Identical particles

The He Hamiltonian

\[ H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{(r_1 - r_2)} \]

describes 2 identical particles

\[ H(1,2) \quad (H(\vec{r}_1, \vec{r}_2)) \]

\[ H(1,2) = H(2,1) \quad \text{symmetric under interchange} \]

What about the energy eigenstates? \( |1,2\rangle \equiv |2,1\rangle \)

\[ \langle \vec{r}_1, \vec{r}_2 | 1,2 \rangle = \chi(\vec{r}_1, \vec{r}_2) \]

Exchange operator: \( \hat{E}_{12} : \)

\[ \hat{E}_{12} |1,2\rangle = 12 |1,2\rangle \]

\[ \hat{E}_{12} \chi(\vec{r}_1, \vec{r}_2) = \chi(\vec{r}_2, \vec{r}_1) \]

\[ [\hat{E}_{12}, H] = 0 \]

\[ \implies \text{we can find common eigenstates} \]

Eigenvalues of \( \hat{E}_{12} : \)

\[ E_{12}^2 (|1,2\rangle) = 11, 2 \rangle \quad \text{physical req.} \]

\[ E_{12}^2 = 1 \]

\[ i \hat{E}_{12} |1,2\rangle \text{ is an eigenstate of } \hat{E}_{12} \]

\[ \hat{E}_{12} |1,2\rangle = \gamma |1,2\rangle = \gamma |1,2\rangle \]

\[ \hat{E}_{12} |1,2\rangle = \gamma^2 |1,2\rangle = |1,2\rangle \]

\[ \gamma^2 = 1 \quad \rightarrow |\gamma = \pm 1| \]

\[ \text{Hermitian!} \]

\[ \hat{E}_{12} |1,2\rangle = \pm |1,2\rangle = (2,1) \]

or \[ -\gamma (1,2) = \gamma (2,1) \] \{ the eigenstate is symmetric or anti-symmetric under exchange \}
We can always make sym. or anti sym. wave fun.
Is there physical realization in here?

More than expected:

Every physical system will have either
symm. or anti symm. kets (wave fun.)

- symmetric: called Bose - Einstein statistics
  bosons - always integer spin

- anti-symmetric: Fermi - Dirac
  fermions - half integer spin

Ex: 2 identical particles feel the same potential
but do not interact (no spin)

\[ H = \frac{\hat{p}_1^2}{2m} + V(r_1) + \frac{\hat{p}_2^2}{2m} + V(r_2) \]

\[ H_1|n\rangle = \frac{\hat{p}_1^2}{2m} + V(r) \]

\[ H \text{ eigenkets } \{ |1, 2\rangle = |n\rangle \otimes |k\rangle \text{ symm. } \]

\[ \psi(r_1, r_2) = \psi_n(r_1) \psi_k(r_2) \]

To make it symm / anti-symmetric, i.e. \( \hat{E}_{12} \) eigenkets

\[ \psi_{kn}(r_1, r_2) \text{ symm. } = \frac{1}{\sqrt{2}} \left( \psi_n(r_1) \psi_k(r_2) + \psi_k(r_1) \psi_n(r_2) \right) \]

\[ |1, 2\rangle = \frac{1}{\sqrt{2}} \left( |n\rangle |k\rangle + |k\rangle |n\rangle \right) \text{ symm. } \]

\[ \text{ anti-symmetric: } \quad + \rightarrow - \]

What if \( n = k \)? only symm. exist \( \psi_{nn} = \psi_n(r_1) \psi_n(r_2) \)
If the particles have spin, we have to take that into account as well:

\[ |n\rangle \rightarrow |n, m_s\rangle \]
\[ \psi (\vec{r}) \rightarrow \psi (\vec{r}) \cdot 1_{m_s} \]
\[ \psi_{nk} (r_1, r_2) |m_{n1}, m_{n2}\rangle \]

\[ \text{will have to be symmetric or antisymmetric.} \]

When we add two spin \( \frac{1}{2} \) together:

\[ \frac{1}{2} \otimes \frac{1}{2} = 1 \otimes 0 \]

\[ \left| \uparrow \uparrow \right> = |s=1, m_s=1\rangle \]
\[ \frac{1}{\sqrt{2}} \left( |\uparrow \downarrow + \downarrow \uparrow \rangle = |s=1, m_s=0\rangle \right. \]
\[ \left. |\downarrow \downarrow \rangle = |s=1, m_s=-1\rangle \right] \]

\[ \frac{1}{\sqrt{2}} \left( |\uparrow \uparrow \rangle - |\downarrow \downarrow \rangle \right) = |s=0, m_s=0\rangle \text{ antisymmetric.} \]

\[ |m_{nj}, m_k\rangle \rightarrow |j, m_j\rangle \]

Using total spin states, the spin state is already symmetric or antisymmetric.

