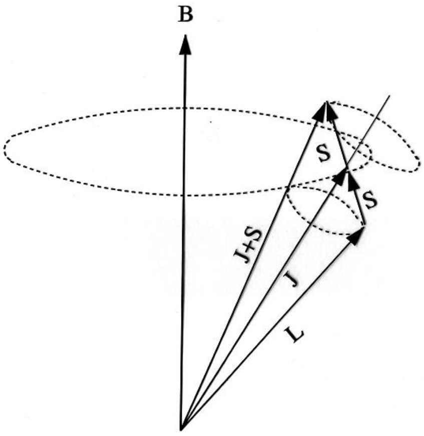
1. **Landé g-factor**

On the basis of Hund's rules, we know S, L, and J. For a given J, there is still $2J+1$ degeneracy, which will be broken by the magnetic field

$$\Delta E_n = \mu_B \mathbf{H} \cdot \langle n|\mathbf{L} + g_e\mathbf{S}|n\rangle + \sum_{n' \neq n} \frac{|\langle n|\mu_B \mathbf{H} \cdot (\mathbf{L} + g_e\mathbf{S})|n'\rangle|^2}{E_n - E_n'} \tag{1}$$



Magnitude and direction of **J** is conserved, the magnitudes of **L** and **S** are conserved, but not their directions (see figure). We need to evaluate

$$\langle JLSJ_z|\hat{L} + g_e\hat{S}|JLSJ_z'\rangle \tag{2}$$

where $g_e \approx 2$ is the electron gyromagnetic ratio. Wickner-Eckart theorem states that

$$\langle JLSJ_z|\hat{L} + 2\hat{S}|JLSJ_z'\rangle = g(JLS)\langle JLSJ_z|\hat{J}|JLSJ_z'\rangle \tag{3}$$

where $g(JLS)$ is the Landé g-factor. To calculate it, we write it more generally as

$$\langle JLSJ_z|\hat{L} + 2\hat{S}|J'L'S'J_z'\rangle = g(JLS)\langle JLSJ_z|\hat{J}|J'L'S'J_z'\rangle \tag{4}$$

where both matrix elements vanish unless $J = J'$, $L = L'$, and $S = S'$. We multiply both sides by $\langle J'L'S'J_z'|\hat{J}|J''L''S''J_z''\rangle$ and sum over all primed states

$$\sum_{J'L'S'J_z'} \langle JLSJ_z|\hat{L} + 2\hat{S}|J'L'S'J_z'\rangle \cdot \langle J'L'S'J_z'|\hat{J}|J''L''S''J_z''\rangle \tag{5}$$

$$= g(JLS) \sum_{J'L'S'J_z'} \langle JLSJ_z|\hat{J}|J'L'S'J_z'\rangle \cdot \langle J'L'S'J_z'|\hat{J}|J''L''S''J_z''\rangle \tag{6}$$

Since the sum is over complete set of states, we can use completeness relation $\sum_\alpha |\alpha\rangle\langle\alpha| = \mathbf{1}$ and obtain

$$\langle JLSJ_z|(\hat{L} + 2\hat{S}) \cdot \hat{J}|JLSJ_z'\rangle = g(JLS)\langle JLSJ_z|\hat{J}^2|JLSJ_z'\rangle \tag{7}$$

which we can evaluate since

$$\hat{S}^2 = (\hat{J} - \hat{L})^2 = \hat{J}^2 + \hat{L}^2 - 2\hat{L} \cdot \hat{J} \tag{8}$$

$$\hat{L}^2 = (\hat{J} - \hat{S})^2 = \hat{J}^2 + \hat{S}^2 - 2\hat{S} \cdot \hat{J} \tag{9}$$

and

$$\langle JLSJ_z|\hat{J}^2|JLSJ_z\rangle = J(J+1) \tag{10}$$
$$\langle JLSJ_z|\hat{L}^2|JLSJ_z\rangle = L(L+1) \tag{11}$$
$$\langle JLSJ_z|\hat{S}^2|JLSJ_z\rangle = S(S+1). \tag{12}$$

