

Chapter 16

Electron Spin

Electron spin hypothesis

Solution to H atom problem gave three quantum numbers, n , l , m .

These apply to all atoms.

Experiments show not complete description. Something missing.

Alkali metals show splitting of spectral lines in absence of magnetic field.

s lines not split

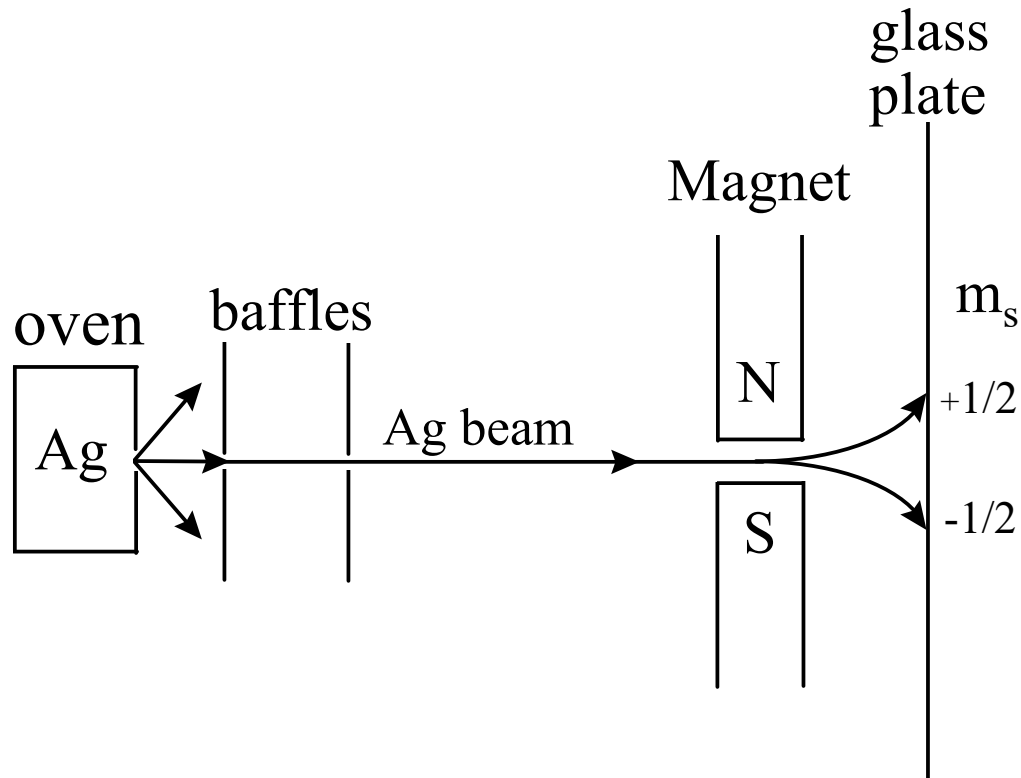
p, d lines split

Na D-line (orange light emitted by excited Na) split by 17 cm^{-1}

Many experiments not explained without electron "spin."

Stern-Gerlach experiment early, dramatic example.

Stern-Gerlach experiment - 1922



Beam of silver atoms deflected by magnetic field gradient.

Single unpaired electron - should not give two lines on glass plate.

s-orbital. No orbital angular momentum. No magnetic moment.

Observed deflection corresponds to one Bohr magneton.

Assume: Electron has intrinsic angular momentum called "spin."

$$s = \frac{1}{2} \hbar$$

$$\underline{S}^2 |s m_s\rangle = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \hbar^2 |s m_s\rangle$$

square of
angular
momentum
operator

$$\underline{S}_z |s m_s\rangle = \pm \frac{1}{2} \hbar |s m_s\rangle$$

projection of
angular
momentum on
z-axis

$$\mu_s = e\hbar/2mc$$

**Electron has magnetic moment.
One Bohr magneton.
Charged particle with angular mom.**

$$\frac{\mu_s}{s} = \frac{e}{mc}$$

$$\frac{\mu_\ell}{\ell} = \frac{e}{2mc}$$

**Ratio twice the ratio for
orbital angular momentum.**

Electronic wavefunction with spin

$$\psi = \psi(x, y, z)$$

$$\psi = \psi(x, y, z, m_s) \longleftarrow \text{with spin}$$

$$m_s = \pm \frac{1}{2}$$

$|s m_s\rangle$ spin angular momentum kets

$$|\chi(m_s)\rangle = \left| \frac{1}{2} \frac{1}{2} \right\rangle, \left| \frac{1}{2} -\frac{1}{2} \right\rangle$$

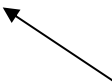
$$\alpha = \left| \frac{1}{2} \frac{1}{2} \right\rangle$$

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

Electronic States in a Central Field

Electron in state of orbital angular momentum ℓ

 $Y_\ell^{m_\ell}(\theta, \varphi)$

m_ℓ  label as orbital angular momentum quantum number

m_s  spin angular momentum quantum number

$$\chi(1/2), \chi(-1/2)$$

$$|\psi(\ell m_\ell m_s)\rangle = |Y_\ell^{m_\ell}\rangle |\chi(m_s)\rangle$$

product space of angular momentum (orbital and spin) eigenvectors

$|\psi(\ell m_\ell m_s)\rangle$ Simultaneous eigenvectors of

$$\underline{L}^2 \quad \underline{L}_z \quad \underline{S}^2 \quad \underline{S}_z$$

$$\underline{L}^2 |\psi\rangle = \ell(\ell + 1) |\psi\rangle$$

$$\underline{L}_z |\psi\rangle = m_\ell |\psi\rangle$$

$$\underline{S}^2 |\psi\rangle = \frac{3}{4} |\psi\rangle$$

← constant - eigenvalues of \underline{S}^2 are $s(s + 1)$, $s = 1/2$

$$\underline{S}_z |\psi\rangle = m_s |\psi\rangle$$

$2(2\ell + 1)$ linearly independent functions of form $|\psi(\ell m_\ell m_s)\rangle$.

Example - p states of an electron

Orbital functions $\ell = 1$

$$\psi(r, \theta, \varphi) = R(r)Y_{\ell}^m(\theta, \varphi)$$

radial

spherical harmonics

orbital angular momentum part

$$Y_1^1 = |11\rangle \quad Y_1^0 = |10\rangle \quad Y_1^{-1} = |1-1\rangle$$

$j_1 m_1 \qquad j_1 m_1 \qquad j_1 m_1$

spin functions

$$\alpha = \left| \begin{array}{cc} 1 & 1 \\ 2 & 2 \end{array} \right\rangle \quad \beta = \left| \begin{array}{cc} 1 & 1 \\ 2 & -2 \end{array} \right\rangle$$

$j_2 m_2 \qquad j_2 m_2$

$$j_1 m_1 = \ell m_{\ell}$$

$$j_2 m_2 = s m_s$$

In the $m_1 m_2$ representation

$$Y_1^1 \alpha = \begin{array}{cc} \ell & s \\ \hline 1 & \frac{1}{2} \end{array} \begin{array}{cc} m_\ell & m_s \\ \hline 1 & \frac{1}{2} \end{array} \rangle = \begin{array}{cc} m_\ell & m_s \\ \hline 1 & \frac{1}{2} \end{array} \rangle$$

$$Y_1^1 \beta = \begin{array}{cc} \ell & s \\ \hline 1 & \frac{1}{2} \end{array} \begin{array}{cc} m_\ell & m_s \\ \hline 1 & -\frac{1}{2} \end{array} \rangle = \begin{array}{cc} m_\ell & m_s \\ \hline 1 & -\frac{1}{2} \end{array} \rangle$$

$$Y_1^0 \alpha = \begin{array}{cc} \ell & s \\ \hline 1 & \frac{1}{2} \end{array} \begin{array}{cc} m_\ell & m_s \\ \hline 0 & \frac{1}{2} \end{array} \rangle = \begin{array}{cc} m_\ell & m_s \\ \hline 0 & \frac{1}{2} \end{array} \rangle$$

$$Y_1^0 \beta = \begin{array}{cc} \ell & s \\ \hline 1 & \frac{1}{2} \end{array} \begin{array}{cc} m_\ell & m_s \\ \hline 0 & -\frac{1}{2} \end{array} \rangle = \begin{array}{cc} m_\ell & m_s \\ \hline 0 & -\frac{1}{2} \end{array} \rangle$$

$$Y_1^{-1} \alpha = \begin{array}{cc} \ell & s \\ \hline 1 & \frac{1}{2} \end{array} \begin{array}{cc} m_\ell & m_s \\ \hline -1 & \frac{1}{2} \end{array} \rangle = \begin{array}{cc} m_\ell & m_s \\ \hline -1 & \frac{1}{2} \end{array} \rangle$$

$$Y_1^{-1} \beta = \begin{array}{cc} \ell & s \\ \hline 1 & \frac{1}{2} \end{array} \begin{array}{cc} m_\ell & m_s \\ \hline -1 & -\frac{1}{2} \end{array} \rangle = \begin{array}{cc} m_\ell & m_s \\ \hline -1 & -\frac{1}{2} \end{array} \rangle$$

