

Chapter 5 Identical Particles

What is the wavefunction and Hamiltonian for 2 particles?

$$H = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\vec{r}_1, \vec{r}_2, t)$$

The Schrödinger equation is $i\hbar \frac{\partial \Psi(\vec{r}_1, \vec{r}_2, t)}{\partial t} = H \Psi(\vec{r}_1, \vec{r}_2, t)$

This is a 7 dimensional PDE $t + 6$ space dimensions

What should the normalization condition be?

$$\int |\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d^3 r_1 d^3 r_2 = 1$$

How to interpret $|\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d^3 r_1 d^3 r_2$?
 " " " $\int |\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d^3 r_1 d^3 r_2$? similar $r_1 \leftrightarrow r_2$

Example H atom $M_1 = M_p, M_2 = m_e, V = -\frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$

Whenever V is only function of $\vec{r}_1 - \vec{r}_2$ can change variables to center of mass coords.

Do the x -coord. The rest are the same.

$$x = x_1 - x_2 \quad X = \frac{x_1 M_1 + x_2 M_2}{M_1 + M_2} \quad M \equiv M_1 + M_2$$

$$x_1 = X + \frac{M_2}{M} x \quad x_2 = X - \frac{M_1}{M} x$$

$$\frac{\partial}{\partial x_i} = \frac{\partial X}{\partial x_i} \frac{\partial}{\partial X} + \frac{\partial x}{\partial x_i} \frac{\partial}{\partial x} = \frac{M_1}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial x} \quad \frac{\partial}{\partial x_2} = \frac{M_2}{M} \frac{\partial}{\partial X} - \frac{\partial}{\partial x}$$

$$\begin{aligned} \frac{1}{M_1} \frac{\partial^2}{\partial x_1^2} + \frac{1}{M_2} \frac{\partial^2}{\partial x_2^2} &= \frac{1}{M} \left(\frac{M_1^2}{M^2} \frac{\partial^2}{\partial X^2} + 2 \frac{M_1}{M} \frac{\partial^2}{\partial X \partial x} + \frac{\partial^2}{\partial x^2} \right) + \frac{1}{M_2} \left(\frac{M_2^2}{M^2} \frac{\partial^2}{\partial X^2} - 2 \frac{M_2}{M} \frac{\partial^2}{\partial X \partial x} + \frac{\partial^2}{\partial x^2} \right) \\ &= \frac{1}{M} \frac{\partial^2}{\partial X^2} + \frac{1}{M} \frac{\partial^2}{\partial x^2} \quad \frac{1}{M} = \frac{1}{M_1} + \frac{1}{M_2} \end{aligned}$$

Very important: If V only depends on \vec{r}_1, \vec{r}_2

$$H = -\frac{\hbar^2}{2m} \nabla_{\vec{R}}^2 - \frac{\hbar^2}{2\mu} \nabla_{\vec{r}}^2 + V(\vec{r}, t)$$

The wave function separates into a part with C.O.M. motion and part with relative motion.

$$\Psi(\vec{R}, \vec{r}, t) = e^{i\vec{k}\cdot\vec{R}} e^{-iE_{com}t/\hbar} \psi(\vec{r}, t)$$

$$E_{com} = \frac{\hbar^2 k^2}{2M}$$

Implication for H atom. Use the solution from Chap 4
but substitute $m_e \rightarrow \mu = m_e m_p / (m_e + m_p)$

This gives a change in energies and wave function
 $(a_0 \text{ has } m_e \text{ in it}) \sim \sqrt{1/1840}$

$$\mu = m_e / (1 + m_e/m_p) \approx m_e (1 - m_e/m_p)$$

If the two particles are identical, the Hamiltonian commutes with the exchange operator

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

$$P^2 \Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_1, \vec{r}_2) \Rightarrow P \Psi_{\pm}(\vec{r}_1, \vec{r}_2) = \pm \Psi_{\pm}(\vec{r}_2, \vec{r}_1) = \Psi(\vec{r}_2, \vec{r}_1)$$

To get a feel for how this works, look at the case where
 $V(\vec{r}_1, \vec{r}_2) = V(\vec{r}_1) + V(\vec{r}_2)$ (non interacting)

$$H^{(1)} = \frac{P^2}{2m} + V(\vec{r}) \quad H^{(1)} \Psi_{\alpha}^{(1)}(\vec{r}) = E_{\alpha}^{(1)} \Psi_{\alpha}^{(1)}(\vec{r})$$

$$\Psi_{\pm \alpha, \beta}(\vec{r}_1, \vec{r}_2) = [\Psi_{\alpha}^{(1)}(\vec{r}_1) \Psi_{\beta}^{(1)}(\vec{r}_2) \pm \Psi_{\beta}^{(1)}(\vec{r}_2) \Psi_{\alpha}^{(1)}(\vec{r}_1)] / \sqrt{2(1 + \delta_{\alpha \beta})}$$

Does the case with $\alpha = \beta$ exist?