\[ |1, 1\rangle \text{ antisym.} \]
\[ \left| n, k \right> \text{ symmetric, } |s=0, m_s=0\rangle \]
\[ \text{or} \]
\[ |n, k\rangle \text{ antisymmetric, } |s=1, m_s=-\frac{1}{2}, 0\rangle \]

\[ n = k \rightarrow |n, k\rangle \text{ symmetric, } |s=0, m_s=0\rangle \]
Works the same way for rows:

\[ S \otimes S = 2S \oplus (2S-1) \oplus \ldots \oplus 0 \]

\[
\uparrow \quad \uparrow \quad \uparrow
\]

sym. and antisym. -- sym.

\[ |i,j\rangle = \Psi_{nm} (\Gamma_1 \Gamma_2)_{sym} |i,j\rangle_{sym} \]

or \[ \Psi_{nm} (\Gamma_1 \Gamma_2)_{as} |i,j\rangle_{as} \]

Special case:

\[ n = m : \Psi_{nm} (\Gamma_1 \Gamma_2) \text{ is necessarily symmetric} \]

\[ \Rightarrow \text{ fermions: } |i,j\rangle_{as} \text{ needed: singlet} \]

\[ \text{ bosons: } |i,j\rangle_{sym} \]

Ex. SHO:

\[ \text{ bosons all have } \uparrow \downarrow \text{ on each level} \]
\[ s = 1 \]

\[ \langle 1 | 1 \rangle = 1 \]

\[ \langle 2 | 1 \rangle = \frac{1}{\sqrt{2}} (\langle 1, 1 \rangle + \langle 1, 1 \rangle) \]

\[ \langle 2 | 0 \rangle = \frac{1}{\sqrt{4}} (\langle 1, -1 \rangle + 2\langle 1, 0 \rangle + \langle 1, -1 \rangle) \]

\[ \langle 2 | -1 \rangle = \frac{1}{\sqrt{2}} (\langle 1, 1 \rangle + \langle 1, -1 \rangle) \]

\[ \langle 2 | -2 \rangle = \langle 1, -1 \rangle \]

\[ \langle 1, 1 \rangle : \text{orthogonal to } \langle 2, 1 \rangle \]

\[ \langle 1, 1 \rangle = \frac{1}{\sqrt{2}} (\langle 1, 1 \rangle - \langle 1, 1 \rangle) \]

\[ \langle 1, 0 \rangle = \frac{1}{\sqrt{2}} (\langle 1, -1 \rangle - \langle 1, -1 \rangle) \]

\[ \langle 1, -1 \rangle = \frac{1}{\sqrt{2}} (\langle 1, 1 \rangle - \langle 1, 1 \rangle) \]

\[ \langle 0, 0 \rangle : \text{orthogonal to } \langle 2, 0 \rangle, \langle 0, 0 \rangle \]

\[ \langle 0, 0 \rangle = \alpha \langle 1, 1 \rangle + \beta \langle 1, 0 \rangle + \alpha \langle 1, 1 \rangle \]

\[ \alpha + 2\beta + \alpha = 0 \rightarrow \beta = -\alpha \]

\[ \langle 0, 0 \rangle = \frac{1}{\sqrt{3}} (\langle 1, 1 \rangle + \langle 1, 0 \rangle + \langle 1, 1 \rangle) \]

\[ \langle 2, 1 \rangle = \sqrt{2 - 3} - \alpha \]

\[ \langle 2, 0 \rangle = \frac{1}{\sqrt{2}} \left( \sqrt{1 + 2} \langle 1, 0 \rangle + \sqrt{1 - 2} \langle -1, -1 \rangle \right) + \sqrt{1 - 2} \langle 1, 0 \rangle + \sqrt{2} \langle 1, 0 \rangle \]

\[ = \frac{1}{\sqrt{6}} (\langle 1, -1 \rangle + 2\langle 1, 0 \rangle + 1, -1) \]
**Ex: He**

2 electrons - spin $\frac{1}{2}$ $\rightarrow$ \( \left| j m \right> \) triplet: sym

\( \downarrow \)

\( \text{Ground state: } n = m = 1 \quad l_z = 0 \)

\( 
\Psi_{11} (r_1, r_2) \text{ is symmetric. } 
\)

\( \downarrow \)

\( \text{Singlet state: } s = 0 \quad \left( \frac{l_{1s}}{l_{1s}} \right) \)

\( \frac{1}{\sqrt{2}} \)

\( \text{Excited state } n \neq m : \text{ both singlet/triplet are possible } \)

\( \rightarrow \) AS wave function is energetically favored

\( \rightarrow \) triplet has lower energy

**Multiparticle atoms**

\( N \) identical electrons: \( \Psi \) is AS under exchange of any 2 electrons

\( \Psi_{n_1 n_2 n_3} (r_1, r_2, r_3) = - \Psi_{n_2 n_1 n_3} (r_2, r_1, r_3) \text{ (spin)} \)

\( \text{etc.} \)

Could all 3 electrons be in the same spatial state?

