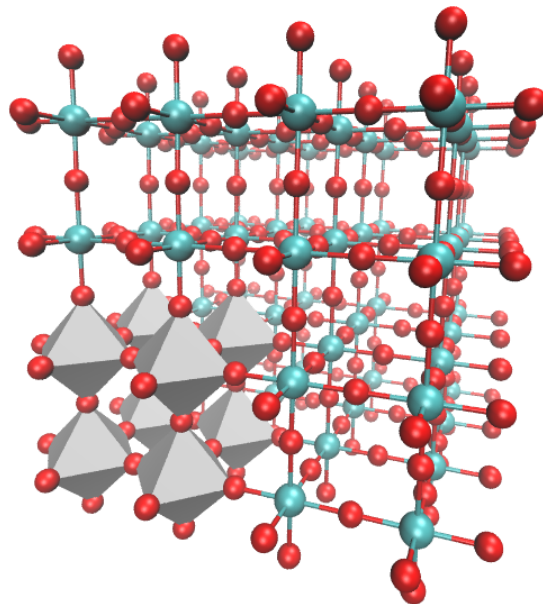




Many-Electron Wavefunctions and Spin Adaptation



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Electronic Wavefunctions

Quick summary

- Determined how to construct operators
- Examined the Hamiltonian operator
- Electronic and nuclear separability (Born-Oppenheimer)
- Time and space separability
- Solvable systems and methods of approximation
- Many-electron atoms and orbital approximation
- Construction of spatial components of Molecular orbitals

- In constructing many electron systems we have so far neglected
 - Angular momentum coupling between different particles
 - Angular momentum coupling between spin and orbital components
 - Antisymmetry of the wavefunction

- In this lecture we will build in the missing parts of the wavefunction to achieve more sophisticated theories beyond Hückle theory

Angular Momentum

Angular momentum operators

- Classically $\mathbf{l} = \mathbf{r} \times \mathbf{p}$

$$\mathbf{l} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = (yp_z - zp_y)\mathbf{i} + (zp_x - xp_z)\mathbf{j} + (xp_y - yp_x)\mathbf{k}$$

- Quantum mechanically $\mathbf{p} \rightarrow \hat{\mathbf{p}} = -i\hbar \nabla$

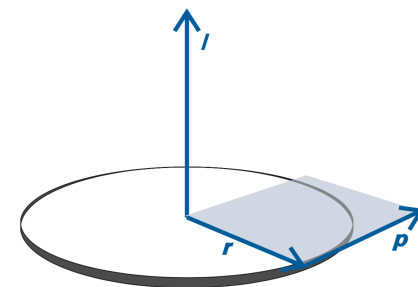
$$\hat{l}_x = (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y) \Rightarrow -i\hbar \left(\hat{y} \frac{\partial}{\partial z} + \hat{z} \frac{\partial}{\partial y} \right)$$

- Commutation relations of the angular momentum operators

$$\begin{aligned} [\hat{l}_x, \hat{l}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\ &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\ &= \hat{y}\hat{p}_x[\hat{p}_z, \hat{z}] - 0 - 0 + \hat{x}\hat{p}_y[\hat{z}, \hat{p}_z] \\ &= i\hbar(-\hat{y}\hat{p}_x + \hat{x}\hat{p}_y) = i\hbar\hat{l}_z \end{aligned}$$

$$[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z \quad [\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y \quad [\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x$$

So cannot simultaneously specify three components with certainty – choose one (conventionally \hat{l}_z) for which wavefunction is an eigenfunction



Canonical commutation relations

$$[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij}$$

$$[\hat{p}_i, \hat{p}_j] = 0 \quad \forall i, j$$

$$[\hat{r}_i, \hat{r}_j] = 0 \quad \forall i, j$$

Angular Momentum

Angular momentum operators

- Total angular momentum is $\hat{l} = \sqrt{\hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2}$ but square root does not make sense as a quantum-mechanical operator so the natural operator for magnitude is $\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$

