Chapter 20
Identical Particles in Quantum Mechanics
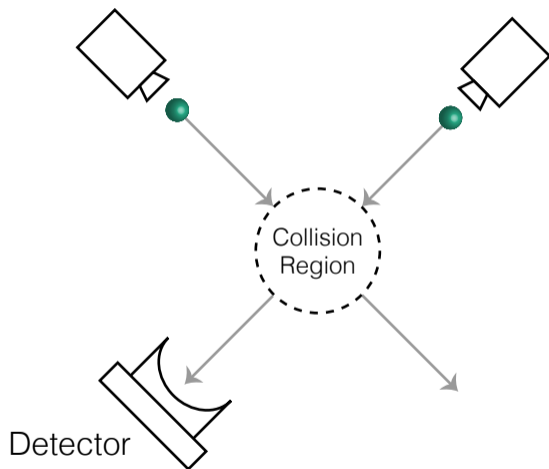
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Chem. 4300
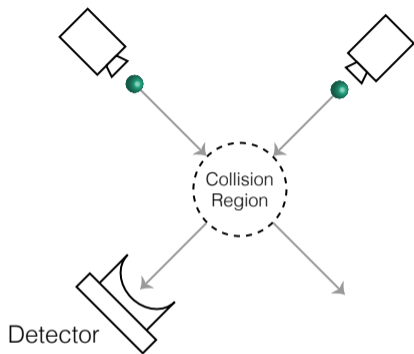
Wolfgang Pauli
1900-1958

Imagine two particles on a collision course

Imagine two particles on a collision course

- If 2 particles were bowling balls we'd have no trouble identifying path of each ball before, after, and during collision.

- Would be obvious if balls were different colors, or different masses. But even if balls were identical in every way we could still track their separate trajectories as long as we can know position and velocity simultaneously.

- But what if this was a collision between 2 electrons?

- Electrons are perfectly identical.

- Uncertainty principle says we cannot track their exact trajectories.

- We could never know which electron enters detector after collision.

- Finite extent of each e^- wave functions leads to overlapping wave functions around collision region and we can't know which wave function belongs to which e^-.

When particles are indistinguishable

QM treatment of 2 e^- system must account for indistinguishability.

Writing Hamiltonian for 2 electrons requires us to use labels,

$$\hat{\mathcal{H}}(1,2) = \frac{\vec{\hat{p}}_1^2}{2m_e} + \frac{\vec{\hat{p}}_2^2}{2m_e} + \hat{V}(\vec{r}_1, \vec{r}_2)$$

To preserve indistinguishability Hamiltonian must be invariant to particle exchange,

$$\hat{\mathcal{H}}(1,2) = \hat{\mathcal{H}}(2,1)$$

If this wasn't true then we would expect measurable differences and that puts us in violation of uncertainty principle.

We must get the same energy with particle exchange:

$$\hat{\mathcal{H}}(1,2)\Psi(\vec{x}_1, \vec{x}_2) = E\Psi(\vec{x}_1, \vec{x}_2), \quad \text{and} \quad \hat{\mathcal{H}}(2,1)\Psi(\vec{x}_2, \vec{x}_1) = E\Psi(\vec{x}_2, \vec{x}_1)$$

Define $\vec{x} = (r, \theta, \phi, \omega)$ with ω defined as spin coordinate which can only have values of α or β, that is, $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$, respectively.

When particles are indistinguishable

$\hat{\mathcal{H}}(1, 2) = \hat{\mathcal{H}}(2, 1)$ doesn't imply that $\Psi(\vec{x}_1, \vec{x}_2)$ is equal to $\Psi(\vec{x}_2, \vec{x}_1)$.

- $|\Psi(\vec{x}_1, \vec{x}_2)|^2$ is probability density for particle 1 to be at $\vec{x}_1$ when particle 2 is at $\vec{x}_2$.
- $|\Psi(\vec{x}_2, \vec{x}_1)|^2$ is probability density for particle 1 to be at $\vec{x}_2$ when particle 2 is at $\vec{x}_1$.
- These two probabilities are not necessarily the same.

But we require that probability density not depend on how we label particles.

