University of Wisconsin
Chemistry 524

Energy Levels in Atoms

Angular Momentum

Energy levels in atoms are described by a term symbol; where a term symbol contains the angular momentum information of the atom.

Each electron in an atom has spin angular momentum, $\mathbf{s_i}$ and orbital angular momentum, $\mathbf{l_i}$.

Each atom has angular momentum, **S, L, and J** where:

$\mathbf{S} = \sum_{i}^{N} \mathbf{s_i}$ total spin angular momentum for N electrons

For 1 electron $S = \frac{1}{2}$

For N electrons when N is odd $S = \frac{N}{2}, \frac{N}{2} -1, \frac{N}{2} -2, \ldots, \frac{1}{2}$

For N electrons when Nis even $S = \frac{N}{2}, \frac{N}{2} -1, \frac{N}{2} -2, \ldots, 0$

$\mathbf{L} = \sum_{i}^{N} \mathbf{l_i}$ total orbital angular momentum for N electrons

For 1 electron L = l

For 2 electrons $|L| = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \ldots, |l_1 - l_2|$

$\mathbf{J} = \mathbf{L} + \mathbf{S}$ total angular momentum of atom

$J = L + S, L + S - 1, \ldots, |L-S|$

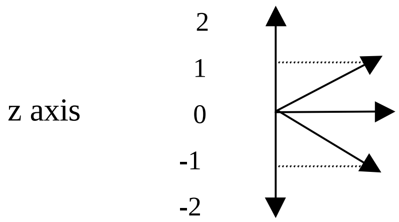
The number of J states, 2S + 1, defines the multiplicity

The term symbol denotes the angular momentum as $^{2S+1}L_J$.

For example, the term symbol, $^2P_{3/2}$ denotes an atom having S = ½ (one unpaired electron), L= 1 (use D for L =2, P for L=1, and S for L=0), and J = 3/2.

Since **J** is a vector, it can point in a number of quantized directions. The quantum number M_J defines the projection of **J** along a given direction (defined as the z axis). The possible quantized directions are given by M_J = J, J-1, J-2, …, -J.

For example, the vector with magnitude J = 2, and M_J = 2,1,0,1, 2, will have the following possible orientations:



The magnetic moment of an atom **μ** is determined by **J** according to:

$$\boldsymbol{\mu} = \frac{-e}{2mc}\mathbf{J}$$

where e is the charge of the electron, m is the mass of the electron, and c is the speed of light.

In the z direction:

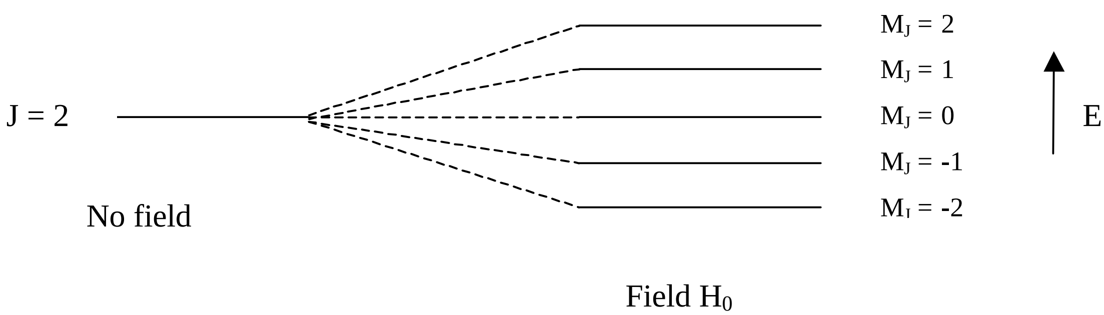
$$\mu_z = \frac{-e\,\hbar}{2mc} M_z$$

where $\hbar = \frac{h}{2p}$ and h = 6.626 x 10^{-34} Js (Planck's Constant)

In an external magnetic field of strength H_0 directed along the z axis; the energy of the atom depends upon the direction that **μ** is pointing:

$$E = -\boldsymbol{\mu} \bullet \mathbf{H} = -H_0\mu_z = \frac{eH_0\hbar}{2mc} M_J$$

Therefore a J = 2 energy level will split into 5 sublevels



The following selection rules govern the allowed energy transitions for atoms:

$\Delta S = 0$
$\Delta L = 0, \pm 1$; $\Delta l = \pm 1$ for 1 electron
$\Delta J = 0, \pm 1$
$\Delta M_J = 0, \pm 1$

Nuclear Magnetic Moments

The nuclei of an atom can have a magnetic moment that will also interact with an external magnetic field.