- \hat{l}^2 commutes with all component operators

$$\begin{aligned} [\hat{l}^2, \hat{l}_z] &= [\hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2, \hat{l}_z] = [\hat{l}_x^2, \hat{l}_z] + [\hat{l}_y^2, \hat{l}_z] + \hat{l}_z^3 - \hat{l}_z^3 = \hat{l}_x \hat{l}_x \hat{l}_z - \hat{l}_z \hat{l}_x \hat{l}_x + \hat{l}_y \hat{l}_y \hat{l}_z - \hat{l}_z \hat{l}_y \hat{l}_y \\ &= \hat{l}_x \hat{l}_x \hat{l}_z - \hat{l}_x \hat{l}_z \hat{l}_x + \hat{l}_x \hat{l}_z \hat{l}_x - \hat{l}_z \hat{l}_x \hat{l}_x + \hat{l}_y \hat{l}_y \hat{l}_z - \hat{l}_y \hat{l}_z \hat{l}_y + \hat{l}_y \hat{l}_z \hat{l}_y - \hat{l}_z \hat{l}_y \hat{l}_y \\ &= \hat{l}_x [\hat{l}_x, \hat{l}_z] + [\hat{l}_x, \hat{l}_z] \hat{l}_x + \hat{l}_y [\hat{l}_y, \hat{l}_z] + [\hat{l}_y, \hat{l}_z] \hat{l}_y = -i\hbar(\hat{l}_x \hat{l}_y + \hat{l}_y \hat{l}_x - \hat{l}_y \hat{l}_x - \hat{l}_x \hat{l}_y) = 0 \end{aligned}$$

$$[\hat{l}^2, \hat{l}_i] = 0 \quad \forall i$$

- The four commutation relations completely describe the theory of angular momentum
- Whenever an observable is described with these commutation relations, it is an angular momentum, even if that is a stretch of the imagination
- We will use \mathbf{j} from here to denote a generic angular momentum

Angular Momentum

Angular momentum operators

- We can specify a stationary state wavefunction with good quantum numbers of \hat{j}^2 and \hat{j}_z but not \hat{j}_x or \hat{j}_y
- Vector model of angular momentum can be used to visualize eigenstates (although \mathbf{j} is really a vector operator and not a classical vector)
- We can write eigenstates as Dirac ket using quantum number labels j and m_j

$$\hat{j}^2 |j, m_j\rangle = \lambda_j |j, m_j\rangle$$

$$\hat{j}_z |j, m_j\rangle = \mu_{m_j} |j, m_j\rangle$$

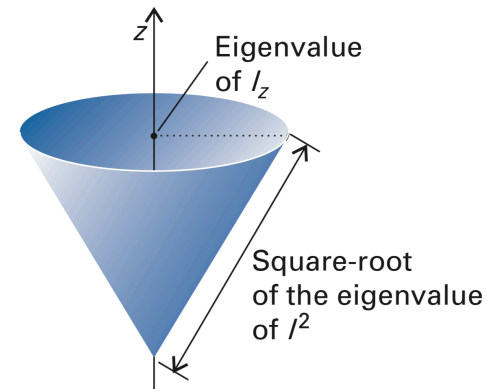
- We already established (particle on the surface of a sphere) that quantum numbers can take on values

$$j = 0, 1, 2, \dots$$

$$m_j = -j, -j + 1, \dots, j$$

- So there are several m_j states for a given eigenvalue λ_j of \hat{j}^2

$$\lambda_j = \hbar^2 j(j+1) \quad \mu_{m_j} = \hbar m_j$$



Angular Momentum

Angular momentum operators

- Permissible j and m_j quantum numbers can also be derived from commutation relations.
- We can define **ladder operators** that raise and lower that transform between different m_j eigenstates

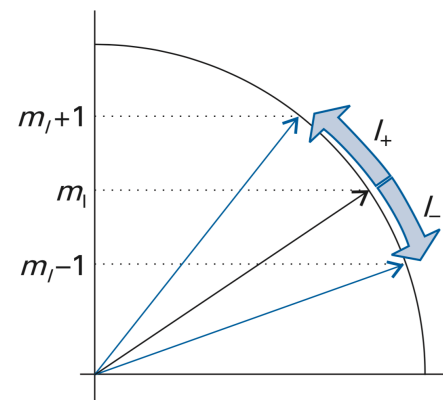
$$\hat{j}_+ = \hat{j}_x + i\hat{j}_y \quad \hat{j}_- = \hat{j}_x - i\hat{j}_y$$

$$[\hat{j}_\pm, \hat{j}^2] = 0 \quad [\hat{j}_z, \hat{j}_\pm] = \pm \hbar \hat{j}_\pm \quad [\hat{j}_+, \hat{j}_-] = 2\hbar \hat{j}_z$$

- The wavefunction $\hat{j}_\pm |j, m_j\rangle$ is an eigenfunction of \hat{j}^2 and \hat{j}_z with eigenvalues λ_j and $\mu_{m_j} \pm \hbar$ respectively

$$\hat{j}_\pm |j, m_j\rangle = \sqrt{j(j+1) - m_j(m_j \pm 1)} \hbar |j, m_j \pm 1\rangle$$

- There is a maximum and minimum value of m_j for which the result of operating with \hat{j}_\pm is zero (falling off the ladder)
- We find that the commutation relations are satisfied if j takes integral or half-integral values but the two series are separate