Actually the wave function is oversimplified because most particles have spin. \hat{P} operates on all quantum numbers.

$$\begin{array}{ll} \text{Spin } 1/2, 3/2, 5/2, \dots & \text{Fermions} \rightarrow \hat{P} \Psi = -\Psi \\ \text{Spin } 0, 1, 2, 3, \dots & \text{Bosons} \rightarrow \hat{P} \Psi = \Psi \end{array}$$

Often the Hamiltonian has little dependence on spin. So Space and spin separates

Example Spin $1/2$

$$\begin{aligned} \Psi(\vec{r}_1, \vec{x}_1, \vec{r}_2, \vec{x}_2) &= \Psi_-(\vec{r}_1, \vec{r}_2) \uparrow_1 \uparrow_2 & \Psi_+(\vec{r}_1, \vec{r}_2) &= -\Psi_-(\vec{r}_2, \vec{r}_1) \\ &= \Psi_-(\vec{r}_1, \vec{r}_2) (\uparrow_1 \downarrow_2 + \downarrow_1 \uparrow_2)/\sqrt{2} & + & " \\ &= \Psi_-(\vec{r}_1, \vec{r}_2) \downarrow_1 \downarrow_2 \\ \text{or} \\ &= \Psi_+(\vec{r}_1, \vec{r}_2) (\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2)/\sqrt{2} & \Psi_+(\vec{r}_1, \vec{r}_2) &= +\Psi_-(\vec{r}_2, \vec{r}_1) \end{aligned}$$

Triplet and Singlet states.

Look at Energy levels of He. Why the pattern?

Sometimes people talk about exchange forces. Suppose only difference $\Psi_{\pm \alpha \beta}(\vec{r}_1, \vec{r}_2)$ is from exchange.

$$\left. \begin{array}{l} \Psi_{-\alpha \beta}(\vec{R} + \frac{\vec{r}_1}{2}, \vec{R} - \frac{\vec{r}_2}{2}) \rightarrow 0 \text{ as } \vec{r} \rightarrow 0 \\ \Psi_{+\alpha \beta}(\vec{R} + \frac{\vec{r}_2}{2}, \vec{R} - \frac{\vec{r}_1}{2}) \rightarrow \text{max as } \vec{r} \rightarrow 0 \end{array} \right] \text{In chemistry, } \Psi_- \text{ is anti-bonding and } \Psi_+ \text{ is bonding}$$

Pauli exclusion principle for fermions.

Look at periodic table

Solids - Pauli exclusion principle leads to the concept of Fermi energy. Accounts for the stability of solids. Also determines the final fate of stars

The Fermi energy at low T: keep adding fermions into the lowest unfilled orbital until you run out of fermions. The energy where you run out is the Fermi energy.

Show some Fermi surfaces for real solids.

Example: Spin $\frac{1}{2}$ in cube (∞ walls), noninteracting

$$E_{n_x n_y n_z}^{(1)} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, 3, \dots \text{ indep.}$$

How many states with $n_x^2 + n_y^2 + n_z^2 \leq n_{\max}^2$?

This is discrete version of finding volume $n_x, n_y, n_z > 0$ and $n_x^2 + n_y^2 + n_z^2 \leq n_{\max}^2$

$$N = 2 \cdot \frac{1}{8} \cdot \frac{4\pi}{3} n_{\max}^3 \quad \text{Error} < 2.5\% \text{ for } n_{\max} = 90$$

$$E_F = \frac{\hbar^2 \pi^2 n_{\max}^2}{2mL^2} = \frac{P_F^2}{2m} = \frac{\hbar^2 k_F^2}{2m} \quad \text{Fermi energy, momentum, wave number}$$

$$k_F = \pi n_{\max}/L = \pi \left(\frac{3N}{\pi}\right)^{1/3}/L = \left(\frac{3\pi^2 N}{V}\right)^{1/3} = (3\pi^2 \rho)^{1/3} \quad \rho = \text{number/vol.}$$

$$P_F = \hbar k_F = \hbar (3\pi^2 \rho)^{1/3} \quad \text{scales like } (N/\text{vol})^{1/3}$$

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3} \quad \text{scales like } (N/\text{vol})^{2/3}$$

How to compute the total Energy?

$$\begin{aligned} E_{\text{TOT}} &= 2 \sum_{n_x n_y n_z} \frac{\pi^2 \hbar^2 (n_x^2 + n_y^2 + n_z^2)}{2mL^2} = \frac{\hbar^2 \pi^2}{mL^2} \frac{1}{8} 4\pi \int_0^{n_{\max}} n^2 n^2 dn \\ &= \frac{\hbar^2 \pi^2}{2mL^2} n_{\max}^2 \pi \frac{n_{\max}^3}{5} = \frac{3}{5} E_F N \end{aligned}$$

$$\text{Degeneracy Pressure } dN = PdV \rightarrow dE = -\frac{2}{3} \frac{E_{\text{TOT}}}{V} dV \quad P = \frac{2}{3} \frac{E_{\text{TOT}}}{V}$$