

Free Study Material from All Lab Experiments



Quantum Mechanics and Applications Chapter - 6 Many Electron Atoms

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Many Electron Atoms

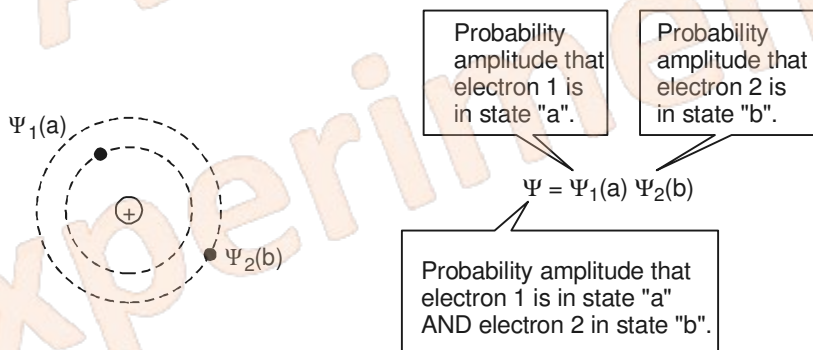
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Syllabus: Pauli's Exclusion Principle. Symmetric and Antisymmetric Wave Functions. Spin orbit coupling. Spectral Notations for Atomic States. Total angular momentum. Spin-orbit coupling in atoms-L-S and J-J coupling.

Q 1. What is Pauli exclusion principle? Explain symmetric and asymmetric wave functions.

Ans. Pauli exclusion principle - No two electrons in an atom can have identical quantum numbers. This is an example of a general principle which applies not only to electrons but also to other particles of half-integer spin (fermions). It does not apply to particles of integer spin (bosons).

Symmetric and asymmetric wave functions - The nature of the Pauli exclusion principle can be illustrated by supposing that electrons 1 and 2 are in states a and b respectively. The wavefunction for the two electron system would be but this wavefunction is unacceptable because the electrons are identical and indistinguishable.



To account for this we must use a linear combination of the two possibilities since the determination of which electron is in which state is not possible to determine.

The wavefunction for the state in which both states "a" and "b" are occupied by the electrons can be written. alllabexperiments.com

$$\Psi = \Psi_1(a)\Psi_2(b) \pm \Psi_1(b)\Psi_2(a)$$

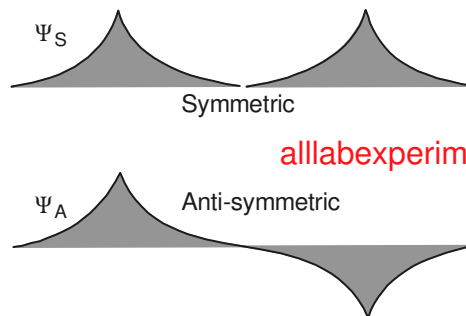
+ Required for bosons.

Probability amplitude that both states "a" and "b" are occupied by electrons 1 and 2 in either order.

– Required for fermions.

The Pauli exclusion principle is part of one of our most basic observations of nature: particles of half-integer spin must have antisymmetric wavefunctions, and particles of integer spin must have symmetric wavefunctions. The minus sign in the above relationship forces the wavefunction to vanish identically if both states are "a" or "b", implying that it is impossible for both electrons to occupy the same state.

The electron distribution around the protons of the hydrogen is described by a quantum mechanical wavefunction, and the wavefunction which describes the two electrons for a pair of atoms can be symmetric or antisymmetric with respect to exchange of the identical electrons. From the Pauli exclusion principle, we know that the wavefunctions for two identical fermions must be antisymmetric. The electron spin part of the wavefunction can be symmetric (parallel spins) or antisymmetric (opposite spins), but then the space part of the wavefunction must be the opposite. That guarantees that the entire wavefunction (the product of the spin and space wavefunctions) is antisymmetric. The two possibilities for the spatial wavefunctions for distant hydrogens are shown below.

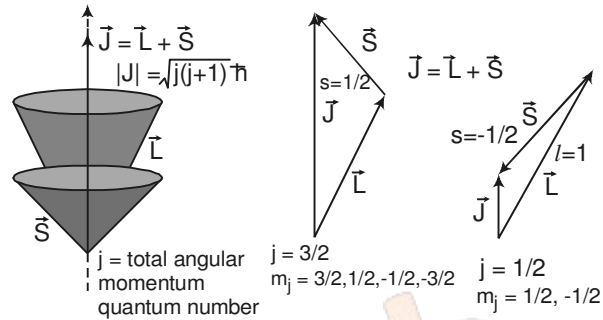


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Q 3. What is Total angular momentum?

