Lecture #13

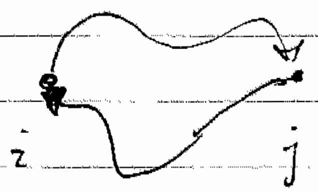
Quantum Many Particle Systems:

N identical particles described by a wavefunction

$\psi(\vec{r}_1, s_1; \vec{r}_2, s_2; \dots \vec{r}_N, s_N)$; $\vec{r}_i$ = position of particle i
s_i = spin of " i

Identical particles $\Rightarrow$ prob. dist. $|\psi|^2$ should not change under exchange of any pair of coordinates:

$$|\psi(\vec{r}_1, s_1; \dots \vec{r}_i, s_i; j; \dots; \vec{r}_N, s_N)|^2$$
$$= |\psi(1, \dots j; i; \dots \vec{r}_N, s_N)|^2$$



$\Rightarrow$ 2 possible symmetries for ψ in 3D

1) ψ is symmetric under pair exchange.
2) ψ is anti-symmetric " " "

$$\psi_S(1, 2, \dots, i, \dots, j, \dots, N) = +\psi_S(1, \dots, j, \dots, i, N)$$
$$\psi_A(1, \dots i, \dots, j, \dots N) = -\psi_A(1, \dots, j, \dots, i, \dots N)$$

(1) particles called Bosons $\rightarrow$ Bose-Einstein stats.
(2) " " Fermions $\rightarrow$ Fermi-Dirac "

Consider a general permutation $\mathbb{P}$ (2)
that interchanges any number of pairs of particles

(1) BE $\Rightarrow \mathbb{P}\Psi = \Psi$
(2) FD $\rightarrow \mathbb{P}\Psi = (-1)^P \Psi$, where

P = # of pair exchanges

$$(-1)^P = \begin{cases} + & \text{for even permutation} \\ - & \text{for odd permutation} \end{cases}$$

Field Theory gives the spin/statistics Theorem:

BE statistics $\longleftrightarrow$ integer spin, $s = 0, 1, 2, \ldots$

FD statistics $\longleftrightarrow$ half-integer spin, $s = \frac{1}{2}, \frac{3}{2}, \ldots$

Consider non-interacting particles.

$$H(1,2,\ldots,N) = \underbrace{H^{(1)}(1) + H^{(1)}(2) + H^{(1)}(3) + \cdots}_{\text{single particle Hamiltonians}}$$

$\rightarrow \Psi(1,2,\ldots,N) = \phi_1(1)\,\phi_2(2)\cdots\phi_N(N)$, ϕ_i is an eigenstate of single-particle Hamiltonian $H^{(1)}(i)$ w/ energy ϵ_i

Does not have proper symmetry.

$$\text{BE}: \quad \psi = \frac{1}{\sqrt{N_P}} \sum_{\{\mathbb{P}\}} \mathbb{P}\psi$$

↑ all possible # of permutations of N particles $= N!$ ($= N_P$)

$$\text{FD}: \psi = \frac{1}{\sqrt{N}} \sum_{\{\mathbb{P}\}} (-1)^P \mathbb{P}\psi$$

This gives the desired symmetry.

In Fermi case, it can be written as a Slater determinante of the single-particle states:

$$\psi_{FD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_i(1) & \phi_i(2) & \cdots & \phi_i(N) \\ \phi_j(1) & \phi_j(2) & \cdots & \phi_j(N) \\ \vdots & \vdots & & \vdots \\ \phi_\ell(1) & \phi_\ell(2) & \cdots & \phi_\ell(N) \end{vmatrix}$$

$$E = \sum_j n_j \epsilon_j \;; \quad n_j = \#\text{ of particles in state } j$$

For FD, $n_j = 0$ or 1 only. Why?

$$\psi(1, 2, \ldots, N) = \phi_1(1)\,\phi_1(2)\,\phi_{i_3}(3) \ldots \phi_{i_N}(N)$$

↑ particles 1 and 2 in same state ϕ_1

When we antisymmetrize:

get $\phi_1(1)\,\phi_1(2) \ldots + (-1)\,\phi_1(2)\,\phi_1(1) \ldots = 0$

for every term

Pauli Exclusion Principle:

No 2 Fermions can occupy the same state, or have the same quantum numbers

For BE stats $\Rightarrow$ no such restriction - $n_j \in \mathbb{Z}$

Specification of non-interacting N particle quantum state is given by occupation numbers $\{n_i\}$.
specifies 1 state of ~~an~~ N particle system

Example: Hetero vs. Homo - Nuclear Molecules:

Internal Modes of a Gas: $E_j = E_{trans} + E_{vib} + E_{rot} + E_{electronic} + E_{nuclear}$

r_0 = equilibrium distance

$I = \mu r_0^2$

$\mu = \frac{m_1 m_2}{m_1 + m_2}$

Non-interacting $\Rightarrow$

$$Z = Z_{trans} Z_{vib} Z_{rot} Z_{elec} Z_{nuclear}$$

Focus on the rotational energy $H = \frac{\hat{L}^2}{2I} \Rightarrow \varepsilon_l = \frac{l(l+1)\hbar^2}{2I}$

define $\varepsilon_{rot} = l(l+1) k \Theta_{rot}$; $\Theta_{rot} \sim 1K = \frac{\hbar^2}{2Ik}$

Consider Heteronuclear atoms: (CO, HD, NO, ...)

with each energy eigenstate, there is the m_l degeneracy $= 2l+1$, $(m_l = (-l, -l+1, \ldots, 0, \ldots l))$

