

LITHIUM ATOM AND ELECTRON SPIN

Lithium atom - nucleus & 3 electrons

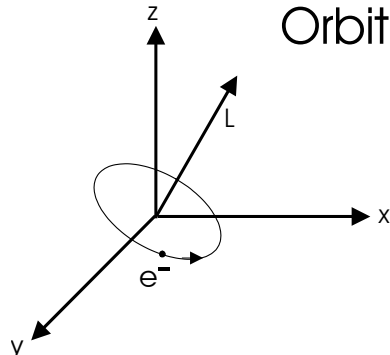
Same approach used for He atom: ground state $\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\phi_{1s}(\mathbf{r}_3)$ in perturbation theory or variational approach *unsuitable even to first order*.

Pauli Exclusion Principle (1925): no more than 2 electrons per orbital, or, no two electrons with all the same quantum numbers. Additional quantum number, now called m_s , was postulated.

Uhlenbeck and Goudsmit (1925) showed that these were two angular momentum states - the electron has intrinsic angular momentum - "SPIN" angular momentum

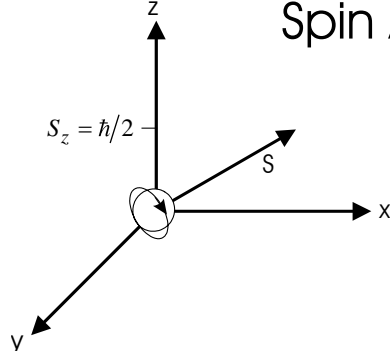
Dirac (1928) developed relativistic quantum theory & derived electron spin angular momentum

Orbital Angular Momentum



\mathbf{L} = orbital angular momentum
 $|\mathbf{L}| = \hbar \sqrt{l(l+1)}$
 l = orbital angular momentum quantum number
 $l \leq n - 1$ for H atom
 $L_z = m \hbar$ z-component of orbital angular momentum
 $m = 0, \pm 1, \pm 2, \dots, \pm l$ magnetic quantum number
 $2(l+1)$ possible values of m

Spin Angular Momentum



\mathbf{S} = spin angular momentum
 $|\mathbf{S}| = \hbar \sqrt{s(s+1)} = \hbar \sqrt{3}/2$
 s = spin angular momentum quantum number
 $s = 1/2$ for electron
 $S_z = m_s \hbar$ z-component of spin angular momentum
 $m_s = \pm 1/2$ spin angular momentum z-component quantum number
 $2(s+1) = 2$ possible values of m_s

Define spin angular momentum operators analogous to orbital angular momentum operators

$$\hat{L}^2 Y_l^m(\theta, \phi) = l(l+1)\hbar^2 Y_l^m(\theta, \phi) \quad l = 0, 1, 2, \dots, n \text{ for H atom}$$

$$L_z Y_l^m(\theta, \phi) = m\hbar Y_l^m(\theta, \phi) \quad m = 0, \pm 1, \pm 2, \dots, \pm n \text{ for H atom}$$

$$\hat{S}^2 \alpha = s(s+1)\hbar^2 \alpha \quad \hat{S}^2 \beta = s(s+1)\hbar^2 \beta \quad s = \frac{1}{2} \text{ always}$$

$$\hat{S}_z \alpha = m_s \hbar \alpha \quad m_s^\alpha = \frac{1}{2} \quad \hat{S}_z \beta = m_s \hbar \beta \quad m_s^\beta = -\frac{1}{2}$$

Spin eigenfunctions α and β are not functions of spatial coordinates!

$$\alpha \equiv \text{"spin up"} \quad \beta \equiv \text{"spin down"}$$

Spin eigenfunctions are orthonormal:

$$\int \alpha^* \alpha d\sigma = \int \beta^* \beta d\sigma = 1 \quad \sigma \equiv \text{spin variable}$$

$$\int \alpha^* \beta d\sigma = \int \beta^* \alpha d\sigma = 0$$

Spin variable has no classical analog.

