UCI Chemistry 249
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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 toal spin, total orbital and total angular momentum, **S**, **L**, and **J** where:

S is the total spin angular momentum for N electrons $\mathbf{S} = \sum_i^N \mathbf{s}_i$

Possible quantum numbers for **S**:

For one electron: S = 1/2.

For N electrons when N is odd: S = N/2, N/2 -1, N/2 -2, … 1/2.

For N electrons when N is even: S = N/2, N/2 -1, N/2 -2, … 0.

L is the total orbital angular momentum for N electrons $\mathbf{L} = \sum_i^N \mathbf{l}_i$

Possible quantum numbers for **L**:

For one electron: L = l.

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

J = **L** + **S** is the total angular momentum of the atom

Possible quantum numbers for J: J = (L + S), (L + S – 1), (L + S – 2), ... | L-S |

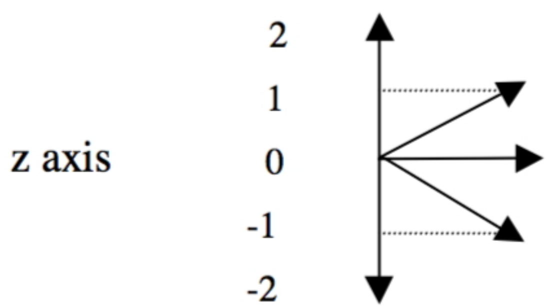
The number of J states, 2S + 1, defines the **multiplicity**

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

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

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

For example, the vector **J** with quantum number J = 2, M_J = 2, 1, 0, -1, -2, and will have the following possible orientations:



Atomic Magnetic Moment

In the weak field limit, the magnetic moment of an atom μ is proportional to **J**:

$$\boldsymbol{\mu} = -g_J \frac{m_B}{\hbar} \mathbf{J}$$

where m_B is the Bohr magneton ($\frac{e\hbar}{2m_e}$) and g_J is the Landé g factor for **J**.

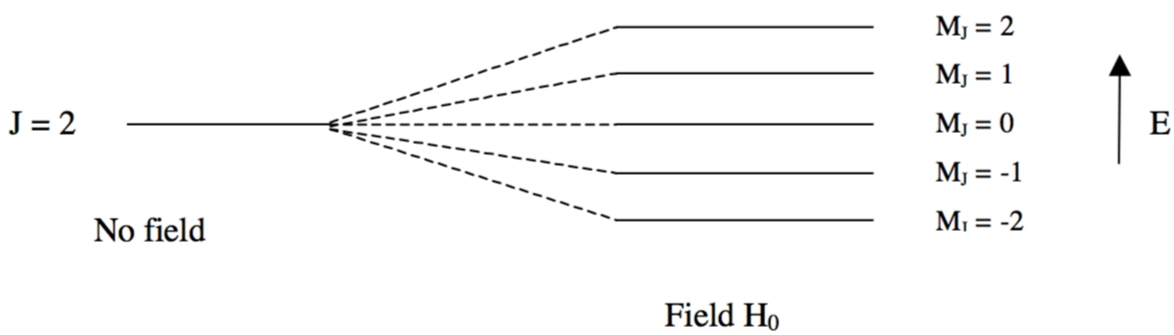
The component of the magnetic moment in the z direction μ_z with eigenvalues:

$$\mu_z = -g_J m_B M_J$$

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:

$$E = -\boldsymbol{\mu} \cdot \boldsymbol{H} = -\mu_z H_0 = g_J m_B H_0 M_J$$

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



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

ΔS = 0

ΔL=0, ±1; Δl= ±1for 1 electron

ΔJ = 0, ±1

ΔMJ = 0, ±1

A **Grotrian Diagram** describes all of the observed absorption lines for an atom.