\( \Psi_{1,1,1} (r_1, r_2, r_3) \text{ symmetric.} \)

\( \left| j m \right> \text{ antisymmetric.} \)

\( \left| n_1, n_2, n_3 \right> \quad \begin{cases} 
\overset{++-}{\rightarrow} \left| 1, 1, 1 \right> \text{ symmetric.} \\
\overset{+--}{\rightarrow} \left| 1, 1, 1 \right> \text{ symmetric.} \\
\overset{-++}{\rightarrow} \left| 1, 1, 1 \right> \text{ symmetric.} \\
\overset{-|- |}{\rightarrow} \left| 1, 1, 1 \right> \text{ symmetric.} \\
\end{cases} \text{ combinations} \)

we fully as
Exchange force

Take 2 (identical) particles in states $n, k$:

\[ |n, k\rangle : \text{if they are distinguishable} \]

\[ 1_{SS} = \frac{1}{\sqrt{2}} \left( |n_1, k_2\rangle + |k_1, n_2\rangle \right) \text{ symmetric} \]

\[ 1_{AS} = \frac{1}{\sqrt{2}} \left( |n_1, k_2\rangle - |k_1, n_2\rangle \right) \text{ antisymmetric} \]

Calculate $\langle (x_1 - x_2)^2 \rangle$ : separation between

\[ (x_1 - x_2)^2 = x_1^2 + x_2^2 - 2x_1x_2 \]

a) $\langle \eta_{n, k} | x_1^2 + x_2^2 - 2x_1x_2 | n, k\rangle = \langle x_1^2 \rangle_n + \langle x_2^2 \rangle_k - 2\langle x_1 \rangle_n \langle x_2 \rangle_k$

\[ = \frac{1}{2} \left( \langle n | x_1^2 \rangle_1 + \langle k | x_1^2 \rangle_2 \right)(x_1^2 + x_2^2 - 2x_1x_2)

\[ + \left( \langle n | x_2^2 \rangle_1 + \langle k | x_2^2 \rangle_2 \right)(x_1^2 + x_2^2 - 2x_1x_2) \]

\[ = \frac{1}{2} \left[ 2\langle x_1^2 \rangle_n + 2\langle x_2^2 \rangle_k - 2\langle x_1 \rangle_n \langle x_2 \rangle_k \right] \]

b) $\langle 5 \{ (x_1 - x_2)^2 \}^2 \rangle = \langle 5 \{ (x_1 - x_2)^2 \}^2 \rangle_n \langle x_n \rangle = \langle x_n \rangle \langle x_n \rangle$

Note:

$\langle nk | x_1^2 | kn\rangle = \langle n| x_1^2 | k\rangle \langle k| x_1 | n\rangle$

$\langle nk | x_1x_2 | kn\rangle = \langle n| x_1x_2 | k\rangle \langle k| x_1x_2 | n\rangle$

$\langle nk | x_1 | kn\rangle = \langle n| x_1 | k\rangle \langle k| x_1 | n\rangle$
\[ \langle A \mid (x_1 - x_2)^2 \mid A \rangle = \langle x^2 \rangle_n + \langle x^2 \rangle_k - 2\langle x \rangle_n \langle x \rangle_k + 2|\langle x \rangle_{nk}|^2 \]

\[ \text{this is the only difference!} \]

Or:

\[ \langle A \mid (x_1 - x_2)^2 \mid A \rangle = \langle s \mid (x_1 - x_2)^2 \mid s \rangle = 4|\langle x \rangle_{nk}|^2 > 0 \]

\[ \langle A \mid (x_1 - x_2)^2 \mid x \rangle = \langle nk \mid (x_1 - x_2)^2 \mid nk \rangle = 2|\langle x \rangle_{nk}|^2 > 0 \]

\[ \Rightarrow \text{antisymmetric states are farther apart} \]
\[ \Rightarrow \text{symmetric states are closer} \]

**EX:**

Take two spin = \( \frac{1}{2} \) fermions

\[ \Rightarrow \text{triplet } (j=1, m) \text{ spin states are symmetric } \Rightarrow \text{wave fun. is AS} \]

\[ \Rightarrow \text{singlet } : (j=0, m=0) \text{ is AS } \Rightarrow \text{wave fun. is S} \]
He has \( 2 \) electrons.

Wave function:

Symmetric states are close

\[ \Rightarrow \text{Coulomb repulsion is large} \]

\[ \Rightarrow \text{singlet combination has higher energy than triplet combination} \]

\[ \Rightarrow \text{He ground state is } j=1 \text{ triplet.} \]

\[
\Delta E = \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad \text{interaction between electrons}
\]

\[ s_{1s}, \psi_{1s,1s} \quad s_{1s}, \psi_{1s,3s} \quad \begin{array}{c} \text{spin} \\ \text{spin} \end{array} \]

\[ s_{1s}, \psi_{1s,1s} \quad s_{1s}, \psi_{1s,3s} \quad \begin{array}{c} \frac{1}{2} \quad s_{1s}, \psi_{1s,1s} \\ \frac{1}{2} \quad s_{1s}, \psi_{1s,3s} \end{array} \]

\[ s_{1s}, \psi_{1s,1s} \quad s_{1s}, \psi_{1s,3s} \quad \begin{array}{c} \text{singlet} \\ \text{triplet} \end{array} \]

\[ \text{A singlet + triplet spin has lower energy} \]

\[ \text{(of course only in excited states!)} \]