

# PHY2005

## Atomic Physics

Lecturer: Dr. Stuart Sim

Room: 02.019

E-mail: [s.sim@qub.ac.uk](mailto:s.sim@qub.ac.uk)

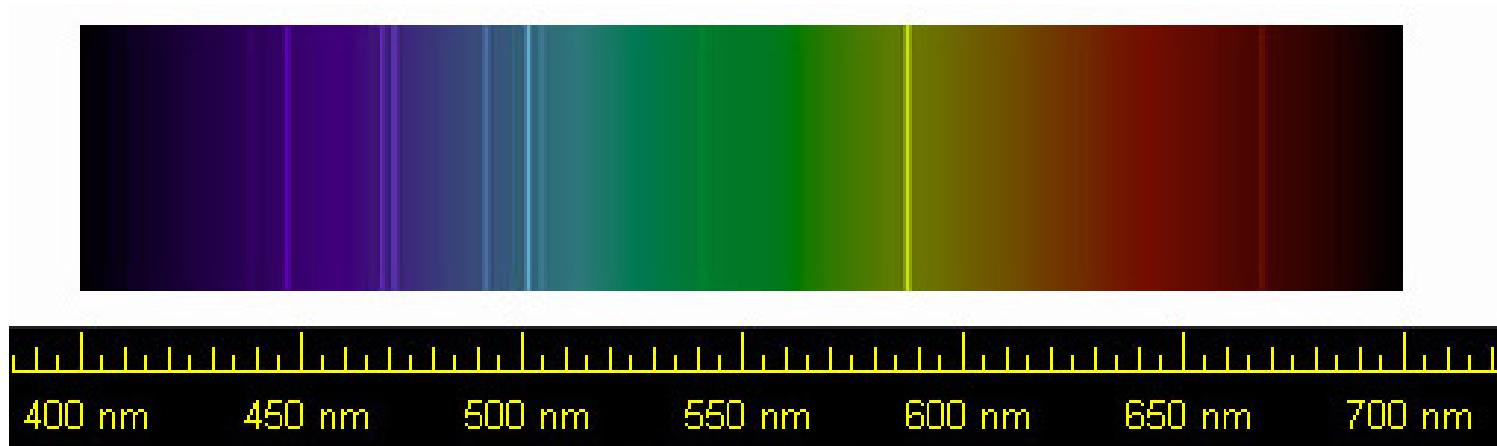
# (7) Multi-electron atoms: Two-electron atoms

## *Learning goals*

1. To study the two-electron atom as the simplest example of the multi-electron case
2. To introduce the Schrödinger equation for a two-electron atom
3. To introduce the concept of *orbitals* in multi-electron atoms and how these are described by a *configuration*
4. To be able to interpret and use spectroscopic notation to describe electron configurations
5. To appreciate that,  $L$  and  $S$  have significant effects on the energy levels of multi-electron atoms
6. To qualitatively understand how the requirements of particle exchange symmetry give rise to the *exchange force* in helium
7. To formalise how the electron-electron interaction in helium can be expressed in terms of the *Coulomb* and *Exchange* integrals

# The helium atom

Spectrum of helium:



# The helium atom

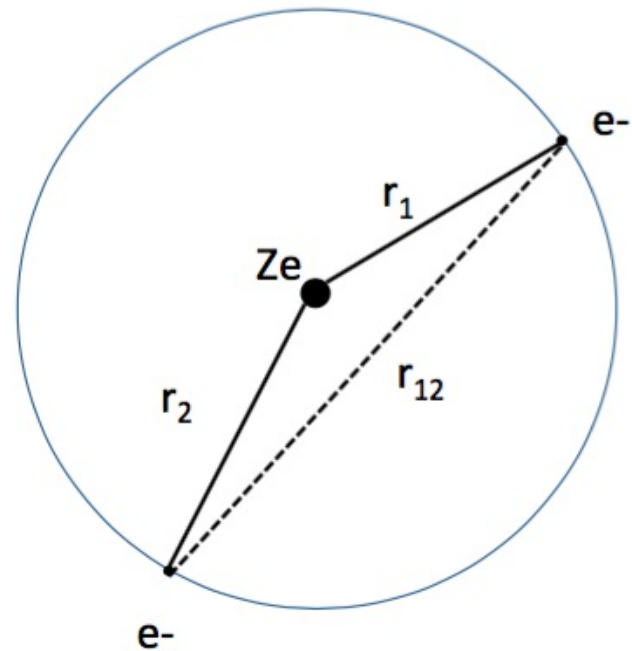
Helios:



# The helium atom

Schematic of helium:

- Two electrons and nucleus



# The helium atom: Schrödinger Equation

Two electrons:

$$-\frac{\hbar^2}{2m_e}\nabla_1^2\psi_T - \frac{\hbar^2}{2m_e}\nabla_2^2\psi_T + V_T\psi_T = E_T\psi_T$$

Three terms in potential energy:

$$V_T = -\frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Last is *not separable*.

# The helium atom: independent electrons

Two electron TISE becomes:

$$\hat{H}_1\psi_T + \hat{H}_2\psi_T = E_T\psi_T$$

Can find solutions:

$$\psi_T = \psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2)$$

Single-particle states  $\psi_\alpha$  and  $\psi_\beta$  known as orbitals.

In this approximation,

$$E_T = E_\alpha + E_\beta$$

# Configurations

Which orbitals are occupied is indicated by *configuration*.

Use spectroscopic notation to give  $n/$  for occupied orbitals.

$l$ -value	letter	origin
0	s	sharp
1	p	principal
2	d	diffuse
3	f	fundamental
4	g	alphabetical
5	h	

List orbitals next to each other.

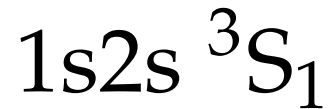
E.g. 1s2p means “one electron with  $n=1$ ,  $l=0$  and one with  $n=2$ ,  $l=1$ ” etc.



# Configuration and Term

Combination of configuration and term is the usual means to identify states of multi-electron atoms:

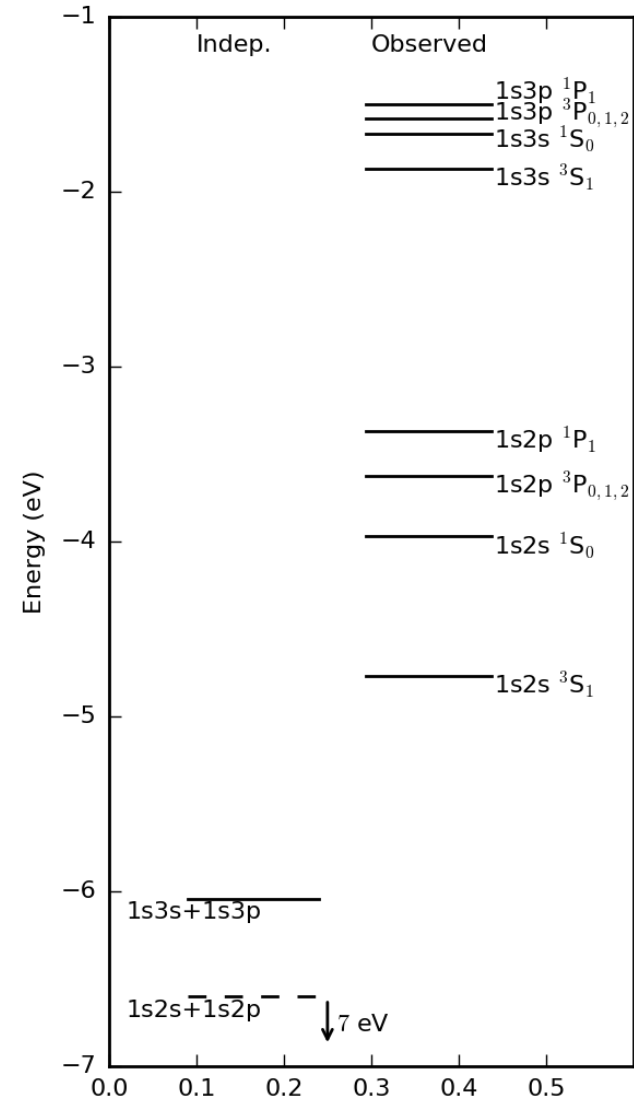
E.g. first excited state of helium is indicated by