Since $\hat{\mathcal{H}}(1, 2) = \hat{\mathcal{H}}(2, 1)$ it must hold that

$$\hat{\mathcal{H}}(1, 2)\Psi(\vec{x}_1, \vec{x}_2) = \hat{\mathcal{H}}(2, 1)\Psi(\vec{x}_1, \vec{x}_2) = E\Psi(\vec{x}_1, \vec{x}_2)$$

and likewise that

$$\hat{\mathcal{H}}(1, 2)\Psi(\vec{x}_2, \vec{x}_1) = \hat{\mathcal{H}}(2, 1)\Psi(\vec{x}_2, \vec{x}_1) = E\Psi(\vec{x}_2, \vec{x}_1)$$

Both $\Psi(\vec{x}_1, \vec{x}_2)$ and $\Psi(\vec{x}_2, \vec{x}_1)$ share same energy eigenvalue, E, so any linear combination of $\Psi(\vec{x}_1, \vec{x}_2)$ and $\Psi(\vec{x}_2, \vec{x}_1)$ will be eigenstate of $\hat{\mathcal{H}}$.

Is there a linear combination that preserves indistinguishability?

Particle Exchange Operator

Introduce new operator to carry out particle exchange.

$$\hat{\mathcal{P}}\Psi(\vec{x}_1, \vec{x}_2) = \Psi(\vec{x}_2, \vec{x}_1) \quad \text{and} \quad \hat{\mathcal{P}}\Psi(\vec{x}_2, \vec{x}_1) = \Psi(\vec{x}_1, \vec{x}_2)$$

Obviously, $\Psi(\vec{x}_1, \vec{x}_2)$ and $\Psi(\vec{x}_2, \vec{x}_1)$ are not eigenstates of $\hat{\mathcal{P}}$.

Calculating $[\hat{\mathcal{P}}, \hat{\mathcal{H}}(1, 2)]$:

$$\begin{aligned}
\left[\hat{\mathcal{P}}, \hat{\mathcal{H}}(1, 2)\right] \Psi(\vec{x}_1, \vec{x}_2) &= \hat{\mathcal{P}}\hat{\mathcal{H}}(1, 2)\Psi(\vec{x}_1, \vec{x}_2) - \hat{\mathcal{H}}(1, 2)\hat{\mathcal{P}}\Psi(\vec{x}_1, \vec{x}_2) \\
&= \hat{\mathcal{P}}E\Psi(\vec{x}_1, \vec{x}_2) - \hat{\mathcal{H}}(1, 2)\Psi(\vec{x}_2, \vec{x}_1) = E\Psi(\vec{x}_2, \vec{x}_1) - E\Psi(\vec{x}_2, \vec{x}_1) \\
&= 0,
\end{aligned}$$

Since $[\hat{\mathcal{P}}, \hat{\mathcal{H}}(1, 2)] = [\hat{\mathcal{P}}, \hat{\mathcal{H}}(2, 1)] = 0$, eigenstates of $\hat{\mathcal{H}}$ and $\hat{\mathcal{P}}$ are the same.

But $\Psi(\vec{x}_1, \vec{x}_2)$ and $\Psi(\vec{x}_2, \vec{x}_1)$ are not eigenstates of $\hat{\mathcal{P}}$.

Eigenstates of $\hat{\mathcal{P}}$ are some linear combinations of $\Psi(\vec{x}_1, \vec{x}_2)$ and $\Psi(\vec{x}_2, \vec{x}_1)$ that preserve indistinguishability.

Symmetric and Anti-Symmetric Wave functions

We can examine the eigenvalues of $\hat{\mathcal{P}}$

$$\hat{\mathcal{P}}\Phi = \lambda\Phi$$

Since $\hat{\mathcal{P}}^2 = 1$ then $\hat{\mathcal{P}}^2\Phi = \Phi$ but also $\hat{\mathcal{P}}^2\Phi = \hat{\mathcal{P}}\lambda\Phi = \lambda^2\Phi = \Phi$

Thus $\lambda^2 = 1$ and find 2 eigenvalues of $\hat{\mathcal{P}}$ to be $\lambda = \pm 1$. We can obtain these 2 eigenvalues with 2 possible linear combinations

$$\Phi_S = \frac{1}{\sqrt{2}}\left[\Psi(\vec{x}_1, \vec{x}_2) + \Psi(\vec{x}_2, \vec{x}_1)\right], \quad \lambda = +1, \quad \text{symmetric combination}$$

and

$$\Phi_A = \frac{1}{\sqrt{2}}\left[\Psi(\vec{x}_1, \vec{x}_2) - \Psi(\vec{x}_2, \vec{x}_1)\right]. \quad \lambda = -1, \quad \text{anti-symmetric combination}$$

Easy to check that $\hat{\mathcal{P}}\Phi_S = \Phi_S$ and $\hat{\mathcal{P}}\Phi_A = -\Phi_A$.

