Electron Spin

Chem 2340

In 1925 Uhlenbeck + Groudsmit: postulated that electrons have spin.

There is no classical analog.

In 1928 Dirac showed that relativistic QM $\longrightarrow$ spin

We postulate that spin is associated with a set of operators that behave like angular momentum operators.

$$\hat{S}^2, \hat{S}_x, \hat{S}_y, \hat{S}_z$$

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z, \quad \left[\hat{S}_y, \hat{S}_z\right] = i\hbar\hat{S}_x \quad \left[\hat{S}_z, \hat{S}_x\right] = i\hbar\hat{S}_y$$

$$\left[\hat{S}^2, \hat{S}_x\right] = 0, \quad \left[\hat{S}^2, \hat{S}_y\right] = 0, \quad \left[\hat{S}^2, \hat{S}_z\right] = 0$$

$$\hat{S}^2\gamma = s(s+1)\hbar^2\gamma$$

$\uparrow$ eigenfunction, possible value of s, 0,1/2, 1, 3/2...

$\hat{S}_z\gamma = m_s\hbar\gamma$, where $m_s = -s, \; -s+1, \ldots, s$

Electrons have s = ½

Photons have s = 1

$$\sqrt{\tfrac{1}{2}\tfrac{3}{2}\hbar^2} = \frac{\sqrt{3}}{2}\hbar =$$ magnitude of spin angular momentum of an electron.

$$m_s = \tfrac{1}{2} \rightarrow \alpha, \quad m_s = -\tfrac{1}{2} \rightarrow \beta$$

$$\hat{S}_z\alpha = \tfrac{1}{2}\hbar\alpha, \quad \hat{S}_z\beta = -\tfrac{1}{2}\hbar\beta$$

$$\hat{S}^2\alpha = \tfrac{3}{4}\hbar^2\alpha, \quad \hat{S}^2\beta = \tfrac{3}{4}\hbar^2\beta$$

Levine adopts m_s as the spin coordinate

$$\alpha = \alpha(m_s); \quad \beta = \beta(m_s)$$

$$\langle \alpha \mid \alpha \rangle = 1, \quad \langle \beta \mid \beta \rangle = 1, \quad \langle \alpha \mid \beta \rangle = 0$$

In going forward we let $d\tau$ denote integration over both spatial and spin coordinates (since spin is discrete this is actually a sum in this case).

H atom: $\psi(x,y,z) \rightarrow \psi(x,y,z)\alpha,\ \ \psi(x,y,z)\beta$

The $\hat{H}$ that we considered for the H atom is independent of spin, so the α or β does not impact the energy.

Actually, one can tack onto H a term that couples $\vec{L}$ and $\vec{S}$. In that case ℓ and s cease to be "perfect" quantum numbers (when both are non-zero)

Let $\{x_i, y_i, z_i, m_{s_i}\} = q_i$

Then for a many particle system $\psi = \psi(q_2, q_1, q_3, \ldots q_n)$

The Permutation Operator

$\hat{P}_{12}$ swaps coordinates of particles 1 and 2

$$\hat{P}_{12}\psi(q_1, q_2, q_3, \ldots q_n) = \psi(q_1, q_2, q_3, \ldots q_n)$$

The eigenvalues of $\hat{P}_{12}$ are ± 1

Interchanging the coordinates of two electrons causes a change in sign of the wave function.

Spin Statistics Theorem

Particles with spin, 1/2, 3/2, etc. are fermions (antisymmetric wavefunctions)

Particles with spin 0,1,2,...are bosons (symmetric wavefunctions)

For a system of identical fermions

$$\psi\left(q_1, q_2, q_3, \ldots q_n\right) = -\psi\left(q_2, q_1, q_3, \ldots q_n\right)$$

This $\Longrightarrow$ that if two electrons have the same coordinates (spin and space): $\psi = 0$

Helium atom

ground state $1s\left(r_1\right)1s\left(r_2\right)\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$

antisymmetry comes from the spin part of the wavefunction

What about the **1s2s** excited state?

1 $\left[1s\left(r_1\right)2s\left(r_2\right) - 2s\left(r_1\right)1s\left(r_2\right)\right] \begin{cases} \alpha(1)\alpha(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \\ \beta(1)\beta(2) \end{cases}$

2 $\left[1s\left(r_1\right)2s\left(r_2\right) + 2s\left(r_1\right)1s\left(r_2\right)\right]\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$

For 2 the antisymmetry comes from the spin function.

This is a singlet state.

For 1 the antisymmetry comes from the spatial function.

This is a triplet state.