Ans. Vector Model for Total Angular Momentum:

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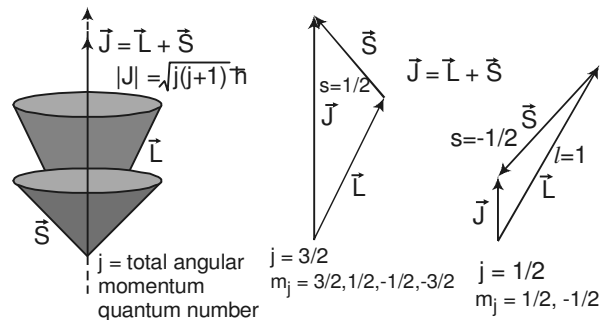
When orbital angular momentum L and electron spin angular momentum S are combined to produce the total angular momentum of an atomic electron, the combination process can be visualized in terms of a vector model. Both the orbital and spin angular momentum are seen as precessing about the direction of the total angular momentum J . This diagram can be seen as describing a single electron, or multiple electrons for which the spin and orbital angular momenta have been combined to produce composite angular momenta S and L respectively.

Q 4. Explain L-S coupling and also explain its spectral term notation.

Ans. Russell-Saunders or L-S Coupling - For multi-electron atoms where the spin-orbit coupling is weak, it can be presumed that the orbital angular momenta of the individual electrons add to form a resultant orbital angular momentum L . Likewise, the individual spin angular momenta are presumed to couple to produce a resultant spin angular momentum S . Then L and S combine to form the total angular momentum"

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

This kind of combination is visualized in terms of a vector model of angular momentum.



This kind of coupling is called L-S coupling or Russell-Saunders coupling, and it is found to give good agreement with the observed spectral details for many light atoms. For heavier atoms, another coupling scheme called "j-j coupling" provides better agreement with experiment.

The vector model illustrated above was applied to a single electron, but a similar model can be applied when multiple electrons contribute to the net angular momentum. If identical electrons are involved, then proper care must be taken to make sure the combinations produce an antisymmetric wavefunction upon exchange of identical electrons. For example, consider the electron configuration of titanium, $(Ar)3d^24s^2$. The 4s electrons contribute to a closed shell and the $3d^2$ electrons contribute the net angular momentum. Under the L-S coupling conditions this gives the following.

$$\vec{L}_1 + \vec{L}_2 = \vec{L}$$

$$\vec{L} = 0, 1, 2, 3, 4$$

$$\vec{S}_1 + \vec{S}_2 = \vec{S}$$

$$S = 0, 1$$

$$\vec{J} = \vec{L} + \vec{S} = 0, 1, 2, 3, 4$$

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These identical electrons must produce an antisymmetric wave function.

$$\Psi = \Psi_{\text{spin}} \Psi_{\text{orbital}}$$

Since $S = 1$ represents a symmetric spin state, it must couple with antisymmetric orbital states $L = 1$ and $L = 3$.

The possibility of $J=5$ is excluded by symmetry considerations for the identical electrons, but the other states can be visualized by the vector model.

Q 5. Explain J-J coupling.

Ans. In light atoms, the interactions between the orbital angular momenta of individual electrons is stronger than the spin-orbit coupling between the spin and orbital angular momenta. These cases are described by "L-S coupling". However, for heavier elements with larger nuclear charge, the spin-orbit interactions become as strong as the interactions between individual spins or orbital angular momenta. In those cases the spin and orbital angular momenta of individual electrons tend to couple to form individual electron angular momenta.

$$J_1 = L_1 + S_1$$

$$J_2 = L_2 + S_2$$

$$J = \sum_i J_i$$

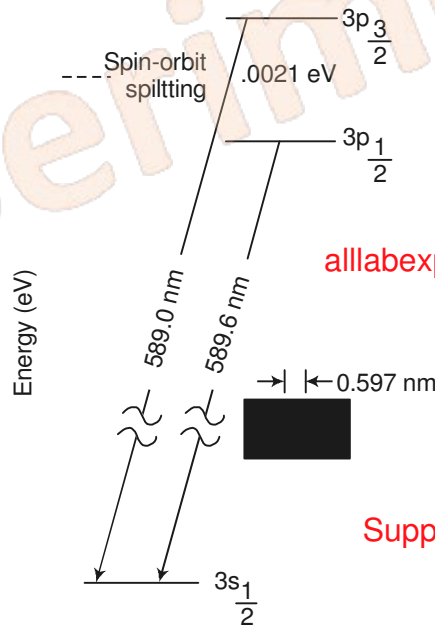
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Another case where the overall L and S are decoupled is the case where there is a very strong external magnetic field is applied.

Q 6. Explain the reason for sodium doublet.

