

10.2: Electron Spin Angular Momentum

Individual electrons possess intrinsic spin characterized by angular momentum quantum numbers s and m_s ; for electrons, $s = 1/2$ and $m_s = 1/2$, or $-1/2$. The $m_s = 1/2$ spin state of the electron is represented by the symbol α and the $m_s = -1/2$ state is represented by β . These spin functions obey:

$$S^2\alpha = \frac{1}{2}\left(\frac{1}{2} + 1\right)\hbar^2\alpha,$$

$$S_z\alpha = \frac{1}{2}\hbar\alpha$$

$$S^2\beta = \frac{1}{2}\left(\frac{1}{2} + 1\right)\hbar^2\beta$$

and

$$S_z\beta = -\frac{1}{2}\hbar\beta.$$

The α (and β) spin functions are connected via lowering S_- and raising S_+ operators, which are defined in terms of the x and y components of S as follows:

$$S_+ = S_x + iS_y$$

and

$$S_- = S_x - iS_y.$$

In particular $S_+\beta = \hbar\alpha$, $S_+\alpha = 0$, $S_-\alpha = \hbar\beta$, and $S_-\beta = 0$. These expressions are examples of the more general relations (these relations are developed in detail in Appendix G) which all angular momentum operators and their eigenstates obey:

$$J^2|j, m\rangle = j(j+1)\hbar^2|j, m\rangle$$

$$J_z|j, m\rangle = m\hbar|j, m\rangle$$

$$J_+|j, m\rangle = \hbar\sqrt{j(j+1) - m(m+1)}|j, m+1\rangle$$

and

$$J_-|j, m\rangle = \hbar\sqrt{j(j+1) - m(m-1)}|j, m-1\rangle$$

In a many-electron system, one must combine the spin functions of the individual electrons to generate eigenfunctions of the total $S_z = \sum_i S_z(i)$ (expressions for $S_x = \sum_i S_x(i)$ and $S_y = \sum_i S_y(i)$ also follow from the fact that the total angular momentum of a collection of particles is the sum of the angular momenta, component-by-component, of the individual angular momenta) and total S^2 operators because only these operators commute with the full Hamiltonian, H, and with the permutation operators P_{ij} . No longer are the individual $S^2(i)$ and $S_z(i)$ good quantum numbers; these operators do not commute with P_{ij} .

Spin states which are eigenfunctions of the total S^2 and S_z can be formed by using angular momentum coupling methods or the explicit construction methods detailed in Appendix (G). In the latter approach, one forms, consistent with the given electronic configuration, the spin state having maximum S_z eigenvalue (which is easy to identify as shown below and which corresponds to a state with S equal to this maximum S_z eigenvalue) and then generating states of lower S_z values and lower S values using the angular momentum raising and lowering operators

$$S_- = \sum_i S_-(i) \text{ and } S_+ = \sum_i S_+(i).$$

To illustrate, consider a three-electron example with the configuration $1s2s3s$. Starting with the determinant $|1s\alpha 2s\alpha 3s\alpha|$, which has the maximum $M_s = \frac{3}{2}$ and hence has $S = \frac{3}{2}$ (this function is denoted $|\frac{3}{2}, \frac{3}{2}\rangle$), apply S_- in the additive form $S_- = \sum_i S_-(i)$ to generate the following combination of three determinants:

$$\hbar [|1s\beta 2s\alpha 3s\alpha| + |1s\alpha 2s\beta 3s\alpha| + |1s\alpha 2s\alpha 3s\beta|],$$

which, according to the above identities, must equal

$$\hbar \sqrt{\frac{3}{2} \left(\frac{3}{2} + 1 \right) - \frac{3}{2} \left(\frac{3}{2} - 1 \right)} \left| \frac{3}{2}, \frac{1}{2} \right\rangle.$$

So the state $\left| \frac{3}{2}, \frac{1}{2} \right\rangle$ with $S = \frac{3}{2}$ and $M_s = \frac{1}{2}$ can be solved for in terms of the three determinants to give

$$\left| \frac{3}{2}, \frac{1}{2} \right\rangle = \frac{1}{\sqrt{3}} [|1s\beta 2s\alpha 3s\alpha| + |1s\alpha 2s\beta 3s\alpha| + |1s\alpha 2s\alpha 3s\beta|].$$

The states with $S = \frac{3}{2}$ and $M_s = \frac{-1}{2}$ and $\frac{-3}{2}$ can be obtained by further application of S_- to $\left| \frac{3}{2}, \frac{1}{2} \right\rangle$ (actually, the $M_s = \frac{-3}{2}$ can be identified as the "spin flipped" image of the state with $M_s = \frac{3}{2}$ and the one with $M_s = \frac{-1}{2}$ can be formed by interchanging all a's and b's in the $M_s = \frac{1}{2}$ state).

