Tutorial 3 : Due today

W7L1 : Identical & Indistinguishable particles

	Bosons	Fermions
many-body states/ wavefunctions	Symmetric (S) w.r.t. exchange	Antisymmetric (AS) w.r.t. exchange

many-body Fermion wavefunction

$$\Psi(x_1, \dots, x_N) \propto \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_N) \\ \phi_2 & & & \vdots \\ \vdots & & & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \dots & \phi_N(x_N) \end{vmatrix} \leftarrow \text{Slater determinant}$$

represent particles (1 to N label the particles)

represent single-particle states (1, 2, .., N label the single-particle states)

Consider the effect of spin

Consider two spin-$\frac{1}{2}$ particles (identical & indistinguishable)

Addition of two spin $\frac{1}{2}$ particles

	Coupled rep. s	m	Uncoupled rep.	
Triplet	1	-1	$\lvert\downarrow_1 \downarrow_2\rangle$	S
	1	0	$\frac{1}{\sqrt{2}}(\lvert\uparrow_1 \downarrow_2\rangle + \lvert\downarrow_1 \uparrow_2\rangle)$	
	1	1	$\lvert\uparrow_1 \uparrow_2\rangle$	
Singlet	0	0	$\frac{1}{\sqrt{2}}(\lvert\uparrow_1 \downarrow_2\rangle - \lvert\downarrow_1 \uparrow_2\rangle)$	AS

$$|\Psi\rangle = \underset{\text{spin}}{|\chi\rangle} \otimes \underset{\text{spatial}}{|\Phi\rangle}$$ — when the Hamiltonian does not depend on spin explicitly.

when we exchange any two particles, $|\Psi\rangle$ must be AS.

$\Rightarrow$ $|\chi\rangle$ AS ; $|\Phi\rangle$ S

OR $|\chi\rangle$ S ; $|\Phi\rangle$ AS.

single particle spatial states
$|\alpha\rangle$, $|\beta\rangle$

Triplet $\quad |\chi\rangle = \begin{cases} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{cases} \otimes |\Phi\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle - |\beta\alpha\rangle\right)$

S $\qquad\qquad$ AS

Singlet $\quad |\chi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \otimes |\Phi\rangle = \begin{cases} |\alpha\alpha\rangle \\ \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle) \\ |\beta\beta\rangle \end{cases}$

AS $\qquad\qquad$ S

Eg Helium atom — Two electrons

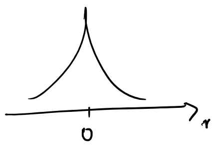
Ground state

1s $\uparrow\downarrow$

1st Excited state (Helium atom)

2s —— $\leftarrow$ one electron is in the 2s orbital

1s $\uparrow$



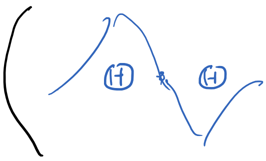
1s , 2s are spherically symmetric.
$\uparrow$ $\quad$ $\uparrow$
$|g\rangle$ $\quad |e\rangle$

symmetric spatial state: $|\Phi^S\rangle = \begin{cases} |gg\rangle \text{ — not possible for excited state} \\ \frac{1}{\sqrt{2}}(|ge\rangle + |eg\rangle) \\ |ee\rangle \text{ — probably not for 1st excited state.} \end{cases}$

Antisymmetric spatial state: $|\Phi^{As}\rangle = \left\{ \frac{1}{\sqrt{2}}(|ge\rangle - |eg\rangle) \right.$

Antisymmetric spatial state: $|\Phi^{as}\rangle = \left\{ \frac{1}{\sqrt{2}}\left(|ge\rangle - |eg\rangle\right)\right.$

can have a node.



$\leftarrow$ H_2 molecule.

The AS spatial state allows the electrons to be farther apart on average.

Due to Coulomb repulsion between electrons, $|\Phi^{as}\rangle$ has a lower energy in the 1st excited state, then $|\Phi^{s}\rangle$

Coulomb interactions are the strongest interactions.

Spin-spin interactions are much smaller.