Angular Momentum

Matrix representations

- The wavefunctions with the same j but different m_j form a closed set
- Thus these wave functions form a basis for a matrix representation using the relations:

$$(\mathbf{j}^2)_{m_j m'_j} = \langle j, m_j | \hat{j}^2 | j', m'_j \rangle = j(j+1)\hbar^2 \delta_{jj'} \delta_{mm'}$$

$$(\mathbf{j}_z)_{m_j m'_j} = \langle j, m_j | \hat{j}_z | j', m'_j \rangle = m_j \hbar \delta_{jj'} \delta_{mm'}$$

$$(\mathbf{j}_{\pm})_{m_j m'_j} = \langle j, m_j | \hat{j}_{\pm} | j', m'_j \rangle = \sqrt{j(j+1) - m'_j(m'_j \pm 1)} \hbar \delta_{jj'} \delta_{mm' \pm 1}$$

- For $j = 1$

$$\mathbf{j}^2 = 2\hbar^2 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{j}_+ = \sqrt{2}\hbar \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$$

$$\mathbf{j}_z = \hbar \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{j}_- = \sqrt{2}\hbar \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix}$$

Angular Momentum

Electron spin

- Eigenfunctions $|j, m_j\rangle$ in 3D space are spherical harmonics $Y(\theta, \phi)$
- No spherical harmonics with half-integer quantum numbers, yet we have determined (experimentally and theoretically) that angular momentum eigenfunctions with such properties should exist (e.g. $j = 1/2$)
- Impossible to write explicit angular form of half-integer wave functions, but can still be characterized by angular momentum representations

$$|\alpha\rangle = \left| \frac{1}{2}, \frac{1}{2} \right\rangle$$

$$\hat{s}^2 |\alpha\rangle = \frac{3}{4} \hbar^2 |\alpha\rangle$$

$$\hat{s}_z |\alpha\rangle = \frac{1}{2} \hbar |\alpha\rangle$$

$$\hat{s}_+ |\alpha\rangle = 0$$

$$\hat{s}_- |\alpha\rangle = \hbar |\beta\rangle$$

$$|\beta\rangle = \left| \frac{1}{2}, -\frac{1}{2} \right\rangle$$

$$\hat{s}^2 |\beta\rangle = \frac{3}{4} \hbar^2 |\beta\rangle$$

$$\hat{s}_z |\beta\rangle = -\frac{1}{2} \hbar |\beta\rangle$$

$$\hat{s}_+ |\beta\rangle = \hbar |\alpha\rangle$$

$$\hat{s}_- |\beta\rangle = 0$$

Angular Momentum

Matrix representations of electron spin

- Just as for the general case, eigenfunctions $|\alpha\rangle$ and $|\beta\rangle$ form a complete set and can be used as a basis – the spinor basis

$$|\alpha\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad s^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad s_z = \frac{1}{2}\hbar \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$|\beta\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad s_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \quad s_- = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

- From these representations we can derive s_x and s_y

$$s_x = \frac{1}{2}(s_+ + s_-) = \frac{1}{2}\hbar \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad s_y = -\frac{i}{2}(s_+ - s_-) = -\frac{i}{2}\hbar \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$$

- The Pauli spin matrices give the symmetry structure of the angular momentum operators

$$s_i = \frac{1}{2}\hbar\sigma_i \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

- Operator matrix representation is diagonal in basis of eigenfunctions
 - $|\alpha\rangle$ and $|\beta\rangle$ are eigenfunctions of s_z but not s_x or s_y



Angular Momentum

Angular momentum coupling

- Many-electron systems have many sources of angular momentum
- Angular momentum is (along with the radial component) the source of energy levels in molecular systems
- Therefore we need to couple together all sources of angular momentum to determine the permissible energy levels in a molecule
- To understand how to express angular momentum of composite system we need to establish commutation relationships
- Imagine two systems rotating independently $|j_1, m_{j_1}\rangle$ and $|j_2, m_{j_2}\rangle$
- Operators that refer to independent components of a system commute
$$[\hat{j}_{1i}, \hat{j}_{2j}] = 0 \quad i, j = \{x, y, z\}$$
- Hence $\hat{j}_{1z}, \hat{j}_{2z}, \hat{j}_1^2$ and \hat{j}_2^2 all commute and uncoupled system can be written as $|j_1, m_{j_1}; j_2, m_{j_2}\rangle$, with $(2j_1 + 1)(2j_2 + 1)$ possibilities

Angular Momentum

Angular momentum coupling

- What about the total angular momentum?

$$\hat{j} = \hat{j}_1 + \hat{j}_2$$

- Is \hat{j} even an angular momentum (obeys four commutation relations)?

