

Two Particle Wavefunctions

We have been focused, so far, this course on spin states like $|+\rangle_x$, $|-\rangle_y$, etc... these are fun toy examples which allow us to see the behavior of quantum systems without getting bogged down in the math.

But, if we want to describe the natural world, we'll have to come back to atoms. If I want to describe the complete state of an electron in, say, a hydrogen atom we'll need to specify

- ① The position space wave function $\Psi(\vec{r})$ which describes how likely it is to find the e^- at a certain place.
- ② The spin state of the electron.

The full state could look something like (c.f. Griffiths problem 41.64)

$$\frac{1}{\sqrt{3}} \underbrace{\psi_{210}(r, \theta, \phi)}_{\text{position space wave functions.}} \chi_+ + \frac{\sqrt{2}}{\sqrt{3}} \underbrace{\psi_{211}(r, \theta, \phi)}_{\text{position space wave functions.}} \chi_-$$

spin states (up/down)

Be careful ... the position space wavefunctions are separate from the spin states ... this does NOT mean

$$\left(\frac{1}{\sqrt{3}} \psi_{210}(r, \theta, \phi) \right) \left(\frac{\sqrt{2}}{\sqrt{3}} \psi_{211}(r, \theta, \phi) \right) \quad \leftarrow \text{ Doesn't make sense.}$$

Some authors will write things like $|\Psi\rangle_{\text{space}} |\chi\rangle_{\text{spin}}$ and make sure to keep the kets separate.

Two Particle Wavefunctions

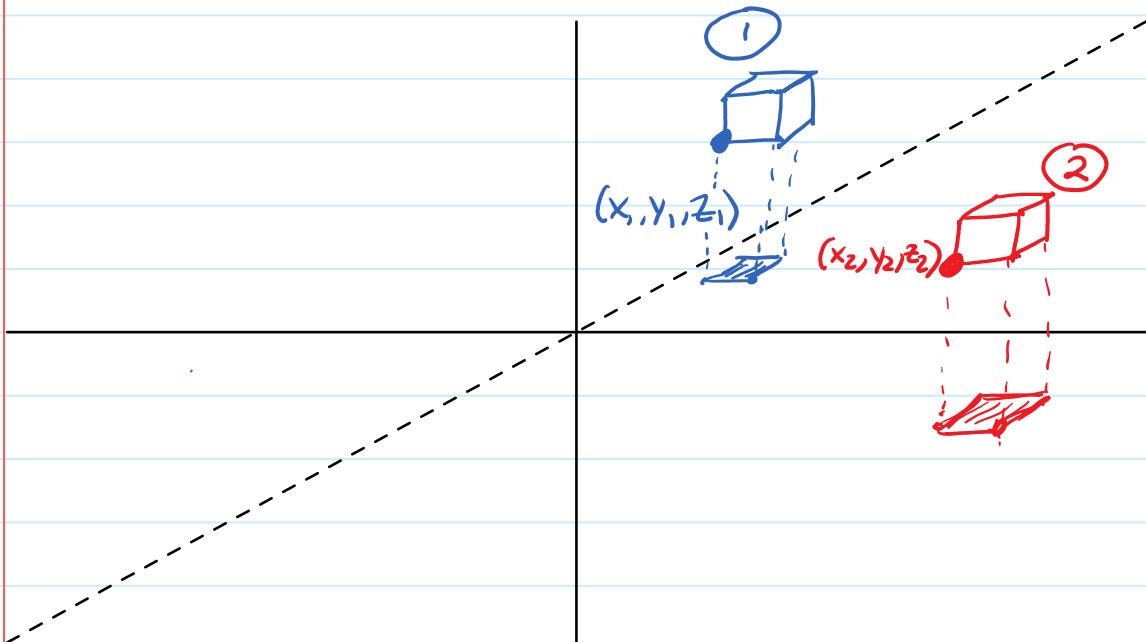
Now, if we want to have any hope of describing atoms beyond hydrogen, we need to start worrying about two particle wave functions.

[Actually, we should even do this for hydrogen ... the proton is a quantum particle, after all!].

Two particle wave functions

A system composed of two particles has its spatial (position) state described by the two-particle wave function.

