

REVIEW #2

DISTINGUISHABLE PARTICLES VS IDENTICAL BOSONS and IDENTICAL FERMIONS

If a system is composed of identical particles, its wavefunction must give the same expectation values if I swap the particle labels. It does not mean that the wavefunction stays the same if I swap the particle labels. In fact, it can get a factor -1 , which does not change expectation values ($(-1)^2=1$).

BOSONS: integer spin particles, wavefunction for system of identical bosons must be symmetric for particle exchange.

E.g. ground state of quantum oscillator with two bosons:

$$\begin{array}{l} |00\rangle ; \text{energy: } \hbar\omega \\ \begin{array}{cc} \nearrow m_1 & \nwarrow m_2 \end{array} \\ \text{excited state: } \frac{|10\rangle + |01\rangle}{\sqrt{2}} ; \text{energy: } 2\hbar\omega \end{array}$$

FERMIONS: semi-integer spin particles, wavefunction for system of identical fermions must be anti-symmetric for particle exchange.

E.g. lowest energy state of quantum oscillator with two fermions:

$$\frac{|10\rangle - |01\rangle}{\sqrt{2}} ; \text{energy: } 2\hbar\omega$$

NOTE: total wavefunction must be symmetric or antisymmetric. Let us now add spin to the wavefunction of two fermions in quantum oscillator. Now I can put them both in $|00\rangle$, I need an anti-symmetric spin part:

lowest energy state of quantum oscillator with two identical fermions including spin

$$|00\rangle \cdot \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} ; \text{energy} = \hbar\omega, \text{total spin} = 0$$

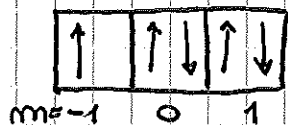
NOTE: $\frac{|10\rangle - |01\rangle}{\sqrt{2}}$ will need to go with symmetric spin function: $|\uparrow\uparrow\rangle, \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}, |\downarrow\downarrow\rangle$

HUND'S RULES

- 1) maximise S , but make sure you satisfy Pauli's exclusion principle (e.g.: if I have two electrons in orbital 1, I can't do $\uparrow\uparrow$, I must have $\uparrow\downarrow$)
- 2) maximise L
- 3) set $J = |L - S|$ if no more than half-shell is filled, and set $J = L + S$ if more than half-shell is filled

Ground state notation: $^{2S+1}L_J$ $L = S, P, D, F$ if $L = 0, 1, 2, 3$

Example: Cl $(3p)^5$



- 1) \Rightarrow put all arrows up, fill boxes, then go back and fill with arrows down
- 2) \Rightarrow start filling from right to left, to maximise $\sum m$

$$S = 3 \cdot \frac{1}{2} + 2 \left(-\frac{1}{2}\right) = \frac{1}{2}$$

↑ arrows up ↓ arrows down

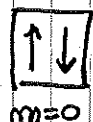
$$L = 2 \cdot 1 + 2 \cdot 0 + 1 \cdot (-1) = 1$$

↑ electrons in $m_l=1$ box ↑ electrons in $m_l=0$ box ↑ electrons in $m_l=-1$ box

$$\Rightarrow {}^2P_{3/2}$$

$$J = L + S = 1 + \frac{1}{2} = \frac{3}{2}$$

Example: He $(1s)^2$



$$S = \frac{1}{2} - \frac{1}{2} = 0, L = 0, J = 0 \Rightarrow {}^1S_0$$

same state: I cannot make anti-symmetric!



This is parahelium, $S = 0$. Since spatial wavefunction is $\psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)$, I need anti-symmetric spin wavefunction: $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$; spin SINGLET.
Excited Helium, in which electrons are in 2 different orbitals, can also be

in a state with spin symmetric wavefunction (spin TRIPLET: $|\uparrow\uparrow\rangle$, $(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$, $|\downarrow\downarrow\rangle$) and anti-symmetric spatial wavefunction. This is called orthohelium, and since exchange force keeps particles more separated, on average, when spatial wavefunction is anti-symmetric for particle exchange, its energy is lower (less Coulomb interaction) than in the corresponding parahelium states.