$$\begin{aligned} [\hat{j}_x, \hat{j}_y] &= [\hat{j}_{1x} + \hat{j}_{2x}, \hat{j}_{1y} + \hat{j}_{2y}] = [\hat{j}_{1x}, \hat{j}_{1y}] + [\hat{j}_{2x}, \hat{j}_{1y}] + [\hat{j}_{1x}, \hat{j}_{2y}] + [\hat{j}_{2x}, \hat{j}_{2y}] \\ &= i\hbar\hat{j}_{1z} + 0 + 0 + i\hbar\hat{j}_{2z} = i\hbar(\hat{j}_{1z} + \hat{j}_{2z}) = i\hbar\hat{j}_z \quad \checkmark \end{aligned}$$

- So \hat{j} is an angular momentum with properties:

$$\hat{j}^2 |j, m_j\rangle = \hbar^2 j(j+1) |j, m_j\rangle$$

$$\hat{j}^z |j, m_j\rangle = \hbar m_j |j, m_j\rangle$$

$$J = \sqrt{j(j+1)}\hbar$$

$$m_j = -j, -j+1, \dots, j$$

Angular Momentum

Angular momentum coupling

- What values of j can exist?
 - If we know j_1 and j_2 , can we know j ?

$$[\hat{j}^2, \hat{j}_1^2] = [\hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2, \hat{j}_1^2] = [\hat{j}_x^2, \hat{j}_1^2] + [\hat{j}_y^2, \hat{j}_1^2] + [\hat{j}_z^2, \hat{j}_1^2]$$

$$\begin{aligned} [\hat{j}_x^2, \hat{j}_1^2] &= [\hat{j}_{1x}^2 + \hat{j}_{2x}^2 + 2\hat{j}_{1x}\hat{j}_{2x}, \hat{j}_1^2] \\ &= [\hat{j}_{1x}^2, \hat{j}_1^2] + [\hat{j}_{2x}^2, \hat{j}_1^2] + 2[\hat{j}_{1x}, \hat{j}_1^2]\hat{j}_{2x} \\ &= 0 + 0 + 0 \end{aligned}$$

- Because \hat{j}_1^2 commutes with $\{\hat{j}_{1i}\}$, and \hat{j}_2^2 commutes with $\{\hat{j}_{2i}\}$, and \hat{j}^2 can be written in terms of the same components:

j_1, j_2 and j can be specified simultaneously

Angular Momentum

Angular momentum coupling

- What values of j can exist?
- If we know m_j , can we know j ? What about if we know m_{j_1} or m_{j_2} ?

$$[\hat{j}^2, \hat{j}_z] = [\hat{j}^2, \hat{j}_{1z} + \hat{j}_{2z}] = [\hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2, \hat{j}_{1z} + \hat{j}_{2z}]$$

$$= [\hat{j}_x^2, \hat{j}_{1z}] + [\hat{j}_y^2, \hat{j}_{1z}] + [\hat{j}_z^2, \hat{j}_{1z}] + [\hat{j}_x^2, \hat{j}_{2z}] + [\hat{j}_y^2, \hat{j}_{2z}] + [\hat{j}_z^2, \hat{j}_{2z}]$$

$$[\hat{j}_x^2, \hat{j}_{1z}] + [\hat{j}_y^2, \hat{j}_{1z}] + [\hat{j}_z^2, \hat{j}_{1z}]$$

$$= [\hat{j}_{1x}^2 + \hat{j}_{2x}^2 + 2\hat{j}_{1x}\hat{j}_{2x}, \hat{j}_{1z}] + [\hat{j}_{1y}^2 + \hat{j}_{2y}^2 + 2\hat{j}_{1y}\hat{j}_{2y}, \hat{j}_{1z}]$$

$$= [\hat{j}_{1x}^2, \hat{j}_{1z}] + 2[\hat{j}_{1x}, \hat{j}_{1z}]\hat{j}_{2x} + [\hat{j}_{1y}^2, \hat{j}_{1z}] + 2[\hat{j}_{1y}, \hat{j}_{1z}]\hat{j}_{2y}$$

$$= [\hat{j}_{1x}^2 + \hat{j}_{1y}^2, \hat{j}_{1z}] - 2i\hbar\hat{j}_{1y}\hat{j}_{2x} + 2i\hbar\hat{j}_{1x}\hat{j}_{2y}$$

$$= [\hat{j}_1^2 - \hat{j}_{1z}^2, \hat{j}_{1z}] - 2i\hbar\hat{j}_{1y}\hat{j}_{2x} + 2i\hbar\hat{j}_{1x}\hat{j}_{2y}$$

$$= 2i\hbar(\hat{j}_{1x}\hat{j}_{2y} - \hat{j}_{1y}\hat{j}_{2x})$$

$$[\hat{j}_x^2, \hat{j}_{2z}] + [\hat{j}_y^2, \hat{j}_{2z}] + [\hat{j}_z^2, \hat{j}_{2z}] = -2i\hbar(\hat{j}_{1x}\hat{j}_{2y} - \hat{j}_{1y}\hat{j}_{2x})$$