Anti-symmetric wave function changes sign when particles are exchanged.

Wouldn't that make particles distinguishable?

No, because sign change cancels when probability or any observable is calculated

$$|\hat{\mathcal{P}}\Phi_A|^2 = |-\Phi_A|^2 = |\Phi_A|^2$$

Symmetric and Anti-Symmetric Wave functions

If you follow similar procedure for 3 identical particles you find

$$\Phi_S = \frac{1}{\sqrt{6}} \left[\Psi(1,2,3) + \Psi(1,3,2) + \Psi(2,3,1) + \Psi(2,1,3) + \Psi(3,1,2) + \Psi(3,2,1) \right]$$

and

$$\Phi_A = \frac{1}{\sqrt{6}} \left[\Psi(1,2,3) - \Psi(1,3,2) + \Psi(2,3,1) - \Psi(2,1,3) + \Psi(3,1,2) - \Psi(3,2,1) \right]$$

- Wave functions for multiple indistinguishable particles must also be either symmetric or anti-symmetric with respect to exchange of particles.

- Mathematically, Schrödinger equation will not allow symmetric wave function to evolve into anti-symmetric wave function and vice versa.

- Particles can never change their symmetric or anti-symmetric behavior under exchange.

Fermions or Bosons

- Particles with half-integer spins $s = 1/2, 3/2, 5/2, \ldots$ are always found to have anti-symmetric wave functions with respect to particle exchange. These particles are classified as *fermions*.

- Particles with integer spins $s = 0, 1, 2, \ldots$ are always found to have symmetric wave functions with respect to particle exchange. These particles are classified as *bosons*.

- When you get to relativistic quantum field theory you will learn how this rule is derived.

- For now we accept this as a postulate of quantum mechanics.

Composite Particles

What about identical composite particles, such as a nucleus composed of proton and neutrons, or an atom composed of protons, neutrons, and electrons?

A composite particle consisting of

- an even number of fermions and any number of bosons is always a boson.

- an odd number of fermions and any number of bosons is always a fermion.

Thus, identical hydrogen atoms are bosons. Note, to be truly identical all hydrogens have to be in the same eigenstate (or same superposition of eigenstates). In practice you'll need ultra low temperatures to get them all in the ground state if you want them to be identical.

Composite Particles

Example

The abundance of lithium isotopes ^{7}Li and ^{6}Li are 92.41% and 7.59%, respectively. Are ^{7}Li and ^{6}Li nuclei classified as bosons or fermions?

Solution: Lithium nuclei contain 3 protons, which are spin $1/2$ particles.

- ^{7}Li nucleus additionally contains 4 neutrons, which are also spin $1/2$ particles.

- Total of 7 spin $1/2$ particles tells us that ^{7}Li nucleus is fermion.

- In contrast, ^{6}Li nucleus contains 3 neutrons.

- Total of 6 spin $1/2$ particles tells us that ^{6}Li nucleus is boson.

Homework: Classify nuclei of isotopes ^{10}B, ^{11}B, ^{12}C, ^{13}C, ^{14}N, ^{15}N, ^{16}O, and ^{17}O as boson or fermion.

Fermi Hole

Fermi Hole

Antisymmetric wave functions (fermions) go to zero if 2 particles have identical coordinates, $\vec{x}_1 = \vec{x}_2$

$$\Phi_A(\vec{x}_1, \vec{x}_1) = \frac{1}{\sqrt{2}} \left[\Psi(\vec{x}_1, \vec{x}_1) - \Psi(\vec{x}_1, \vec{x}_1) \right] = 0$$

- Recall $\vec{x} = (r, \theta, \phi, \omega)$ or $\vec{x} = (\vec{r}, \omega)$ where ω is spin state.
- Zero probability of 2 fermions having $\vec{x}_1 = \vec{x}_2$
- Identical fermions can occupy same point in space, $\vec{r}_1 = \vec{r}_2$, only if spin states are different. Otherwise, wave function goes to zero.
- Identical fermions with same spin states avoid each other.
- This avoidance is sometimes described as an *exchange force*, but technically it is not a force.
- It's just a property of indistinguishable particles with anti-symmetric wave functions, i.e., identical fermions.
- Region around each electron that is excluded to other electrons with same spin is called a *Fermi hole*.