Each of these is multiplied by $R(r)$.

$$j_1 j_2 = \ell s$$

Total angular momentum - jm representation

Two states of total angular momentum

$$j = j_1 + j_2 = \ell + s = \frac{3}{2}$$

$$j = j_1 + j_2 - 1 = |j_1 - j_2| = \ell - s = \frac{1}{2}$$

The jm kets are

$$\left| \frac{3}{2} \frac{3}{2} \right\rangle \quad \left| \frac{3}{2} \frac{1}{2} \right\rangle \quad \left| \frac{3}{2} -\frac{1}{2} \right\rangle \quad \left| \frac{3}{2} -\frac{3}{2} \right\rangle \quad \left| \frac{1}{2} \frac{1}{2} \right\rangle \quad \left| \frac{1}{2} -\frac{1}{2} \right\rangle$$

Spin-orbit Coupling

An electron, with magnetic moment moves in the electric field of rest of atom (or molecule).

$$W = -(\vec{E} \times \vec{V}) \cdot \vec{\mu}$$

↑
energy

classical energy of magnetic dipole $\vec{\mu}$ moving in electric field \vec{E} with velocity \vec{V}

$$\vec{\mu} = -\frac{|e|\hbar}{2mc} \vec{S}$$

spin magnetic moment of electron

Then

$$W = \frac{|e|\hbar}{2mc} (\vec{E} \times \vec{V}) \cdot \vec{S}$$

Using

$$|e|\vec{E} = -\vec{\text{grad}} \phi$$

← Coulomb potential (usually called V , but V is velocity)

and

$$\vec{p} = m\vec{V}$$

$$\underline{W} = \frac{1}{2m^2c} (\underline{\text{grad}} \phi \times \underline{\vec{p}}) \cdot \underline{\vec{S}}$$

Hydrogen like atoms

$$\phi = -\frac{ze^2}{4\pi\epsilon_0 r} \quad \text{Coulomb potential}$$

unit vector

$$\underline{\text{grad}} \phi = \frac{ze^2}{4\pi\epsilon_0 r^2} \left(\frac{\underline{\vec{r}}}{r} \right) = \frac{ze^2}{4\pi\epsilon_0 r^3} \underline{\vec{r}} \quad \text{vector derivative of potential}$$

Substituting

$$\underline{H}_{so} = \frac{ze^2}{8\pi\epsilon_0 m^2 c} \frac{1}{r^3} (\underline{\vec{r}} \times \underline{\vec{p}}) \cdot \underline{\vec{S}}$$

$$(\underline{\vec{r}} \times \underline{\vec{p}}) \longrightarrow \underline{\vec{L}} \quad \text{orbital angular momentum}$$

$$\underline{H}_{so} = \frac{ze^2}{8\pi\epsilon_0 m^2 c} \frac{1}{r^3} \underline{\vec{L}} \cdot \underline{\vec{S}}$$

operates on
radial part of
wavefunction

operates on
orbital ang. mom.
part of wavefunction

operates on
spin ang. mom.
part of wavefunction

One unpaired electron – central field (Sodium outer electron)

$$\phi = V(r)$$

$$\vec{\text{grad}} V(r) = \frac{\partial V(r)}{\partial r} \frac{1}{r} \vec{r}$$

result of operating on
radial part of wavefunction

$$\underline{H}_{so} = \frac{1}{2m^2c} \frac{1}{r} \frac{\partial V(r)}{\partial r} \underline{\vec{L}} \cdot \underline{\vec{S}} = a(r) \underline{\vec{L}} \cdot \underline{\vec{S}}$$

Many electron system

$$\underline{H}_{so} = \frac{1}{2m^2c} \sum_i \left[\frac{1}{r_i} \frac{\partial V(r_i)}{\partial r_i} \right] \underline{\vec{L}}_i \cdot \underline{\vec{S}}_i = \sum_i a_i(r) \underline{\vec{L}}_i \cdot \underline{\vec{S}}_i$$

Ignore terms involving, $\underline{\vec{L}}_i \cdot \underline{\vec{S}}_j$, the orbital angular momentum of one electron with the spin of another electron. Extremely small.

Spin-orbit coupling piece of Hamiltonian

$$\underline{H}_{so} = a(r)\underline{\vec{L}} \cdot \underline{\vec{S}}$$

H-like atom – spatial part of operator

$$\underline{H}_{so}(r) = \frac{ze^2}{8\pi\epsilon_0 m^2 c} \frac{1}{r^3}$$

$$E = \int_{-\infty}^{\infty} \psi^*(r) \underline{H}_{so} \psi(r) d\tau$$

Normalization constant (eq.7.63) contains

$$\therefore E \propto z \cdot z^{3/2} \cdot z^{3/2} \quad \longrightarrow \quad a(r) \propto z^4$$

heavy atom effect
similar for all atoms
and molecules

H – little S.O. coupling
Br – sizable S.O. coupling

Heavy atom effect and **external heavy atom effect** important in many processes.

$$\underline{H}_{so} = a(r)\underline{\vec{L}} \cdot \underline{\vec{S}}$$

The $a(r)$ part is independent of the angular momentum states.

Consider $\underline{\vec{L}} \cdot \underline{\vec{S}}$

$$\underline{\vec{L}} \cdot \underline{\vec{S}} = \underline{L}_x \underline{S}_x + \underline{L}_y \underline{S}_y + \underline{L}_z \underline{S}_z$$

Rearranging the expressions for the angular momentum raising and lowering operators

$$\underline{S}_x = \frac{1}{2}(\underline{S}_+ + \underline{S}_-)$$

$$\underline{S}_y = \frac{1}{2i}(\underline{S}_+ - \underline{S}_-)$$

$$\underline{L}_x = \frac{1}{2}(\underline{L}_+ + \underline{L}_-)$$

$$\underline{L}_y = \frac{1}{2i}(\underline{L}_+ - \underline{L}_-)$$

Substituting

$$\underline{\vec{L}} \cdot \underline{\vec{S}} = \underline{L}_z \underline{S}_z + \frac{1}{2}(\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+)$$

↙
↖

diagonal
off-diagonal

Spin-Orbit Coupling in the m_1m_2 representation

$$\vec{L} \cdot \vec{S} = \underline{L}_z \underline{S}_z + \frac{1}{2}(\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+) \quad \text{not diagonal in the } m_1m_2 \text{ representation}$$

States in the m_1m_2 representation

$$\left| 1 \frac{1}{2} \right\rangle \quad \left| 1 -\frac{1}{2} \right\rangle \quad \left| 0 \frac{1}{2} \right\rangle \quad \left| 0 -\frac{1}{2} \right\rangle \quad \left| -1 \frac{1}{2} \right\rangle \quad \left| -1 -\frac{1}{2} \right\rangle$$

The spin-orbit coupling Hamiltonian matrix in the m_1m_2 representation is a 6×6 .

