

Chemistry 126 – Molecular Spectra & Molecular Structure

Week # 1 Supplemental Notes – The Electronic Structure of Atoms

I. THE HYDROGEN ATOM

A. Quantum Mechanical Formulation

1. Energies

The non-relativistic Hamiltonian operator for a hydrogen-like atom consisting of one electron and one positively charged nucleus, without any external fields, is:

$$\mathcal{H} = -\frac{\hbar^2}{2\mu} \vec{\nabla}^2 - \frac{Ze^2}{r} = \frac{\vec{p}^2}{2\mu} + V(\vec{r}) \quad (1.1)$$

where $Z = 1$ for hydrogen, 2 for He^+ , 3 for Li^{2+} , etc... $\mu = m_p m_e / (m_p + m_e) \approx m_e$ is the reduced mass, $\vec{p} = -i\hbar \vec{\nabla}$, and $V(\vec{r}) = -Ze^2/r$ is the centrosymmetric Coloumb potential.

The wavefunctions ψ , which contain all the information knowable about the states of the atom, can be obtained by solving the time-independent Schrödinger equation:

$$\mathcal{H}\psi = E\psi \quad (1.2)$$

In spherical coordinates, this equation becomes

$$r^2 \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] \psi + \frac{2\mu r^2}{\hbar^2} [E - V(r)] \psi = L^2 \psi \quad , \quad (1.3)$$

where

$$L^2 = - \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (1.4)$$

There is no physical reason for asymmetry, and so the wavefunction can be factored as

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \quad . \quad (1.5)$$

When this form is substituted into (1.3), we obtain

$$\begin{aligned} \frac{r^2}{R(r)} \left[\left(\frac{d^2}{dr^2} R(r) + \frac{2}{r} \frac{dR(r)}{dr} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] R(r) \right] = \\ - \frac{1}{Y(\theta, \phi)} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} Y(\theta, \phi) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) \right] = \text{constant} = \lambda \quad . \quad (1.6) \end{aligned}$$

Here the partial derivatives in r become full derivatives since R is a function of r only. Note that the left-hand side in (1.6) depends on r only and the right-hand side on the angle variables only, so that both must be constant. If we replace $R(r) = F(r)/r$, then

$$\frac{d^2 F(r)}{dr^2} + \frac{2\mu}{\hbar^2} [E - V(r)] F(r) = \frac{\lambda}{r^2} F(r) \quad , \quad (1.7a)$$

$$L^2 Y(\theta, \phi) = \lambda Y(\theta, \phi) \quad (1.7b)$$

Assume on physical grounds that Y and its first derivatives are continuous, single-valued and finite everywhere. Then equation (1.7b) gives $Y(\theta, \phi) = Y_{l,m}(\theta, \phi)$, the spherical harmonics, with $\lambda = l(l+1)$ and $m = l, l-1, \dots, -l$.

For the radial function $F(r)$, the boundary condition that $V(r) \rightarrow 0$ as $r \rightarrow \infty$ gives:

$$\frac{d^2 F(r)}{dr^2} + \frac{2\mu}{\hbar^2} E F(r) = 0 \quad \text{as } r \rightarrow \infty . \quad (1.8)$$

This is the Schrödinger equation for the free particle, which has the solutions:

$$F(r) = \exp[\pm r \sqrt{-2\mu E/\hbar^2}] . \quad (1.9)$$

If $E < 0$, only $F(r) \sim e^{-ar}$ is possible for ψ to be finite everywhere. If $E > 0$, both the $+$ and $-$ solutions will work. We thus examine solutions for bound states ($E < 0$) of the form $F(r) = e^{-ar} f(r)$, where $a = (-2\mu E/\hbar^2)^{1/2}$.

In the following, we will use atomic units, in which $e = \hbar = m_e = 1$. The unit of length $a_0 = \hbar^2/m_e e^2$ is equal to the first Bohr radius. With this unit of length, the unit of energy is the hartree $= e^2/a_0$. For more details, see the accompanying notes on units (A1-3).