Angular Momentum

Angular momentum coupling

- What values of j can exist?
 - If we know m_j , can we know j ? What about if we know m_{j_1} or m_{j_2} ?

$$[\hat{j}^2, \hat{j}_z] = 0$$

$$[\hat{j}^2, \hat{j}_{1z}] = 2i\hbar(\hat{j}_{1x}\hat{j}_{2y} - \hat{j}_{1y}\hat{j}_{2x})$$

$$[\hat{j}^2, \hat{j}_{2z}] = -2i\hbar(\hat{j}_{1x}\hat{j}_{2y} - \hat{j}_{1y}\hat{j}_{2x})$$

- Because \hat{j}^2 commutes with \hat{j}_z :
 - j and m_j can be specified simultaneously
- Because \hat{j}^2 does not commute with \hat{j}_{1z} or \hat{j}_{2z} :
 - j and m_{j_1}/m_{j_2} cannot be specified simultaneously
- Hence in the coupled picture:

$$|j_1, m_{j_1}; j_2, m_{j_2}\rangle \Rightarrow |j_1, j_2; j, m_j\rangle$$

Angular Momentum

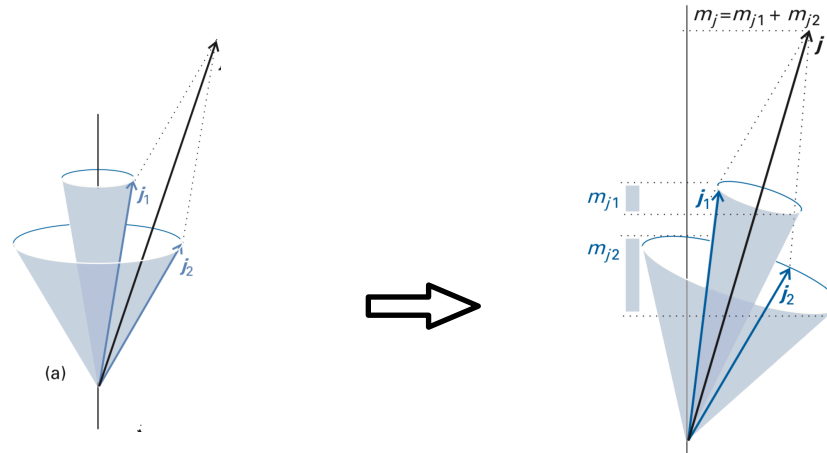
Angular momentum coupling

- Allowed values of $m_j = m_{j_1} + m_{j_2}$ which follows from $\hat{j}_z = \hat{j}_{1z} + \hat{j}_{2z}$
- Allowed values of j follow from $m_{j_1} = -j_1, -j_1 + 1, \dots, j_1$ where there are $(2j_1 + 1)(2j_2 + 1) = 4j_1j_2 + 2j_1 + 2j_2 + 1$ allowed states
- $m_j^{max} = j_1 + j_2$ is obtained one way:
 - $(m_{j_1} = j_1 \text{ and } m_{j_2} = j_2)$
 - $(2j + 1) = 2j_1 + 2j_2 + 1$ different possible m_j
- $m_j^{max} = j_1 + j_2 - 1$ is obtained two ways:
 - $(m_{j_1} = j_1 - 1 \text{ and } m_{j_2} = j_2) \text{ or } (m_{j_1} = j_1 \text{ and } m_{j_2} = j_2 - 1)$
 - $(2j + 1) = 2j_1 + 2j_2 - 1$ different possible m_j
- Clebsch-Gordan series obtained by continuing until all states identified

$$|j_1 - j_2| \leq j \leq j_1 + j_2$$

Angular Momentum

Angular momentum coupling



Uncoupled

- Indeterminate j

Coupled

- Indeterminate m_j

- Clebsch-Gordan coefficients describe the coupling weights

$$|j_1, j_2; J, M_J\rangle = \sum_{m_{j1} m_{j2}} C(m_{j1}, m_{j2}) |j_1, m_{j1}; j_2, m_{j2}\rangle$$

$$C(m_{j1}, m_{j2}) = \langle j_1, m_{j1}; j_2, m_{j2} | j_1, j_2; J, M_J \rangle$$