Calculating the matrix elements

Kets are diagonal for the $\underline{L}_z \underline{S}_z$ piece of the Hamiltonian. For example

$$\underline{L}_z \underline{S}_z \left| \underset{m_\ell m_s}{1 \frac{1}{2}} \right\rangle = \frac{1}{2} \left| \underset{m_\ell m_s}{1 \frac{1}{2}} \right\rangle \quad \underline{L}_z \text{ brings out } m_\ell \text{ and } \underline{S}_z \text{ brings out } m_s.$$

$$\frac{1}{2}(\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+) \quad \text{not diagonal}$$

Apply $\frac{1}{2}(\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+)$ to the six kets.

Examples

$$\frac{1}{2}(\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+) \left| 1 \frac{1}{2} \right\rangle = 0 \quad \text{can't raise above largest values}$$

$$\frac{1}{2}(\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+) \left| 1 -\frac{1}{2} \right\rangle = \frac{\sqrt{2}}{2} \left| 0 \frac{1}{2} \right\rangle$$

Left multiply by $\left\langle 0 \frac{1}{2} \right|$

$$\left\langle 0 \frac{1}{2} \right| \frac{1}{2}(\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+) \left| 1 -\frac{1}{2} \right\rangle = \frac{\sqrt{2}}{2} \quad \text{matrix element}$$

$$\underline{H}_{so} = a(r) \left[\underline{L}_z \underline{S}_z + \frac{1}{2} (\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+) \right]$$

put kets along top

$$\underline{H}_{so} = a(r) \begin{array}{c} \langle 1 \frac{1}{2} | \\ \langle 1 - \frac{1}{2} | \\ \langle 0 \frac{1}{2} | \\ \langle 0 - \frac{1}{2} | \\ \langle -1 \frac{1}{2} | \\ \langle -1 - \frac{1}{2} | \end{array} \begin{bmatrix} \boxed{\frac{1}{2}} & & & & & \\ & \boxed{\begin{matrix} -\frac{1}{2} & \sqrt{2}/2 \\ \sqrt{2}/2 & 0 \end{matrix}} & & & & \\ & & \boxed{\begin{matrix} 0 & \sqrt{2}/2 \\ \sqrt{2}/2 & -\frac{1}{2} \end{matrix}} & & & \\ & & & \boxed{\frac{1}{2}} & & \\ & & & & & \end{bmatrix} \begin{array}{c} | 1 \frac{1}{2} \rangle \\ | 1 - \frac{1}{2} \rangle \\ | 0 \frac{1}{2} \rangle \\ | 0 - \frac{1}{2} \rangle \\ | -1 \frac{1}{2} \rangle \\ | -1 - \frac{1}{2} \rangle \end{array}$$

put bras down left side

example

$$\left\langle 0 \frac{1}{2} \left| \frac{1}{2} (\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+) \right| 1 - \frac{1}{2} \right\rangle = \frac{\sqrt{2}}{2}$$

Matrix is block diagonal.

Matrix – Block Diagonal

Each block is independent. Diagonalize separately.

Form determinant from block with λ (eigenvalue) subtracted from diagonal elements.

$$\begin{vmatrix} -\frac{1}{2} - \lambda & \sqrt{2}/2 \\ \sqrt{2}/2 & -\lambda \end{vmatrix} = 0$$

The two blocks are the same. Only need to solve one of them.

The two 1×1 blocks are diagonal – eigenvalues.

Expand the determinant. Solve for λ . Each block multiplied by $a(r)$.

$$1/2\lambda + \lambda^2 - 1/2 = 0$$

$$\lambda = -1/4 \pm 3/4$$

$$\lambda = [1/2 \text{ or } -1]$$

$$\lambda = \frac{1}{2}a(r)$$

$$\lambda = -1a(r)$$

The two 2×2 blocks each give these results.

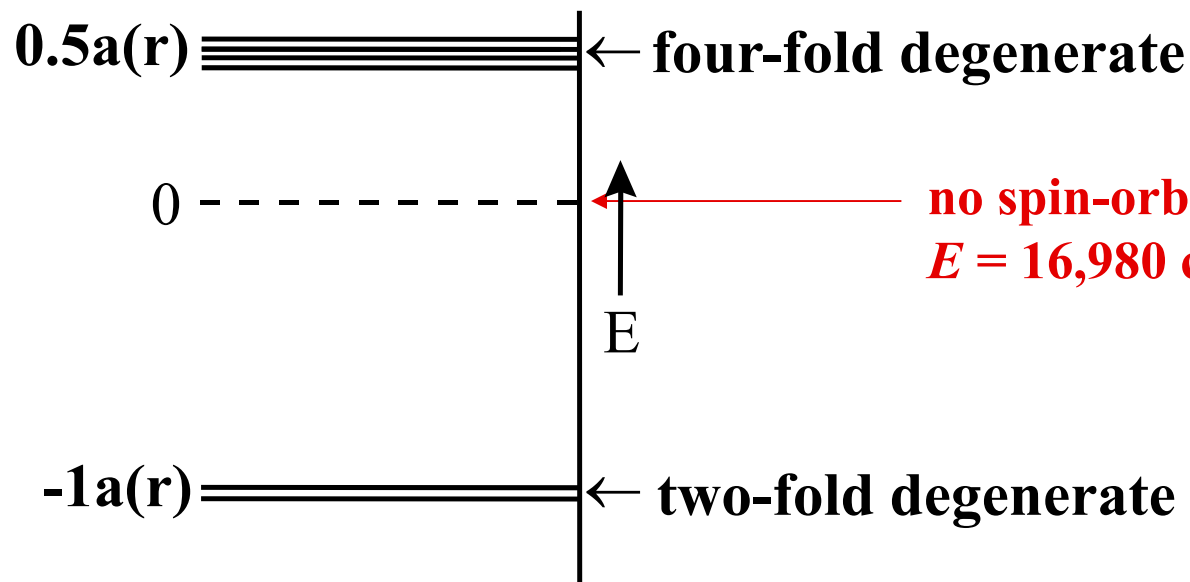
The two 1×1 blocks each give $1/2a(r)$.

Therefore,

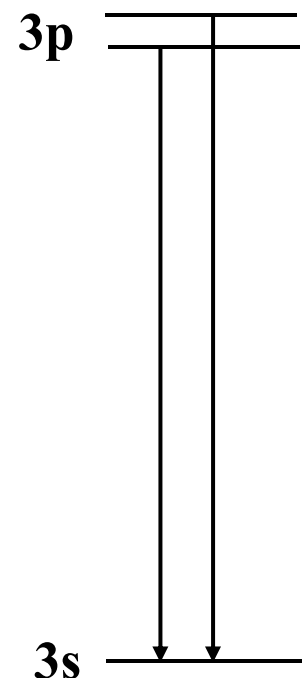
4 eigenvalues of $1/2a(r)$.

2 eigenvalues of $-1a(r)$.

Energy level diagram



fluorescence



Na D-line (3p to 3s transition) split by 17 cm^{-1} .

$$17 \text{ cm}^{-1} = \frac{3}{2} a(r).$$

$$a(r) = 11.3 \text{ cm}^{-1}.$$

Ratio $\frac{a(r)}{E} = 7 \times 10^{-4}$

Ratio small, but need spin-orbit coupling to explain line splitting.

Spin-orbit Coupling in the jm representation

The jm kets are

$$\left| \frac{3}{2} \frac{3}{2} \right\rangle \quad \left| \frac{3}{2} \frac{1}{2} \right\rangle \quad \left| \frac{3}{2} -\frac{1}{2} \right\rangle \quad \left| \frac{3}{2} -\frac{3}{2} \right\rangle \quad \left| \frac{1}{2} \frac{1}{2} \right\rangle \quad \left| \frac{1}{2} -\frac{1}{2} \right\rangle$$

However

$$a(r) \underline{\vec{L}} \cdot \underline{\vec{S}}$$

is in the $m_1 m_2$ representation.