Angular momentum of electron spin leads to a magnetic moment, just like orbital angular momentum.

Electron orbital magnetic moment Electron spin magnetic moment

$$\boldsymbol{\mu}_L = -\frac{e}{2m_e} \mathbf{L}$$

$$\boldsymbol{\mu}_s = -\frac{e}{2m_e} g \mathbf{S}$$

$$|\boldsymbol{\mu}_L| = -\frac{e\hbar}{2m_e} \sqrt{l(l+1)} \equiv -\beta_0 \sqrt{l(l+1)} \quad |\boldsymbol{\mu}_s| = -\frac{e\hbar}{2m_e} g \sqrt{s(s+1)} = -\beta_0 g \sqrt{s(s+1)}$$

$$\mu_{L_z} = -\frac{e}{2m_e} L_z = -\frac{e\hbar}{2m_e} m = -\beta_0 m \quad \mu_{s_z} = -\frac{e}{2m_e} g S_z = -\frac{e\hbar}{2m_e} g m_s = -\beta_0 g m_s \approx \pm \beta_0$$

$$\beta_0 \equiv \text{Bohr magneton}$$

$$g \equiv \text{"electronic g factor"} = 2.0023$$

Total electron wavefunction has both SPATIAL and SPIN parts
Each part is normalized so the total wavefunction is normalized

$$\Psi(x, y, z, \sigma) = \psi(x, y, z,)\alpha(\sigma) \text{ or } \psi(x, y, z,)\beta(\sigma)$$

e.g. for H atom the ground state total wavefunctions (in atomic units) are

$$\Psi_{100\frac{1}{2}} = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr} \alpha \quad \Psi_{100\frac{-1}{2}} = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr} \beta$$

which are orthogonal and normalized.

HE ATOM

We wrote approximate He atom wavefunctions as products of 1-electron wavefunctions, e.g.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)$$

with an adjustable value of the nuclear charge Z .

Including spin, we invoke the Pauli Exclusion Principle and write

$$\Psi(1,2) = \frac{1}{\sqrt{2}} [1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2)] = -\Psi(2,1)$$

This avoids distinguishing between the 2 electrons, and is *antisymmetric* with respect to interchange of identical particles (Pauli exclusion principle): the sign of the total wavefunction must change! (True for fermions)

Other particles (bosons) may have *symmetric* total wavefunctions.

Can write $\Psi(1,2)$ in *Slater determinant* form:

$$\Psi(1,2) = \frac{1}{\sqrt{2}} [1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2)] = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

automatically antisymmetric with respect to interchange of any two rows or columns (interchange of any two particles), even for > 2 electrons

gives zero if any two rows or columns are identical
(two particles in same total wavefunction)

For 2 electrons (*not* more generally), spatial and spin wavefunctions separable:

$$\Psi(1,2) = 1s(\mathbf{r}_1)\alpha(\sigma_1)1s(\mathbf{r}_2)\beta(\sigma_2) - 1s(\mathbf{r}_1)\beta(\sigma_1)1s(\mathbf{r}_2)\alpha(\sigma_2) = 1s(\mathbf{r}_1)1s(\mathbf{r}_2) \begin{vmatrix} \alpha(\sigma_1) & \beta(\sigma_1) \\ \alpha(\sigma_2) & \beta(\sigma_2) \end{vmatrix}$$

For > 2 electrons, Slater determinant takes the form

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & u_2(1) & \cdots & u_N(1) \\ u_1(2) & u_2(2) & \cdots & u_N(2) \\ \vdots & \vdots & & \vdots \\ u_1(N) & u_2(N) & \cdots & u_N(N) \end{vmatrix}$$

where the u 's are product spatial x spin wavefunctions.

LITHIUM ATOM

Slater determinant form of total wavefunction:

$$\Psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

In this case, and in general, spatial and spin wavefunctions cannot be separated.