We get

$$g(JLS)J(J+1) = \langle JLSJ_z|\hat{L}\cdot\hat{J}|JLSJ_z\rangle - 2\langle JLSJ_z|\hat{S}\cdot\hat{J}|JLSJ_z\rangle \tag{13}$$
$$= \frac{1}{2}[J(J+1) + L(L+1) - S(S+1)] + [J(J+1) + S(S+1) - L(L+1)] \tag{14}$$

which finally yields

$$g(JLS) = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{15}$$

2. **Total angular momentum**

(a) Commutation relations for the orbital and spin angular momenta

$$\mathbf{L} \times \mathbf{L} = i\mathbf{L} \Leftrightarrow [L_i, L_j] = i \sum_k \varepsilon_{ijk} L_k, \tag{16}$$

$$\mathbf{S} \times \mathbf{S} = i\mathbf{S} \Leftrightarrow [S_i, S_j] = i \sum_k \varepsilon_{ijk} S_k, \tag{17}$$

$$[L_i, S_j] = 0 \tag{18}$$

Here, we have used the Levi-Civita symbol in writing cross producs. Levi-Civita symbol ε_{ijk} is defined as

$$\varepsilon_{ijk} = \begin{cases} +1 & \text{if } (i,j,k) \text{ is } (x,y,z), (y,z,x) \text{ or } (z,x,y), \\ -1 & \text{if } (i,j,k) \text{ is } (z,y,x), (x,z,y) \text{ or } (y,x,z), \\ 0 & \text{if } x = y \text{ or } y = z \text{ or } z = x \end{cases} \tag{19}$$

With these, the ith component of cross product is $(\mathbf{a} \times \mathbf{b})_i = \sum_{j=1}^{3} \sum_{k=1}^{3} \varepsilon_{ijk} a^j b^k$ or simply $(\mathbf{a} \times \mathbf{b})_i = \varepsilon_{ijk} a^j b^k$ in Einstein notation (implied summation).
Using the last commutation relation we can show

$$\begin{aligned} [\mathbf{L}, \mathbf{S}] &= [L_x \hat{\mathbf{e}}_x + L_y \hat{\mathbf{e}}_y + L_z \hat{\mathbf{e}}_z, S_x \hat{\mathbf{e}}_x + S_y \hat{\mathbf{e}}_y + S_z \hat{\mathbf{e}}_z] \\ &= [L_x, S_x] + [L_y, S_y] + [L_z, S_z] = 0. \end{aligned} \tag{20}$$

Then $(\mathbf{J} = \mathbf{L} + \mathbf{S})$,

$$[\mathbf{L} + g_0\mathbf{S}, \hat{\mathbf{n}} \cdot \mathbf{J}] = [\mathbf{L}, \hat{\mathbf{n}} \cdot \mathbf{L}] + \underbrace{[\mathbf{L}, \hat{\mathbf{n}} \cdot \mathbf{S}]}_{=0} + g_0 \underbrace{[\mathbf{S}, \hat{\mathbf{n}} \cdot \mathbf{L}]}_{=0} + g_0 [\mathbf{S}, \hat{\mathbf{n}} \cdot \mathbf{S}] \tag{21}$$

Consider the ith component of the commutator (and $\hat{\mathbf{n}} \cdot \mathbf{J} = n_j J_j$ with implicit summation over j):

$$\begin{aligned} ([\mathbf{L} + g_0\mathbf{S}, \hat{\mathbf{n}} \cdot \mathbf{J}])_i &= [L_i, n_j L_j] + g_0[S_i, n_j S_j] = n_j [L_i, L_j] + g_0 n_j [S_i, S_j] \\ &= n_j i \sum_k \varepsilon_{ijk} L_k + g_0 n_j i \sum_k \varepsilon_{ijk} S_k = i \sum_k \varepsilon_{ijk} n_j (L_k + g_0 S_k) \end{aligned}$$

and finally writing explicitly the implicit sum over j:

$$i \sum_{jk} \varepsilon_{ijk} n_j (L_k + g_0 S_k) = i(\hat{\mathbf{n}} \times (\mathbf{L} + g_0 \mathbf{S}))_i \tag{22}$$