Can't operate \underline{H}_{SO} directly on the jm kets.

Use table of Clebsch-Gordan coefficient to take jm kets into $m_1 m_2$ rep., operate, then convert back to jm rep. (Done in this manner in book.)

Alternatively, rewrite operator so it can operate on the jm kets.

We need the operator, $a(r)\underline{\vec{L}} \cdot \underline{\vec{S}}$, which is an $m_1 m_2$, in the jm

$$\underline{J} = \underline{L} + \underline{S}$$

$$\underline{J}^2 = (\underline{L} + \underline{S})^2 = \underline{L}^2 + \underline{S}^2 + 2\underline{L} \cdot \underline{S}$$

So

$$\underline{L} \cdot \underline{S} = 1/2(\underline{J}^2 - \underline{L}^2 - \underline{S}^2)$$

Recall that a jm ket, $|Jm\rangle$, is an abbreviation for $|j_1 j_2 Jm\rangle$.

So for the spin-orbit coupling problem, the jm ket is

$$|lsJm\rangle$$

l is an eigenket of the \underline{L}^2 operator.

s is an eigenket of the \underline{S}^2 operator.

and

J is an eigenket of the \underline{J}^2 operator.

Therefore, the jm kets are eigenkets of the $\underline{L} \cdot \underline{S}$ operator.

Operate $a(r)\underline{\bar{L}} \cdot \underline{\bar{S}}$ **on** $\left| \frac{3}{2} \frac{3}{2} \right\rangle$ $\underline{\bar{L}} \cdot \underline{\bar{S}} = 1/2(\underline{\bar{J}}^2 - \underline{\bar{L}}^2 - \underline{\bar{S}}^2)$

$$\begin{aligned}
 a(r)\underline{\bar{L}} \cdot \underline{\bar{S}} \left| \frac{3}{2} \frac{3}{2} \right\rangle &= a(r)1/2(\underline{\bar{J}}^2 - \underline{\bar{L}}^2 - \underline{\bar{S}}^2) \left| \frac{3}{2} \frac{3}{2} \right\rangle \\
 &= a(r)1/2(\underline{\bar{J}}^2 - \underline{\bar{L}}^2 - \underline{\bar{S}}^2) \left| 1 \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle \\
 &= a(r)1/2 \left(\frac{15}{4} - 2 - \frac{3}{4} \right) \left| 1 \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle \\
 &= 1/2a(r) \left| 1 \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle
 \end{aligned}$$

Therefore,

$$a(r)\underline{\bar{L}} \cdot \underline{\bar{S}} \left| \frac{3}{2} \frac{3}{2} \right\rangle = \frac{1}{2}a(r) \left| \frac{3}{2} \frac{3}{2} \right\rangle$$

$\left| \frac{3}{2} \frac{3}{2} \right\rangle$ **is an eigenket of** $a(r)\underline{\bar{L}} \cdot \underline{\bar{S}}$ **with eigenvalue** $1/2a(r)$

The jm kets are

$$\left| \frac{3}{2} \frac{3}{2} \right\rangle \quad \left| \frac{3}{2} \frac{1}{2} \right\rangle \quad \left| \frac{3}{2} -\frac{1}{2} \right\rangle \quad \left| \frac{3}{2} -\frac{3}{2} \right\rangle \quad \left| \frac{1}{2} \frac{1}{2} \right\rangle \quad \left| \frac{1}{2} -\frac{1}{2} \right\rangle$$

Since $\frac{1}{2}(\underline{J}^2 - \underline{L}^2 - \underline{S}^2)$

does not operate on the m of the jm kets, $|lsJm\rangle$, all of the kets with $J = 3/2$ give the same eigenvalue, $1/2a(r)$.

$$\begin{aligned} &\text{Then operating on } \left| \frac{1}{2} \frac{1}{2} \right\rangle \\ &a(r)\frac{1}{2}(\underline{J}^2 - \underline{L}^2 - \underline{S}^2) \left| \frac{1}{2} \frac{1}{2} \right\rangle \\ &= a(r)\frac{1}{2}(\underline{J}^2 - \underline{L}^2 - \underline{S}^2) \left| 1 \frac{1}{2} \frac{1}{2} \frac{1}{2} \right\rangle \\ &= a(r)\frac{1}{2} \left(\frac{3}{4} - 2 - \frac{3}{4} \right) \left| 1 \frac{1}{2} \frac{1}{2} \frac{1}{2} \right\rangle \\ &= -1a(r) \left| \frac{1}{2} \frac{1}{2} \right\rangle \end{aligned}$$

Applying \underline{H}_{SO} to all jm kets  Eigenkets

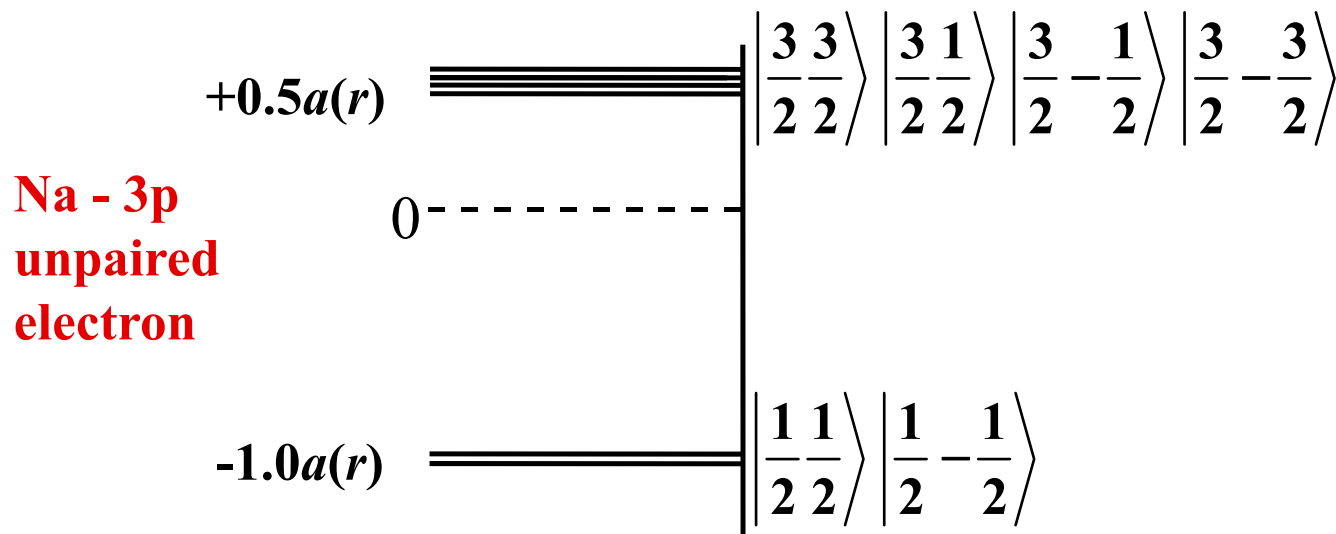
The jm representation kets are the eigenkets because \underline{H}_{SO} couples the orbital and spin angular momenta.

Coupled representation eigenkets.

The jm kets

$$\left| \frac{3}{2} \frac{3}{2} \right\rangle \quad \left| \frac{3}{2} \frac{1}{2} \right\rangle \quad \left| \frac{3}{2} -\frac{1}{2} \right\rangle \quad \left| \frac{3}{2} -\frac{3}{2} \right\rangle \quad \longrightarrow \quad \text{eigenvalues} - +0.5a(r)$$

$$\left| \frac{1}{2} \frac{1}{2} \right\rangle \quad \left| \frac{1}{2} -\frac{1}{2} \right\rangle \quad \longrightarrow \quad \text{eigenvalues} - -1.0a(r)$$



**The jm representation kets will be the eigenkets
whenever a term in Hamiltonian couples
two types of angular momenta.**

Examples:

Hyperfine Interaction $-\gamma \underline{\vec{I}} \cdot \underline{\vec{S}}$

Coupling of electron spin and nuclear spin.

