Lecture 3 - Atoms + Solids

Last time, introduced spin-statistics theorem:

integer spin = boson = + exchange
half-integer spin = fermion = − exchange

Consequences:

See supplement online

- Two fermions can't occupy same single particle state (including spin)
- Two bosons can.
- Two fermions in different states more likely to be found far apart
- Two bosons more likely to be found close together
- Symmetry doesn't matter if single particle states have no overlap.

Sometimes think about this using "exchange forces"

"Quantum" force that attracts bosons + repels fermions

Force doesn't come from Hamiltonian, but it is real
→ takes a lot of energy to push two fermions together

Spin effects:
With spin, typically have

$$\psi(\vec{r}_1,\vec{s}_1;\vec{r}_2,\vec{s}_2) = \psi(r_1,r_2)\,\chi(s_1,s_2)$$ - spin decoupled

$$P\psi(\vec{r}_1,\vec{s}_1;\vec{r}_2,\vec{s}_2) = \psi(\vec{r}_2,\vec{s}_2;\vec{r}_1,\vec{s}_1)$$

singlet:
$\chi = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$
total $S = 0$

Need overall ψ to have correct exchange

For instance, if $\chi(s_1, s_2) =$ spin singlet
then $\chi(s_2, s_1) = -\chi(s_1, s_2)$

Then for fermions, need $\psi(r_1, r_2)$ symmetric
bosons need antisymmetric

Last point:

How do we symmetrize wave function for more than two particles?

Say N states $\psi_a, \psi_b, \dots \psi_n$
N particles $r_1, r_2, \dots r_N$

For bosons, just sum all permutations of states & particles:

$$\psi(r_1, r_2, \dots r_N) = A[\psi_a(r_1)\psi_b(r_2)\dots\psi_n(r_N) + \psi_b(r_1)\psi_c(r_2)\dots\psi_c(r_N) + \dots \text{ all other combinations}]$$

For fermions harder, need to keep track of signs. Can use "Slater determinant":

$$\psi(r_1 \dots r_N) = \begin{vmatrix} \psi_a(r_1) & \psi_b(r_1) & \dots & \psi_n(r_1) \\ \psi_a(r_2) & \psi_b(r_2) & \dots & \psi_n(r_2) \\ \vdots & & & \\ \psi_a(r_N) & \psi_b(r_N) & \dots & \psi_n(r_N) \end{vmatrix}$$

Evaluate with normal rules for determinants

Can use Pauli exclusion principle to understand
multi-electron atoms.

For instance, He has 2 electrons.

To first approximation, say they don't interact.
Then each electron in a single particle hydrogen state

Lowest energy: both in 1s state
only possible for spin singlet

First excited state, one e^- in 2s state

Could now have spin singlet or triplet,
Which has lower energy?

If spin singlet, spatial ψ is symmetric
$\Rightarrow$ electrons like to be close
Spin triplet, spatial part is antisymmetric
$\Rightarrow$ electrons further apart.

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

$\Rightarrow$ spin triplet state is lower. - correct

Section 5.2 discusses in more detail,
explains spectroscopic notation

I'll let you read it,

Now talk about solids, particularly metals

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

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

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!

Develop model: Free Electron Gas

Box potential $V(x,y,z) = 0 \qquad 0<x<l_x$
$0<y<l_y$
$0<z<l_z$
$= \infty \qquad$ else

Can write $U = U_x(x) + U_y(y) + U_z(z)$
each 1D infinite square well

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

We know square well solutions:

$$X(x) = \sqrt{\frac{2}{l_x}} \sin \frac{n_x \pi}{l_x} x$$

integer $n_x > 0$

So 3D wavefunctions are

$$\psi_{n_x n_y n_z}(x,y,z) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right)$$

V = volume $l_x l_y l_z$

with energies $$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right)$$

$$= \frac{\hbar^2 k^2}{2m}$$

for $\vec{k} = \left(\frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z}\right)$

But that's not the whole story...
even free electrons satisfy exchange requirement

Only two electrons in each state (n_x, n_y, n_z)
[those two e^-'s are in spin singlet]

So if we have a lot of e^-'s, we'll occupy
a lot of states.

→ What is total energy of electron gas?

Use geometrical construction
Allowed wave vectors $\vec{k}$ form grid in "k-space"