Reminder : HW Quiz this Wednesday

$\ell = 0, \cdots, n-1$
$m_\ell = -\ell, \cdots, \ell$

$\psi_{n\ell m}(r, \theta, \phi)$ are "hydrogenic" wavefunctions $(e \to Ze)$

<u>Periodic Table</u>

$Z=1$ Hydrogen $\psi_{100}\,\chi_{\pm}$

$Z=2$ Helium $\psi^1_{100}\,\psi^2_{100}\,\frac{1}{\sqrt{2}}(\chi^1_+\chi^2_- - \chi^1_-\chi^2_+)$

$Z=3$ Lithium $\underbrace{\psi_{100}\,\psi_{100}\,\psi_{2\ell m}}_{\text{must be symmetric}}\ \underbrace{\chi^1\chi^2\chi^3}_{\text{must be antisymmetric}}$

Larger ℓ values (for a given n) are <u>higher</u> in energy due to inner-electron screening of nucleus.

$Z=3 \Rightarrow \psi_{100}\,\psi_{100}\,\psi_{200}$

For $Z=19$ (potassium) the $n=3, \ell=2$ state is higher in energy than $n=4, \ell=0$!

Nomenclature: $n = 1, 2, \ldots$
$\ell = 0(s), 1(p), 2(d), 3(f), 4(g) \ldots$

$(1s)^2(2s)^2(2p)^2$ carbon $Z=6$

$(1s)^2(2s)^2(2p)^3$

$\hookrightarrow \ell = 1 \Rightarrow m_\ell = -1, 0, 1 \Rightarrow$ can hold 6 total electrons

$$\overbrace{\psi^1_{100}\psi^2_{100}}^{L=0}\,\underbrace{\frac{1}{\sqrt{2}}(\chi^1_+\chi^2_- - \chi^1_-\chi^2_+)}_{S=0}$$

$(1s)^2(2s)^2(2p)^2$ $\ell = 1$

$L=0$

$$\psi^3_{200}\psi^4_{200}\,\underbrace{\frac{1}{\sqrt{2}}(\chi^3_+\chi^4_- - \chi^3_-\chi^4_+)}_{S=0}$$

Total ang. mom. 1,2 $\ell_1 = 0, \ell_2 = 0, s_1 + s_2 = 0$
3,4 $\ell_3 = 0, \ell_4 = 0, s_3 + s_4 = 0$ } Altogether this gives 0 cont.
5,6 $\ell_5 = 1, \ell_6 = 1$

required symm.: $\psi^5_{210}\psi^6_{210}, \psi^5_{211}\psi^6_{211}$ $\Rightarrow s_1 + s_2 = 0$

Symm. or antisymm: $\psi^5_{210}\psi^6_{211}$ $\Rightarrow s_1 + s_2 = 0, 1$

When adding $L_{tot} = L^5 + L^6 = 2, 1, 0$ w/ $S_{tot} = s_1 + s_2 = 0, 1$

then $J_{tot} = 3, 2, 1, 0$

Hund's Rules (problem 5.13 in book)

$^{2S+1}L_J$

total spin

total ang. mom.

total orb. ang. mom.

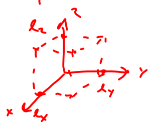
Solids

Focus is on detached loosely bound valence electrons which roam the solid.

2 approximations

Free-electron gas : Treats electrons as P.I.B.

Bloch's theory : Periodic potential



Free-electron Gas

$$V(x,y,z) = \begin{cases} 0 & 0 < x,y,z < \ell_x, \ell_y, \ell_z \\ \infty & \text{otherwise} \end{cases}$$

From H.W. #4.2

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin\left(\frac{n_x \pi}{\ell_x} x\right) \sin\left(\frac{n_y \pi}{\ell_y} y\right) \sin\left(\frac{n_z \pi}{\ell_z} z\right)$$

$$n_x, n_y, n_z = 1, 2, 3 \cdots$$

Note: $\psi(0) = 0 = \psi(x=\ell_x, y, z) = \psi(x, y=\ell_y, z)$

$$E_{n_x n_y n_z} = \frac{\hbar^2}{2m}\left(\frac{n_x^2 \pi^2}{\ell_x^2} + \frac{n_y^2 \pi^2}{\ell_y^2} + \frac{n_z^2 \pi^2}{\ell_z^2}\right) = \frac{\hbar^2}{2m} k^2$$

$$\vec{k} \equiv \left(\frac{n_x \pi}{\ell_x}, \frac{n_y \pi}{\ell_y}, \frac{n_z \pi}{\ell_z}\right)$$

Let's go to k-space (also called reciprocal space)

N - # of atoms in solid (big for macroscopic)

q - # of free-electrons per atom (typically 1~2)

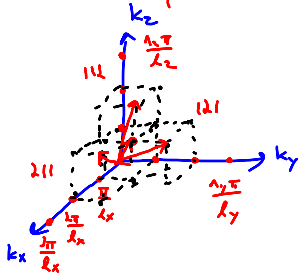
Nq - total # of free electrons in sample

$\rho = \frac{Nq}{V} = \frac{Nq}{\ell_x \ell_y \ell_z}$ = free-electron density

Electrons are fermions $\Rightarrow$ Pauli exclusion principle

$\Rightarrow$ 2 electrons in each $\psi_{n_x n_y n_z}$ state.

k-space is the space of allowed $\vec{k}$-vectors



<u>At low T</u>

$N_q = 1 \quad \hat{k} = (1,1,1)$

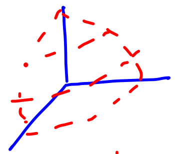
$N_q = 2 \quad \hat{k}_{1,2} = (1,1,1)$

$N_q = 3 \quad \hat{k}_{1,2} = (111)\ , \ \hat{k}_3 = (112), (121), (211)$

⋮

$N_q = 8$ can live in $(111)(112)(121)(211)$

As $N_q \to$ large we fill up an octant of k-space.



we only use $k_{xyz} > 0$