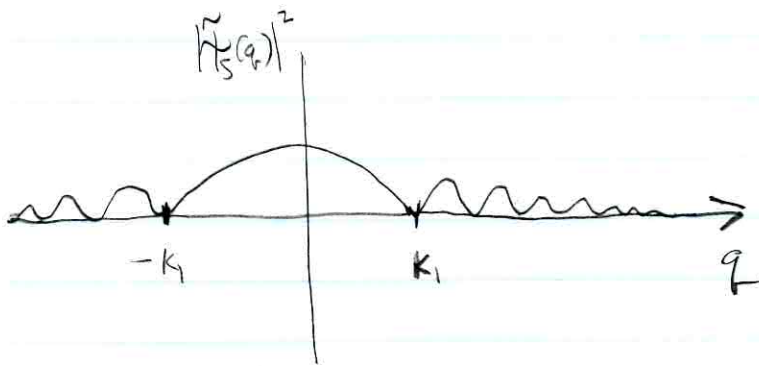
$$\tilde{\Psi}_A(q) = \frac{1}{\sqrt{2\pi}} \int dx e^{-iqx} \Psi_A(x)$$

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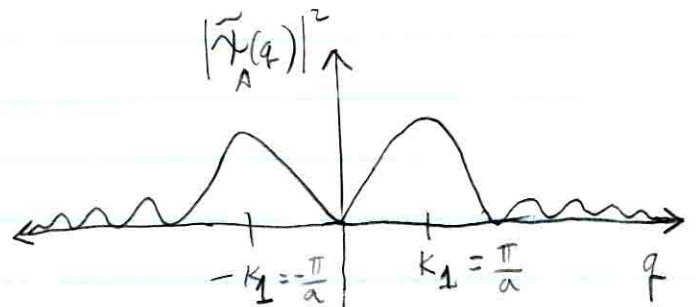
$$(k_1 = \frac{\pi}{a})$$

$$\psi_S(x) \approx \frac{1}{\sqrt{a}} |\sin(k_1 x)| \Rightarrow \tilde{\psi}_S(q) = \sqrt{\frac{2}{\pi a}} \left\{ \frac{\sin\left[\frac{(q+k_1)a}{2}\right]}{(k_1+q)} + \frac{\sin\left[\frac{(q-k_1)a}{2}\right]}{(k_1-q)} \right\}$$

$$\psi_A(x) \approx \frac{1}{\sqrt{a}} \cos(k_1 x) \Rightarrow \tilde{\psi}_A(q) = \frac{1}{\sqrt{2\pi a}} \left\{ \frac{\sin[(q-k_1)a]}{(k_1-q)} + \frac{\sin[(q+k_1)a]}{(k_1+q)} \right\}$$



► $|\tilde{\psi}_S(q)|^2$ is peaked at $q \approx 0$

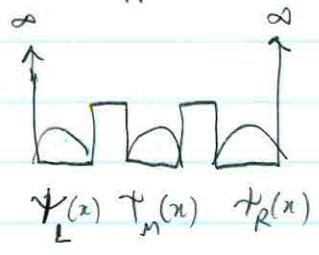


$|\tilde{\psi}_A(q)|^2$ is peaked at $q = \pm k_1 = \pm \frac{\pi}{a}$

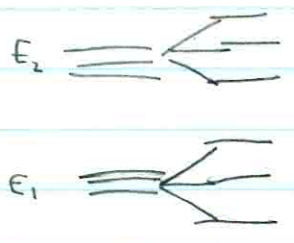
Since $\psi_S(x)$ is made of longer wavelengths (low q) waves, while $\psi_A(x)$ is made of waves peaked at $\approx \pm \frac{\pi}{a}$ (because it has a node at $x=0$!).

Since $E = \int dq |\tilde{\psi}(q)|^2 \frac{\hbar^2 q^2}{2m}$, $\psi_S(x)$ has lower kinetic energy!

What happens when we have 3 wells?



$$\Psi(x) = a_L \Psi_L(x) + a_M \Psi_M(x) + a_R \Psi_R(x)$$



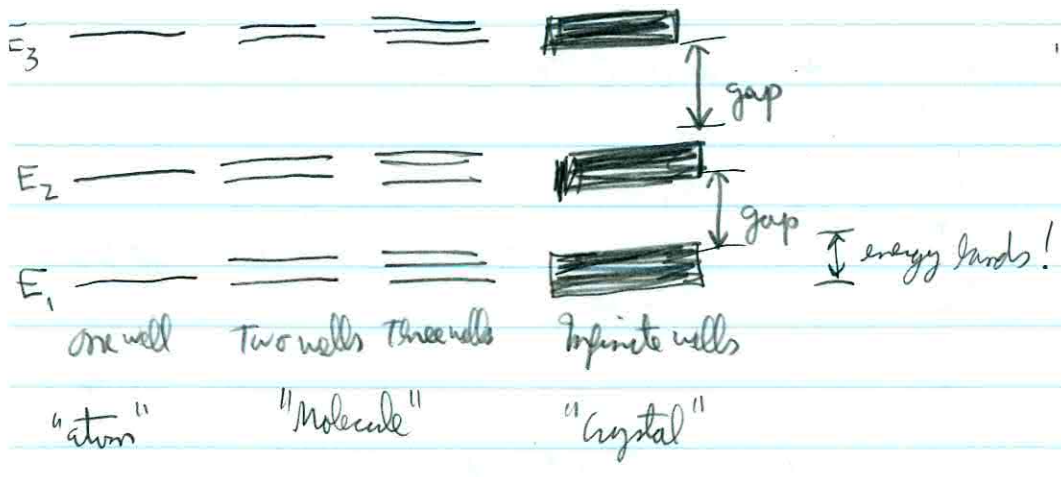
	a_L	a_M	a_R
E_2	+	+	+
E_2	+	+	-
E_1	+	-	+
E_1	-	+	+