The nuclear magnetic moment is given by:

$\boldsymbol{\mu} = \gamma\, \mathbf{I}$ where γ is the gyromagnetic ratio and **I** is the spin angular momentum of the nucleus

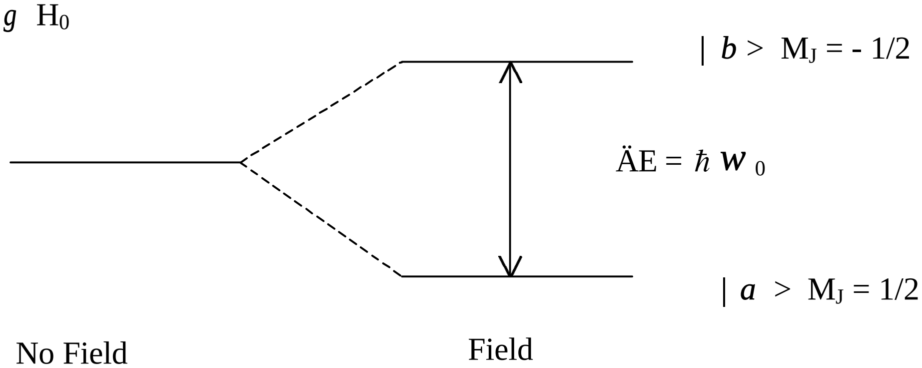
for a proton I = ½ and M_I = + ½ and – ½ (defined as α and β respectively)

In the presence of an external magnetic field the energy will depend on the orientation of magnetic moment with respect to the field according to:

$$E = -\boldsymbol{\mu} \bullet \mathbf{H} = -\gamma\, I_z H_0 = -\hbar\, \gamma\, H_0 M_I$$

for the proton: $E_\alpha = -\frac{\hbar}{2}\gamma\, H_0 = -\frac{\hbar}{2}\omega_0$ and $E_\beta = \frac{\hbar}{2}\gamma\, H_0 = \frac{\hbar}{2}\omega_0$

where $\omega_0 = \gamma\, H_0$



For an external magnetic field, H_0, of 23490 Gauss , $\frac{\omega_0}{2\pi}$ = 100.00 MHz