Angular Momentum

Angular momentum coupling

- $C(m_{j1}, m_{j2}) = 0$ unless $m_j = m_{j1} + m_{j2}$ and
- e.g. $\left| \frac{1}{2}, \pm \frac{1}{2}; \frac{1}{2}, \pm \frac{1}{2} \right\rangle$ $j_{min} = \left| \frac{1}{2} - \frac{1}{2} \right| = 0$ $j_{max} = \frac{1}{2} + \frac{1}{2} = 1$

So the Clebsch-Gordan series is $J = 1, 0$ with coupled eigenstates:

$$\left| \frac{1}{2}, \frac{1}{2}; 1, +1 \right\rangle = \left| \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2} \right\rangle$$

$$\left| \frac{1}{2}, \frac{1}{2}; 1, -1 \right\rangle = \left| \frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, -\frac{1}{2} \right\rangle$$

The only
uncoupled
determinant with
 $M = m_{j1} + m_{j2}$

$$\left| \frac{1}{2}, \frac{1}{2}; 1, 0 \right\rangle = C_1 \left| \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, -\frac{1}{2} \right\rangle + C_2 \left| \frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, \frac{1}{2} \right\rangle$$

$$\left| \frac{1}{2}, \frac{1}{2}; 0, 0 \right\rangle = C_1 \left| \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, -\frac{1}{2} \right\rangle + C_2 \left| \frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, \frac{1}{2} \right\rangle$$



Electronic Wavefunctions

Incorporating electron spin

- Electronic Hamiltonian depends only on electron spatial coordinates
- Wavefunction has component that depends on electron intrinsic spin
 - Electron described by spatial and spin coordinates

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$

- Wavefunction is a function of spin and spatial coordinates

$$\Psi(\mathbf{x}_1, \mathbf{x}_1, \dots, \mathbf{x}_{N_{elec}})$$

Spin and spatial orbitals

- Orbital is a one-electron wavefunction - molecular orbital
- Spatial orbital $\psi(\mathbf{r})$ describes the spatial element of an electron
- Orthonormal and in infinite limit, they are complete

$$f(\mathbf{r}) = \sum_i^{\infty} c_i \psi_i(\mathbf{r}) \qquad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

- Spin function $\sigma(\omega)$ added to spatial orbital to form spin orbital

$$\chi(\mathbf{x}) = \psi(\mathbf{r})\sigma(\omega)$$



Electronic Wavefunctions

Pauli exclusion principle

- Just including spin does not make a difference because Hamiltonian has no dependence on spin
- But fermionic systems (such as electronic wavefunctions) are **antisymmetric** with respect to exchange of particles
- Thus, wavefunction must be both an eigenfunction of the Hamiltonian operator **and** antisymmetric

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_{N_{\text{elec}}}) = -\Psi(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots, \mathbf{x}_{N_{\text{elec}}})$$

- We need to find a way to construct the wavefunction such it is antisymmetric
- If two coordinates are identical antisymmetry demands wavefunction is zero

$$\Psi(\mathbf{x}_1, \mathbf{x}_1) = -\Psi(\mathbf{x}_1, \mathbf{x}_1) \Rightarrow \Psi(\mathbf{x}_1, \mathbf{x}_1) = 0$$

- Antisymmetry is the origin of the Pauli exclusion principle



Electronic Wavefunctions

Hartree product wavefunction

- Build many-electron wavefunction based on electron configuration picture
 - Wavefunction product of basis orbitals is eigenfunction

$$|\Psi\rangle = \prod_{i=1}^{N_{\text{elec}}} |\chi_i(\mathbf{x}_i)\rangle$$

- Eigenfunction of non-interacting system

$$\hat{H} = \sum_{i=1}^{N_{\text{elec}}} h(i)$$

- Energy is sum of orbital energies

$$E = \sum_{i=1}^{N_{\text{elec}}} \varepsilon_i$$

- But such a wavefunction is not antisymmetric

$$\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\dots\chi_N(\mathbf{x}_N) = \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)\dots\chi_N(\mathbf{x}_N)$$

Electronic Wavefunctions

Slater determinants

- Hartree product wavefunction is not antisymmetric - not acceptable
- Linear combinations of permuted Hartree products can be made antisymmetric

$$\hat{A} = \frac{1}{N_{\text{elec}}!} \sum_{\pi \in S_n} \epsilon_{\pi} \hat{\pi}$$

Permutation operator

Parity of permutation (± 1)

$\hat{A}^2 = \hat{A}$
 $\hat{A}^\dagger = \hat{A}$
 $\hat{H}\hat{A} = \hat{A}\hat{H}$

$S_3 = \{\hat{1}, \hat{\pi}_{12}, \hat{\pi}_{13}, \hat{\pi}_{23}, \hat{\pi}_{12}\hat{\pi}_{13}, \hat{\pi}_{12}\hat{\pi}_{23}\}$

$$|\Psi\rangle = \sqrt{N_{\text{elec}}!} \hat{A} \left| \prod_{i=1}^{N_{\text{elec}}} \chi_i(\mathbf{x}_i) \right\rangle$$