# Electron-electron repulsion: effect on energies

The observed energy levels of He differ significantly from independent electron approximation:

- Always less negative
- Different terms have different energies
- L-value has large effect
- S-value also has large effect



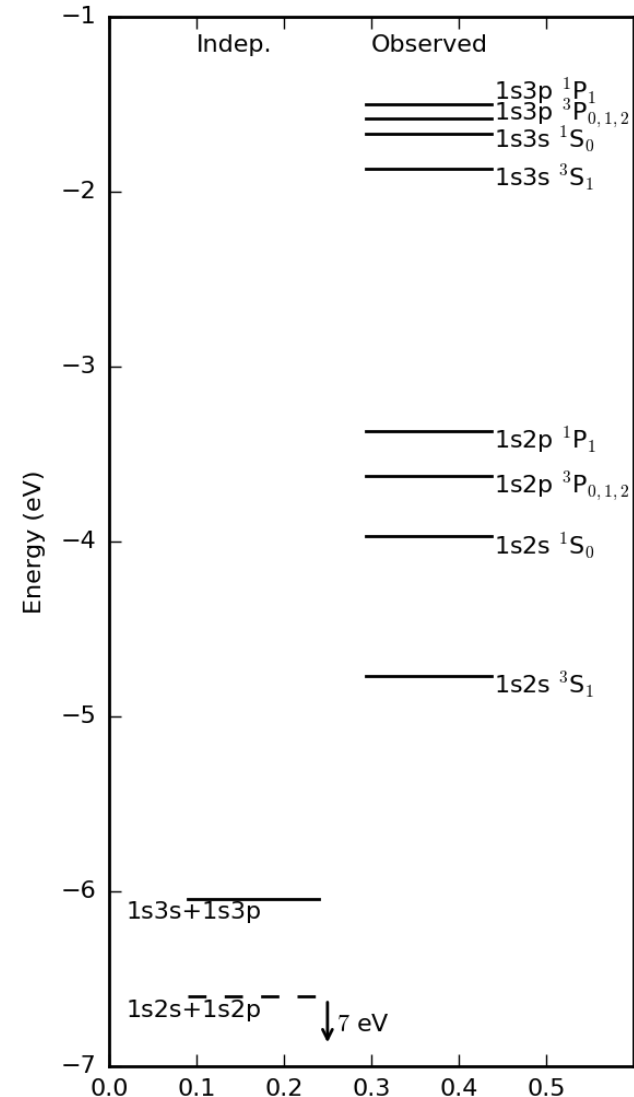
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Qualitative influence of L makes intuitive sense (space distribution of electrons).

But S ....? Need to investigate...



# Orbitals and indistinguishability

The wavefunction

$$\psi_T = \psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2)$$

does not respect the *indistinguishability* of the electrons. As in PHY2001, the (space) wavefunction must have definite symmetry under particle exchange:

Exchange symmetric:

$$\psi_S = \frac{1}{\sqrt{2}} (\psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) + \psi_\alpha(\mathbf{r}_2)\psi_\beta(\mathbf{r}_1))$$

or exchange antisymmetric:

$$\psi_A = \frac{1}{\sqrt{2}} (\psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) - \psi_\alpha(\mathbf{r}_2)\psi_\beta(\mathbf{r}_1))$$

# Proximity of electrons

Consider both exchange symmetries if the electron positions are close to each other (i.e.  $\mathbf{r}_2 \rightarrow \mathbf{r}_1$ ):

$$\psi_A \rightarrow 0 \text{ as } \mathbf{r}_2 \rightarrow \mathbf{r}_1$$

while

$$\psi_S \rightarrow \sqrt{2}\psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_1) \text{ as } \mathbf{r}_2 \rightarrow \mathbf{r}_1$$

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thus expect Coulomb repulsion to be larger for symmetric than anti-symmetric wavefunction, *even through the same orbitals are occupied!*

# Symmetrised spin wavefunctions

There are four distinct spin states for pair of electrons.