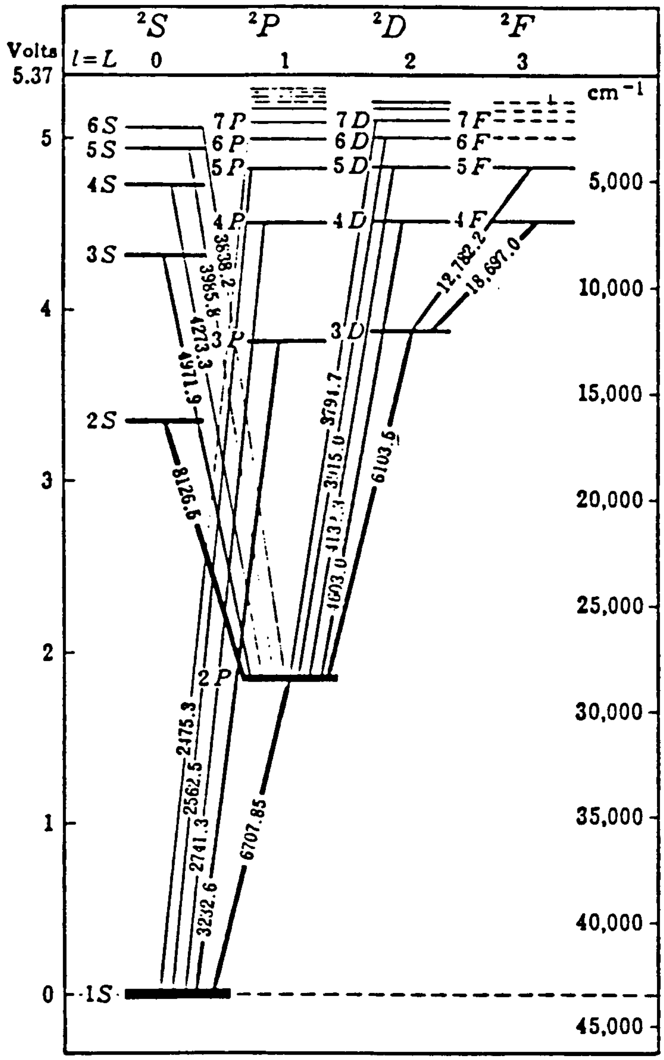


Fig. 24. Energy Level Diagram of the Li Atom [after Grotrian (8)]. The wave lengths of the spectral lines are written on the connecting lines representing the transitions. Doublet structure (see Chapter II) is not included. Some unobserved levels are indicated by dotted lines. The true principal quantum numbers for the S terms are one greater than the empirical running numbers given (see p. 61); for the remaining terms, they are the same.

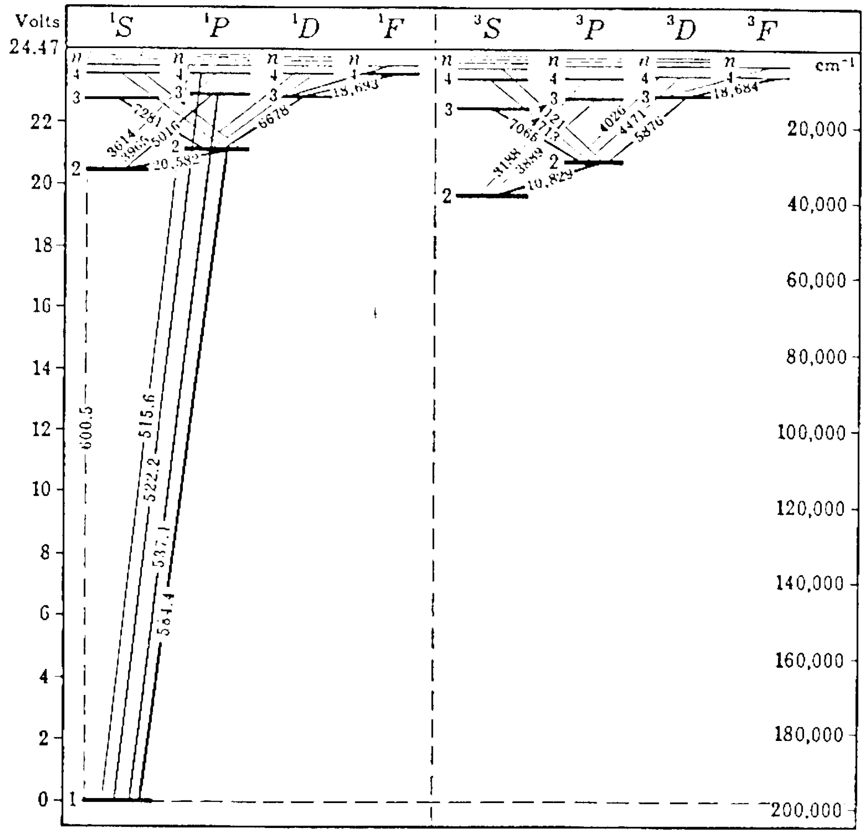


Fig. 27. Energy Level Diagram for Helium. The running numbers and true principal quantum numbers of the emission electron are here identical. The series in the visible and near ultraviolet regions correspond to the indicated transitions between terms with $n \geqq 2$.

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[23] The weak intercombination line reported by Lyman at 591.6 Å is an Ne line according to Dorgelo (55).