Of the eight total spin states (each electron can take on either α or β spin and there are three electrons, so the number of states is 2^3), the above process has identified proper combinations which yield the four states with $S = \frac{3}{2}$. Doing so consumed the determinants with $M_s = \frac{3}{2}$ and $\frac{-3}{2}$, one combination of the three determinants with $M_s = \frac{1}{2}$, and one combination of the three determinants with $M_s = \frac{-1}{2}$. There still remain two combinations of the $M_s = \frac{1}{2}$ and two combinations of the $M_s = \frac{-1}{2}$ determinants to deal with. These functions correspond to two sets of $S = \frac{1}{2}$ eigenfunctions having $M_s = \frac{1}{2}$ and $\frac{-1}{2}$. Combinations of the determinants must be used in forming the $S = \frac{1}{2}$ functions to keep the $S = \frac{1}{2}$ eigenfunctions orthogonal to the above $S = \frac{3}{2}$ functions (which is required because S^2 is a hermitian operator whose eigenfunctions belonging to different eigenvalues must be orthogonal). The two independent $S = \frac{1}{2}, M_s = \frac{3}{2}$ states can be formed by simply constructing combinations of the above three determinants with $M_s = \frac{1}{2}$ which are orthogonal to the $S = \frac{3}{2}$ combination given above and orthogonal to each other. For example,

$$\left| \frac{1}{2}, \frac{1}{2} \right\rangle = \frac{1}{\sqrt{2}} [|1s\beta 2s\alpha 3s\alpha| - |1s\alpha 2s\beta 3s\alpha| + 0x|1s\alpha 2s\alpha 3s\beta|],$$

$$\left| \frac{1}{2}, \frac{1}{2} \right\rangle = \frac{1}{\sqrt{6}} [|1s\beta 2s\alpha 3s\alpha| + |1s\alpha 2s\beta 3s\alpha| - 2x|1s\alpha 2s\alpha 3s\beta|],$$

are acceptable (as is any combination of these two functions generated by a unitary transformation). A pair of independent orthonormal states with $S = \frac{1}{2}$ and $M_s = \frac{-1}{2}$ can be generated by applying S_- to each of these two functions (or by constructing a pair of orthonormal functions which are combinations of the three determinants with $M_s = \frac{-1}{2}$ and which are orthogonal to the $S = \frac{3}{2}, M_s = \frac{-1}{2}$ function obtained as detailed above).

The above treatment of a three-electron case shows how to generate quartet (spin states are named in terms of their spin degeneracies $2S+1$) and doublet states for a configuration of the form $1s2s3s$. Not all three-electron configurations have both quartet and doublet states; for example, the $1s^2 2s$ configuration only supports one doublet state. The methods used above to generate $S = \frac{3}{2}$ and $S = \frac{1}{2}$ states are valid for any three-electron situation; however, some of the determinantal functions vanish if doubly occupied orbitals occur as for $1s^2 2s$. In particular, the $|1s\alpha 1s\alpha 2s\alpha|$ and $|1s\beta 1s\beta 2s\beta|$ $M_s = \frac{3}{2}, \frac{-3}{2}$ and $|1s\alpha 1s\alpha 2s\beta|$ and $|1s\beta 1s\beta 2s\alpha|$ $M_s = \frac{1}{2}, \frac{-1}{2}$ determinants vanish because they violate the Pauli principle; only $|1s\alpha 1s\beta 2s\alpha|$ and $|1s\alpha 1s\beta 2s\beta|$ do not vanish. These two remaining determinants form the $S = \frac{1}{2}, M_s = \frac{1}{2}, \frac{-1}{2}$ doublet spin functions which pertain to the $1s^2 2s$ configuration. It should be noted that all closed-shell components of a configuration (e.g., the $1s^2$ part of $1s^2 2s$ or the $1s^2 2s^2 2p^6$ part of $1s^2 2s^2 2p^6 3s^1 3p^1$) must involve α and β spin functions for each doubly occupied orbital and, as such, can contribute nothing to the total M_s value; only the open-shell components need to be treated with the angular momentum operator tools to arrive at proper total-spin eigenstates.

In summary, proper spin eigenfunctions must be constructed from antisymmetric (i.e., determinantal) wavefunctions as demonstrated above because the **total** S^2 and **total** S_z remain valid symmetry operators for many-electron systems. Doing so results in the spinadapted wavefunctions being expressed as combinations of determinants with coefficients determined via spin angular momentum techniques as demonstrated above. In configurations with closed-shell components, not all spin functions are possible because of the antisymmetry of the wavefunction; in particular, any closed-shell parts must involve $\alpha\beta$ spin pairings for each of the doubly occupied orbitals, and, as such, contribute zero to the total M_s .

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