Ans. The sodium spectrum is dominated by the bright known as the sodium D-lines at 588.9950 and 589.5924 nanometer. From the energy level diagram it can be seen that these lines are emitted in a transition from the 3p to the 3s levels.

The Sodium Doublet: The well known bright doublet which is responsible for the bright yellow light from a sodium lamp may be used to demonstrate several of the influences which cause splitting of the emission lines of atomic spectra. The transition which gives rise to the doublet is from the 3p to the 3s level, levels which would be the same in the hydrogen atom. The fact that the 3s (orbital quantum number = 0) is lower than the 3p ($l=1$) is a good example of the dependence of atomic energy levels on angular momentum. The 3s electron penetrates the 1s shell more and is less effectively shielded than the 3p electron, so the 3s level is lower (more tightly bound).



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The fact that there is a doublet shows the smaller dependence of the atomic energy levels on the total angular momentum. The 3p level is split into states with total angular momentum $j=3/2$ and $j=1/2$ by the magnetic energy of the electron spin in the presence of the internal magnetic field caused by the orbital motion. This effect is called the spin-orbit effect.

Q 7. Solve LS coupling for two different "p-shell" electrons pp and pd coupling.

Ans.

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- As an example, take a 2-electron atom:

$$nl_1, n'l_2 \quad (n \neq n')$$

$$\begin{cases} L = |l_1 - l_2| + 1, \dots, l_1 + l_2 \\ S = |s_1 - s_2| + 1, \dots, s_1 + s_2 \end{cases}$$

$$\left(s_1 = s_2 = \frac{1}{2} \right) \Rightarrow S = 0 \text{ or } S = 1$$

(single and triplets)

- Example 1 :

$$l_1 = l_2 = 1 \Rightarrow \text{configuration: } np, np$$

$$L = 0 \text{ or } L = 1 \text{ or } L = 2$$

\Rightarrow possible terms are:

$${}^1S, {}^1P, {}^1D, {}^3S, {}^3P, {}^3D$$

- Example 2 :

$$l_1 = 1, l_2 = 2 \Rightarrow \text{configuration: } np, n'd$$

$$L = 1 \text{ or } L = 2 \text{ or } L = 3$$

\Rightarrow possible terms are :

$${}^1P, {}^1D, {}^1F, {}^3P, {}^3D, {}^3F$$

Electrons in the same orbital (equivalent electrons)

when $l_1 = l_2$ then same spin states $s_1 = 1/2$ and $s_2 = 1/2$ can't exist due to Pauli exclusion principle, then it is states as np^2

Example 1:

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$$n_1 = n_2, l_1 = l_2 = 1 \Rightarrow \text{configuration : } np^2$$

(the case for example : C, Si, Ge

$$\Rightarrow \text{possible terms : } {}^1S, {}^1D, {}^3P$$

(other terms possible for $npn p'$ are forbidden due to the Pauli principle)

Example 2:

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$$n_1 = n_2 = n_3, l_1 = l_2 = l_3 = 1$$

$$\Rightarrow \text{configuration : } np^3$$

(the case fore, for example : N, P, As

$$\Rightarrow \text{possible terms : } {}^2P, {}^2D, {}^4S$$

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

addition of angular momenta

$$\begin{cases} J = |L - S|, |L - S| + 1, \dots, L + S \\ M_J = -J, J + 1, \dots, J \end{cases}$$

For every atomic terms, there are $(2S + 1)$ fine-structure levels

(or $(2L + 1)$ if $L < S$)

Example 1 :