Small splitting in Na optical spectrum.

Structure in ESR spectra.

Electronic triplet states - coupling of two unpaired electrons.

Have diagonalized \underline{H}_{SO} in $m_1 m_2$ representation.
Have shown that jm kets are eigenkets.

A unitary transformation \underline{U}
will take the non-diagonal matrix $\underline{H}_{SO}^{m_1 m_2}$ in the $m_1 m_2$ representation
into the diagonal matrix \underline{H}_{SO}^{jm} in the jm representation.

$$\underline{H}_{SO}^{jm} = \underline{U} \underline{H}_{SO}^{m_1 m_2} \underline{U}^{-1}$$

\underline{U} is the matrix of Clebsch-Gordan Coefficients.

$$\underline{H}_{so} = a(r) \begin{array}{c} \langle 1 \frac{1}{2} | \\ \langle 1 -\frac{1}{2} | \\ \langle 0 \frac{1}{2} | \\ \langle 0 -\frac{1}{2} | \\ \langle -1 \frac{1}{2} | \\ \langle -1 -\frac{1}{2} | \end{array} \begin{array}{c} | 1 \frac{1}{2} \rangle \\ | 1 -\frac{1}{2} \rangle \\ | 0 \frac{1}{2} \rangle \\ | 0 -\frac{1}{2} \rangle \\ | -1 \frac{1}{2} \rangle \\ | -1 -\frac{1}{2} \rangle \end{array} \left[\begin{array}{cccccc} \frac{1}{2} & & & & & \\ & \boxed{\begin{array}{cc} -\frac{1}{2} & \sqrt{2}/2 \\ \sqrt{2}/2 & 0 \end{array}} & & & & \\ & & & 0 & \sqrt{2}/2 & \\ & & & \sqrt{2}/2 & -\frac{1}{2} & \\ & & & & & \frac{1}{2} \end{array} \right]$$

$m_1 m_2$ matrix

**Both are block diagonal.
Only need to work with
corresponding blocks.**

$j_1 = 1$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	j	
$j_2 = 1/2$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	m	
1	$\frac{1}{2}$							
1	$-\frac{1}{2}$							
0	$\frac{1}{2}$							
0	$-\frac{1}{2}$						$\sqrt{\frac{2}{3}}$	$\sqrt{\frac{1}{3}}$
-1	$\frac{1}{2}$						$\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{2}{3}}$
-1	$-\frac{1}{2}$							1
m_1	m_2							

**Table of
Clebsch-Gordan
coefficients**

Multiplying the 2×2 blocks

$$\underline{\underline{U}} \quad \underline{\underline{H}}_{so} \quad \underline{\underline{U}}^{-1}$$

$$\begin{pmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{2}}{2} \\ \frac{\sqrt{2}}{2} & 0 \end{pmatrix} \begin{pmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \end{pmatrix} =$$

$$\begin{pmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \end{pmatrix} \begin{pmatrix} \frac{1}{2}\sqrt{\frac{1}{3}} & -\sqrt{\frac{2}{3}} \\ \frac{1}{2}\sqrt{\frac{2}{3}} & \sqrt{\frac{1}{3}} \end{pmatrix} =$$

$$\begin{pmatrix} 1/2 & 0 \\ 0 & -1 \end{pmatrix}$$

**diagonal matrix with
eigenvalues on the diagonal**

Electron Spin, Antisymmetrization of Wavefunctions, and the Pauli Principle

In treating the He atom, electron spin was not included.

Electron - particle with intrinsic angular momentum, spin

$$S = 1/2 \quad m_s = \pm 1/2$$

$$|1/2 \ 1/2\rangle = |\alpha\rangle$$

$$|1/2 \ -1/2\rangle = |\beta\rangle$$

Excited States of He neglecting Spin

Ground State of He - perturbation theory

$$\underline{H'} = \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad \text{perturbation}$$

Zeroth order wavefunctions (any level)

Product of H atom orbitals

$$|\psi_{n_1\ell_1m_1}(1)\rangle |\psi_{n_2\ell_2m_2}(2)\rangle = |\psi_{n_1\ell_1m_1}(1) \psi_{n_2\ell_2m_2}(2)\rangle$$

(1) → **electron 1; coordinates** (r_1, θ_1, ϕ_1)

(2) → **electron 2; coordinates** (r_2, θ_2, ϕ_2)

Zeroth order energy

$$E_{n_1 n_2}^0 = -4Rhc \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

$$R = \frac{\mu e^4}{8\epsilon_0^2 h^3 c} \quad \mu - \text{reduced mass of H atom}$$

First excited state energy

zeroth order

$$E^0 = -5Rhc$$

since $n_1 = 1$ and $n_2 = 2$
 $n_2 = 1$ and $n_1 = 2$ **same energy**

First Excited Configuration

States corresponding to zeroth order energy - 8 fold degenerate

$$|1s(1)\rangle|2s(2)\rangle \quad |1s(1)\rangle|2p_y(2)\rangle$$

$$|2s(1)\rangle|1s(2)\rangle \quad |2p_y(1)\rangle|1s(2)\rangle$$

$$|1s(1)\rangle|2p_x(2)\rangle \quad |1s(1)\rangle|2p_z(2)\rangle$$

$$|2p_x(1)\rangle|1s(2)\rangle \quad |2p_z(1)\rangle|1s(2)\rangle$$

All have same zeroth order energy.

All have

$$n_1 = 1 \quad \text{and} \quad n_2 = 2$$

or $n_2 = 1 \quad \text{and} \quad n_1 = 2$

Degenerate perturbation theory problem

System of equations (matrix)

Form determinant

	1	2	3	4	5	6	7	8		
1	1s(1)2s(2)	$J_s - E'$	K_s							= 0
2	2s(1)1s(2)	K_s	$J_s - E'$							
3	1s(1)2p _x (2)			$J_{p_x} - E'$	K_{p_x}					
4	2p _x (1)1s(2)			K_{p_x}	$J_{p_x} - E'$					
5	1s(1)2p _y (2)					$J_{p_y} - E'$	K_{p_y}			
6	2p _y (1)1s(2)					K_{p_y}	$J_{p_y} - E'$			
7	1s(1)2p _z (2)							$J_{p_z} - E'$	K_{p_z}	
8	2p _z (1)1s(2)							K_{p_z}	$J_{p_z} - E'$	

E' - eigenvalues

J's - diagonal matrix elements

K's - off diagonal matrix elements

Block diagonal

Four 2x2 blocks

$$J_s = \iint 1s(1)2s(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 1s(1)2s(2) d\tau_1 d\tau_2$$

$$K_s = \iint 1s(1)2s(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 2s(1)1s(2) d\tau_1 d\tau_2$$

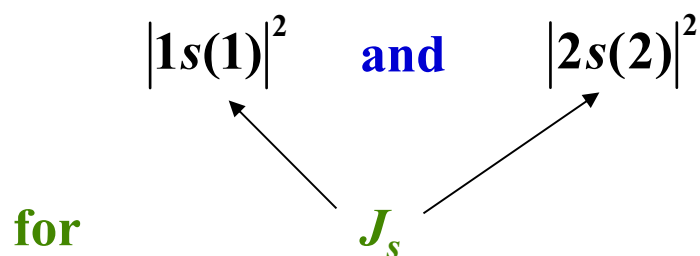
$$J_{p_x} = \iint 1s(1)2p_x(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 1s(1)2p_x(2) d\tau_1 d\tau_2$$

$$K_{p_x} = \iint 1s(1)2p_x(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 2p_x(1)1s(2) d\tau_1 d\tau_2$$

$(J_{p_y}, K_{p_y}, J_{p_z}, K_{p_z} \Rightarrow \text{replace } x \text{ with } y \text{ and } z)$

J 's - Coulomb Integrals

Classically represent average Coulomb interaction energy of two electrons with probability distribution functions



K 's - Exchange Integrals

No classical counter part.

