Wavefunctions, One Particle

Hamiltonian $\widehat{\mathcal{H}}(\widehat{\vec{r}}, \widehat{\vec{p}}, \widehat{\vec{s}})$

Wavefunction $\psi_n(\vec{r}, \vec{s})$

$\vec{r}$ and $\vec{s}$ are the variables.

n is a state index and could have several parts.

For an e^- in hydrogen $\psi = \psi_{n,l,m_l,m_s}(\vec{r}, \vec{s})$

$$\widehat{\mathcal{H}}(\widehat{\vec{r}}, \widehat{\vec{p}}, \widehat{\vec{s}})\, \psi_n(\vec{r}, \vec{s}) = E_n\, \psi_n(\vec{r}, \vec{s})$$

$\psi_n(\vec{r},\vec{s})$ often factors into space and spin parts.

$$\psi_n(\vec{r},\vec{s}) = \psi^{\text{space}}_{n'}(\vec{r})\,\psi^{\text{spin}}_{n''}(\vec{s})$$

$\psi^{\text{space}}_n(x) \propto e^{-\alpha x^2/2} H_n(\sqrt{\alpha}\,x)$ H.O. in 1 dimension

$\psi^{\text{space}}_n(\vec{r}) \propto e^{i\vec{k}\cdot\vec{r}}$ free particle in 3 dimensions

$\psi^{\text{spin}}_{n''}(\vec{s})$

Spin is an angular momentum so for a given value of the magnitude S there are $2S+1$ values of m_S.

For the case of $S = 1/2$ the eigenfunctions of the z component of $\vec{s}$ are $\phi_{1/2}(\vec{s})$ and $\phi_{-1/2}(\vec{s})$

$$\widehat{S}_z\,\phi_{1/2}(\vec{s}) \;=\; \frac{\hbar}{2}\,\phi_{1/2}(\vec{s})$$

$$\widehat{S}_z\,\phi_{-1/2}(\vec{s}) \;=\; -\frac{\hbar}{2}\,\phi_{-1/2}(\vec{s})$$

$\psi^{\text{spin}}_{n''}(\vec{s})$ is not necessarily an eigenfunction of $\widehat{S}_z$. For example one might have

$$\psi^{\text{spin}}_{n''}(\vec{s}) = \frac{1}{\sqrt{2}}\,\phi_{1/2}(\vec{s}) + \frac{1}{\sqrt{2}}\,\phi_{-1/2}(\vec{s})$$

In some cases $\psi_n(\vec{r},\vec{s})$ may not factor into space and spin parts. For example one may find

$$\psi_n(x,\vec{s}) = f(x)\,\phi_{1/2}(\vec{s}) + g(x)\,\phi_{-1/2}(\vec{s})$$

Many Distinguishable Particles, Same Potential, No Interaction

Lump space and spin variables together

$\vec{r}_1, \vec{s}_1 \rightarrow 1 \quad \vec{r}_2, \vec{s}_2 \rightarrow 2$ etc.

$$\hat{\mathcal{H}}(1, 2, \cdots N) = \hat{\mathcal{H}}_0(1) + \hat{\mathcal{H}}_0(2) + \cdots \hat{\mathcal{H}}_0(N)$$

In this expression the single particle Hamltonians all have the same functional form but each has arguments for a different particle.

The same set of single particle energy eigenstates is available to every particle, but each may be in a different one of them. The energy eigenfunctions of the system can be represented as products of the single particle energy eigenfunctions.

$$\psi_{\{n\}}(1,2,\cdots N) = \psi_{n_1}(1)\psi_{n_2}(2)\cdots\psi_{n_N}(N)$$

$\{n\} \equiv \{n_1, n_2, \cdots n_N\}$. There are N #s, but each n_i could have an infinite range.

$$\hat{\mathcal{H}}(1,2,\cdots N)\,\psi_{\{n\}}(1,2,\cdots N) = E_{\{n\}}\,\psi_{\{n\}}(1,2,\cdots N)$$