Just like the space wavefunction, the spin wavefunction must have definite symmetry. There are four possibilities:

Triplet of symmetric spin states:

exchange symmetric  $(+1/2, +1/2)$

exchange symmetric  $\frac{1}{\sqrt{2}} [(+1/2, -1/2) + (-1/2, +1/2)]$

exchange symmetric  $(-1/2, -1/2)$

Singlet with antisymmetric spin:

exchange antisymmetric  $\frac{1}{\sqrt{2}} [(+1/2, -1/2) - (-1/2, +1/2)]$

# Symmetrised spin wavefunctions

This “triplet” + “singlet” split exactly corresponds to the allowed  $S$  quantum numbers:

For  $S=1$ , there are three values of  $M_S$  ( $= -1, 0, +1$ )

- these three are the symmetric triple states

For  $S=0$ , there is only one value of  $M_S$  ( $= 0$ )

- this is the singlet antisymmetric state



# Pauli principle

We have met the Pauli principle before. It is often stated in one of two ways:

1. No two identical fermions can have the same set of quantum numbers (special form)
2. The complete wavefunction for a system of fermions must be antisymmetric under particle exchange (more general form)

Remember:

$$\text{complete eigenfunction} = \psi \times \sigma$$

# Pauli principle: the *Exchange Force* for two electrons

For the complete wavefunction to be antisymmetric:

$S = 1$  spin states pair with  $\psi_A$  spatial wavefunctions

$S = 0$  spin states pair with  $\psi_S$  spatial wavefunctions.

Since we know the symmetric space function allows the electrons to be closer to each other (= more repulsion energy), the  $S=0$  states will have higher energy.

Known as the *Exchange Force*.

# Electron repulsion as a “perturbation”

The repulsion can be approximately incorporated as a perturbation (example of *1<sup>st</sup> order perturbation theory*):

This means include it in energy as an extra term (*expectation value*):

$$E_T = E_\alpha + E_\beta + \left\langle \frac{e^2}{4\pi\epsilon_0 r_{12}} \right\rangle$$

