Exercise 9 - Recap

1 Systems with Multiple Particles

1.1 Atoms

Consider an atom with Z electrons and Z protons. Then,

$$\hat{H} = \sum_{j=1}^{Z} \left(\underbrace{\left(-\frac{\hbar^2}{2m}\nabla_j^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{|\vec{r}_j|} \right)}_{\hat{H} \text{ of } j\text{-th electron in hydr. state}} + \underbrace{\frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{k=1,k\neq j}^{Z} \frac{e^2}{|\vec{r}_j - \vec{r}_k|}}_{\text{interaction between electrons}} \right).$$

The second term causes a mathematical problem: We can no longer solve the S.E. exactly. First, we neglect this term. Then electrons are each sitting in single-particle hydrogenic state. However, electrons are indistiguishable, therefore we have to consider linear combinations. By assuming there are only two particles, we get:

Spatial:

$$\psi_{\pm} = C\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right)$$

$\psi_{\pm}$ is the two particle state (spatial part of the wavefunction).

Spin:

$$\chi(s) = \begin{cases} \uparrow\uparrow & \Rightarrow \text{Triplet} \\ \downarrow\downarrow & \Rightarrow \text{Triplet} \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) & \Rightarrow \text{Triplet} \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) & \Rightarrow \text{Singlet} \end{cases}$$

The first three states are called triplet (symmetric), the last one singlet (antisymmetric).

The overall wavefunction will be the product of spatial and spin parts.

1.2 Fermions and Bosons

A fermion is a QM particle with half-integer sping, a boson is a QM particle with integer spin. Thus, electrons are fermions.
Axiom: The overall wavefunction for a multiple particle system of identical fermions must be antisymmetric with respect to exchange of any two particles. For bosons, it must be symmetric. So for an electron (fermion), the overall wavefunction is

$$\psi_+ \cdot (\text{singlet}) \quad \text{or} \quad \psi_- \cdot (\text{triplet}).$$

1.3 Exchange Operator

Define the exchange operator:

$$\hat{P}f(\vec{r}_1, \vec{r}_2) \rightarrow f(\vec{r}_2, \vec{r}_1)$$

This operator switches the position of two particles. Note that $[\hat{P}, \hat{H}] = 0$, i.e. $\hat{P}$ and $\hat{H}$ share the same eigenfunctions ψ_+ and ψ_-. The eigenvalues are ± 1.

1.4 Pauli's Exclusion Principle

There is no way to place two electrons in exactly the same state (i.e. with the same n, l, m_l, m_s) and still have an antisymmetric state.
Motivation: Assume two fermions share the same quantum numbers. Then,

$$\begin{aligned}\psi_+ &= C\left(\psi_{n,l,m_l}(\vec{r}_1)\psi_{n,l,m_l}(\vec{r}_2) + \psi_{n,l,m_l}(\vec{r}_1)\psi_{n,l,m_l}(\vec{r}_2)\right), \\ &= 2C\psi_{n,l,m_l}(\vec{r}_1)\psi_{n,l,m_l}(\vec{r}_2) \\ \psi_- &= C\left(\psi_{n,l,m_l}(\vec{r}_1)\psi_{n,l,m_l}(\vec{r}_2) - \psi_{n,l,m_l}(\vec{r}_1)\psi_{n,l,m_l}(\vec{r}_2)\right) \\ &= 0.\end{aligned}$$

In order to obtain a physical solution, we must therefore pick ψ_+. Thus, the sping must be antisymmetic(singlet) in order to have an antisymmetric wavefunction; that is

$$\chi_{m_s} = \frac{1}{2}(\uparrow\downarrow - \downarrow\uparrow).$$

With a triplet (in particular $\uparrow\uparrow$ or $\downarrow\downarrow$) the overall wavefunction cannot be antisymmetric. Therefore, the two electrons cannot share the same quantum numbers.