Alternatively, through explicit calculation:

$$[\mathbf{L}, \hat{n} \cdot \mathbf{L}] = L_x \hat{\mathbf{e}}_x (n_x L_x + n_y L_y + n_z L_z) - (n_x L_x + n_y L_y + n_z L_z) L_x \hat{\mathbf{e}}_x + \dots \tag{23}$$

$$= ((L_x L_y - L_y L_x) n_y + (L_x L_z - L_z L_x) n_z) \,\hat{\mathbf{e}}_x + \dots \tag{24}$$

$$= ([L_x, L_y] n_y + [L_x, L_z] n_z) \,\hat{\mathbf{e}}_x + \dots \tag{25}$$

$$= i(L_z n_y + L_y n_z) \hat{\mathbf{e}}_x + \dots \tag{26}$$

with y and z components omitted for brevity. The last line can be identified as the x-component of a cross product

$$i\hat{\mathbf{n}} \times \mathbf{L} = i \begin{pmatrix} \hat{\mathbf{e}}_x & \hat{\mathbf{e}}_x & \hat{\mathbf{e}}_x \\ n_x & n_y & n_z \\ L_x & L_y & L_z \end{pmatrix}. \tag{27}$$

After similar treatment for the $g_0[\mathbf{S}, \hat{\mathbf{n}} \cdot \mathbf{S}]$ term, the final result is obtained.

(b) A state $|0\rangle$ with zero total angular momentum satisfies.

$$J_x|0\rangle = J_y|0\rangle = J_z|0\rangle = 0 \tag{28}$$

Rewrite the expectation value of the commutator from (a)

$$\begin{aligned}\langle 0|([\mathbf{L} + g_0\mathbf{S}, \hat{\mathbf{n}} \cdot \mathbf{J})_i]|0\rangle &= \langle 0|i\varepsilon_{ijk} n_j (L_k + g_0 S_k)|0\rangle \\ &= i\varepsilon_{ijk} n_j \langle 0|(L_k + g_0 S_k)|0\rangle \\ &= i(\hat{\mathbf{n}} \times \langle 0|(\mathbf{L} + g_0\mathbf{S}_k)|0\rangle)_i. \end{aligned} \tag{29}$$

So,

$$\langle 0|[\mathbf{L} + g_0\mathbf{S}, \hat{\mathbf{n}} \cdot \mathbf{J}]|0\rangle = i\hat{\mathbf{n}} \times \langle 0|(\mathbf{L} + g_0\mathbf{S}_k)|0\rangle. \tag{30}$$

Since $J_i|0\rangle = 0$ and J_i is hermitian, also $\langle 0|J_i = 0$ applies. Therefore, after opening the commutator, we get

$$\langle 0|[\mathbf{L} + g_0\mathbf{S}, \hat{\mathbf{n}} \cdot \mathbf{J}]|0\rangle = \langle 0|(\mathbf{L} + g_0\mathbf{S}) n_j J_j|0\rangle - \langle 0|n_j J_j (\mathbf{L} + g_0\mathbf{S})|0\rangle \tag{31}$$

$$= 0 \tag{32}$$

$$= i\hat{\mathbf{n}} \times \langle 0|(\mathbf{L} + g_0\mathbf{S}_k)|0\rangle, \ \forall \hat{\mathbf{n}}. \tag{33}$$

Therefore, also

$$\langle 0|(\mathbf{L} + g_0\mathbf{S}_k)|0\rangle = 0. \tag{34}$$

Alternatively, on the basis of Wickner-Eckart theorem

$$\langle 0|(\mathbf{L} + g_0\mathbf{S}_k)|0\rangle = g(JLS)\langle 0|\mathbf{J}|0\rangle = 0. \tag{35}$$