For the singlet state $\hat{S}^2\psi = 0\psi$, So $S = 0$, $M_s = 0$

For the triplet state $\hat{S}^2\psi = 2(1)\hbar^2\psi$, So $S = 1$, $M_s = -1, 0, 1$

How does this impact the energy?

consider $\left\langle \psi_S \mid \hat{H} \mid \psi_S \right\rangle = \frac{1}{2}\int \left[1s(1)2s(2)+2s(1)1s(2)\right]\hat{H}\left[1s(1)2s(2)+2s(1)1s(2)\right]d\tau$

Here we have integrated out the spin. So $d\tau \Rightarrow d\vec{r}_1 d\vec{r}_2$

$$E_s = \int 1s(1)2s(2)\hat{H}1s(1)2s(2)d\tau + \int 1s(1)2s(2)\hat{H}2s(1)1s(2)d\tau$$

Now consider $\left\langle \psi_T \mid \hat{H} \mid \psi_T \right\rangle = \frac{1}{2}\int \left[1s(1)2s(2)-2s(1)1s(2)\right]\hat{H}\left[1s(1)2s(2)-2s(1)1s(2)\right]d\tau$

$$= \frac{1}{2}\int 1s(1)2s(2)\hat{H}1s(1)2s(2)d\tau - \int 1s(1)2s(2)\hat{H}2s(1)1s(2)d\tau$$

Again the spin has been integrated out.

The 2nd integral is the exchange integral K

K is positive, so the triplet is below the singlet, and the states are split by 2K.

He atom in its ground state: Slater determinant

$$\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} = \left|1s\overline{1s}\right|$$

Shorthand nomenclature

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

$$= \frac{1}{\sqrt{2}}1s(1)1s(2)(\alpha\beta - \beta\alpha)$$

The energy can be approximated as

$$E = \langle 1s(r_1)1s(r_2) \mid H \mid 1s(r_1)1s(r_2)\rangle$$

$$= 2E_1^{(0)} + \int \left|1s(r_1)\right|^2 \frac{1}{r_{12}} \left|1s(r_2)\right|^2 d\vec{r}_1 d\vec{r}_2$$

$$= 2E_1^{(0)} + J_{1s,1s}$$

J = Coulomb repulsion

1s2s Triplet $(1s2s - 2s1s)\alpha\alpha$

Singlet $(1s2s + 2s1s)(\alpha\beta - \beta\alpha)$

$$E(T) = E_{1s}^{(0)} + E_{2s}^{(0)} + J_{1s,2s} - K_{1s,2s}$$

$$E(S) = E_{1s}^{(0)} + E_{2s}^{(0)} + J_{1s,2s} + K_{1s,2s}$$

Now lets consider the Li atom

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix} = \left|1s\overline{1s}2s\right|$$

Note: the short-hand nomenclature for a Slater determinant

$$= \frac{1}{\sqrt{6}}\left(1s\overline{1s}2s - 1s2s\overline{1s} - \overline{1s}1s2s + \overline{1s}2s1s + 2s1s\overline{1s} - 2s\overline{1s}1s\right)$$

Note that this can not be written as a spatial function times a spin function

One can show that we only need to consider:

$$\left\langle 1s\overline{1s}2s \mid H \mid 1s\overline{1s}2s - 1s2s\overline{1s} - \overline{1s}1s2s + \overline{1s}2s1s + 2s1s\overline{1s} - 2s\overline{1s}1s \right\rangle$$

$$= \left\langle 1s\overline{1s}2s \mid H \mid 1s\overline{1s}2s \right\rangle - \left\langle 1s\overline{1s}2s \mid H \mid 2s\overline{1s}1s \right\rangle$$

It doesn't matter which of the six terms we retain on the left.

$$2E_{1s}{}^{(0)} + E_{2s}{}^{(0)} + J_{1s,1s} + 2J_{1s,2s} - K_{1s,2s}$$

$$E^{(0)} = -275.5 \text{ eV}, \quad E^{(1)} = 83.5 \text{ eV} \rightarrow E^{(0)} + E^{(1)} = -192.0 \text{ eV}$$

