SPIN FUNCTIONS AND PAULI EXCLUSION PRINCIPLE

1. Spin is a vector quantity like angular momentum [its components have commutation relations like the angular momentum operators] except:

   (a) The spin of a single electron is fixed in magnitude

$$\sqrt{\langle s^2 \rangle} = \sqrt{s(s+1)\hbar^2} = \sqrt{\frac{3}{4}}\hbar \Rightarrow s = \frac{1}{2}$$

   (b) The spin can have only one of two directions

$$\hat{S}_z \Gamma(\sigma_1) = \pm \frac{\hbar}{2} \Gamma(\sigma_1)$$

2. Wavefunctions for spin:

   (a) Coordinate σ is discrete (only +1/2 or –1/2)

Γ (σ) — can be only one of two eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$

↗ spin function ↑ variable

$$\alpha(\sigma) = \delta_{\sigma,1/2}$$

$$\beta(\sigma) = \delta_{\sigma,-1/2}$$

$$\hat{S}^2 \alpha(\sigma) = s(s+1)\hbar^2 \alpha(\sigma) = 1/2(1/2+1)\hbar^2 \alpha(\sigma)$$

$$\hat{S}^2 \beta(\sigma) = s(s+1)\hbar^2 \beta(\sigma) = 1/2(1/2+1)\hbar^2 \beta(\sigma)$$

$$\hat{S}_z \alpha(\sigma) = \frac{\hbar}{2} \alpha(\sigma)$$

$$\hat{S}_z \beta(\sigma) = -\frac{\hbar}{2} \beta(\sigma)$$

3. We integrate over continuous variables (like r, x, y, z), e.g., orthogonality

$$\int \psi_i^*(r) \psi_j(r) d\tau = \delta_{ij}$$

but for discrete variable σ, we sum over the possible coordinate values:

$$"\int \alpha(\sigma)\beta(\sigma)\ d\sigma" = \sum_{\sigma=1/2,-1/2} \alpha(\sigma)\beta(\sigma) = \underbrace{\alpha(1/2)\beta(1/2)}_{1\ \cdot\ 0} + \underbrace{\alpha(-1/2)\beta(-1/2)}_{0\ \cdot\ 1} = \mathbf{0}\quad = 0$$

or

$$"\int \alpha(\sigma)\alpha(\sigma)\ d\sigma" = \sum_{\sigma=1/2,-1/2} \alpha(\sigma)\alpha(\sigma) = \underbrace{\alpha(1/2)\alpha(1/2)}_{1\ \cdot\ 1} + \underbrace{\alpha(-1/2)\alpha(-1/2)}_{0\ \cdot\ 0} = \mathbf{1}\quad = 1$$

Thus $\alpha(\sigma)$ and $\beta(\sigma)$ are *orthonormal* functions of the discrete variable σ.

PAULI EXCLUSION PRINCIPLE

1. Electrons are indistinguishable (as also are other identical particles) and thus the wavefunction must change by a phase factor (+ or – for real wavefunctions) under the exchange of the coordinates of two electrons

$$(x_1, y_1, z_1, \sigma_1) \leftrightarrow (x_2, y_2, z_2, \sigma_2)$$

2. A wavefunction for a system of two or more electrons must be *antisymmetric* (change sign) under the interchange of the space and spin coordinates of any pair of electrons.