Electronic Wavefunctions

Slater determinants

- The resulting expansion is the same as obtained from a determinant

$$|\Psi\rangle = \sqrt{N_{\text{elec}}!} \hat{A} \left| \prod_{i=1}^{N_{\text{elec}}} \chi_i(\mathbf{x}_i) \right\rangle$$

$$|\Psi\rangle = \frac{1}{\sqrt{N_{\text{elec}}!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \dots & \chi_n(1) \\ \chi_1(2) & \chi_2(2) & \dots & \chi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(n) & \chi_2(n) & \dots & \chi_n(n) \end{vmatrix}$$

- Recall the properties of determinants:
 1. $\det(A)=0$ if any two rows/columns equal - Pauli exclusion
 2. Sign changes when row/column interchanged - antisymmetric

Shorthand notation: $|\Psi\rangle = |\chi_1(1)\chi_2(2)\dots\chi_{N_{\text{elec}}}(N_{\text{elec}})\rangle$

Electronic Wavefunctions

Spin Properties of Slater Determinants

- Wavefunction must be antisymmetric with respect to both spatial and spin components so if spin is symmetric, space is antisymmetric

$$|0,0\rangle = \frac{1}{\sqrt{2}} \{ \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2) \} \frac{1}{\sqrt{2}} \{ \alpha(\omega_1)\beta(\omega_2) - \beta(\omega_1)\alpha(\omega_2) \}$$

$$|1,0\rangle = \frac{1}{\sqrt{2}} \{ \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2) \} \frac{1}{\sqrt{2}} \{ \alpha(\omega_1)\beta(\omega_2) + \beta(\omega_1)\alpha(\omega_2) \}$$

- Can a single determinant always achieve the spin and spatial antisymmetry?

$$\begin{aligned} |\psi_a(\mathbf{r}_1)\alpha(\omega_1)\psi_b(\mathbf{r}_2)\beta(\omega_2)\rangle &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(\mathbf{r}_1)\alpha(\omega_1) & \psi_b(\mathbf{r}_1)\beta(\omega_1) \\ \psi_a(\mathbf{r}_2)\alpha(\omega_2) & \psi_b(\mathbf{r}_2)\beta(\omega_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \{ \psi_a(\mathbf{r}_1)\alpha(\omega_1)\psi_b(\mathbf{r}_2)\beta(\omega_2) - \psi_a(\mathbf{r}_2)\alpha(\omega_2)\psi_b(\mathbf{r}_1)\beta(\omega_1) \} \neq |0,0\rangle \end{aligned}$$



Electronic Wavefunctions

Spin Properties of Slater Determinants

- Which spin operators is the Slater determinant an eigenfunction?

$$\begin{aligned} \hat{S}_z & \left(\frac{1}{\sqrt{2}} \{ \psi_a(\mathbf{r}_1) \alpha(\omega_1) \psi_b(\mathbf{r}_2) \beta(\omega_2) - \psi_a(\mathbf{r}_2) \alpha(\omega_2) \psi_b(\mathbf{r}_1) \beta(\omega_1) \} \right) \\ &= \frac{1}{\sqrt{2}} \sum_i \hat{s}_z(\omega_i) \{ \psi_a(\mathbf{r}_1) \alpha(\omega_1) \psi_b(\mathbf{r}_2) \beta(\omega_2) - \psi_a(\mathbf{r}_2) \alpha(\omega_2) \psi_b(\mathbf{r}_1) \beta(\omega_1) \} \\ &= \frac{1}{\sqrt{2}} \left(\frac{1}{2} - \frac{1}{2} \right) \psi_a(\mathbf{r}_1) \alpha(\omega_1) \psi_b(\mathbf{r}_2) \beta(\omega_2) \\ &\quad - \frac{1}{\sqrt{2}} \left(-\frac{1}{2} + \frac{1}{2} \right) \psi_a(\mathbf{r}_2) \alpha(\omega_2) \psi_b(\mathbf{r}_1) \beta(\omega_1) \end{aligned}$$

So Slater determinant is an eigenfunction of \hat{S}_z

Electronic Wavefunctions

Spin Properties of Slater Determinants

- Which spin operators is the Slater determinant an eigenfunction?

