Identical Particles: Pauli Exclusion Principle

Besides using direct product spaces to build up the Hilbert space for a particle moving in more than one dimension, i.e. $|\vec{r}\rangle = |x\rangle \otimes |y\rangle \otimes |z\rangle$, or including additional (non-spatial) degrees of freedom that are intrinsic properties of the particle like spin; i.e. $|\vec{r}, s, m_s\rangle = |\vec{r}\rangle \otimes |s, m_s\rangle$. We also used and will use this construction to build the Hilbert space of states for systems of more than one particle. (These are all cases of systems with many degrees of freedom).

Indeed we can consider the combined system consisting of 2-particles of mass m_1, m_2 (so they are distinguishable). Their Hilbert space of states $\mathcal{H}$ is just the direct product space of the individual particle Hilbert spaces $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$, now labelling the spaces by particle 1 or particle 2.

The coordinate basis in each space provides a direct product basis

$$|\vec{r}_1, \vec{r}_2\rangle = |\vec{r}_1\rangle \otimes |\vec{r}_2\rangle$$

As well so would any 2 sets of CSCO in the 1 particle spaces $\mathcal{H}_i$. ex. $|\vec{p}_1, \vec{p}_2\rangle = |\vec{p}_1\rangle \otimes |\vec{p}_2\rangle$

or $|\vec{r}_1, \vec{p}_2\rangle = |\vec{r}_1\rangle \otimes |\vec{p}_2\rangle$.

Hence any 2-particle state can be expanded in terms of these states

$$|\psi\rangle = \int d^3r_1\, d^3r_2 \, \langle \vec{r}_1, \vec{r}_2 | \psi \rangle \, |\vec{r}_1, \vec{r}_2\rangle$$

(all at time t)

$\langle \vec{r}_1, \vec{r}_2 | \psi \rangle = \psi(\vec{r}_1, \vec{r}_2)$ ← 2 particle wavefunction.

The state evolves in time according to Sch. Eq.

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle$$

$$\Rightarrow \quad i\hbar \frac{\partial}{\partial t} \langle \vec{r}_1, \vec{r}_2 | \psi(t) \rangle = \langle \vec{r}_1, \vec{r}_2 | H | \psi(t) \rangle$$

$$\psi(\vec{r}_1, \vec{r}_2, t)$$

Now

$$\langle \vec{r}_1, \vec{r}_2 | H | \psi(t) \rangle = \int d^3r_1' d^3r_2' \times$$

$$\times \underbrace{\langle \vec{r}_1, \vec{r}_2 | H | \vec{r}_1', \vec{r}_2' \rangle}_{\text{but } H = H(\vec{R}_1, \vec{P}_1, \vec{R}_2, \vec{P}_2)} \underbrace{\langle \vec{r}_1', \vec{r}_2' | \psi(t) \rangle}_{= \psi(\vec{r}_1', \vec{r}_2'; t)}$$

$$\Rightarrow$$

$$\langle \vec{r}_1, \vec{r}_2 | H(\vec{R}_1, \vec{P}_1, \vec{R}_2, \vec{P}_2) | \vec{r}_1', \vec{r}_2' \rangle$$

$$= H\left(\vec{r}_1, \tfrac{\hbar}{i}\vec{\nabla}_1; \vec{r}_2, \tfrac{\hbar}{i}\vec{\nabla}_2\right) \underbrace{\langle \vec{r}_1, \vec{r}_2 | \vec{r}_1', \vec{r}_2' \rangle}_{= \delta^3(\vec{r}_1 - \vec{r}_1') \times \delta^3(\vec{r}_2 - \vec{r}_2')}$$

$$\Rightarrow$$

$$\langle \vec{r}_1, \vec{r}_2 | H | \psi(t) \rangle = H\left(\vec{r}_1, \tfrac{\hbar}{i}\vec{\nabla}_1, \vec{r}_2, \tfrac{\hbar}{i}\vec{\nabla}_2\right) \times \psi(\vec{r}_1, \vec{r}_2; t)$$

& Hence

$$\boxed{i\hbar \frac{\partial}{\partial t} \psi(\vec{r}_1, \vec{r}_2; t) = H\left(\vec{r}_1, \tfrac{\hbar}{i}\vec{\nabla}_1, \vec{r}_2, \tfrac{\hbar}{i}\vec{\nabla}_2\right) \times \psi(\vec{r}_1, \vec{r}_2; t)}$$

Aside: 2 cases

1) Separable $H = H_1 + H_2$ with

$H_i = H_i(\vec{r}_i, \vec{p}_i)$ only.

