Lecture 38: Indistinguishable Particles & the Pauli Exclusion Principle

A. Introduction

- We have seen that QM places restrictions on the knowledge that can be obtained for single-particle systems.
- QM places additional restrictions, which are closely linked to spin.
- The foundations of these additional restrictions can be understood without considering spin.

- Let's first consider identical particles sharing the same space.

\[ \text{spinless} \]

\[ \Rightarrow \text{Identical: not distinguishable - e.g., electrons, protons, ...} \]

\[ \Rightarrow \text{Same space: Not physically isolated - there is some place where both particles can be found} \]

- Need a 2-particle Schrödinger Equation:

\[ \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_2^2} \right) \psi(x_1, x_2) + U(x_1, x_2) \psi(x_1, x_2) = E \psi(x_1, x_2) \]

\[ \Rightarrow E: \text{total energy of system} \]

\[ x_1, x_2: \text{position coordinates of particle 1, 2} \]

\[ \psi(x_1, x_2): \text{2-particle wave function} \]

\[ U(x_1, x_2): \text{total potential energy of 2-particle system} \]

- Let's first consider the familiar case of the infinite well
B. 2-particles in a box (without spin)

*$^*$ Use separation of variables (as usual):

$$\Psi(x_1, x_2) = \Psi_a(x_1) \Psi_b(x_2)$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi_a(x_1)}{\partial x_1^2} - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi_b(x_2)}{\partial x_2^2} + U(x_1, x_2) = E$$

*$^*$ The solution is dictated by $U(x_1, x_2)$, as usual

*$^*$ If $U(x_1, x_2)$ contains terms of mutual interaction, which would typically depend on $|x_1 - x_2|$, then separation is not possible.

*$^*$ If particles don’t interact, then only external forces act, and $U(x_1, x_2) = U_1(x_1) + U_2(x_2)$

$$\Rightarrow SE \text{ is separable if problem reduces to that of 2 independent SEs for the 2 particles, with}$$

$$E = E_a + E_b \quad \& \quad \Psi(x_1, x_2) = \Psi_a(x_1) \Psi_b(x_2)$$

$$\Updownarrow E_a = \frac{\hbar^2 \pi^2}{2m L^2} \quad \Psi_a = \sqrt{\frac{2}{L}} \sin \frac{n \pi x}{L}$$

C. Indistinguishable particles

*$^*$ Sticking with 2 particles in an infinite well, let’s consider the case of $n_1 = 4 \quad \& \quad n_2 = 3$

$$\Rightarrow \Psi(x_1, x_2) = \Psi_4(x_1) \Psi_3(x_2)$$

*$^*$ The probability density of finding particle 1 @ $x_1$ & particle 2 @ $x_2$ is $|\Psi(x_1, x_2)|^2 = |\Psi_4(x_1)|^2 |\Psi_3(x_2)|^2$

$\Rightarrow$ The probability of finding particle 1 @ $x_1 = \frac{3}{5}$:

$$P_1(\frac{3}{5}) = |\Psi_4(\frac{3}{5})|^2 \int_0^L |\Psi_3(x_2)|^2 dx_2 = \frac{1}{4} (\frac{3}{5})^2 = 0$$

$$\Rightarrow \frac{\frac{1}{2}}{\frac{3}{5}} \sin^2 \left( \frac{4\pi x}{L} \right) = 0$$

$$\Rightarrow 1 \text{ (particle 2 must be somewhere)}$$
The probability of finding particle 2 at $x_2 = \frac{L}{2}$:

$$P_2(\frac{L}{2}) = |\Psi_2(\frac{L}{2})|^2 \int_0^L |\Psi_1(x)|^2 \, dx_1 = |\Psi_2(\frac{L}{2})|^2 = \frac{L}{2} \sin^2(\frac{2\pi}{L} \frac{L}{2}) = \frac{L}{2}$$

\hspace{1cm} \text{Uh Oh! This doesn't make sense: the 2 particles are indistinguishable so how can one be forbidden from a particular region while the other is allowed to be there.}

\hspace{1cm} \text{This would violate the presumption of indistinguishability}

\hspace{1cm} \text{Thus, we have a new restriction: the probability density must be unchanged upon the exchange of the 2 particles: } x \rightarrow x_2, \ x_2 \rightarrow x

\hspace{1cm} \text{So we must modify the wavefunction } \Psi_n(x_1) \Psi_m(x_2) \text{ in such a way that it still satisfies the S.E., but also yields a probability density that is "Symmetric" relative to the exchange of particles}

\hspace{1cm} \text{There are 2 ways to do this:}

1) $\Psi_n(x_1, x_2) = \Psi_n(x_1) \Psi_m(x_2) + \Psi_m(x_1) \Psi_n(x_2) \leftarrow \text{Symmetric}$

2) $\Psi_n(x_1, x_2) = \Psi_n(x_1) \Psi_m(x_2) - \Psi_m(x_1) \Psi_n(x_2) \leftarrow \text{Antisymmetric}$

\hspace{1cm} \text{Upon exchange of particles, } x_1 \rightarrow x_2 \text{ & } x_2 \rightarrow x_1

\hspace{1cm} \Psi_n(x_1, x_2) = \Psi_n(x_1, x_2) \left\{ \begin{array}{l} |\Psi_n(x_1, x_2)|^2 = |\Psi_n(x_1, x_2)|^2 \\ |\Psi_a(x_1, x_2)|^2 = |\Psi_a(x_1, x_2)|^2 \end{array} \right.$

\hspace{1cm} \text{Both probability densities are symmetric}
I. Different ways to represent the wavefunction

Assume "n" represents the entire set of quantum numbers for a particular state:

\[ n = \{n, \ell, m_\ell, m_s\} \Rightarrow \Psi_n(x) = \Psi_{n, \ell, m_\ell, m_s}(x) = \Psi_{n, \ell, m_\ell, m_s}(1) \]

For an electron, the spin projection is either +\( \frac{1}{2} \) or -\( \frac{1}{2} \), so we can represent this as \( \uparrow \) or \( \downarrow \).