Many Distinguishable Particles, Same Potential, Pairwise Interaction

$$\hat{\mathcal{H}}(1,2,\cdots N) = \sum_{i=1}^{N} \hat{\mathcal{H}}_0(i) + \tfrac{1}{2} \sum_{i \neq j} \hat{\mathcal{H}}_{\text{int}}(i,j)$$

The $\psi_{\{n\}}(1,2,\cdots N)$ are no longer energy eigenfunctions; however, they could form a very useful basis set for the expansion of the true energy eigenfunctions.

Indistinguishable Particles

$$\hat{P}_{ij}\, f(\cdots i \cdots j \cdots) \equiv f(\cdots j \cdots i \cdots)$$

$$(\hat{P}_{ij})^2 = \hat{I} \quad \Rightarrow \quad \text{eigenvalues of } \hat{P}_{ij} \text{ are } +1, -1$$

It is possible to construct many-particle wavefunctions which are symmetric or anti-symmetric under this interchange of two particles.

$$\hat{P}_{ij}\, \psi^{(+)} = \psi^{(+)} \qquad\qquad \hat{P}_{ij}\, \psi^{(-)} = -\,\psi^{(-)}$$

Identical $\Rightarrow$ no physical operation distinguishes between particle i and particle j. Mathematically, this means that for all physical operators $\hat{\mathcal{O}}$

$$[\hat{\mathcal{O}}, \hat{P}_{ij}] = 0$$

$\Rightarrow$ eigenfunctions of $\hat{\mathcal{O}}$ must also be eigenfunctions of $\hat{P}_{ij}$.

$\Rightarrow$ energy eigenfunctions ψ_E must be either $\psi_E^{(+)}$ or $\psi_E^{(-)}$.

$\Rightarrow$ states differing only by the interchange of the spatial and spin coordinates of two particles are the <u>same</u> state.

Relativistic quantum mechanics requires

$$\text{integer spin} \leftrightarrow \psi_E{}^{(+)} \qquad \text{[Bosons]}$$

$$\text{half-integer spin} \leftrightarrow \psi_E{}^{(-)} \qquad \text{[Fermions]}$$

Composite Particles

- Composite Fermions and Composite Bosons
- Count the number of sign changes as all the constituents are interchanged
- Well defined statistics (F-D or B-E) as long as the internal degrees of freedom are not excited

The constitutents of nuclei and atoms are e, p & n.
Each has $S = 1/2$.

N even $\Rightarrow$ even # of exchanges.

$\psi \rightarrow (+)\psi \Rightarrow$ B-E

also N even $\Rightarrow$ integer spin

N odd $\Rightarrow$ odd # of exchanges.

$\psi \rightarrow (-)\psi \Rightarrow$ F-D

also N odd $\Rightarrow$ half-integer spin

Particle	Nuclear Spin	Electrons	Statistics
H (H^1)	$\frac{1}{2}$	1	B-E
D (H^2)	1	1	F-D
T (H^3)	$\frac{1}{2}$	1	B-E
He^3	$\frac{1}{2}$	2	F-D
He^4	0	2	B-E
Li^6	1	3	F-D
Li^7	$\frac{3}{2}$	3	B-E
H_2	0 or 1	2	B-E
x_2	integer	()×2	B-E

Let $\alpha(\vec{r},\vec{s})$, $\beta(\vec{r},\vec{s}),\cdots$ be single particle wavefunctions.

A product many-particle wavefunction, $\alpha(1)\beta(2)$, does not work.