$\Rightarrow$

$$\psi(\vec{r}_1, \vec{r}_2; t) = e^{-\frac{i}{\hbar} E t} \psi_E(\vec{r}_1, \vec{r}_2)$$

$\Rightarrow$

$$E\psi_E = H\psi_E = H_1\psi_E + H_2\psi_E$$

Ansatz: Separation of variables

$$\psi_E = \psi_{E_1}(\vec{r}_1) \times \psi_{E_2}(\vec{r}_2)$$

$$E = E_1 + E_2$$

This means in the abstract space that

$$|\psi(t)\rangle = |\ \rangle e^{-\frac{iE_1 t}{\hbar}} \otimes |\ \rangle e^{-\frac{i}{\hbar} E_2 t}$$

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2) Non-separable $H \neq H_1 + H_2$

a) Special case of change of coordinates ex. $H = H_{cm} + H_{rel}$, etc. ↑ i.e. $V = V(\vec{r}_1 - \vec{r}_2)$

2) b) In general it is not possible to write system as many independent 1 particle problems.

Now suppose these 2 particles were indistinguishable (they are identical — same mass, spin, electric charge etc. — no physical measurement can tell them apart — more precisely - 2 physical situations that differ by their interchange are indistinguishable) let's continue to label one particle 1 and the other particle 2.

The system wavefunction $\Psi(\vec{r}_1, \vec{r}_2)$ — or just $\Psi(1,2)$ has the interpretation that

$|\Psi(1,2)|^2$ is the prob. density that particle 1 is in the volume d^3r_1 about $\vec{r}_1$ AND particle 2 is in the volume d^3r_2 about $\vec{r}_2$.

Let P_{12} be the interchange or permutation operator so that

$$P_{12}\,\psi(1,2) = \psi(2,1) \quad . \quad P_{12}$$

interchanges all the 1 & 2 labels of the particles in the wavefunction, i.e. coordinates & spin.

If $\psi(1,2)$ is a stationary state

$$H\,\psi(1,2) = E\,\psi(1,2) \quad \text{and}$$

$H(1,2) = H(2,1)$

H is invariant under interchange of the particles, that is $[P_{12}, H] = 0$

(i.e. $P_{12}\,H(1,2)\,P_{12}$; $P_{12}^2 = 1 \Rightarrow$

$= H(2,1) = H(1,2)$ if invariant $\Rightarrow$

$P_{12} H(1,2) = H(1,2)\,P_{12}$)

So that $[H, P_{12}]\,\psi(1,2) = 0$

Hence $H\underbrace{P_{12}\psi(1,2)}_{\psi(2,1)} = P_{12}\underbrace{H\psi(1,2)}_{= E\psi(1,2)}$

Then $\boxed{H\psi(2,1) = E\,\psi(2,1)}$

Thus $\psi(1,2)$ and $\psi(2,1)$ are degenerate in energy, this is called <u>exchange degeneracy</u>. Consequently the linear combination

$$\Psi(1,2) \equiv A\psi(1,2) + B\psi(2,1)$$

is an eigenstate of H with eigenvalue E.