Exact energy = -203.5 eV

If we optimize the exponents E = -201.2 eV

He **1s2s** excited states and Slater determinants

$$\frac{1}{\sqrt{2}}\begin{vmatrix}1s2s\\1s2s\end{vmatrix} = \frac{1}{\sqrt{2}}(1s2s - 2s1s)\alpha\alpha$$

$$\chi_1 = \frac{1}{\sqrt{2}}\begin{vmatrix}1s\overline{2s}\\1s\overline{2s}\end{vmatrix} = \frac{1}{\sqrt{2}}\left(1s\overline{2s} - \overline{2s}1s\right) = \frac{1}{\sqrt{2}}(1s2s\alpha\beta - 2s1s\beta\alpha)$$

$$\chi_2 = \frac{1}{\sqrt{2}}\begin{vmatrix}\overline{1s}2s\\\overline{1s}2s\end{vmatrix} = \frac{1}{\sqrt{2}}\left(\overline{1s}2s - 2s\overline{1s}\right) = \frac{1}{\sqrt{2}}(1s2s\beta\alpha - 2s1s\alpha\beta)$$

Note that χ_1 and χ_2 do not correspond to the singlet and triplet wavefunctions that we considered previously.

Lets consider: $\frac{1}{\sqrt{2}}(\chi_1 + \chi_2)$

$$= \tfrac{1}{2}\left[1s2s\alpha\beta - 2s1s\beta\alpha + 1s2s\beta\alpha - 2s1s\alpha\beta\right]$$

$$= \tfrac{1}{2}\left[1s2s(\alpha\beta + \beta\alpha) - 2s1s(\alpha\beta + \beta\alpha)\right]$$

$$= \tfrac{1}{2}(1s2s - 2s1s)(\alpha\beta + \beta\alpha)$$

which is the M_s**=0** component of the triplet

$$\frac{1}{\sqrt{2}}(\chi_1 - \chi_2) = \frac{1}{2}(1s2s + 2s1s)(\alpha\beta - \beta\alpha)$$

is the wavefunction for the singlet.

If we use either χ_1 or χ_2 as the wavefunction in an electronic structure code, we would be describing a linear combination of the singlet and triplet states.

We can treat the triplet with a single Slater determinant, by using the $\alpha\alpha$ spin arrangement.

Now lets consider the next few elements of the periodic table.

Be atom:	$\left\|1s\overline{1s}2s\overline{2s}\right\|$	^1S
B atom:	$\left\|1s\overline{1s}2s\overline{2s}2p\right\|$	^2P
C atom:	$\left\|1s\overline{1s}2s\overline{2s}2p^2\right\|$	?

The C atom presents the first real challenge

M_L +1   0   -1

There are 15 possible arrangements of the two p electrons

D_1	↑↓	—	—	$M_L=2$, $M_s=0$	^1D
D_2	—	—	↑↓	$M_L=-2$, $M_s=0$	^1D
D_3	↑	↑	—	$M_L=1$, $M_s=1$	^3p
D_4	↑	↓	—	$M_L=1$, $M_s=0$	(^1D, ^3P)
D_5	↓	↑	—	$M_L=1$, $M_s=0$	
D_6	↓	↓	—	$M_L=1$, $M_s=-1$	^3P
D_7	—	↑	↑	$M_L=-1$, $M_s=1$	^3P
D_8	—	↓	↑	$M_L=-1$, $M_s=0$	(^1D, ^3P)
D_9	—	↑	↓	$M_L=-1$, $M_s=0$	
D_{10}	—	↓	↓	$M_L=-1$, $M_s=-1$	^3P
D_{11}	—	↑↓	—	$M_L=0$, $M_s=0$	
D_{12}	↑	—	↑	$M_L=0$, $M_s=1$	(^3P)
D_{13}	↑	—	↓	$M_L=0$, $M_s=0$	
D_{14}	↓	—	↑	$M_L=0$, $M_s=0$	
D_{15}	↓	—	↓	$M_L=0$, $M_s=-1$	(^3P)

We can immediately see that there is a ^1D and a ^3P state. This accounts for $1 \times 5 + 3 \times 3 = 14$ combinations.

This means that there is also a ^1S state.

^3D, ^1P, or ^3S would violate the Pauli principle.

There are 3 arrangements with $M_L=0$, $M_s=0$

These give rise to ^1D, ^1S, ^3P

There are 3 arrangements with $M_L=0$, $M_s=1$ and one with $M_L=0$, $M_s=-1$.

These are associated with ^3P

^{1}D

$$p_1 p_1 (\alpha\beta - \beta\alpha)$$

$$p_{-1} p_{-1} (\alpha\beta - \beta\alpha)$$

^{3}P

$$(p_1 p_0 - p_0 p_1)\alpha\alpha$$

$$(p_1 p_0 - p_0 p_1)\beta\beta$$

$$(p_1 p_0 - p_0 p_1)(\alpha\beta + \beta\alpha)$$

$(p_1 p_0 + p_0 p_1)(\alpha\beta - \beta\alpha)$ must be ^{1}D, etc.