(c.f. G. Herzberg, Atomic Spectra and Atomic Structure)

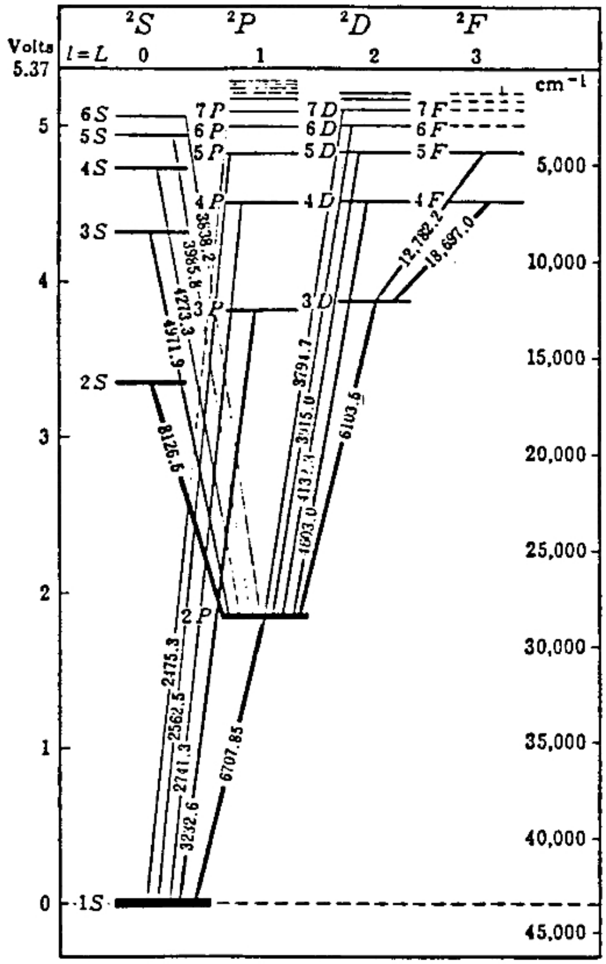


Fig. 24. Energy Level Diagram of the Li Atom [after Grotrian (8)]. The wave lengths of the spectral lines are written on the connecting lines representing the transitions. Doublet structure (see Chapter II) is not included. Some unobserved levels are indicated by dotted lines. The true principal quantum 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.

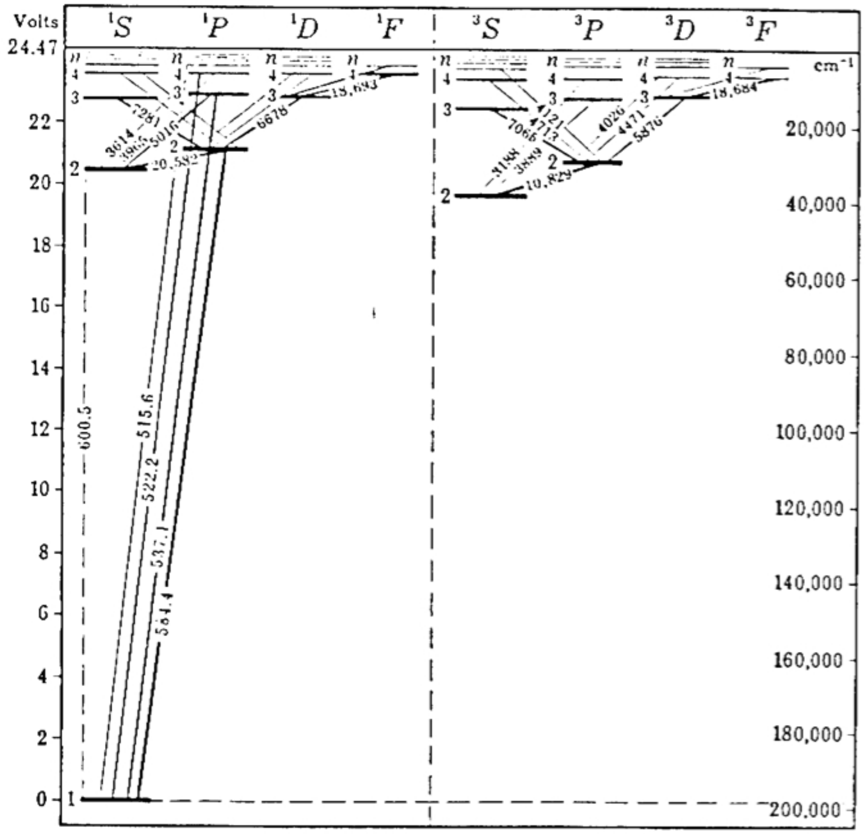


Fig. 27. Energy Level Diagram for Helium. The running numbers and true principal quantum numbers of the emission electron are here identical. The series in the visible and near ultraviolet regions correspond to the indicated transitions between terms with $n \geqq 2$.

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