Now since the particles are identical, labelling them by 1 and 2 as we have done can have <u>no</u> physical consequences. Hence the probability density $|\Psi(2,1)|^2$ should be the same as $|\Psi(1,2)|^2$

$$|\Psi(1,2)|^2 = |\Psi(2,1)|^2$$

$$|A|^2|\psi(1,2)|^2 + |B|^2|\psi(2,1)|^2 + A^*B\,\psi^*(1,2)\psi(2,1) + AB^*\psi(1,2)\psi^*(2,1)$$

$$= |A|^2|\psi(2,1)|^2 + |B|^2|\psi(1,2)|^2 + A^*B\,\psi^*(2,1)\psi(1,2) + AB^*\psi(2,1)\psi^*(1,2).$$

$\Rightarrow$

1) $|A|^2 = |B|^2 \Rightarrow B = Ae^{i\varphi}$ with $\varphi \in \mathbb{R}$.

2) $A^*B = AB^* \Rightarrow \frac{A^*}{A} = \frac{B^*}{B} = \frac{A^* e^{-i\varphi}}{Ae^{+i\varphi}} = \frac{A^*}{A} e^{-2i\varphi}$

$\Rightarrow \boxed{e^{-2i\varphi} = 1}$

So $\varphi = n\pi$, $n = 0, \pm 1, \pm 2, \ldots$

So $B = Ae^{in\pi} = (-1)^n A$.

$= \begin{cases} A & , n = \text{even} \\ -A & , n = \text{odd}. \end{cases}$

Thus only 2 cases:

$$\Psi_{\pm}(1,2) = A\left[\Psi(1,2) \pm \Psi(2,1)\right]$$

with A an overall normalization constant.

New Physical Law: (consequence of relativistic q.f.t.)

+ sign in wavefunction required for 2 identical integer spin particles called Bosons — symmetric wavefunction under particle interchange

− sign in wavefunction required for 2 identical half odd integer particles called Fermions antisymmetric wavefunction under particle interchange.

This is known as the spin-statistics theorem — verified many times experimentally — i.e. periodic table of elements.

Suppose particle 1 was in a basis eigenstate $|\vec{r}_1 = \vec{a}\rangle$ or $|\alpha_1\rangle$ where $A^{(1)}|\alpha_1\rangle = \alpha_1|\alpha_1\rangle$ is CSCO

and particle 2 was in a similar basis eigenstate say $|\vec{r}_2 = \vec{b}\rangle$ or $|\alpha_2\rangle$ of $A^{(2)}$

If 2 bosons, then they are in the symmetric normalized state

$$|\vec{a},\vec{b},S\rangle = \begin{cases} \frac{1}{\sqrt{2}}\left[|\vec{a},\vec{b}\rangle + |\vec{b},\vec{a}\rangle\right] & \text{if } \vec{a}\neq\vec{b} \\ |\vec{a},\vec{a}\rangle & \text{if } \vec{a}=\vec{b} \end{cases}$$

More general symmetric state can be expanded in terms of the normalized

$$|\vec{r}_1,\vec{r}_2,S\rangle \equiv \frac{1}{\sqrt{2}}\left[|\vec{r}_1,\vec{r}_2\rangle + |\vec{r}_2,\vec{r}_1\rangle\right]$$

then

$$|\psi_S\rangle = \frac{1}{2}\int d^3r_1\, d^3r_2 \langle \vec{r}_1\vec{r}_2 S|\psi_S\rangle \, |\vec{r}_1,\vec{r}_2,S\rangle$$

$|\psi_S\rangle$ ↗ symmetric state

with the symmetric wavefunction

$$\psi_S(\vec{r}_1,\vec{r}_2) = \psi_S(\vec{r}_2,\vec{r}_1)$$

$$\equiv \langle \vec{r}_1,\vec{r}_2 S|\psi_S\rangle$$

Also, note the normalization

$$1 = \langle\psi_S|\psi_S\rangle = \int \frac{d^3r_1 d^3r_2}{2} |\psi_S(\vec{r}_1,\vec{r}_2)|^2$$

If 2 fermions, then they are in the antisymmetric normalized state

$$|\vec{a}, \vec{b}, A\rangle = \frac{1}{\sqrt{2}}\{|\vec{a}, \vec{b}\rangle - |\vec{b}, \vec{a}\rangle\}$$

Notice if the fermions are in the same state $\vec{a} = \vec{b}$ then

$$|\vec{a}, \vec{a}, A\rangle = 0 \; !$$

An antisymmetric wavefunction cannot be constructed for fermions in the same state.

