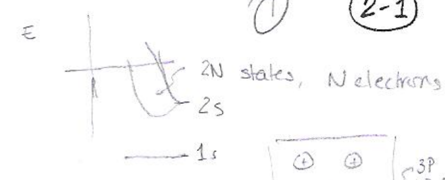
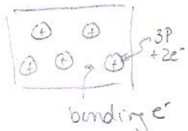
Last time: Li 3e $1s^2 2s^1$

chemical bonding → continuous band





Topics:

Electrons in an ideal metal → particle in a box

Solve for $\psi(x)$

Show that $\psi(x) \to \psi_n(x)$ solutions

Show that E is quantized ⇒ specific quantum states

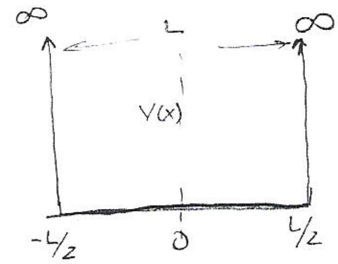
Derive density of states

Distribution of electrons within those states

Last time:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\cdot\psi(x) = E\cdot\psi(x)$$

metals → free electrons in a box



$V(x) = 0$ for $|x| \leq L/2$ inside

$V(x) = \infty$ for $|x| > L/2$ outside

solve for $\psi(x)$ within the box

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\,\psi(x)$$

or $\psi_0 e^{\pm ikx}$

solutions are of the form

$$\psi(x) = A\cos kx + B\sin kx \qquad \text{where } k = \frac{(2mE)^{1/2}}{\hbar}$$

use boundary conditions to get $A, B, k(E)$

$\psi(x) = 0$ @ $x = \pm L/2$

$\psi(L/2) = 0 = A\cos(kL/2) + B\sin(kL/2)$

$\psi(-L/2) = 0 = A\cos(-kL/2) + B\sin(-kL/2)$

$\cos(-x) = \cos(x)$

$\sin(-x) = -\sin(x)$

$A = B = 0$ is trivial solution

add: $2A\cos(k\,L/2) = 0$
subtract: $2B\sin(k\,L/2) = 0$

} no ~~single~~ value of k makes these both true for arbitrary A, B (non-zero)

$\Rightarrow$ 2 solution sets.

0, π, 2π, 3π etc.

set ① $A = 0$ and $\sin(kL/2) = 0 \Rightarrow \frac{kL}{2} = n'\pi \Rightarrow k_n = \frac{n\pi}{L}$ n = even

π/2, 3π/2, etc.

set ② $B = 0$ and $\cos(kL/2) = 0 \Rightarrow \frac{kL}{2} = (n'+\tfrac{1}{2})\cdot\pi \Rightarrow k_n = \frac{n\pi}{L}$ n = odd

$n \equiv$ principle quantum #

k is quantized, not continuous.