Product basis set not correct zeroth order set of functions.

Exchange - Integrals differ by an Exchange of electrons.

$$K_s = \iint 1s(1)2s(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 2s(1)1s(2) d\tau_1 d\tau_2$$

Other matrix elements are zero.

Example

$$\iint 1s(1)2s(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} 1s(1)2p_z(2) d\tau_1 d\tau_2 = 0$$

odd function - changes sign on inversion through origin

Other functions are even.

Integral of even function times odd function over all space = 0.

Eigenvalues (E')

- 1) Set determinant = 0
 - 2) Expand
- Four 2×2 blocks
 3 blocks for p orbitals
 identical

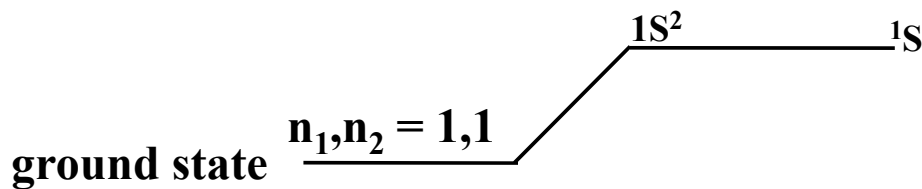
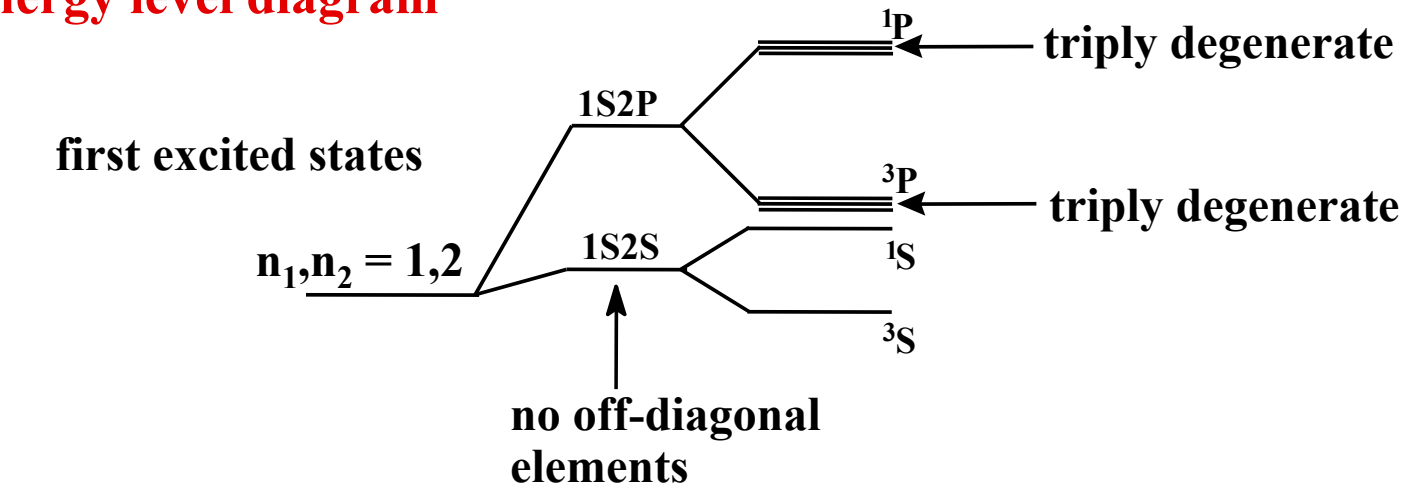
$$E' = J_s + K_s$$

$$J_s - K_s$$

$$J_{p_i} + K_{p_i} \longleftarrow \text{triple root, } p_x, p_y, p_z$$

$$J_{p_i} - K_{p_i} \longleftarrow \text{triple root, } p_x, p_y, p_z$$

Energy level diagram



**S configuration more stable.
 S orbital puts more electron
 density close to nucleus -
 greater Coulombic attraction.**

Eigenfunctions

$$E' = J_s + K_s \quad \frac{1}{\sqrt{2}} \{1s(1)2s(2) + 2s(1)1s(2)\}$$

$$E' = J_s - K_s \quad \frac{1}{\sqrt{2}} \{1s(1)2s(2) - 2s(1)1s(2)\}$$

$$E' = J_{p_i} + K_{p_i} \quad \frac{1}{\sqrt{2}} \{1s(1)2p_i(2) + 2p_i(1)1s(2)\}$$

$i = x, y, z$

$$E' = J_{p_i} - K_{p_i} \quad \frac{1}{\sqrt{2}} \{1s(1)2p_i(2) - 2p_i(1)1s(2)\}$$

Symmetric and Antisymmetric Combinations

+ \longrightarrow combination symmetric.
Symmetric with respect to the interchange of
electron coordinates (labels).

$$\underline{P}|\psi\rangle = 1|\psi\rangle$$

P is the permutation operator.

P interchanges the labels of two electrons (labels - coordinates)

Applying **P** to the wavefunction gives back identical function times 1.

- → **combination antisymmetric.**
Antisymmetric with respect to the interchange of electron coordinates (labels).
Switching coordinates of two electrons gives function back multiplied by -1 .

$$\begin{aligned} \underline{P}|\psi\rangle &= \underline{P} \frac{1}{\sqrt{2}} \{1s(1)2s(2) - 2s(1)1s(2)\} \\ &= \frac{1}{\sqrt{2}} \{1s(2)2s(1) - 2s(2)1s(1)\} \\ &= -1 \frac{1}{\sqrt{2}} \{1s(1)2s(2) - 2s(1)1s(2)\} \\ &= -1|\psi\rangle \end{aligned}$$

**Both + and – functions are
eigenfunctions of permutation operator.**

Symmetric function \longrightarrow **eigenvalue +1**
Antisymmetric function \longrightarrow **eigenvalue –1**

**All wavefunctions for a system containing two or more identical particles
are either symmetric or antisymmetric with respect to exchange of a pair
of electron labels (positions).**

**Many electron wavefunctions must be eigenfunctions of the
permutation operator.**

Inclusion of electron spin in He atom problem

Two spin 1/2 particles \longrightarrow 4 possible states.

In $m_1 m_2$ representation

$$\alpha(1)\alpha(2)$$

$$\alpha(1)\beta(2)$$

$$\beta(1)\alpha(2)$$

$$\beta(1)\beta(2)$$

The two functions, $\alpha(1)\beta(2)$ and $\alpha(2)\beta(1)$
are neither symmetric nor antisymmetric.

$m_1 m_2$ representation not proper representation
for two (or more) electron system.

Transform into jm representation

In jm representation

$\alpha(1)\alpha(2)$	$= 11\rangle$	
$\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$	$= 10\rangle$	symmetric
$\beta(1)\beta(2)$	$= 1-1\rangle$	spin = 1
$\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$	$= 00\rangle$	antisymmetric
		spin = 0

Eight spatial functions.

H independent of spin.

**Each of 8 orbital functions can be multiplied by
the 4 spin functions.**

32 total (spin×orbital) functions.

$$1s(1)2s(2)\alpha(1)\alpha(2)$$

$$2s(1)1s(2)\alpha(1)\alpha(2)$$

$$1s(1)2p_x(2)\alpha(1)\alpha(2)$$

⋮

$$1s(1)2s(2) \cdot \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) + \beta(1)\alpha(2))$$

⋮

Secular determinant looks like

$$\begin{vmatrix} \square & & & \\ & \square & & \\ & & \square & \\ & & & \square \end{vmatrix} = 0$$

Block diagonal same as before except the correct zeroth order functions are obtained by multiplying each of the previous spatial functions by the four spin functions.