If we assume $\mu = m_e$, then $a = (-2E)^{1/2}$, and equation (1.7a) becomes

$$\frac{d^2 f(r)}{dr^2} - 2a \frac{df(r)}{dr} + \left[2\frac{Z}{r} - \frac{l(l+1)}{r^2} \right] f(r) = 0 . \quad (1.10)$$

Equation (1.10) can be solved by expanding $f(r)$ in an infinite power series

$$f(r) = r^s \sum_{v=0}^{\infty} A_v r^v \quad (1.11)$$

where $s > 0$ so that f is finite as $r \rightarrow 0$.

If we evaluate the derivatives df/dr and $d^2 f/dr^2$ in series form and collect terms with common powers, the radial equation becomes:

$$\sum_{v=0}^{\infty} A_v \{ [(v+s-1)(v+s) - l(l+1)] r^{v+s-2} - 2[a(v+s) - z] r^{v+s-1} \} = 0 . \quad (1.12)$$

Obviously, the factor multiplying each power of r must vanish separately; in particular, the lowest term with $v=0$ gives

$$A_0 \{ (s-1)s - l(l+1) \} r^{s-2} = 0 . \quad (1.13)$$

$\Rightarrow s = l+1 > 0$. Moreover, there is a recursion relation for the coefficients A_v :

$$\frac{A_v}{A_{v-1}} = \frac{2[(l+v)a - z]}{[v^2 + (2l+1)v]} . \quad (1.14)$$

As $v \rightarrow \infty$, $A_v/A_{v-1} \sim 2a/v$ which has exactly the same asymptotic behavior as:

$$e^{2ar} = \sum_{v=0}^{\infty} \frac{(2a)^v}{v!} r^v \quad (1.15)$$

so that $F(r) = e^{-ar} f(r) \sim e^{-ar} e^{+2ar} \sim e^{ar}$ in the limit $v \rightarrow \infty$. The boundary condition that $F(r)$ be finite as $r \rightarrow \infty$ requires that the series expansion must terminate at some value v_{max} which we call $v_{max} = n - l - 1$. That is, $A_v \equiv 0$ for all $v > v_{max}$, and in particular $A_{v_{max}+1} = A_{n-l} = 0$. Then, the recursion formula gives:

$$\frac{A_{n-l}}{A_{n-l-1}} = \frac{2[(l+n-l)a - z]}{[(n-l)^2 + (2l+1)(n-1)]} \quad (1.16)$$

so that $an - Z = 0$ (1.17)
and since $a = (-2E)^{1/2}$, we find

$$E = -Z^2/2n^2 \quad \text{in atomic units,} \quad (1.18a)$$

or
$$E = -\frac{\mu e^4 Z^2}{2\hbar^2} \frac{1}{n^2} . \quad (1.18b)$$

Thus, for the bound states of a hydrogenic atom, we find

- * the energy is independent of l and m (at this level of approximation)
- * there are n^2 degenerate states. Note that this is a special property of a pure Coulomb potential. The $(2l+1)$ -fold degeneracy associated with the l quantum number is a characteristic of any ordinary spherically symmetric system for which the hamiltonian is invariant under any rotations, reflection and inversions in 3-dimensional space. $n = v_{max} + l + 1$ is called the principle quantum number.

The natural unit of energy in (1.18b) is the Rydberg, $R_{\infty} = m_e e^4 / 4\pi\hbar^3 c = 109737.31572 \text{ cm}^{-1}$ for infinite nuclear mass. For the electron-proton system, $\mu=0.9994557 m_e$, and so $R_H = 109677.585 \text{ cm}^{-1}$. The hartree is $2R_{\infty}$.