Instead, use a sum of all possible permutations:

$$\Psi_2^{(+)} = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\alpha(2)\beta(1))$$

$$\Psi_N^{(+)} = \frac{1}{\sqrt{N!}}\frac{1}{\sqrt{\prod_\alpha n_\alpha!}}\sum_{\text{permutations}}(\alpha(1)\beta(2)\gamma(3)\cdots)$$

The antisymmetric version results in a familiar form, a determinant.

$$\Psi_2^{(-)} = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

$$\Psi_N^{(-)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \alpha(1) & \beta(1) & \gamma(1) & \cdots \\ \alpha(2) & \beta(2) & \gamma(2) & \cdots \\ \alpha(3) & \beta(3) & \gamma(3) & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix}$$

$\rightarrow$ states

$\downarrow$ particles

- $\Psi_N^{(-)} = 0$ if 2 states are the same since 2 columns are equal: Pauli Principle.

- $\Psi_N^{(-)} = 0$ if 2 particles have the same $\vec{r}$ and $\vec{s}$ since 2 rows are equal.

- Specification: indicate which s.p. ψs are used. $\{n_\alpha, n_\beta, n_\gamma, \cdots\}$ An ∞ # of entries, each ranging from 0 to N but with $\sum_\alpha n_\alpha = N$.

$|1,0,1,1,0,0,\cdots\rangle$ Fermi-Dirac

$|2,0,1,3,6,1,\cdots\rangle$ Bose-Einstein

$\sum_{\alpha}{}' \epsilon_\alpha n_\alpha = E$ Prime indicates $\sum_\alpha n_\alpha = N$

Example Atomic configurations

$(1S)^2(2S)^2(2P)^6 \leftrightarrow$ Ne

$(1S)^2(2S)^2(2P)^6(3S)^1 \leftrightarrow$ Na

$(1S)^1(2S)^1 \leftrightarrow$ He*

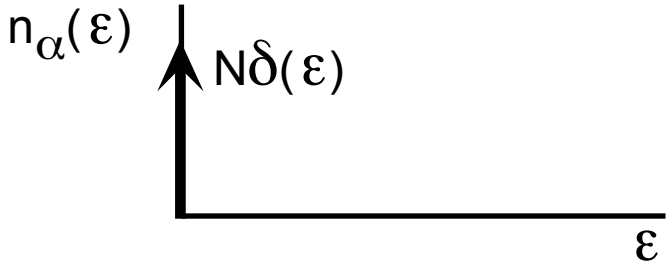
Statistical Mechanics Try Canonical Ensemble

$$
\begin{aligned}
Z(N,V,T) &= \sum_{\text{states}} e^{-E(\text{state})/kT} \\
&= \sum_{\{n_\alpha\}}{}' \; e^{-E(\{n_\alpha\})/kT} \\
&= \sum_{\{n_\alpha\}}{}' \left(\prod_{\alpha} e^{-\epsilon_\alpha n_\alpha/kT} \right)
\end{aligned}
$$

This can not be carried out. One can not interchange the $\sum$ over occupation numbers and the $\prod$ over states because the occupation numbers are not independent ($\sum n_\alpha = N$).

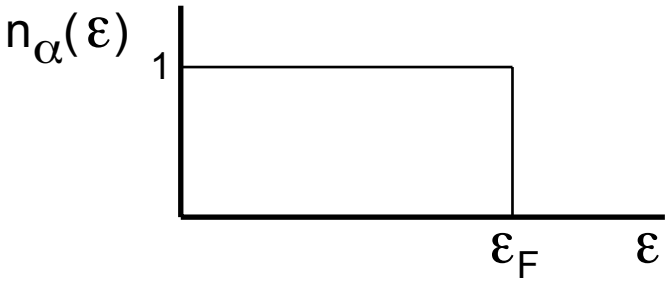
T=0 LOWEST POSSIBLE TOTAL ENERGY

BOSE: ALL N PARTICLES IN LOWEST ε SINGLE PARTICLE STATE



FERMI: LOWEST N SINGLE PARTICLE STATES EACH USED ONCE

$\varepsilon < \varepsilon_F$, ε_F CALLED THE FERMI ENERGY



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