set ① $\psi(x) = B\sin\left(\frac{n\pi x}{L}\right)$ n = even

set ② $\psi(x) = A\cos\left(\frac{n\pi x}{L}\right)$ n = odd

to solve for A & B, normalize according to

$$\int_{-L/2}^{L/2} \psi^*(x)\,\psi(x)\,dx = 1$$

use $\int \cos^2 z\,dz = \tfrac{1}{2}z + \tfrac{1}{4}\sin 2z$

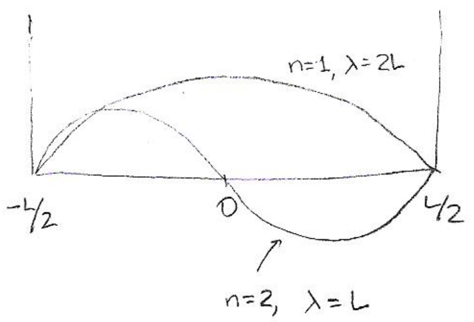
} $\Rightarrow A = B = \sqrt{2/L}$

solution: $\psi_n(x) = \sqrt{2/L}\,\sin\left(\frac{n\pi x}{L}\right)$ n = even

$= \sqrt{2/L}\,\cos\left(\frac{n\pi x}{L}\right)$ n = odd

} eigenfunctions

wave eq'n: $\psi(x) = A\cdot\cos\left(\frac{2\pi x}{\lambda}\right) = A\cos kx$



$\lambda_n = \frac{2L}{n}$ $k_n = \frac{2\pi}{\lambda_n}$

wavelength

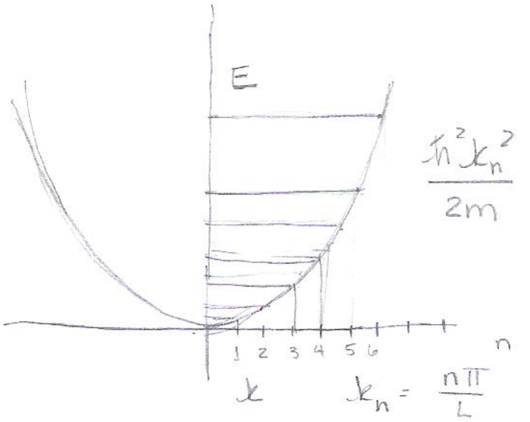
wave vector by definition

Showed above: $k_n = \frac{n\pi}{L} = \frac{(2mE)^{1/2}}{\hbar}$

$$\Rightarrow E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2} = \frac{n^2 h^2}{8mL^2} \quad \text{also quantized,} \quad h = 2\pi\hbar$$

$$E_n = \frac{\hbar^2 k_n^2}{2m} \quad \text{quantum} \qquad p = \hbar k$$

$$E = \frac{p^2}{2m} \quad \text{classical}$$



$$\Psi(x,t) = \psi(x) \cdot T(t)$$

$$\Psi(x,t) = \psi_n(x)\, e^{-i(E_n/\hbar)\cdot t}$$

as $n \uparrow$ $\Delta E \uparrow$ $\Rightarrow$ not approaching classical limit

resolution: need to treat in 3-D

<u>assume</u> cubic box: $L_x = L_y = L_z = L$.

$\psi(x) \rightarrow \psi(x,y,z) \Rightarrow$ 3 quantum #'s: $n_x\ n_y\ n_z$

$$E_{n_x,n_y,n_z} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) \qquad \vec{k} = \frac{\pi}{L}(n_x \hat{k}_x + n_y \hat{k}_y + n_z \hat{k}_z)$$

$$|\vec{k}| = \frac{\pi}{L}(n_x^2 + n_y^2 + n_z^2)^{1/2} \qquad E = \frac{\hbar^2 |k|^2}{2m}$$

Does this mean $\Delta E \downarrow$ as $n \uparrow$ (as $E \uparrow$) ?

1-D $\quad E = \frac{h^2}{8mL^2} n^2$

E $\left(\frac{h^2}{8mL^2}\right)$

E			# states
16	↑↓	n = 4	2
9	↑↓	n = 3	2
4	↑↓	n = 2	2
1	↑↓	n = 1 ("n = 0")	2
0			

3-D. $\quad E = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$

$\frac{h^2}{8mL^2}$

E	{n}	# states
14	123	12
12	222	2
11	311	6
9	221	6
6	211	6
3	111	2
	(000)	

6 $\quad$ 211 → 211, 121, 112

9 $\quad$ 221 → 221, 212, 122.

11 $\quad$ 311 → 311, 131, 113

14 $\quad$ 123 → 123, 312, 231, 132, 213, 321

Yes, as $E \uparrow$, $\Delta E \downarrow$, approaches classical limit (continuous)

ΔE ← measure of quantization.

In which states do the electrons exist?

In which energy levels?

→ Density of states: # of states available between E & $E + dE$ for placing electrons.