Notation of energy levels:

n	l	m	state	
1	0	0	1s	
2	0	0	2s	
		1	0	2p ₀
		1	± 1	2p _{± 1}
3	0	0	3s	
		1	0	3p ₀
		1	± 1	3p _{± 1}
		2	0	3d ₀
		2	± 1	3d _{± 1}
		2	± 2	3d _{± 2}

etc

The energy level diagram for H is reproduced in Figure 1.1, with possible transitions indicated. Radiative transitions between states nlm and $n'l'm'$ are possible only if the quantum number l, m changes by $\Delta l = l' - l = \pm 1$, $\Delta m = m' - m = 0, \pm 1$. There are no limitations on the quantum numbers n and n' .

The hydrogen spectrum consists of clearly defined series of lines with wavelengths λ satisfying the following formulas:

$$\begin{aligned} 1/\lambda &= R_H(1-1/n^2) \quad n=2,3,4,\dots \text{ Lyman series,} \\ 1/\lambda &= R_H(1/2^2-1/n^2) \quad n=3,4,5,\dots \text{ Balmer series,} \\ 1/\lambda &= R_H(1/3^2-1/n^2) \quad n=4,5,6,\dots \text{ Paschen series,} \\ 1/\lambda &= R_H(1/4^2-1/n^2) \quad n=5,6,7,\dots \text{ Brackett series,} \\ 1/\lambda &= R_H(1/5^2-1/n^2) \quad n=6,7,8,\dots \text{ Pfund series.} \end{aligned}$$

The longest (vacuum) wavelength lines of these series are, respectively, $\lambda=1215.68 \text{ \AA}$ (Ly α), 6562.79 \AA (H α), $1.875 \text{ }\mu\text{m}$ (P α), $4.051 \text{ }\mu\text{m}$ (Br α) and $7.456 \text{ }\mu\text{m}$ (Pfund α). The subsequent lines in a series, lying at shorter wavelengths, are denoted with β, γ , etc.... For example, the main lines of the Balmer series lie in the visible-near UV region of the spectrum:

$$\begin{aligned} \text{H } \alpha &: 6562.73 \text{ \AA} \quad n=3-2 \\ \text{H } \beta &: 4861.33 \text{ \AA} \quad n=4-2 \\ \text{H } \gamma &: 4340.47 \text{ \AA} \quad n=5-2 \\ \text{H } \delta &: 4101.74 \text{ \AA} \quad n=6-2 \\ &\text{etc....} \end{aligned}$$

The difference between energy $E = 0$ ($n \rightarrow \infty$) and E_n is called the ionization energy of level n . The ionization energy from the ground level $n=1$ is $E_\infty - E_1 = R_H$. The ionization energies for the first three series correspond to $\lambda = 912 \text{ \AA}$, 3648 \AA and 8208 \AA . For $\lambda < \lambda_i$, the spectrum is continuous.

2. Wave functions

The total wavefunction is

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi) = \frac{F_{nl}(r)}{r}Y_{lm}(\theta, \phi) \quad (1.19)$$

for the 3 quantum numbers n, l, m . Note, however, that the energy depends on n only. The series expansion (1.11) can be written in terms of Laguerre polynomials, which have exactly the same recursion relation for the coefficients

$$L_{n+1}^{2l+1}(r) = \sum_{k=0}^{n-l-1} B_k r^k \quad (1.20)$$

In order for B_{n-l-1} to remain finite, it is necessary that $n - l - 1 \geq 0$, so that for each n, l can have only the values $l = 0, 1, \dots, n - 1$. The properly normalized form of the radial function is

