Two-Electron Wave Functions

Electrons are indistinguishable, so are photons and other fundamental particles. Interchanging particle **1** and **2** should give the same combined probability density $|\psi(\mathbf{1,2})|^2 = |\psi(\mathbf{2,1})|^2$ in quantum mechanics. That can be achieved in two ways by combining two single-particle wave functions $\psi_\alpha(\mathbf{1})$, $\psi_\beta(\mathbf{2})$ into a two-particle wave function $\psi(\mathbf{1,2})$:

$$\psi^S(\mathbf{1,2}) = [\, \psi_\alpha(\mathbf{1})\cdot\psi_\beta(\mathbf{2}) + \psi_\alpha(\mathbf{2})\cdot\psi_\beta(\mathbf{1}) \,] / \sqrt{2}$$
Symmetric for integer spin: Bosons, e.g. **photons, ^{4}He**

$$\psi^A(\mathbf{1,2}) = [\, \psi_\alpha(\mathbf{1})\cdot\psi_\beta(\mathbf{2}) - \psi_\alpha(\mathbf{2})\cdot\psi_\beta(\mathbf{1}) \,] / \sqrt{2}$$
Antisymmetric for half-integer spin: Fermions, e.g. **electrons**

$1\leftrightarrow2$

α, β are the quantum numbers of the two particles (for example n, l, m_l).

The **one-electron** wave functions consists of a **spatial** part and a **spin** part (quantum notes p. 17):

$$\boxed{\psi_\alpha(\mathbf{1}) = \psi_\alpha(\mathbf{r}_1) \cdot \chi_1}$$

$\chi_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \uparrow$ for $m_s = +\tfrac{1}{2}$

$\chi_1 = \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \downarrow$ for $m_s = -\tfrac{1}{2}$

In the **two-electron** wave function either the spatial or the spin part can be antisymmetric, the other is symmetric:

$$\boxed{\psi^A(\mathbf{1,2}) = \begin{cases} \psi^S(\mathbf{r}_1,\mathbf{r}_2) \cdot \chi^A(\mathbf{1,2}) \\ \psi^A(\mathbf{r}_1,\mathbf{r}_2) \cdot \chi^S(\mathbf{1,2}) \end{cases}}$$

spatial part: $\quad \psi^S(\mathbf{r}_1,\mathbf{r}_2) = [\, \psi_\alpha(\mathbf{r}_1)\cdot\psi_\beta(\mathbf{r}_2) + \psi_\alpha(\mathbf{r}_2)\cdot\psi_\beta(\mathbf{r}_1) \,] / \sqrt{2}$

$\qquad\qquad\quad \psi^A(\mathbf{r}_1,\mathbf{r}_2) = [\, \psi_\alpha(\mathbf{r}_1)\cdot\psi_\beta(\mathbf{r}_2) - \psi_\alpha(\mathbf{r}_2)\cdot\psi_\beta(\mathbf{r}_1) \,] / \sqrt{2}$

spin part: $\quad \chi^A(\mathbf{1,2}) = [\uparrow_1 \downarrow_2 - \uparrow_2 \downarrow_1] / \sqrt{2} \qquad m_s = 0 \quad S=0$, singlet

$$\chi^S(\mathbf{1,2}) = \begin{cases} \uparrow_1 \uparrow_2 & m_s = +1 \\ [\uparrow_1 \downarrow_2 + \uparrow_2 \downarrow_1] / \sqrt{2} & m_s = 0 \\ \downarrow_1 \downarrow_2 & m_s = -1 \end{cases} \quad S=1, \text{ triplet}$$

The spin part is an explicit example of angular momentum addition (quantum notes p. 18):
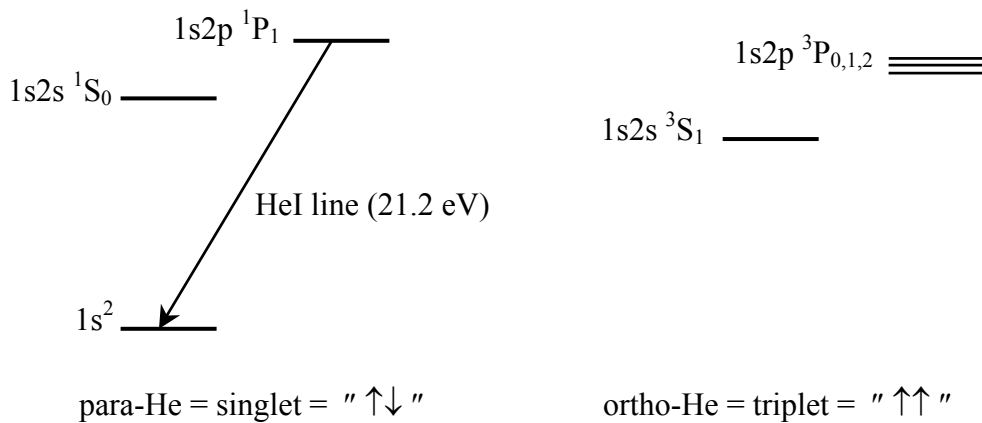
$$s_1 = \tfrac{1}{2}, \quad s_2 = \tfrac{1}{2}, \quad S = |s_1 - s_2|, \dots, s_1 + s_2 = \begin{cases} 0 & m_s = -S, \dots, +S = 0 \\ 1 & m_s = -S, \dots, +S = -1, 0, +1 \end{cases}$$