It can be shown (see more in lecture notes) that

$$\left\langle \frac{e^2}{4\pi\epsilon_0 r_{12}} \right\rangle = J \pm K$$



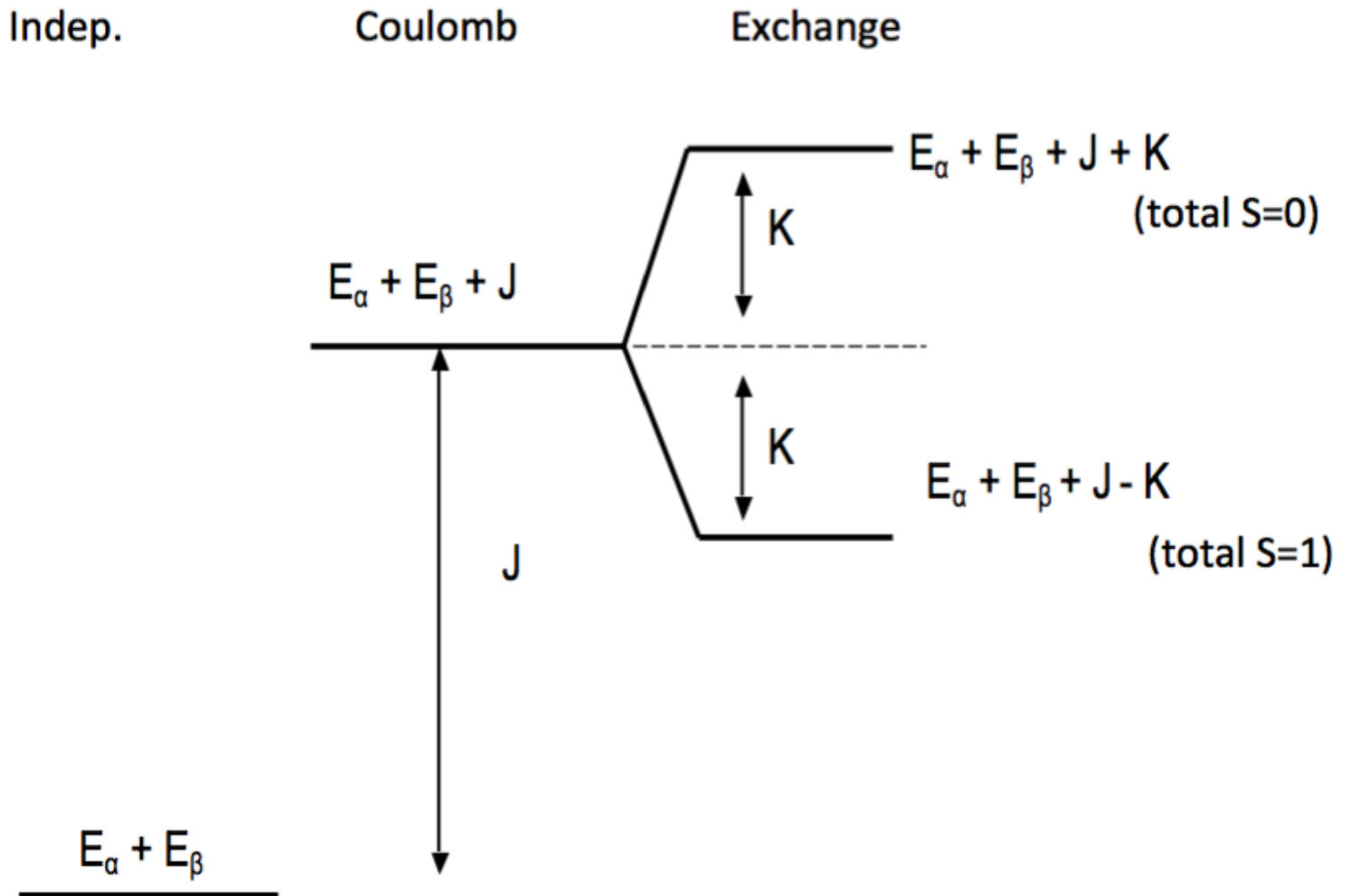
J called Coulomb Integral

K called Exchange Integral

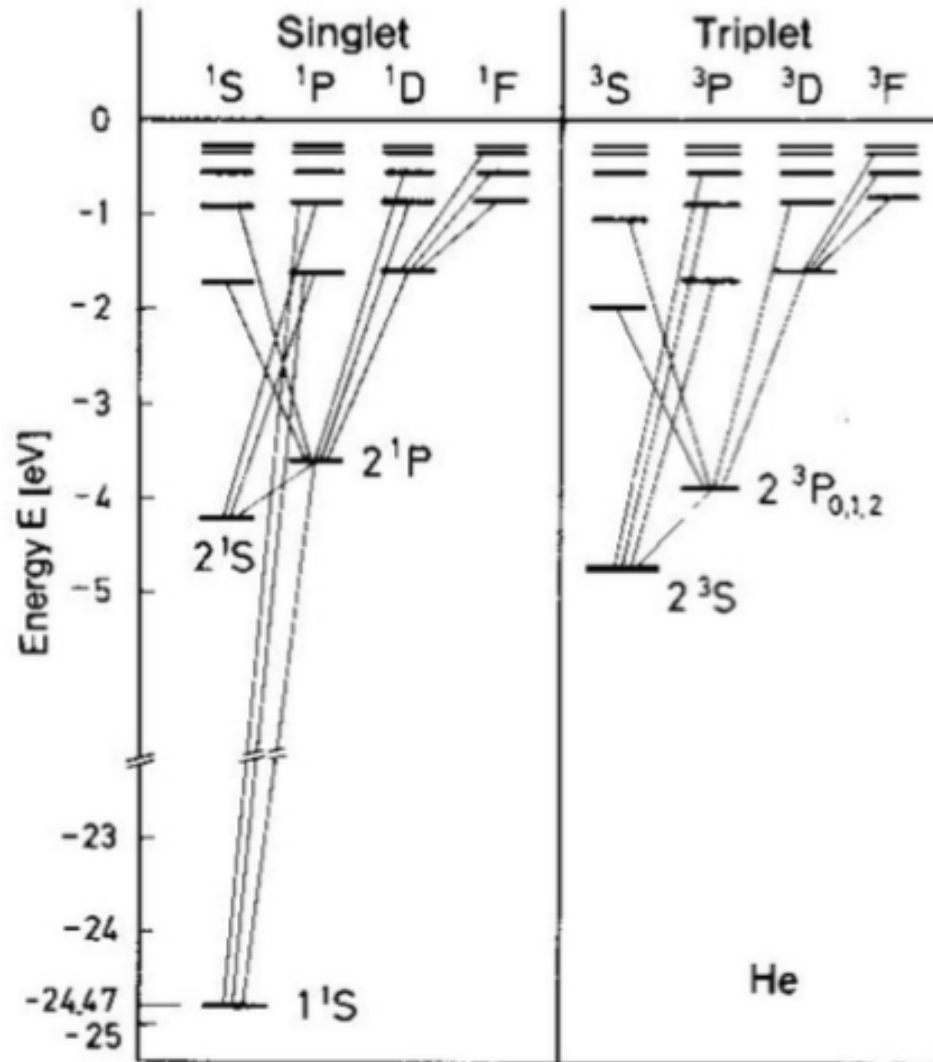
+ for S=0

- For S=1

# Electron repulsion: Coulomb and Exchange Integrals



# He atom: energy level diagram



# He atom: ground configuration and the Pauli principle

## Why no $1s^2 \ ^3S_1$ state?

Would require  $S=1$  (i.e. symmetric spin state)

- So would have  $\psi_A$  (i.e. anti-symmetric space wavefunction)
- But  $\psi_A = \frac{1}{\sqrt{2}} (\psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) - \psi_\alpha(\mathbf{r}_2)\psi_\beta(\mathbf{r}_1))$  is zero if both orbitals are the same (i.e. if  $\alpha=\beta$ )
- I.e. there is no anti-symmetric space wavefunction to use!
- So only the  $S=0$  (i.e. anti-symmetric spin state) solution is allowed

# Summary/Revision

- For multi-electron atoms, the formulation of the Schrödinger equation is a simple generalisation of what we have seen for single-electron atoms.
- The electron-electron interaction term generally makes analytic solution of the multi-electron Schrödinger equation impossible.
- If the electron-electron interaction is ignored, the wavefunction can be expressed in terms of occupied single-electron *orbitals*.
- For a multi-electron atom, it is usual to indicate which orbitals are occupied by giving the *configuration* in spectroscopic notation.
- The electron-electron interaction has very significant effects on the energy levels of atoms: since this interaction is repulsive, it will raise the total energy compared to a calculation in which it is neglected.

# Summary/Revision

- Since the space distribution of the electrons depends on their  $l$  quantum numbers, the value of  $L$  affects the strength of the electron-electron repulsion, and therefore the total energy.
- The total wavefunction must be antisymmetric with respect to particle exchange (general expression of the Pauli principle for electrons). This is achieved *either* by having a symmetric space wavefunction and antisymmetric spin wavefunction or *vice versa*.
- For the two-electron atom, if the total spin is  $S = 1$  then the spin wavefunction is symmetric under particle exchange. If  $S = 0$  the spin wavefunction is antisymmetric.
- Since symmetric space wavefunctions place the electrons closer to each other than antisymmetric wavefunctions,  $S = 1$  states have lower energies than  $S = 0$  states.
- In the two-electron atom, the electron-electron interaction can be formally expressed in terms of the *Coulomb* and *Exchange* integrals.
- In the two-electron atom, the Pauli principle forbids both electrons occupying the same orbital with an antisymmetric space wavefunction. Thus the ground configuration  $1s^2$  has no  $^3S$  term.