Example 1s2s orbitals

$$\frac{1}{\sqrt{2}}[1s(1)2s(2) + 2s(1)1s(2)] \cdot \alpha(1)\alpha(2)$$

$$\frac{1}{\sqrt{2}}[1s(1)2s(2) + 2s(1)1s(2)] \cdot \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\frac{1}{\sqrt{2}}[1s(1)2s(2) + 2s(1)1s(2)] \cdot \beta(1)\beta(2)$$

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

Totally Symmetric
(1-3 spat. & spin sym.
4 spat. & spin antisym.)

$$\frac{1}{\sqrt{2}}[1s(1)2s(2) - 2s(1)1s(2)] \cdot \alpha(1)\alpha(2)$$

$$\frac{1}{\sqrt{2}}[1s(1)2s(2) - 2s(1)1s(2)] \cdot \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

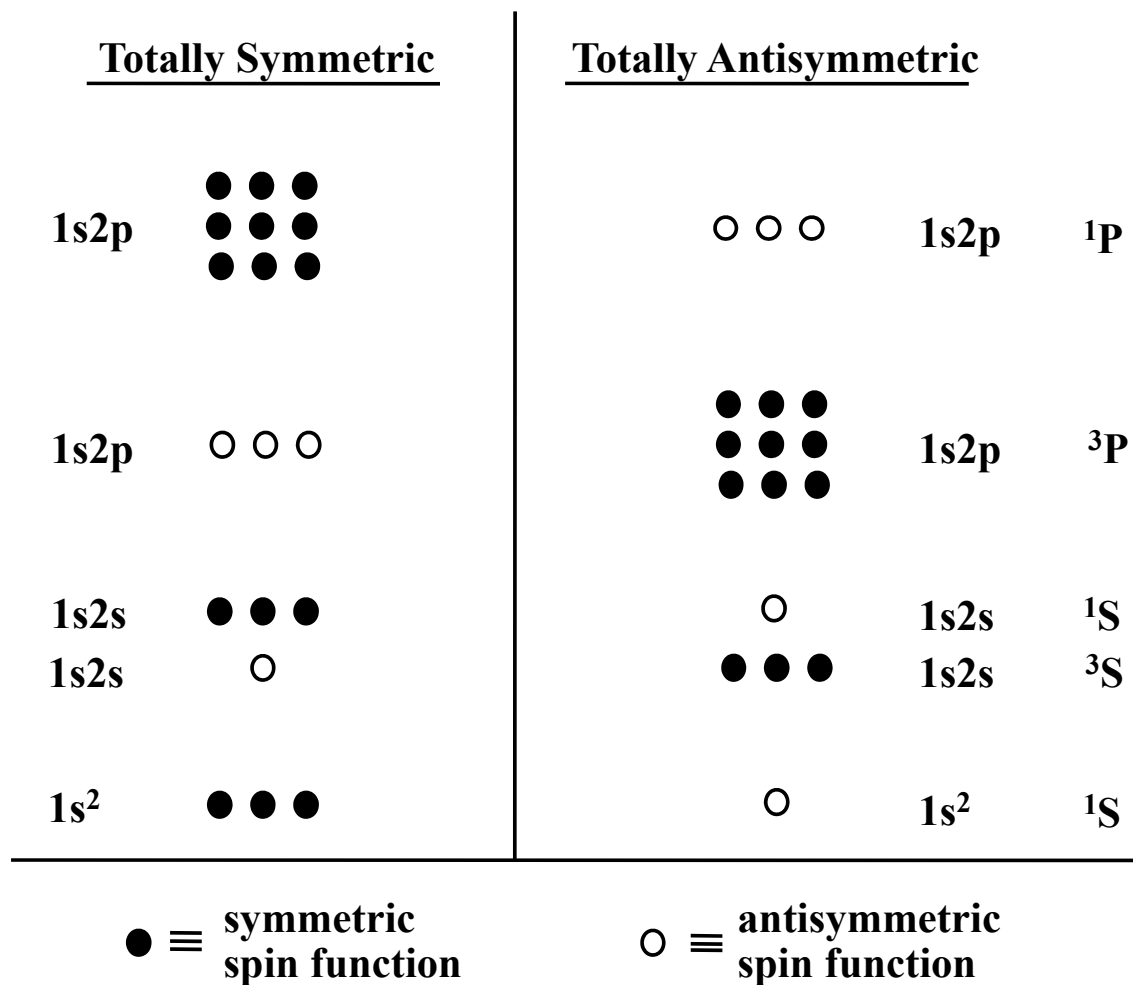
$$\frac{1}{\sqrt{2}}[1s(1)2s(2) - 2s(1)1s(2)] \cdot \beta(1)\beta(2)$$

$$\frac{1}{\sqrt{2}}[1s(1)2s(2) + 2s(1)1s(2)] \cdot \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Totally Antisymmetric
(5-7 spat. antisym; spin sym.
8 spat. sym.; spin antisym.)

Energy Level Diagram

Divided according to totally symmetric or totally antisymmetric.



No perturbation can mix symmetric and antisymmetric states. (H does not Change a symmetric function into an antisymmetric function and vice versa.)

Which functions occur in nature?

Totally symmetric or totally antisymmetric

→ Answer with experiments.

All experiments → States occurring in nature are always

Totally Antisymmetric

Example - ground state of He atoms not paramagnetic, spins paired.

<u>Totally Symmetric</u>		<u>Totally Antisymmetric</u>	
1s2p	● ● ● ● ● ● ● ● ●	○ ○ ○	1s2p 1P
1s2p	○ ○ ○	● ● ● ● ● ● ● ● ●	1s2p 3P
1s2s	● ● ●	○	1s2s 1S
1s2s	○	● ● ●	1s2s 3S
1s ²	● ● ●	○	1s ² 1S

● ≡ symmetric spin function ○ ≡ antisymmetric spin function

Assume:

The wavefunction representing an actual state of a system containing two or more electrons must be totally antisymmetric in the coordinates of the electrons; i.e., on interchanging the coordinates of any two electrons the wavefunction must change sign.

Q.M. statement of the Pauli Exclusion Principle

(Applies to any Fermions.)

To see equivalence of Antisymmetrization and Pauli Principle

Antisymmetric functions can be written as determinants.

**A(1) represents an orbital×spin function for one electron,
for example, $1s(1)\alpha(1)$,
and B, C, ... N are others, then**

$$\psi = \begin{vmatrix} A(1) & B(1) & \cdots & N(1) \\ A(2) & B(2) & \cdots & N(2) \\ \vdots & \vdots & & \vdots \\ A(N) & B(N) & \cdots & N(N) \end{vmatrix}$$

**Expand the determinant gives the antisymmetrized wavefunction.
Totally antisymmetric because interchange of any two rows
changes the sign of the determinant.**

Example - He ground state

$$1s(1) \alpha(1) = 1s(1) \quad \text{(no bar means } \alpha \text{ spin)}$$

$$1s(1) \beta(1) = \overline{1s(1)} \quad \text{(bar means } \beta \text{ spin)}$$

$$\left| \begin{array}{cc} 1s(1) \overline{1s(1)} \\ 1s(2) \overline{1s(2)} \end{array} \right| = 1s(1) \overline{1s(2)} - 1s(2) \overline{1s(1)}$$

$$= 1s(1)\alpha(1)1s(2)\beta(2) - 1s(2)\alpha(2)1s(1)\beta(1)$$

$$= 1s(1)1s(2) [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

(symmetric spatial,
antisymmetric spin)

Correct antisymmetric ground state function.

Another important property of determinants

Two Columns of Determinant Equal \longrightarrow Determinant Vanishes

Pauli Principle

For a given orbital there are only two possible
orbital \times spin functions,

i. e., those obtained by multiplying the orbital function by α or β spin functions.

Thus, no more than two electrons can occupy the same orbital in an atom,
and the two must have their spins opposed,

that is,

no two electrons can have the same values of all four quantum numbers
 n, ℓ, m_ℓ, m_s

otherwise two columns will be equal and the determinant,
the wavefunction, vanishes.