So for the total wavefunction to be AS for the fermions, $|\chi\rangle$, the spin part, must be S.

We need $|\chi^{s}\rangle \longrightarrow$ triplet spin state.

$S = 1$

<u>Approximation Methods</u> to find the energy eigenvalues of time-independent Hamiltonians or properties of time-dependent states.

Needed because very few Hamiltonians can be solved exactly.

What can be solved?

- Hydrogen atom — only for Hamiltonian with kinetic and Coulombic terms
- Infinite square well
- Harmonic oscillator.

<u>Examples of approximation methods</u>

- Born-Oppenheimer approximation
- Central Potential approximation for multi-electron atoms

} before recess week.

- Variational principle
- Time-independent perturbation theory
- Time-dependent — " —

<u>Variational Principle</u>

- To estimate the ground state energy of a Hamiltonian H.

Assume $\exists$ eigenstates of H:

$$H|\psi_n\rangle = E_n|\psi_n\rangle \quad , n \geq 0$$

(we do not know what E_n and $|\psi_n\rangle$ are.)

Consider any ("trial") state $|\phi\rangle$ in the Hilbert space. (normalized)

we can show that $\boxed{\langle\phi|H|\phi\rangle \geq E_0}$

Proof:

We write $|\phi\rangle = \sum_n c_n |\psi_n\rangle$

$c_n = \langle\psi_n|\phi\rangle$

$\langle\phi|\psi_n\rangle = c_n^*$

$$(|\phi\rangle = \mathbb{1}\, |\phi\rangle = \sum_n |\psi_n\rangle\langle\psi_n|\phi\rangle$$

$\{|\psi_n\rangle, n\geq 0\}$ a complete o.n. basis

Thoughts

· $\langle\psi_n|H|\psi_n\rangle = E_n$

· orthonormal o.n. $\{|\psi_n\rangle, n\geq 0\}$ span the Hilbert space.

Pick $|\psi_n\rangle$

$\downarrow$

$\langle\psi_n|H|\psi_n\rangle = E_n$

Pick $|\phi\rangle = \frac{1}{\sqrt{2}}(|\psi_1\rangle + |\psi_3\rangle)$

$$\langle\phi|H|\phi\rangle$$
$$= \langle\phi|H\sum_n c_n|\psi_n\rangle$$
$$= \sum_n c_n \langle\phi|H|\psi_n\rangle$$
$$= \sum_n c_n \langle\phi|E_n|\psi_n\rangle$$
$$= \sum_n E_n c_n \langle\phi|\psi_n\rangle$$
$$= \sum_n E_n c_n c_n^*$$
$$= \sum_n E_n |c_n|^2$$

$E_n \geq E_0$ for all n

So

$$\langle\phi|H|\phi\rangle = \sum_n E_n |c_n|^2$$
$$\geq \sum_n E_0 |c_n|^2$$
$$= E_0 \sum_n |c_n|^2$$
$$= E_0$$

since $\sum_n |c_n|^2 = 1$

$(\langle\phi|\phi\rangle = 1)$ //

In the basis of $\{|\psi_n\rangle, n\geq 0\}$

H can be written as the matrix

$$\begin{array}{cc} & \langle\psi_1|H|\psi_3\rangle \\ H = & \begin{pmatrix} E_0 & 0 & 0 & 0 \\ 0 & E_1 & & \\ 0 & & E_2 & \\ 0 & & & \ddots \end{pmatrix} \\ \langle\psi_3|H|\psi_1\rangle & \end{array}$$

$$\langle\phi|H|\phi\rangle$$
$$= \frac{1}{\sqrt{2}}(\langle\psi_1| + \langle\psi_3|)H(\frac{1}{\sqrt{2}}|\psi_1\rangle + |\psi_3\rangle)$$
$$= \frac{1}{2}(\overbrace{\langle\psi_1|H|\psi_1\rangle}^{E_1} + \overbrace{\langle\psi_3|H|\psi_3\rangle}^{E_3}$$
$$+ \underbrace{\langle\psi_1|H|\psi_3\rangle}_{0} + \underbrace{\langle\psi_3|H|\psi_1\rangle}_{0})$$
$$= \frac{1}{2}E_1 + \frac{1}{2}E_3$$

Eg. of application

(A) Select a 'trial' wavefunction $|\phi\rangle$

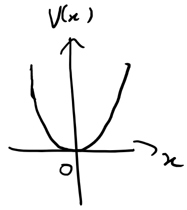
Typically depends on some parameters, which you optimize in order to minimize $\langle\phi|H|\phi\rangle$ and approach E_0, the ground state energy as closely as possible.