$\Psi(\vec{r}_1, \vec{r}_2, t)$. The statistical interpretation is, as expected,



Probability of finding particle 1 in box ① and particle 2 in box ② is

$$P = \underbrace{\iiint_{V_1} dx_1 dy_1 dz_1}_{\text{Integrate } x_1, y_1, z_1 \text{ over volume of box 1}} \iiint_{V_2} dx_2 dy_2 dz_2 |\Psi(\vec{r}_1, \vec{r}_2, t)|^2$$

$\underbrace{V_2}_{\text{Integrate } x_2, y_2, z_2 \text{ over volume of box 2.}}$

Two Particle Wavefunctions

It gets cumbersome to write all this out, so we use the shorthand:

$$\int_{V_1, V_2} |\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d\vec{r}_1 d\vec{r}_2$$

$d\vec{r}_1 = dx_1 dy_1 dz_1$ $d\vec{r}_2 = dx_2 dy_2 dz_2$

To be normalized, $\int_{\text{all space}} |\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d\vec{r}_1 d\vec{r}_2 = 1$

This means $\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty}$

integrate over entire volume of space.

This two particle wavefunction must satisfy the Schrödinger equation.

it $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$ where \hat{H} is the Hamiltonian for both particles.

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + \underbrace{V(\vec{r}_1, \vec{r}_2, t)}_{\text{All potential energy}}$$

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$$

$$\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}$$

"Kinetic energy $\frac{\hat{p}_1^2}{2m}$ "

"Kinetic energy $\frac{\hat{p}_2^2}{2m}$ "

Separating time dependence

As you might expect, if $V(\vec{r}_1, \vec{r}_2, t)$ is independent of time, you can separate variables

Two Particle Wavefunctions

Guess $\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2) \phi(t)$ and plug in to the Schrödinger equation.

$$i\hbar [\dot{\psi} \cdot \dot{\phi}] = -\frac{\hbar^2}{2m} (\nabla_1^2 \psi) \phi - \frac{\hbar^2}{2m} (\nabla_2^2 \psi) \phi + V \cdot \psi \cdot \phi$$

divide by $\psi \cdot \phi$

$$\frac{i\hbar \dot{\phi}}{\phi} = \frac{1}{\psi} \left[-\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) \psi + V \right] = E$$

Both sides must be constant (call it "E")

$$\textcircled{1} \quad \dot{\phi}(t) = -\frac{iE}{\hbar} \phi(t) \rightarrow \phi(t) = e^{-iEt/\hbar}$$

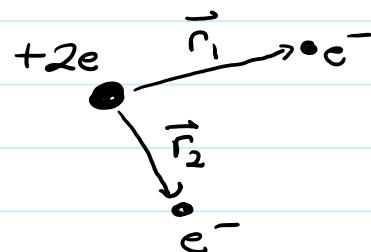
$$\textcircled{2} \quad \hat{H} \psi(\vec{r}_1, \vec{r}_2) = E \psi(\vec{r}_1, \vec{r}_2) \quad (\text{Time independent Schrödinger equation for 2 particles}).$$

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2) e^{-iEt/\hbar}$$

As we did last semester, you have to specify $V(\vec{r}_1, \vec{r}_2)$ and solve the (time independent) Schrödinger equation to determine the wave function.

Example: The Helium atom

The potential energy is :



$$V(\vec{r}_1, \vec{r}_2) = \underbrace{\frac{k(2e)(-e)}{r_1}}_{\text{PE from nucleus.}} + \underbrace{\frac{k(2e)(-e)}{r_2}}_{\text{PE from nucleus.}} + \underbrace{\frac{k(-e)(-e)}{|\vec{r}_1 - \vec{r}_2|}}_{\text{repulsion between electrons.}}$$

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The time-independent Schrödinger equation is:

$$-\frac{\hbar^2}{2m} \left[\nabla_1^2 + \nabla_2^2 \right] \psi(\vec{r}_1, \vec{r}_2) - ke^2 \left[\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|r_1 - r_2|} \right] \psi(r_1, r_2) = E \psi(r_1, r_2)$$

Try separation of variables ... always the first line of attack.

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1) \psi_b(\vec{r}_2)$$

$$-\frac{\hbar^2}{2m} \left[\psi_b \nabla_1^2 \psi_a + \psi_a \nabla_2^2 \psi_b \right] - ke^2 \left[\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|r_1 - r_2|} \right] \psi_a \psi_b = E \psi_a \psi_b$$

Divide by $\psi_a \psi_b$

$$-\frac{\hbar^2}{2m} \left[\frac{\nabla_1^2 \psi_a}{\psi_a} + \frac{\nabla_2^2 \psi_b}{\psi_b} \right] - ke^2 \left[\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|r_1 - r_2|} \right] - E = 0$$

Can we separate the \vec{r}_1 dependence from \vec{r}_2 ? The electron repulsion term (circled) makes it impossible.