3. **Proof that the Two-Electron Ground State of a Spin-Independent Hamiltonian is Singlet**

(a) Energy of a two-electron system:

$$E[\psi] = \int d\vec{r_1} d\vec{r_2} \left\{ \frac{\hbar^2}{2m} \left[|\vec{\nabla}_1 \psi|^2 + |\vec{\nabla}_2 \psi|^2 \right] + V(\vec{r_1}, \vec{r_2}) |\psi|^2 \right\}, \tag{36}$$

where ψ is a universal spin-independent wavefunction. The common formula for energy expectation value can be obtained through integration by parts. Consider the kinetic energy

$$\int d\vec{r_1} |\vec{\nabla}_1 \psi|^2 = \int d\vec{r_1} (\vec{\nabla}_1 \psi) \cdot (\vec{\nabla}_1 \psi)^* \tag{37}$$

For the x-component

$$\int dx \left(\frac{\partial}{\partial x} \psi \right) \left(\frac{\partial}{\partial x} \psi^* \right) = \left(\frac{\partial}{\partial x} \psi \right) (\psi^*) \Bigg|_{-\infty}^{\infty} - \int dx \left(\frac{\partial}{\partial x^2} \psi \right) \psi^* \tag{38}$$

The first term on the right vanishes under the assumption that $\psi(x \to \infty) = 0$ (and that ψ is normalized $\int d\vec{r_1} d\vec{r_2} \psi^* \psi = 1$), and consequently $\frac{\partial}{\partial x} \psi(x \to \infty) = 0$. Other components are handled similarly (plus the trivial potential term) to yield:

$$E = \int d\vec{r_1} d\vec{r_2} \left\{ \psi^* \left[-\frac{\hbar^2}{2m} \vec{\nabla}_1^2 \psi - \frac{\hbar^2}{2m} \vec{\nabla}_2^2 \psi + V(\vec{r_1}, \vec{r_2}) \psi \right] \right\} = \int d\vec{r_1} d\vec{r_2} \psi^* H \psi. \tag{39}$$

Alternatively, one could have used Green's identity: $\int_U \left(\psi^* \nabla^2 \psi + \nabla \psi \cdot \nabla \psi^* \right) dV = \oint_{\partial U} \psi^* \left(\nabla \psi \cdot \mathbf{n} \right) dS$, where ∂U is boundary of the integration volume U. Due to the boundary condition for ψ right hand side is zero.

This way we proved that E is indeed an expectation value of given Hamiltonian. In other words, according to the variational principle, minimizing the energy functional with respect to the wave function yields the ground state energy:

$$E_g = \min_{\{\psi\}} E \tag{40}$$

If the space part is symmetric, according to Pauli exclusion principles the spin part has to be antisymmetric and there is only one such combination $1/\sqrt{2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$, for which $S = 0$, and the ground state is singlet. The energy is $E = E_s$. If the space part is antisymmetric, the spin part is symmetric with three possible combinations, $|\uparrow\uparrow\rangle$, $1/\sqrt{2}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$, and $|\downarrow\downarrow\rangle$, all having $S = 1$. Then the ground state is triplet with $E = E_t$.

(b) Assuming that ψ is real, we realize that

$$\int |\nabla \psi|^2 = \int (\nabla \psi) \cdot (\nabla \psi^*) = \int (\nabla \psi) \cdot (\nabla \psi) \tag{41}$$

$$= \int (\nabla \pm \psi) \cdot (\nabla \pm \psi) = \int (\nabla |\psi|) \cdot (\nabla |\psi|) = \int |\nabla |\psi||^2 \tag{42}$$

(consider here "$\pm$" to be point-wise either plus or minus). Thus, for spatially antisymmetric real wave functions, the energy can be obtained from the same energy functional as for the spatially symmetric case, i.e., $E[\psi] = E[|\psi|]$. However, since we know that the energy is minimized by the symmetric wave function ψ_s at energy E_s, we may conclude that the energy E_t for the antisymmetric ground state ψ_t must be higher (or equal when the two electrons do not interact).