configuration : $npn'p'$

$${}^3D \Rightarrow J = 3, 2, 1 \Rightarrow {}^3D_1, {}^3D_2, {}^3D_3$$

$${}^1D \Rightarrow J = 2 \Rightarrow {}^1D_2$$

$${}^3P \Rightarrow J = 2, 1, 0 \Rightarrow {}^3P_0, {}^3P_1, {}^3P_2$$

$${}^1P \Rightarrow J = 1 \Rightarrow {}^1P_1$$

$${}^3S \Rightarrow J = 1 \Rightarrow {}^3S_1$$

$${}^1S \Rightarrow J = 0 \Rightarrow {}^1S_0$$

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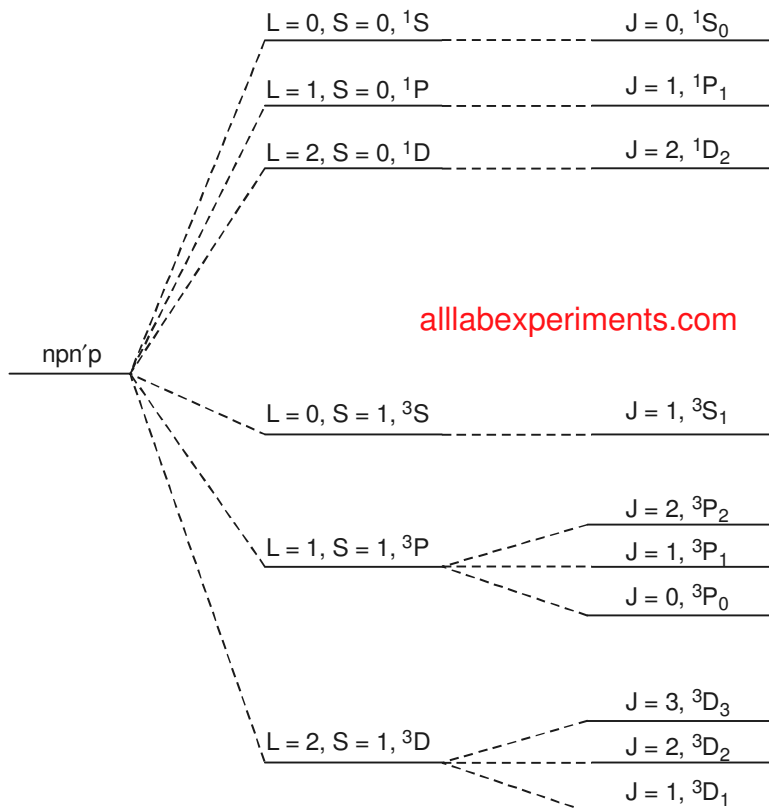
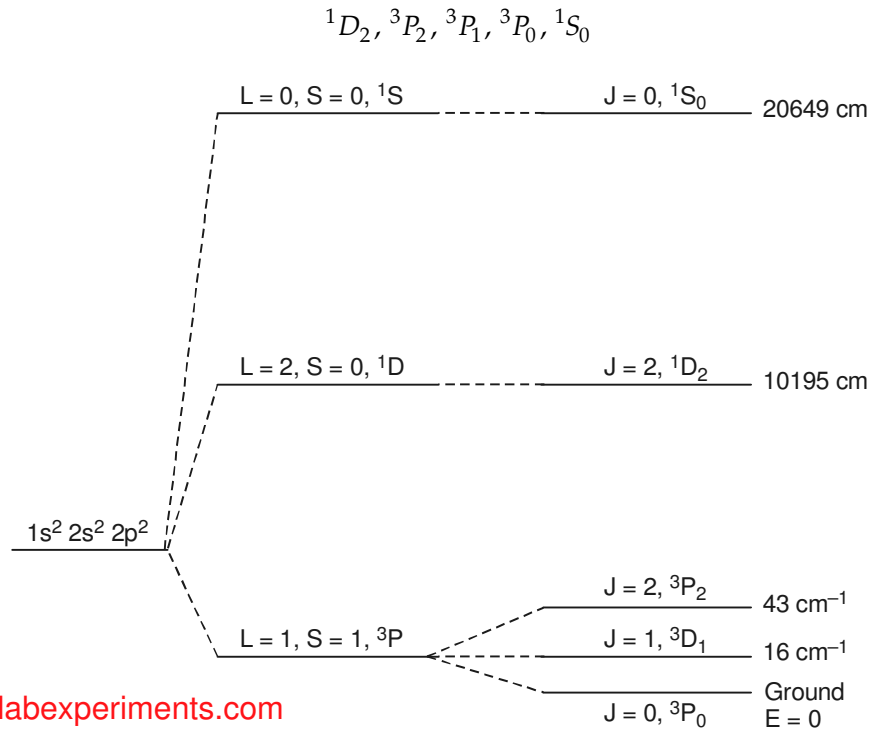


Figure the splitting of the configuration $np n'p$ by the electrotonic perturbation H_1 and the spin-orbit perturbation H_2

• example 2 :

configuration : np^2



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Q 9. Give some examples of JJ Coupling.

Ans.

- As an example, take a 2- electron atom :

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$l_1 = 0, l_2 = 1 \Rightarrow$ configuration : $ns, n'p$

$$\begin{cases} l_1=0 \\ l_2=1 \end{cases} \quad \text{and} \quad \begin{cases} s_1=1/2 \\ s_2=1/2 \end{cases}$$

$$(j_i = |l_i - s_i|, |l_i - s_i| - 1, \dots, l_i + s_i)$$

$\Rightarrow j_1 = 1/2$ and $j_2 = 3/2, 1/2$

\Rightarrow Two possibilities :

$$\left(\frac{1}{2}, \frac{1}{2}\right) \text{ and } \left(\frac{1}{2}, \frac{3}{2}\right)$$