If we ignore the electron-electron interaction, we can separate variables. So let's do that ... it's not ideal, but we'll take what we can get.

$$-\frac{\hbar^2}{2m} \left[\frac{\nabla_1^2 \psi_a(\vec{r}_1)}{\psi_a(\vec{r}_1)} - \frac{2ke^2}{r_1} \right] = +\frac{\hbar^2}{2m} \left[\frac{\nabla_2^2 \psi_b(\vec{r}_2)}{\psi_b(\vec{r}_2)} - \frac{2ke^2}{r_2} \right] + E$$

Both sides must be constant, call it E_a

$$-\frac{\hbar^2}{2m} \nabla_1^2 \psi_a(\vec{r}_1) + \frac{2ke^2}{r_1} \psi_a(\vec{r}_1) = E_a \psi_a(\vec{r}_1)$$

$$-\frac{\hbar^2}{2m} \nabla_2^2 \psi_b(\vec{r}_2) + \frac{2ke^2}{r_2} \psi_b(\vec{r}_2) = (E - E_a) \psi_b(\vec{r}_2)$$

Two Particle Wavefunctions

When the electrons do not interact, we've separated the Schrödinger equation into two independent equations. This will always be the case for non interacting particles.

We actually don't need to do any more work ... these are Schrödinger equations for the Hydrogen atom with one small difference:

$$e^2 \rightarrow 2e^2 \quad (\text{since the nucleus has charge } +2e).$$

So, we know the solutions:

$$\Psi_a(\vec{r}_1) = \Psi_{nem}(r_1, \theta_1, \phi_1) \quad \text{depends on "Bohr radius"} \\ \alpha_{He} = \frac{\hbar^2}{k^2 m_e \cdot (2e^2)} = \frac{1}{2} \cdot (5.3 \times 10^{-10} \text{ m})$$

$$E_a = \frac{k^2 (2e^2)^2}{2\hbar^2} \cdot \frac{1}{n^2} \\ = \frac{4 \cdot (-13.6 \text{ eV})}{n^2}$$

These 2's (highlighted) are the modification due to $H \rightarrow He$.
And, $\Psi_b(\vec{r}_2)$ is of course the same.

$$\Psi_b(\vec{r}_2) = \Psi_{n'e'm'}(r_2, \theta_2, \phi_2) \quad \text{with } E - E_a = \frac{4 \cdot (-13.6 \text{ eV})}{(n')^2}$$

And, the full wave function and energies are:

$$\Psi(\vec{r}_1, \vec{r}_2) = \Psi_a(\vec{r}_1) \Psi_b(\vec{r}_2) = \Psi_{nem}(\vec{r}_1) \Psi_{n'e'm'}(\vec{r}_2)$$

$$\text{and } E_{nn'} = 4(-13.6 \text{ eV}) \left[\frac{1}{n^2} + \frac{1}{(n')^2} \right]$$

Two Particle Wavefunctions

Ground State of Helium (neglecting $e^- - e^-$ repulsion)

$$\Psi_0(\vec{r}_1, \vec{r}_2) = \Psi_{100}(\vec{r}_1) \Psi_{100}(\vec{r}_2) \quad \text{with } a \rightarrow \frac{a}{2} = a_{He}$$

(Half the Bohr radius)

Recall for Hydrogen $\Psi_{100}^H(\vec{r}_1) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$, so for helium,

$$\Psi_{100}(\vec{r}_1) = \sqrt{\frac{2^3}{\pi a^3}} e^{-\frac{2r_1}{a}} \quad \text{and}$$

$$\Psi_0(\vec{r}_1, \vec{r}_2) = \frac{8}{\pi a^3} e^{-\frac{2r_1}{a}} e^{-\frac{2r_2}{a}} = \underline{\underline{\frac{8}{\pi a^3} e^{-\frac{2(r_1+r_2)}{a}}}}$$

And, we predict the ground state energy $E_0 = -4 \cdot 13.6 \text{ eV} \left[\frac{1}{1^2} + \frac{1}{1^2} \right]$

$$E_0 = -8 \cdot 13.6 \text{ eV} = \underline{\underline{-109 \text{ eV}}}$$

Experiments show that the actual ground state energy is -79 eV
our estimate isn't very good (30% error) ... but it's because we
neglected the $e^- - e^-$ repulsion. We'll learn how to deal with
this in time ...