E.g.: one electron in (1s) and one in (2s):

orthohelium:
$$\frac{\psi_{100}(\vec{r}_1)\psi_{200}(\vec{r}_2) - \psi_{200}(\vec{r}_1)\psi_{100}(\vec{r}_2)}{\sqrt{2}} \cdot |\uparrow\uparrow\rangle$$

parahelium:
$$\frac{\psi_{100}(\vec{r}_1)\psi_{200}(\vec{r}_2) + \psi_{200}(\vec{r}_1)\psi_{100}(\vec{r}_2)}{\sqrt{2}} \cdot \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}$$

parahelium energy > orthohelium energy

FREE ELECTRON GAS

ρ = electron density = $\frac{n}{V}$ ← number of ^{free} electrons contributed by each atom. Typical numbers: $\sim 6 \cdot 10^{23}$ electrons per mole

k_F = Fermi wavenumber = $(3\pi^2\rho)^{1/3}$

E_F = Fermi energy = $\frac{\hbar^2 k_F^2}{2m}$ ← electron mass: $0.5 \text{ MeV}/c^2$

T_F = Fermi temperature = $\frac{E_F}{k_B}$ ← Boltzmann constant. Remember:

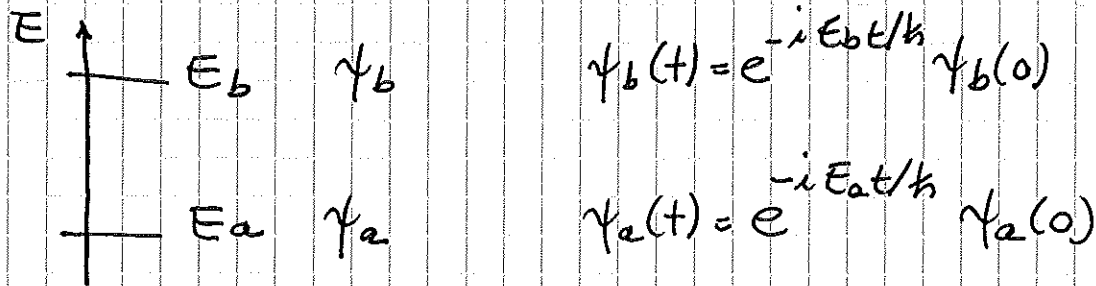
$k_B \cdot 300\text{K} = 1/40 \text{ eV}$

characteristic thermal energy at temperature T : $E = k_B T$

v_F = Fermi velocity = $\sqrt{\frac{2E_F}{m}}$

TIME-DEPENDENT PERTURBATION THEORY

Typically, we have a 2-state system; at $t=0$, we are in state ψ_a ; we turn on a perturbation for a time T , and ask ourselves what is the probability that, at time T , we are in state ψ_b (the other one).



We start with state:

$$\psi(t) = C_a(t) \psi_a(t) + C_b(t) \psi_b(t) \Rightarrow \psi(0) = \psi_a(0)$$

$\downarrow C_a(0)=1$ $\downarrow C_b(0)=0$

At time $t=T$, we are in:

$$\psi(T) = C_a(T) \psi_a(T) + C_b(T) \psi_b(T)$$

$$P_{a \rightarrow b}(T) = \text{probability that, at time } T, \text{ we are in state } \psi_b = |C_b(T)|^2$$

Most important formula:

$$\dot{C}_b(t) \approx -\frac{i}{\hbar} e^{i(E_b - E_a)t/\hbar} \langle \psi_b | H' | \psi_a \rangle$$

valid only at first order

Special case: $\langle \psi_b | H' | \psi_a \rangle$ does not depend on t :

$$P_{a \rightarrow b}(T) = |C_b(T)|^2 = \frac{|\langle \psi_b | H' | \psi_a \rangle|^2 \sin^2\left(\frac{E_b - E_a}{2\hbar} T\right)}{(E_b - E_a)^2}$$

(if $\langle \psi_b | H' | \psi_a \rangle$ does depend on t , bite the bullet and do the integral: $C_b(T) = -\frac{i}{\hbar} \int_0^T e^{i(E_b - E_a)t/\hbar} \langle \psi_b | H' | \psi_a \rangle dt$)