This is the Pauli-Exclusion Principle

Two identical fermions cannot be in the same state.

The general anti-symmetric fermion state can be expanded in terms of

$$|\vec{r}_1, \vec{r}_2 A\rangle = \frac{1}{\sqrt{2}}\left[|\vec{r}_1, \vec{r}_2\rangle - |\vec{r}_2, \vec{r}_1\rangle\right]$$

$$|\psi_A\rangle = \frac{1}{2}\int d^3r_1 \, d^3r_2 \, \langle \vec{r}_1 \vec{r}_2, A | \psi_A\rangle |\vec{r}_1 \vec{r}_2, A\rangle$$

Now check consistency

$$\langle \vec{r}_1 \vec{r}_2 A | \psi_A \rangle = \frac{1}{2} \int d^3r_1' \, d^3r_2' \, \langle \vec{r}_1' \vec{r}_2' A | \psi_A \rangle \, \frac{1}{2} \left[\langle \vec{r}_1 \vec{r}_2 | - \langle \vec{r}_2 \vec{r}_1 | \right] \left[| \vec{r}_1' \vec{r}_2' \rangle - | \vec{r}_2' \vec{r}_1' \rangle \right]$$

$$= \frac{1}{2} \frac{1}{2} \int d^3r_1' \, d^3r_2' \, \langle \vec{r}_1' \vec{r}_2' A | \psi_A \rangle \times$$

$$\times \left[\delta^3(\vec{r}_1 - \vec{r}_1') \delta^3(\vec{r}_2 - \vec{r}_2') - \delta^3(\vec{r}_1 - \vec{r}_2') \delta^3(\vec{r}_2 - \vec{r}_1') - \delta^3(\vec{r}_2 - \vec{r}_1') \delta^3(\vec{r}_1 - \vec{r}_2') + \delta^3(\vec{r}_2 - \vec{r}_2') \delta^3(\vec{r}_1 - \vec{r}_1') \right]$$

$$= \frac{1}{4} \left\{ \langle \vec{r}_1 \vec{r}_2 A | \psi_A \rangle - \langle \vec{r}_2, \vec{r}_1 A | \psi_A \rangle - \langle \vec{r}_2 \vec{r}_1 A | \psi_A \rangle + \langle \vec{r}_2 \vec{r}_1 A | \psi_A \rangle \right\}$$

$$= \langle \vec{r}_1 \vec{r}_2 A | \psi_A \rangle \quad \checkmark$$

So define $\psi_A(\vec{r}_1, \vec{r}_2) = \langle \vec{r}_1, \vec{r}_2 | A | \psi_A \rangle$

and $1 = \langle \psi_A | \psi_A \rangle = \int \frac{d^3r_1 d^3r_2}{2} |\psi_A(\vec{r}_1, \vec{r}_2)|^2$

Now recall that spin $\frac{1}{2}$ particles have an additional degree of freedom — spin — so the basis states are

$$|\vec{r}, s, m_s\rangle = |\vec{r}\rangle \otimes |s, m_s\rangle$$
$$= |\vec{r}\rangle \otimes |\tfrac{1}{2}, \pm\tfrac{1}{2}\rangle$$

for each spin $\frac{1}{2}$ fermion. Hence the wavefunction of the fermion is a spinor

$$\psi_{m_s}(\vec{r}) = \begin{pmatrix} \psi_\uparrow(\vec{r}) \\ \psi_\downarrow(\vec{r}) \end{pmatrix}$$

For a 2 identical particles spin $\frac{1}{2}$ system then the wavefunction will be antisymmetric under the exchange of all degrees of freedom of each fermion — space & spin!