Non-interacting Identical Particles

Non-interacting Identical Particles

For 2 non-interacting identical particles the Hamiltonian for system is sum of one particle Hamiltonians,

$$\hat{\mathcal{H}}(\vec{x}_1, \vec{x}_2) = \hat{\mathcal{H}}(\vec{x}_1) + \hat{\mathcal{H}}(\vec{x}_2)$$

Single particle Hamiltonians must have same form for particles to be identical.

Schrödinger Eq. solutions for non-interacting particles can be written

$$\boxed{\Psi_{\text{total}}(\vec{x}_1, \vec{x}_2) = \psi(\vec{x}_1)\psi(\vec{x}_2) \qquad \text{non-interacting particles}}$$

$\psi(\vec{x}_1)$ and $\psi(\vec{x}_2)$ are individual particle wave functions. *Non-interacting identical particles will be starting approximation for multi-electron atoms and molecules.*

Pauli exclusion principle

If 2 non-interacting particles are fermions, e.g., e^-, then we need to construct antisymmetric wave function,

$$\Phi_A(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \left[\psi(\vec{x}_1)\psi(\vec{x}_2) - \psi(\vec{x}_2)\psi(\vec{x}_1) \right]$$

to preserve indistinguishability of 2 electrons.

Remember! There is zero probability of 2 fermions having same coordinates, $\vec{x}_1 = \vec{x}_2$.

Non-interacting fermions have stronger constraint, aka the *Pauli exclusion principle:* two fermions cannot occupy identical wave functions, that is, same quantum states.

Slater determinant

For N identical and non-interacting fermions occupying n different quantum states, labeled as $\psi_a, \psi_b, \ldots, \psi_n$, the anti-symmetric wave function can be expressed as a determinant

$$\Phi_A(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(\vec{x}_1) & \psi_b(\vec{x}_1) & \cdots & \psi_n(\vec{x}_1) \\ \psi_a(\vec{x}_2) & \psi_b(\vec{x}_2) & \cdots & \psi_n(\vec{x}_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_a(\vec{x}_N) & \psi_b(\vec{x}_N) & \cdots & \psi_n(\vec{x}_N) \end{vmatrix}$$

also known as a *Slater determinant*.

Example

Approximate ground state wave function of 3 electrons in lithium atom ($1s^2 2s$) as non-interacting fermions using H-like spin orbitals.

Solution: Using the Slater determinant approach gives

$$\Phi_A = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\,\alpha(1) & 1s\,\beta(1) & 2s\,\alpha(1) \\ 1s\,\alpha(2) & 1s\,\beta(2) & 2s\,\alpha(2) \\ 1s\,\alpha(3) & 1s\,\beta(3) & 2s\,\alpha(3) \end{vmatrix}$$

$$\Phi_A = \frac{1}{\sqrt{3!}} \left\{ 1s\,\alpha(1) \begin{vmatrix} 1s\,\beta(2) & 2s\,\alpha(2) \\ 1s\,\beta(3) & 2s\,\alpha(3) \end{vmatrix} - 1s\,\beta(1) \begin{vmatrix} 1s\,\alpha(2) & 2s\,\alpha(2) \\ 1s\,\alpha(3) & 2s\,\alpha(3) \end{vmatrix} + 2s\,\alpha(1) \begin{vmatrix} 1s\,\alpha(2) & 1s\,\beta(2) \\ 1s\,\alpha(3) & 1s\,\beta(3) \end{vmatrix} \right\}$$

$$\Phi_A = \frac{1}{\sqrt{3!}} \left\{ 1s\,\alpha(1) \Big(1s\,\beta(2)\,2s\,\alpha(3) - 2s\,\alpha(2)\,1s\,\beta(3) \Big) - 1s\,\beta(1) \Big(1s\,\alpha(2)\,2s\,\alpha(3) - 2s\,\alpha(2)1s\,\alpha(3) \Big) \right.$$
$$\left. + 2s\,\alpha(1) \Big(1s\,\alpha(2)\,1s\,\beta(3) - 1s\,\beta(2)\,1s\,\alpha(3) \Big) \right\}$$

Slater determinant

Slater determinants enforce anti-symmetric wave functions. Any time 2 columns or rows are identical the determinant is zero.

For example, if we try to place 3 identical electrons into the 1s orbital we find

$$\Phi_A = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\,\alpha(1) & 1s\,\beta(1) & 1s\,\alpha(1) \\ 1s\,\alpha(2) & 1s\,\beta(2) & 1s\,\alpha(2) \\ 1s\,\alpha(3) & 1s\,\beta(3) & 1s\,\alpha(3) \end{vmatrix} = 0$$