For an electron in the H atom, its spatial parts are represented by \( r, \theta, \phi \) so the representation is:

\[ \Psi_n(r, \theta, \phi) \Rightarrow \Psi_n(r, \theta, \phi, \uparrow) \]

A more compact way is to use "Ket" notation:

\[ |n, \ell, m_\ell, m_s\rangle = \Psi_{n, \ell, m_\ell, m_s}(r, \theta, \phi) \]

\[ \Rightarrow \Psi_{1,0,0,1}(r, \theta, \phi) = 100 \uparrow \]

\[ \Rightarrow \Psi_{1,0,0,1}(r, \theta, \phi)^* = \langle 100 \uparrow | \downarrow \text{ conjugate} \]

Normalization:

\[ \langle n | n \rangle = \langle n, \ell, m_\ell, m_s | n, \ell, m_\ell, m_s \rangle = 1 \]

So, symmetric + antisymmetric wavefunctions are:

\[ \Psi_S \equiv |n, \ell_1, m_{\ell_1}, m_s_1, n, \ell_2, m_{\ell_2}, m_s_2\rangle \leftarrow \text{Symmetric} \]

\[ \Psi_A \equiv |n, \ell_1, m_{\ell_1}, m_s_1, n, \ell_2, m_{\ell_2}, m_s_2\rangle - |n, \ell_2, m_{\ell_2}, m_s_2, n, \ell_1, m_{\ell_1}, m_s_1\rangle \leftarrow \text{Antisymmetric} \]

Where \( n_i = \{n_i, \ell_i, m_{\ell_i}, m_{s_i}\} \)

E. Pauli Exclusion Principle

Whether the wavefunction should be symmetric or antisymmetric depends on the spin. This can be explained only by relativistic QM, but the results are experimentally verified.
Bosons: Particles with integer spin: \( s = 0, 1, 2, \ldots \)

\[ \Rightarrow \text{Symmetric Wavefunction} \]

Fermions: Particles with half integer spin: \( s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots \)

\[ \Rightarrow \text{Antisymmetric Wavefunction} \]

\& For 2 fermions occupying states \( |n_1> \) \& \( |n_2> \), then the wavefunction must be antisymmetric: 
\[ \psi_a = |n_1> |n_2> - |n_2> |n_1> \]

(We can use the convention that the first ket always represents particle 1: \( \psi_a = |n_1> |n_2> - |n_2> |n_1> \))

\& If \( n_1 = n_2 = n \), then 
\[ \psi_a = |n> |n> - |n> |n> = 0 \]

So no two fermions can have the same set of quantum \#s

No two indistinguishable fermions may have the same set of quantum numbers in an isolated system

\& This principle was discovered by Wolfgang Pauli in 1924 and he obtained the Nobel Prize in 1945.

\& Since bosons have a symmetric wavefunction, the Pauli exclusion principle does not apply to them!

\& Identical bosons are more likely to be found close to each other compared to "spin-free" particles

\& Fermions are less likely to be found close together

\[ \Rightarrow \text{See Harris, pg 304-306} \]
An asymmetric probability density.

\[ P(x_1, x_2) = \psi_1^*(x_1, x_2) \psi_2^*(x_1, x_2) \]

\[ = \frac{1}{L^4} \sin^2 \frac{\pi x_1}{L} \sin^2 \frac{\pi x_2}{L} \]

This probability density violates the premise of indistinguishability: It is not symmetric upon reflection about the line \( x_1 = x_2 \) (no exchange symmetry).

Symmetric and antisymmetric probability densities when \( n = 3 \) and \( n = 4 \) states are occupied.

\[ P_s (x_1, x_2) = \psi_1^*(x_1, x_2) \]

\[ = \frac{1}{2} \left[ \psi_1^2(x_1, x_2) + \psi_1^2(x_2, x_1) \right] \]

\[ = \frac{1}{2} \left[ \psi_1^2(x_1, x_2) + \psi_1^2(x_2, x_1) \right] \]

\[ = \frac{1}{L} \left[ \psi_1^2(x_1, x_2) - \psi_1^2(x_2, x_1) \right] \]

\[ = \frac{1}{L} \left[ \psi_1^2(x_1, x_2) - \psi_1^2(x_2, x_1) \right] \]

\[ = \psi_1(x_1) \psi_1(x_2) \]

\[ = \psi_1(x_1) \psi_1(x_2) \]

\[ \psi_1(x) = \sin \frac{\pi x}{L}, \quad \psi_2(x) = \sin \frac{3\pi x}{L} \]

- Both \( P_s \) and \( P_a \) are symmetric about the line \( x_1 = x_2 \), so they are symmetric with respect to the exchange of particles.

- \( P_s \Rightarrow \) The probability density is largest near \( x_1 = x_2 \), so the two particles are likely to be found close together.

- \( P_a \Rightarrow \) The probability density is smallest near \( x_1 = x_2 \), so the two particles are not likely to be found close together.

- Bosons are social. Fermions are shy!!