The general basis is of the form

$$|\vec{r}_1, \vec{r}_2\rangle \otimes |m_{s_1}\rangle \otimes |m_{s_2}\rangle$$

Again we can make symmetric & anti-symmetric combinations of the position & spin basis states separately

"A" singlet, "S" triplet

$|\vec{r}_1, \vec{r}_2\, A\rangle$, $|\vec{r}_1, \vec{r}_2, S\rangle$

$|m_S\, S, T\rangle \propto |m_{s_1}\rangle \pm |m_{s_2}\rangle$

Some have antisymmetric states, 2 ways

$|\vec{r}_1, \vec{r}_2\, S\rangle \otimes |\quad s=0, m=0\rangle$

$|\vec{r}_1, \vec{r}_2\, A\rangle \otimes |\, s=1, m=-1, 0, +1\rangle$

For the wavefunctions we would have

$$\psi_A(\vec{r}_1, \vec{r}_2, \underbrace{m_1, m_2}_{s=m=0}) = \psi_S(\vec{r}_1, \vec{r}_2)\, \frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 1 \\ -1 \\ 0 \end{bmatrix}$$

← anti-symmetric when interchange ↑↓

$$\psi_{1A}(\vec{r}_1, \vec{r}_2; \underbrace{m_1, m_2}_{=(1,\pm,0)}) = \psi_A^{\underbrace{m}_{=(S,M)}}(\vec{r}_1, \vec{r}_2)\, e_m$$

$$e_{\substack{+ \\ 0 \\ -}} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix}$$

← symmetric

In fact Helium is an example of such a case. The Hamiltonian is complicated but the Coulombic part is simply : $Z=2$

$$H = \left\{ -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

↖ electron Coul. repulsion.

Ignore last term — this is then 2- hydrogenic Hamiltonian.

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{n_1 l_1 m_1}(\vec{r}_1)\,\psi_{n_2 l_2 m_2}(\vec{r}_2)$$

The energy

$$E = 4(E_{n_1} + E_{n_2}) \quad (Z=2)$$

$$= -54.4\,eV\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

Groundstate $E_0 = -54.4\,eV(1+1)$

$$= -109\,eV$$

Since $\psi = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)$

is symmetric the 2 electron spin wavefunction must be antisymmetric

This is the singlet state $|0,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$

$$\longrightarrow \frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\\-1\\0\end{pmatrix}$$

$$= \frac{1}{\sqrt{2}}\left[\begin{pmatrix}1\\0\end{pmatrix}\otimes\begin{pmatrix}0\\1\end{pmatrix} - \begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}\right]$$

The spins are oppositely aligned.

(Experimentally the $E_0^{exp} = -78.975\,eV$.

The $e^- - e^-$ repulsion provides a positive contribution to raise the energy from $-109\,eV \rightarrow -79\,eV$ as we will calculate by R-S PT & Variational methods later)

The excited states are

$$\psi_{n\ell m}\,\psi_{100}$$

(if both e⁻ excited the atom decays rapidly & ionizes itself — so only consider longer lived states above)

Now we can make spatially symmetric & antisymmetric wavefunctions →

$$\psi_S = \frac{1}{\sqrt{2}}\left(\psi_{nem}(\vec{r}_1)\psi_{100}(\vec{r}_2) + \psi_{100}(\vec{r}_1)\psi_{nem}(\vec{r}_2)\right)$$

$$\psi_A = \frac{1}{\sqrt{2}}\left(\quad " \quad - \quad " \quad \right)$$

The Total spatial x spin wavefunction must be antisymmetric Since we have

$$\psi_S \cdot \frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\\-1\\0\end{pmatrix} = \text{parahelium}$$

antisymmetric spin state (Singlet)

ground state is parahelium state.

$$\psi_A \cdot \chi \begin{cases} \begin{pmatrix}1\\0\\0\\0\end{pmatrix} \\ \frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\\1\\0\end{pmatrix} \\ \begin{pmatrix}0\\0\\0\\1\end{pmatrix} \end{cases} = \text{orthohelium}$$

symmetric spin state (triplet)

Since spatial e^- closer for symmetric (para) case $\Rightarrow$ e-e repulsion energy higher

$\Rightarrow$ parahelium energy states slightly higher than ortho states, verified experimentally.

This example, as others, brings up the whole issue of how to calculate (estimate) the energy eigenvalues when we cannot solve the Schrödinger equation exactly.