Differs by a "global phase" $e^{i\pi} = -1$

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

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

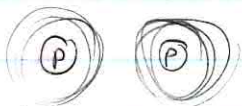


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2) The Linear combination of atomic orbitals (LCAO) method

There is nothing special about the choice of square well potentials made in the previous section. We can derive 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 an H_2 molecule



$|T_L\rangle$ $|T_R\rangle$

The ^{two} lowest energy orbital excitations of the H_2 molecule can be found assuming

a two state Hilbert space formed by $\{|T_L\rangle, |T_R\rangle\}$. As an approximation, we make $\langle T_L | T_R \rangle \approx 0$. The Schrodinger eqn becomes:

$$\underbrace{H(c_1|T_L\rangle + c_2|T_R\rangle)}_{|T\rangle} = E \underbrace{(c_1|T_L\rangle + c_2|T_R\rangle)}_{|T\rangle}$$

We get two eqns by multiplying by $\langle T_L |$ and $\langle T_R |$, respectively:

$$\begin{aligned} c_1 \underbrace{\langle T_L | H | T_L \rangle}_{E_0} + c_2 \underbrace{\langle T_L | H | T_R \rangle}_{-V} &= c_1 E \\ c_1 \underbrace{\langle T_R | H | T_L \rangle}_{-V^*} + c_2 \underbrace{\langle T_R | H | T_R \rangle}_{E_0} &= c_2 E \end{aligned} \Rightarrow \underbrace{\begin{pmatrix} E_0 - V \\ -V^* & E_0 \end{pmatrix}}_H \underbrace{\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}}_{\vec{c}} = E \underbrace{\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}}_{\vec{c}}$$

Use the ^{orthogonal} transformation $\hat{O} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$ to diagonalize: $\hat{O}^* \hat{O} = \mathbb{1}$

$$\underbrace{(\hat{O}^* \cdot H \cdot \hat{O})}_{=\mathbb{1}} (\hat{O}^* \cdot \vec{c}) = E (\hat{O}^* \cdot \vec{c})$$

assume V is real

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$$\langle \vec{\sigma}^\dagger | \hat{H} | \vec{\sigma} \rangle = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} E_0 - V & \\ & E_0 + V \end{pmatrix} \begin{pmatrix} 1 \\ 1 \\ 1 \\ -1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} E_0 - V & E_0 + V \\ E_0 - V & -E_0 - V \end{pmatrix} = \begin{pmatrix} E_0 - V & 0 \\ 0 & E_0 + V \end{pmatrix}$$

$$\vec{\sigma}^\dagger \vec{\psi} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} c_1 + c_2 \\ c_1 - c_2 \end{pmatrix} = \begin{cases} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ when } c_1 = c_2 = \frac{1}{\sqrt{2}} \\ \begin{pmatrix} 0 \\ 1 \end{pmatrix} \text{ when } c_1 = -c_2 = \frac{1}{\sqrt{2}} \end{cases}$$

The eigenstates are:

$$|\psi_S\rangle = \frac{1}{\sqrt{2}} (|\psi_L\rangle + |\psi_R\rangle) \quad \text{with energy } (E_0 - V)$$

$$|\psi_A\rangle = \frac{1}{\sqrt{2}} (|\psi_L\rangle - |\psi_R\rangle) \quad \text{with energy } (E_0 + V).$$

Note: Energy splitting is given by $2V = -2 \langle \psi_L | \hat{H} | \psi_R \rangle = -2 \int \psi_L^*(x) \hat{H} \psi_R(x) dx > 0$

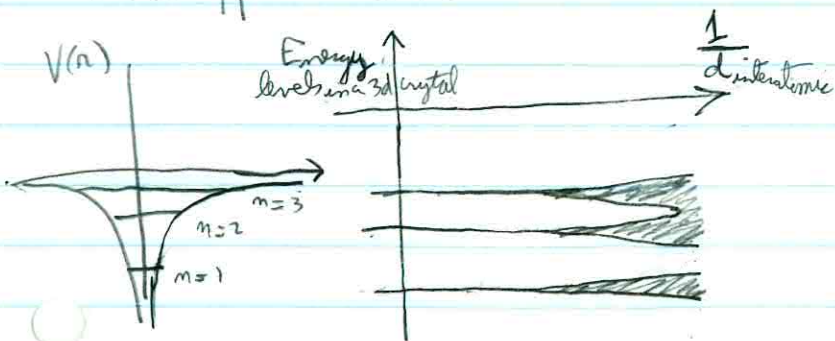
$$\text{for } \hat{H} \approx -\frac{\hbar^2}{2m} \nabla^2 :$$

$$2V = +\frac{\hbar^2}{m} \int \psi_L^* \nabla^2 \psi_R dx = -\frac{\hbar^2}{m} \int (\nabla \psi_L^*) \cdot (\nabla \psi_R) dx > 0$$

$\psi_L \psi_R$ Negative!

In the overlap region, derivatives have opposite signs!

What happens in 3d?



In 1d, there is never In 3d, band overlap can happen.
 band overlap.

5 lectures on energy bands:

- 1) Multiple wells, LCAO
- 2) Kronig-Penney, Bloch's theorem, Bravais lattices
- 3) Crystals, Bravais lattices, x-ray scattering, General prop. Bloch's theorem, density of states
- 4) Finite crystals, examples of band structures, tight binding approx., nearly free electron approx.
- 5) k-p theory, molecular bonds, crystal symmetry.