Lecture 3 - Atoms & Solids

Last time, introduced spin-statistics theorem:

- Integer spin = boson = + exchange
- Half-integer spin = fermion = - exchange

Consequences:

- 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

\[ 2 \left( \sigma_x \hat{s}_x, \sigma_y \hat{s}_y, \sigma_z \hat{s}_z \right) = 2 \left( \sigma_x, \sigma_y, \sigma_z \right) \times \left( \hat{s}_x, \hat{s}_y, \hat{s}_z \right) \] spin decoupled

\[ \hat{F} \times \left( \sigma_x \hat{s}_x, \sigma_y \hat{s}_y, \sigma_z \hat{s}_z \right) \]
Need overall \( \gamma \) to have correct exchange

Singlet:

\[
\{ \gamma_0 \}_{(1-1)} \]

For instance, if \( \gamma(s_1, s_2) \) = spin singlet

then \( \gamma(s_1, s_1) = -\gamma(s_1, s_2) \)

Then, for fermions, need \( \gamma(c_1, c_2) \) symmetric

bosons need antisymmetric

Last point:

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

Say \( N \) states, \( 2f_a, 2f_b, ... 2f_N \)

\( N \) particles \( c_1, c_2, ... c_N \)

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

\[
\gamma(c_1, c_2, ... c_N) = A \left[ \gamma_a(c_1) \gamma_b(c_2) ... \gamma_N(c_N) + \gamma_b(c_1) \gamma_c(c_2) ... \gamma_N(c_N) + ... \text{ all other combinations} \right]
\]

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

\[
\gamma(c_1, c_2, ... c_N) = \begin{vmatrix}
\gamma_a(c_1) & \gamma_b(c_1) & ... & \gamma_N(c_1) \\
\gamma_a(c_2) & \gamma_b(c_2) & ... & \gamma_N(c_2) \\
& \ddots & \ddots & \ddots \\
\gamma_a(c_N) & \gamma_b(c_N) & ... & \gamma_N(c_N)
\end{vmatrix}
\]

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 Z1 is symmetric

2) electrons like to be close

Spin triplet, spatial part is antisymmetric

2) electrons further apart

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

=> 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 \( U(x, y, z) = \begin{cases} 0 & 0 < x < L_x \\ 0 < y < L_y \\ 0 < z < L_z \\ \infty & \text{else} \end{cases} \)

Can write \( U = U_x(x) + U_y(y) + U_z(z) \)
each 2D infinite square well

So wave function separates
\[ \psi(x, y, z) = X(x) Y(y) Z(z) \]
We know square well solutions:

\[ \chi(x) = \sum_{n_x} \frac{1}{\sqrt{2}} \sin \left( \frac{n_x \pi}{L_x} x \right) \]

So 3D wavefunctions are

\[ \chi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{V}} \sin \left( \frac{n_x \pi}{L_x} x \right) \sin \left( \frac{n_y \pi}{L_y} y \right) \sin \left( \frac{n_z \pi}{L_z} z \right) \]

where \( V = \text{volume} = L_x L_y L_z \)

with energies

\[ E_{n_x n_y n_z} = \frac{\hbar^2 k^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \]

\[ = \frac{\hbar^2 k^2}{2m} \]

for \( k = \left( \frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z} \right) \)

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 \( k \) form grid in "k-space"