Helium

Helium, the prototype of a two-electron system, has two distinct sets of levels where the two electrons have "antiparallel" / "parallel" spins: singlet / triplet = para- / ortho-He. All optical transitions between them are dipole-forbidden by the $\Delta S{=}0$ rule (quantum notes p. 21). The ground state $1s^2$ does not exist in ortho-He ("parallel" spins) because the antisymmetric spatial wave function $\psi^A(\mathbf{r}_1,\mathbf{r}_2)$ vanishes if electrons 1 and 2 have the same quantum numbers $\alpha = \beta = 1s$. This is an example of **Pauli's exclusion principle for Fermions**, which forbids identical quantum numbers for both electrons. It is a consequence of the antisymmetric wave function.
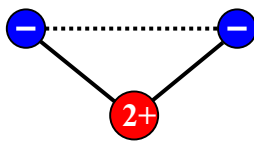
Level structure of He:

(For the terminology see quantum notes p. 20)

$$1s2p\ {}^1P_1 \quad \underline{\qquad}$$
$$1s2s\ {}^1S_0 \quad \underline{\qquad}$$
HeI line (21.2 eV)
$$1s^2 \quad \underline{\qquad}$$

$$1s2p\ {}^3P_{0,1,2} \quad \underline{\overline{\equiv}}$$
$$1s2s\ {}^3S_1 \quad \underline{\qquad}$$

para-He = singlet = ″↑↓″   ortho-He = triplet = ″↑↑″

Two-Electron Schrödinger Equation in He

$$-\hbar^2/2m_e \left[(\partial/\partial\mathbf{r}_1)^2 + (\partial/\partial\mathbf{r}_2)^2 \right] \psi^A_n(\mathbf{1,2}) \ + \ V \cdot \psi^A_n(\mathbf{1,2}) \ = \ E_n \cdot \psi^A_n(\mathbf{1,2})$$

$$V = \ -\frac{2e^2}{|\mathbf{r}_1|} \ - \frac{2e^2}{|\mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}$$

——— Attraction of each electron to the nucleus

·········· Repulsion between the two electrons

Exchange Interaction

The average (= expectation value) of the Coulomb interaction between the two electrons is obtained by taking the integral over the antisymmetric two-electron function (only the spatial part is shown):

$$\langle V_{ee} \rangle = \iint \psi^A(\mathbf{r}_1,\mathbf{r}_2)^* \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|} \psi^A(\mathbf{r}_1,\mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2$$

$$= + e^2 \iint \psi_\alpha^*(\mathbf{r}_1)\psi_\alpha(\mathbf{r}_1) \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|} \psi_\beta^*(\mathbf{r}_2)\psi_\beta(\mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2 \qquad \textbf{Coulomb} \text{ integral}$$

$$- e^2 \iint \psi_\alpha^*(\mathbf{r}_1)\psi_\alpha(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|} \psi_\beta^*(\mathbf{r}_2)\psi_\beta(\mathbf{r}_1) \, d\mathbf{r}_1 d\mathbf{r}_2 \qquad \textbf{Exchange} \text{ integral}$$

Coulomb repulsion between electrons is often reduced by **exchange attraction**, due to the minus sign in the antisymmetrized wave function. The exchange interaction is responsible for **magnetism**.

Many-Electron Wave Functions

The antisymmetrized wave function for N electrons is the Slater determinant

$$\psi(\mathbf{1}, \dots, \mathbf{N}) = (N!)^{-\frac{1}{2}} \cdot \det \begin{pmatrix} \psi_\alpha(\mathbf{1}) & \psi_\beta(\mathbf{1}) & \cdots & \psi_\zeta(\mathbf{1}) \\ \psi_\alpha(\mathbf{2}) & & & \vdots \\ \vdots & & & \vdots \\ \psi_\alpha(\mathbf{N}) & & \cdots & \psi_\zeta(\mathbf{N}) \end{pmatrix}$$

An infinite number of particles is described by quantum field theory, for example an infinite number of virtual electrons and photons by quantum electrodynamics, or a huge number of 10^{23} electrons in a solid. In that case it is often sufficient to use an effective single-electron wave function in the average potential of all other electrons and to populate the energy levels according to the average occupancy $\langle n \rangle$:

Bose-Einstein statistics (Bosons):

$$\langle n \rangle = \frac{1}{\exp[\, E/k_B T \,] - 1}$$

k_B = Boltzmann constant

Fermi-Dirac statistics (Fermions)

$$\langle n \rangle = \frac{1}{\exp[\, (E-E_F)\, /\, k_B T \,] + 1}$$

E_F = Fermi level = chemical potential