Example - He ground state with both spins α

$$\psi = \begin{vmatrix} 1s(1) & 1s(1) \\ 1s(2) & 1s(2) \end{vmatrix}$$

$$\begin{vmatrix} 1s(1) & 1s(1) \\ 1s(2) & 1s(2) \end{vmatrix} = 1s(1)\alpha(1)1s(2)\alpha(2) - 1s(2)\alpha(2)1s(1)\alpha(1) = 0$$

Requirement of antisymmetric wavefunctions is the equivalent of the Pauli Principle.

Singlet and Triplet States

Totally Antisymmetric

term symbols

○ ○ ○ 1s2p 1P

● ● ●
● ● ● 1s2p 3P
● ● ●

○ 1s2s 1S
● ● ● 1s2s 3S

○ $1s^2$ 1S

● ≡ symmetric spin function ○ ≡ antisymmetric spin function

- → singlet states, sym. orbital function × (single) antisym. spin function.
- → triplet states, antisym. orbital function × (three) sym. spin functions.

For same orbital configuration

Triplet States lower in energy than singlet states
because of electron correlation.

Triplet \longrightarrow **sym. spin.** Therefore, **antisym. orbital**

For example:

$$\psi_T = [1s(1)2s(2) - 2s(1)1s(2)] \times \begin{cases} \alpha(1)\alpha(2) & \Rightarrow |11\rangle \\ \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(1)) & \Rightarrow |10\rangle \\ \beta(1)\beta(2) & \Rightarrow |1-1\rangle \end{cases}$$

Singlet \longrightarrow **antisym. spin.** Therefore, **sym. orbital**

$$\psi_S = [1s(1)2s(2) + 2s(1)1s(2)] \times \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1)) \Rightarrow |00\rangle$$

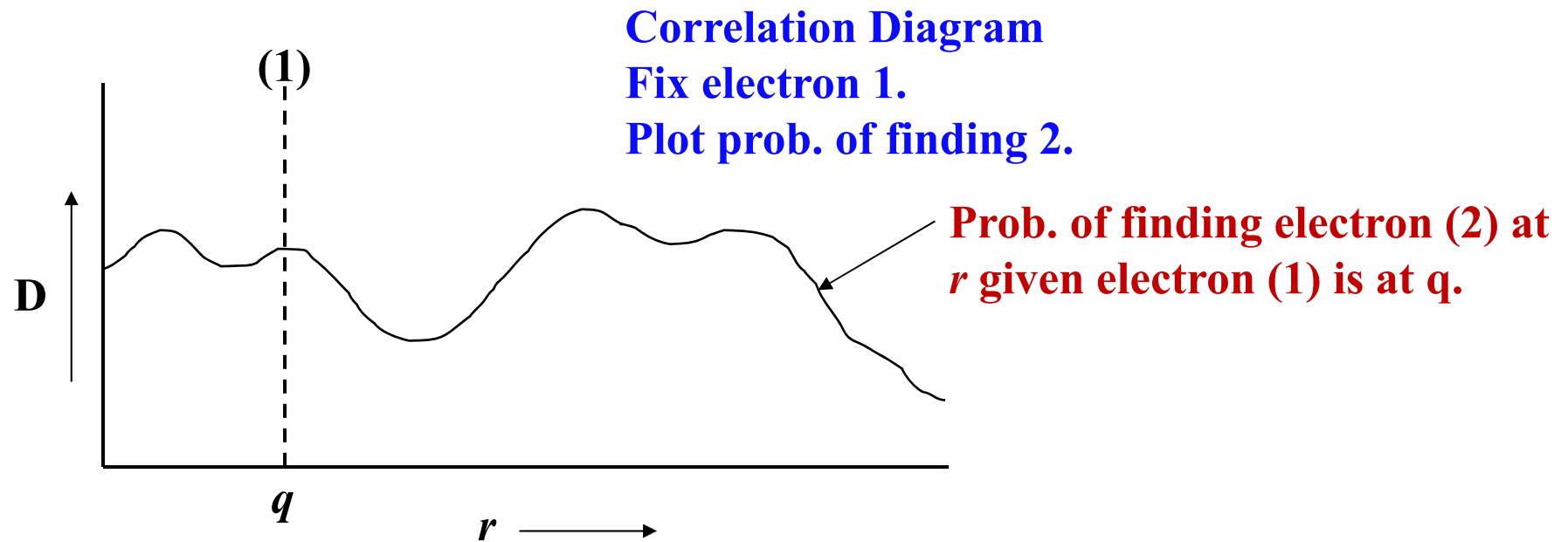
Singlet - 2 electrons can be at the same place.

Consider a point with coordinates, q .

$$\psi_S = [1s(1)2s(2) + 2s(1)1s(2)]$$

$$\psi_S = [1s(q)2s(q) + 2s(q)1s(q)]$$

$$\psi_S = 2[1s(q)2s(q)]$$



(schematic illustration)

**Triplet - 2 electrons cannot be at the same place.
2 electrons have node for being in same place.**

Consider a point with coordinates, q (any q).

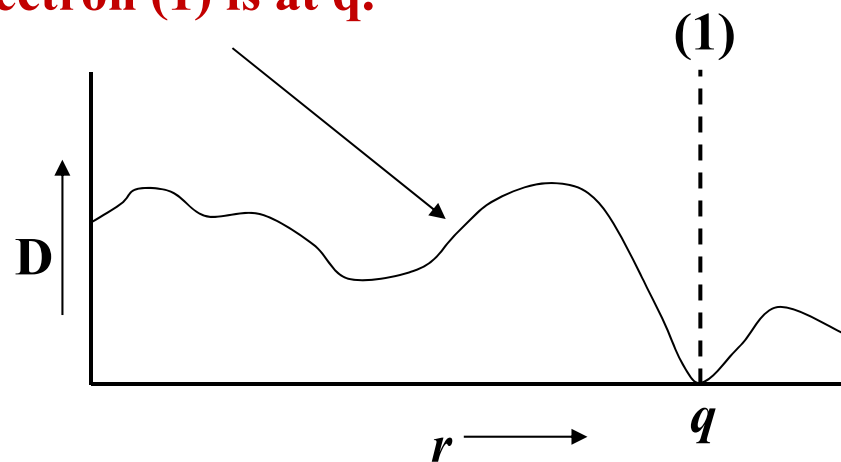
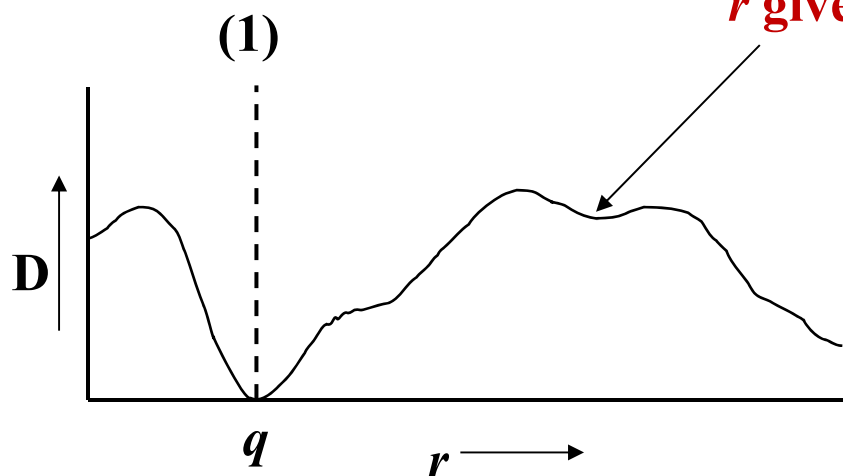
$$\psi_T = [1s(1)2s(2) - 2s(1)1s(2)]$$

$$\psi_T = [1s(q)2s(q) - 2s(q)1s(q)]$$

$$\psi_T = 0$$

**Correlation Diagram
Fix electron 1.
Plot prob. of finding 2.**

**Prob. of finding electron (2) at
 r given electron (1) is at q .**



(schematic illustrations)

In triplet state

Electrons are anti-correlated.

Reduces electron-electron repulsion.

Lowers energy below singlet state of same orbital configuration.