Lecture 5

Last time talked about general consequences of exchange symmetry:
- bosons effectively attract one another
- fermions effectively repel

One important point I left out: spin

Should really write $12\uparrow = \Psi(\vec{r}_1, \vec{r}_2) \left| \chi(s_1, s_2) \right>$

$\left| \chi \right>$ is a two-particle spin state

Need $\Psi(\vec{r}_1, \vec{r}_2)$ to satisfy exchange

$\rho(\Psi) = \Psi(\vec{r}_2, \vec{r}_1) \left| \chi(s_2, s_1) \right> = \pm 12\uparrow$

For instance, suppose two electrons in spin singlet

$\left| \chi \right> = \left( \left| \uparrow \downarrow \right> - \left| \downarrow \uparrow \right> \right) / \sqrt{2}$

Then $\rho(\Psi) = - \left| \chi \right>$

Already gives minus sign, so need $\Psi(\vec{r}_1, \vec{r}_2) = + \Psi(\vec{r}_2, \vec{r}_1)$

That's why we can put two electrons in each atomic state:

$\left| \Psi \right> = \Phi_a(r_1) \Phi_b(r_2) \left| \chi_{\text{singlet}} \right>$ has right exchange symmetry

With this, we have what we need to understand atoms.
For instance, in He, have two electrons

To first approx, say they don't interact... each electron in a single-particle hydrogenic state

\[ \text{Lowest energy: both in } 1s \text{ state} \]
\[ \Rightarrow \text{requires spin singlet} \]

Correct: experimentally, ground state He atoms have \( S = 0 \)

First excited state: put one electron in 2s state
Could have either \( S = 0 \) or \( S = 1 \)... which has lower energy?

If \( S = 0 \), \( \Psi(1, 1, 1) \) is symmetric
\[ \Rightarrow \text{electrons closer together} \]
\( S = 1 \), \( \Psi(1, 1, 1) \) antisymmetric, electrons farther apart

But since electrons both have negative charge,
costs EM energy to have close together

\[ \Rightarrow \text{Spin triplet state is lower energy... correct} \]

Section 5.2.2 talks about the rest of the periodic table.

I'll let you read it. Notation is important... to describe a multi-electron atomic state, write

\[ \Psi(L, S) \]

where \( S = \text{total spin} \)
\[ (2S + 1 = \text{degeneracy}) \]

\[ L = \text{letter for total orbital momentum} \]
\[ 0 > S > 1 > A, \text{ etc.} \]
and \( J = \) total angular momentum \( L+S \)

So first excited state of He would have \( S=1 \)
\( L=0 \) (combining of two S states)
\( J=1 \) (since \( S=1+L=0 \) \( \implies \) \( J=1 \))

write \( ^3S_1 \)

Exchange effects also very important for solids particularly metals.

Solid = bunch of atoms meshed together
Metal = each atom gives up a few electrons that are free to drift through material.

That's why metals conduct.
Put some electrons in one side of wire, take some out on other.

This is a complicated system.
Electrons interact with ionic cores & each other.

Simplest model: say electrons are free particles in a box.

Turns out to work tolerably well!

Model called Free Electron Gas.
Say electrons in box potential

\[ U(x, y, z) = \begin{cases} 0 & \text{if } 0 < x < l_x, \\ 0 < y < l_y, \\ 0 < z < l_z \\ \infty & \text{otherwise} \end{cases} \]

Can write \( U = U_x(x) + U_y(y) + U_z(z) \)

each a 1D infinite square well

So wave function separates \( \psi(x, y, z) = X(x) Y(y) Z(z) \)

We know square well solutions \( X(x) = \sqrt{\frac{2}{l_x}} \sin \left( \frac{n_x \pi}{l_x} x \right) \)

integer \( n_x > 0 \)

So 3D wave functions are

\[ \psi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{2}{V}} \sin \left( \frac{n_x \pi}{l_x} x \right) \sin \left( \frac{n_y \pi}{l_y} y \right) \sin \left( \frac{n_z \pi}{l_z} z \right) \]

\( V = \text{volume} = l_x l_y l_z \)

with energies

\[ E_{n_x, n_y, n_z} = \frac{k^2}{2m} \left( \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) \]

\[ \frac{\hbar^2}{2m} \left( \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) \]

for \( \hbar = \frac{\pi}{l_x} x + \frac{\pi}{l_y} y + \frac{\pi}{l_z} z \)

But that's not whole story... electrons satisfy exchange requirement... only two electrons in each state

(in S=0 combination)
So a lot of electrons will occupy a lot of states.

How to account for this?

Use geometrical construction

Allowed $k$’s form grid in “k-space”

If we have $N$ atoms, and each donates $e$ electrons, then $N_0e$ electrons total ($\sim$ Avogadro’s #)

Occupy \( \frac{N_0}{2} \) points in k-space

Since $E \propto k^2$, lowest energy configuration is sphere

Actually 1/8 of sphere: $n\'s$ must be positive

Say radius of sphere is $k_F \equiv$ Fermi wave vector

Then “volume” = \( \frac{1}{8} \times \left( \frac{4}{3} \pi k_F^3 \right) = \frac{\pi^2}{3} \)

Each state occupies volume $\Delta k^3 = \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{2} \pi k_F^3$

So number of points in sphere is $\frac{\frac{\pi^2}{3} k_F^3}{\frac{1}{2} \pi k_F^3} = \frac{1}{6} \pi^2 k_F^3 \cdot \frac{3}{2}$

Set equal \( \frac{N_0}{2} \Rightarrow N_0 = \frac{1}{3} \pi^2 k_F^3 \cdot \frac{3}{2} \)
Solve for $k_F$: 

$$k_F = \left( \frac{3\pi^2 \rho}{2} \right)^{1/3}$$

for 

$$\rho = \frac{N}{V} = \text{density of electrons.}$$

So ground state is all states with $|k| < k_F$ filled.

states with $|k| > k_F$ empty.

Cell boundary between filled & unfilled states = Fermi surface (here a sphere).

Energy of surface = Fermi energy

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 \rho}{2} \right)^{2/3}$$

States with $E < E_F$ are filled.

Finally, set total energy of gas

Write

$$E_{\text{tot}} = \int E(k) \rho(k) \, d^3k$$

$$E(k) = \frac{\hbar^2 k^2}{2m}$$

$$\rho(k) = \frac{\text{Number of states}}{\text{Volume in k-space}} = \text{"density of states"}$$

$$= \frac{2}{(2\pi)^3} = \frac{2V}{\pi^3}$$

So

$$E_{\text{tot}} = \int_0^{k_F} \frac{\hbar^2 k^2}{2m} \frac{2V}{\pi^3} \frac{4\pi k^3 \, dk}{8} \approx \frac{2}{8} \text{ of sphere}$$

$$= \frac{V}{2\pi^2} \frac{4\pi}{m} \int_0^{k_F} k^2 \, dk = \frac{V}{2\pi^2} \frac{4}{5} \frac{k_F^5}{5}$$

So

$$E_{\text{tot}} = \frac{V}{2\pi^2} \frac{4\pi}{m} \left( \frac{3\pi^2 \rho}{2} \right)^{2/3} = \text{total energy of electron gas}$$