'Trial' wavefunction $|\phi\rangle$

— should be normalized
— should satisfy boundary conditions

Eg. 1D Harmonic Oscillator

$$H = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{T} + \underbrace{\frac{1}{2}m\omega^2 x^2}_{V} \equiv T + V$$



spatially symmetric

Trial wavefunction

$$\psi_b(x) = A\exp(-bx^2)$$ Gaussian, A normalization constant.

$$A = \left(\frac{2b}{\pi}\right)^{1/4}$$

Use $\int_{-\infty}^{\infty} e^{-\alpha x^2}dx = \sqrt{\frac{\pi}{\alpha}}$

$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2}dx = \frac{\sqrt{\pi}}{2\alpha^{3/2}}$

Need $\langle\psi_b|H|\psi_b\rangle = \langle\psi_b|T|\psi_b\rangle + \langle\psi_b|V|\psi_b\rangle$

$$\langle\psi_b|T|\psi_b\rangle = |A|^2\left(-\frac{\hbar^2}{2m}\right)\int dx\, e^{-bx^2}\frac{d^2}{dx^2}\left(e^{-bx^2}\right)$$

$$= |A|^2\frac{\hbar^2 b}{2m}\int dx\, e^{-bx^2}(1-2bx^2)e^{-bx^2}$$

$$= |A|^2\frac{\hbar^2 b}{m}\int dx\,(1-2bx^2)\,e^{-2bx^2}$$

$$= \sqrt{\frac{2b}{\pi}}\frac{\hbar^2 b}{m}\left(\sqrt{\frac{\pi}{2b}} - \frac{2b}{2}\frac{\sqrt{\pi}}{(2b)^{3/2}}\right)$$

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

$$\langle\psi_b|V|\psi_b\rangle = |A|^2\frac{1}{2}m\omega^2\int dx\, e^{-bx^2}x^2 e^{-bx^2}$$

$$= \sqrt{\frac{2b}{\pi}}\frac{1}{2}m\omega^2\left(\int dx\, x^2 e^{-2bx^2}\right)$$

$$= \sqrt{\frac{2b}{\pi}}\frac{1}{2}m\omega^2\frac{\sqrt{\pi}}{2(2b)^{3/2}}$$

$$= \frac{m\omega^2}{8b}$$

$$\langle\psi_b|H|\psi_b\rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$

Using the variational principle, we want to estimate E_0 by minimizing $\langle\psi_b|H|\psi_b\rangle$ wrt b.

$$\frac{d}{db}\langle \psi_b | H | \psi_b \rangle = 0$$

$$\frac{d}{db}\left(\frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b} \right) = 0$$

$$\frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0$$

$$b^2 = \frac{m^2\omega^2}{4\hbar^2}$$

$$b = \pm \frac{m\omega}{2\hbar}$$

For minimum: $\frac{d^2}{db^2}\left(\langle \psi_b | H | \psi_b \rangle \right) > 0$

$$\Rightarrow b = \frac{m\omega}{2\hbar}$$

So the estimate for the ground state:

$$\langle \psi_b | H | \psi_b \rangle \Big|_{b=\frac{m\omega}{2\hbar}} = \frac{\hbar^2}{2m} \cdot \frac{m\omega}{2\hbar} + \frac{m\omega^2}{8} \frac{2\hbar}{m\omega} = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \frac{\hbar\omega}{2}$$

actually the exact answer for the ground state eigenvalue.

- Exact because the ground state wavefunction for the harmonic oscillator is actually a gaussian.