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \left\{ \frac{1}{2}(\hat{S}_+ + \hat{S}_-) \right\}^2 + \left\{ \frac{-i}{2}(\hat{S}_+ - \hat{S}_-) \right\}^2 + \hat{S}_z^2 = \hat{S}_+ \hat{S}_- + \hat{S}_z^2$$

$$\begin{aligned} & \hat{S}_+ \hat{S}_- \left(\frac{1}{\sqrt{2}} \{ \psi_a(\mathbf{r}_1) \alpha(\omega_1) \psi_b(\mathbf{r}_2) \beta(\omega_2) - \psi_a(\mathbf{r}_2) \alpha(\omega_2) \psi_b(\mathbf{r}_1) \beta(\omega_1) \} \right) \\ &= \frac{1}{\sqrt{2}} \sum_i \hat{S}_+(\omega_i) \sum_j \hat{S}_-(\omega_j) \{ \psi_a(\mathbf{r}_1) \alpha(\omega_1) \psi_b(\mathbf{r}_2) \beta(\omega_2) - \psi_a(\mathbf{r}_2) \alpha(\omega_2) \psi_b(\mathbf{r}_1) \beta(\omega_1) \} \\ &= \frac{1}{\sqrt{2}} \{ \psi_a(\mathbf{r}_1) \alpha(\omega_1) \psi_b(\mathbf{r}_2) \beta(\omega_2) + \psi_a(\mathbf{r}_1) \beta(\omega_1) \psi_b(\mathbf{r}_2) \alpha(\omega_2) \\ & \quad - \psi_a(\mathbf{r}_2) \beta(\omega_2) \psi_b(\mathbf{r}_1) \alpha(\omega_1) - \psi_a(\mathbf{r}_2) \alpha(\omega_2) \psi_b(\mathbf{r}_1) \beta(\omega_1) \} \end{aligned}$$

Right multiplying by the ket and using orthonormality of spin functions gives

$$\langle \hat{S}^2 \rangle = 1 - \langle \psi_a(\mathbf{r}_1) | \psi_b(\mathbf{r}_1) \rangle \langle \psi_a(\mathbf{r}_2) | \psi_b(\mathbf{r}_2) \rangle$$

So Slater determinant is only an eigenfunction of \hat{S}^2 if $\langle \psi_a | \psi_b \rangle = 1$

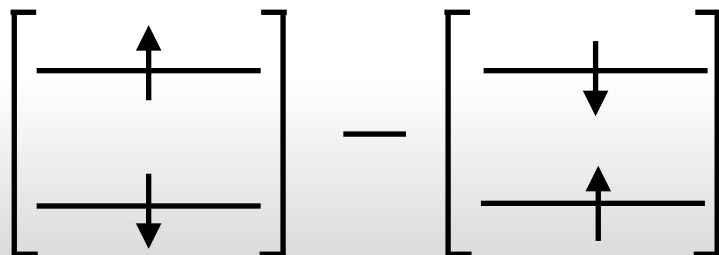


Electronic Wavefunctions

Spin Properties of Slater Determinants

- More generally, to obtain a wavefunction that is always an eigenfunction of \hat{S}^2 , combinations of Slater determinants must be used

$$\begin{aligned} & |\psi_a(\mathbf{r}_1)\alpha(\omega_1)\psi_b(\mathbf{r}_2)\beta(\omega_2)\rangle - |\psi_a(\mathbf{r}_1)\beta(\omega_1)\psi_b(\mathbf{r}_2)\alpha(\omega_2)\rangle \\ &= \frac{1}{\sqrt{2}}\{\psi_a(\mathbf{r}_1)\alpha(\omega_1)\psi_b(\mathbf{r}_2)\beta(\omega_2) - \psi_a(\mathbf{r}_2)\alpha(\omega_2)\psi_b(\mathbf{r}_1)\beta(\omega_1)\} \\ &\quad - \frac{1}{\sqrt{2}}\{\psi_a(\mathbf{r}_1)\beta(\omega_1)\psi_b(\mathbf{r}_2)\alpha(\omega_2) - \psi_a(\mathbf{r}_2)\beta(\omega_2)\psi_b(\mathbf{r}_1)\alpha(\omega_1)\} \\ &= \frac{1}{\sqrt{2}}\{\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)\}\frac{1}{\sqrt{2}}\{\alpha(\omega_1)\beta(\omega_2) - \alpha(\omega_2)\beta(\omega_1)\} = |0,0\rangle \end{aligned}$$





Summary

- Angular momentum
 - Angular momentum operators
 - Commutators of angular momentum
 - Ladder operators
 - Matrix representations
 - Half-integer spin
 - Coupling of Angular momentum
 - Coupling of orbital and intrinsic angular momentum
 - Russell-Saunders and jj-coupling limits
- Spin-adapted many-electron wavefunctions
 - Spin and spatial orbitals
 - Hartree-product wavefunction
 - Antisymmetry as the origin of the Pauli principle
 - Slater determinant wavefunction