Pauli Exclusion Principle

Ground State of He:

$\Psi_{He}(1,2) = \Psi_{1s}(1)\ \Psi_{1s}(2)$ *spin part

$\Psi_{He}(1,2) = \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2)]$

Indistinguishable from: $\Psi_{He}(1,2) = \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\beta(1)\ \alpha(2)]$

Take linear combinations with equal weight:

$\Psi_s = {}^1/\sqrt{2}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) + \beta(1)\ \alpha(2)]$

$\Psi_a = {}^1/\sqrt{2}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)]$

Exchange labels $\rightarrow \Psi^2$ stays the same, but:

$\Psi_s \rightarrow \Psi_s$

$\Psi_a \rightarrow \quad {}^1/\sqrt{2}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(2)\ \beta(1) - \beta(2)\ \alpha(1)]$

$\qquad = - {}^1/\sqrt{2}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)]$

$\Psi_a \rightarrow - \Psi_a$

$\Psi_s = {}^1/\sqrt{2}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) + \beta(1)\ \alpha(2)]$

$\Psi_a = {}^1/\sqrt{2}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)]$

$\qquad$ SPATIAL PART * SPIN PART

$\qquad\quad$ symmetric $\qquad$ antisymmetric

Pauli Exclusion Principle: The wavefunction is overall antisymmetric with respect to exchange of spin labels.

Guaranteeing Antisymmetry: Determinantal Wavefunctions:

$\Psi_a = {}^1/\sqrt{2}\ \begin{vmatrix} \Psi_{1s}(1)\alpha(1) & \Psi_{1s}(1)\beta(1) \\ \Psi_{1s}(2)\alpha(2) & \Psi_{1s}(2)\beta(2) \end{vmatrix}$ rows: different electrons
columns: different wavefunctions

He Excited State: $1s^1 2s^1$ $\qquad$ $1s\boxed{\uparrow}\ 2s\boxed{\downarrow}$ $\qquad$ or $\ 1s\boxed{\uparrow}\ 2s\boxed{\uparrow}$

$\Psi^{ex}_{He}(1,2) = \Psi_{1s}(1)\ \Psi_{2s}(2) \Rightarrow \Psi^{ex}_{He}(1,2) = {}^1/\sqrt{2}\ (\Psi_{1s}(1)\ \Psi_{2s}(2) \pm \Psi_{1s}(2)\ \Psi_{2s}(1))$

SPIN PARTS $\qquad \alpha(1)\alpha(2)$ $\qquad\qquad\qquad$ $\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)$

$\qquad\qquad\qquad \beta(1)\beta(2)$

$\qquad\qquad \alpha(1)\ \beta(2) + \beta(1)\ \alpha(2)$

${}^1\Psi^{ex} = {}^1/\sqrt{2}\ (\Psi_{1s}(1)\ \Psi_{2s}(2) + \Psi_{1s}(2)\ \Psi_{2s}(1))\ [\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)]$ $\qquad$ singlet

$\qquad\qquad\quad$ SPATIAL PART $\qquad\qquad$ SPIN PART

$$^3\Psi^{ex} = \frac{1}{\sqrt{2}} (\Psi_{1s}(1)\,\Psi_{2s}(2) - \Psi_{1s}(2)\,\Psi_{2s}(1)) \begin{bmatrix} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \end{bmatrix} \text{ triplet}$$

$$\text{Li:}1s^2\,2s^1: 1s\,\boxed{\uparrow\downarrow}\,2s\,\boxed{\uparrow} \qquad \Psi_a = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

For N electrons, normalization $= \frac{1}{\sqrt{N!}}$

Doublet: H atom: $\quad 1s(1) \begin{bmatrix} \alpha(1) \\ \beta(1) \end{bmatrix}$

$S = (\Sigma\, m_s)_{max}$ $\qquad$ total spin quantum number

Spin Multiplicity: $g_S = (2S + 1)$

electronic structure calculation programs list instead:

$$\langle \hat{S}^2 \rangle = \langle S^2 \rangle = \langle S*S \rangle = S(S+1)\hbar^2$$

Spin State	Example[*]	S	Multiplicity	$\langle S*S \rangle / \hbar^2$
↑↓ spin paired	Most molecules	0	1	0
↑	H, Li, B, F, Na, Cu(II) organic radicals	½	2	0.75
↑↑	C, O, Si, S, Ni(II), O_2, excited triplet states	1	3	2.0
↑↑↑	N, P, As, V, V(II), Cr(III), Co, Co(II)	1½	4	3.75
↑↑↑↑	Cr, Cr(II), Mn(III), Fe, Fe(II), Co(III), B_2	2	5	6.0
↑↑↑↑↑	Mn, Mn(II), Fe(III),	2½	6	8.75

* Atomic examples are for ground states.

Deviation from these <S*S> values in molecular orbital calculations shows that some excited state character (of higher multiplicity) is being mixed into the desired state. This error is called spin contamination. More complete atomic basis sets or better-optimized geometries often correct this problem.[1]

References:
1. W. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, <u>Ab Initio Molecular Orbital Theory</u>, Wiley, New York, NY, 1986.