$U = \frac{\partial \ln Z}{\partial \beta}(-)$

$c_v = \frac{\partial U}{\partial T}$

degeneracy

$$Z_{rot} = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\ell(\ell+1)\theta_{rot}/T} \approx \int_0^\infty (2\ell+1) e^{-\ell(\ell+1)\frac{\theta}{T}} \underset{T \gg \theta_r}{\approx} \frac{T}{\theta_r}$$

(5)

$\mathcal{Z}_{rot} = (Z_{rot})^N$ for N molecules. $\Rightarrow c_v = Nk = \frac{\partial U}{\partial T}$

Homonuclear Molecules ($H_2, O_2, D_2, \ldots$) are more complicated (statistics // indistinguishability)

$$\Psi = \psi_{electronic} \psi_{vib} \psi_{rot} \cdot \psi_{nuclear}$$

$$\mathbb{P}\psi_{vib} = \psi_{vib} \quad \text{(a function of } |R_1 - R_2|)$$

$$\mathbb{P}\psi_{electronic} = \pm \psi_{electronic} \quad \text{(depending on the particular orbital)}$$

We classify orbitals by $\vec{L}$ component along the molecular axis.

Denote states by $\Lambda = |M_L|$ $\quad$ $- - \circledcirc - - \bullet - - \to z$

So too with spin

Λ	name
0	Σ
1	Π
2	Δ

Think about symmetry with respect to particle exchange

Recall the orbital wavefunctions are

$\psi_{orbit} \propto Y_{\ell m}(\theta, \phi)$ (rotational eigenstates)

$$Y_{\ell,m}(\theta, \phi) \propto P_\ell^m(\cos\theta) e^{im\phi}$$

Exchange of nuclei corresponds to $\theta \to \pi - \theta$

$\phi \to \phi + \pi$

$$\therefore P_\ell^m[\cos(\pi-\theta)] = (-1)^{\ell+m} P_\ell^m[\cos\theta]$$

and $$e^{i(\phi+\pi)m} = (-1)^m e^{i\phi m}$$

$$\Rightarrow \mathbb{P}\psi_{\text{rotation}} = (-1)^\ell \psi_{\text{rotation}}$$

Consider now H_2, and consider the nuclear spins.

Nucleus of 4 protons $\rightarrow$ nuclear spin of $I_1 = \frac{1}{2}$,
eigenstates of total nuclear spin $I = I_1 + I_2$,
correspond to $I = 1$, $I_z = 1, 0, -1$ AND
$I = 0$, $I_z = 0$ (from QM) ; $|\psi\rangle = |I_1, I_{1,z}\rangle |I_2, I_{2,z}\rangle$

symmetric (even)
$$|1,1\rangle = |\tfrac{1}{2},\tfrac{1}{2}\rangle_1 |\tfrac{1}{2},\tfrac{1}{2}\rangle_2$$
$$|1,0\rangle = \tfrac{1}{\sqrt{2}}\left[|\tfrac{1}{2},\tfrac{1}{2}\rangle_1 |\tfrac{1}{2},-\tfrac{1}{2}\rangle_2 + |\tfrac{1}{2},-\tfrac{1}{2}\rangle_1 |\tfrac{1}{2},\tfrac{1}{2}\rangle_2\right]$$
$$|1,-1\rangle = |\tfrac{1}{2},-\tfrac{1}{2}\rangle_1 |\tfrac{1}{2},-\tfrac{1}{2}\rangle_2$$

Antisymmetric (odd)
$$|0,0\rangle = \tfrac{1}{\sqrt{2}}\left[|\tfrac{1}{2},\tfrac{1}{2}\rangle_1 |\tfrac{1}{2},-\tfrac{1}{2}\rangle_2 - |\tfrac{1}{2},-\tfrac{1}{2}\rangle_1 |\tfrac{1}{2},\tfrac{1}{2}\rangle_2\right]$$

have this definate symmetry because Hamiltonian commutes with $\mathbb{P}$.

The transition rates between nuclear spin states is small, so the two spin orientations are often considered as two different components (2 species of a gas) of H_2 (7)

We specify the nuclear and rotational states as

$$\psi_{tot} = \psi_{N.S.}(I, I_z) \otimes \psi_{rot}(l, m) \otimes \psi_{rest}$$ ← symmetric under exchange.

$$\therefore \mathbb{P}\psi_{N.S.} = \begin{cases} +1, & I=1 \\ -1, & I=0 \end{cases} \otimes \psi_{N.S.}$$

$$\mathbb{P}\psi_{rot} = (-1)^l \psi_{rot}(l,m)$$

$\Rightarrow$ if $I=1$ and l = even
if $I=0$ and l = odd } symmetric wavefunction → forbidden because H is a Fermion

$\Rightarrow$ $I=1$ and l = odd
$I=0$ and l = even } anti-symmetric wavefunction → allowed.

call para-H_2 the H_2 w/ spin 0
ortho-H_2 the H_2 w/ spin 1

then $$Z_{para} = \sum_{\substack{l=\text{even} \\ l=0,2,4,\dots}}^{\infty} (2l+1)\, e^{-l(l+1)\Theta_r/T}$$

3 states for $I_z = 1, 0, -1$

$$Z_{ortho} = (3) \sum_{l=1,3,5,\dots}^{\infty} (2l+1)\, e^{-l(l+1)\Theta/T}$$

$$\therefore Z_{rot}^{tot} = Z_{para} + Z_{ortho}$$

Probability that a molecule is in the ortho (or para) state [regardless of l] is given by

$$\text{Prob[ortho]} = \frac{Z_{ortho}}{Z_{ortho} + Z_{para}}, \quad \text{Prob[para]} = \frac{Z_{para}}{Z_{ortho} + Z_{para}}$$

as $T \gg \Theta_r$; $\sum_l \approx \int dl$

$$\Rightarrow \quad \text{Prob (ortho)} = 3/4, \quad \text{Prob (para)} = \frac{1}{4}$$