$$\int F_{nl}(r)F_{n'l}(r)dr = \delta_{nn'} \quad (1.21)$$

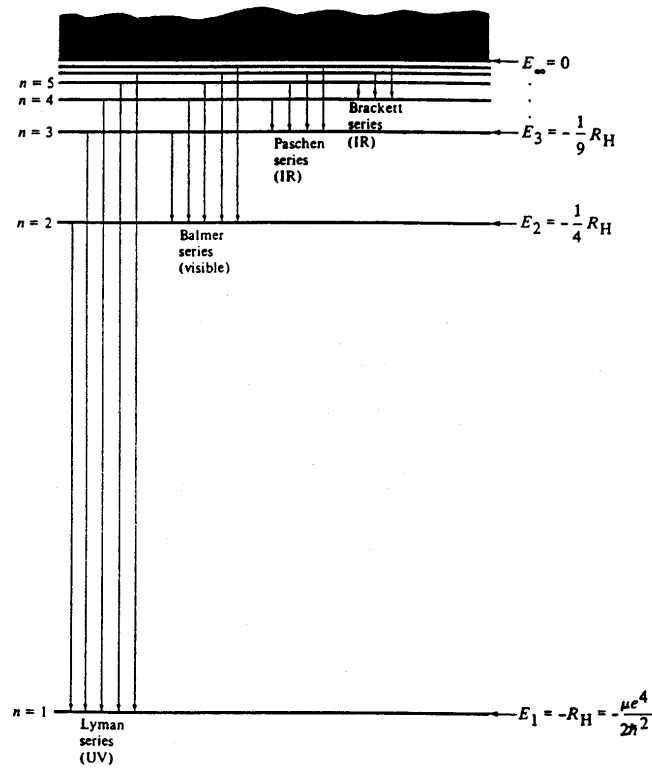


Figure 1.1 – Energy levels and spectroscopic transitions of the hydrogen atom.

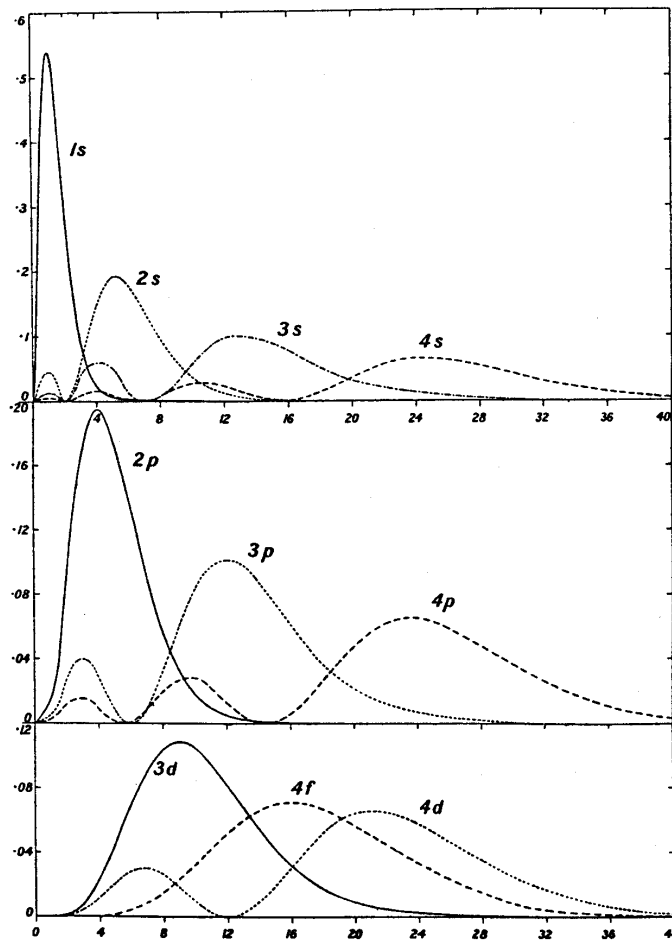


Figure 1.2– Radial probability distribution $R^2(nl)$ for several of the lowest H atom levels.

with

$$F_{nl}(r) = \left[\frac{(n-l-1)!Z}{n^2[(n+l)!]^3} \right]^{1/2} \left(\frac{2Zr}{n} \right)^{l+1} e^{-Zr/n} L_{n+1}^{2l+1} \left(\frac{2Zr}{n} \right) . \quad (1.22)$$

The first three radial functions are:

$$F_{10} = 2Z^{3/2}r e^{-Zr} \quad (1.23a)$$

$$F_{20} = \left(\frac{Z}{2} \right)^{3/2} (2 - Zr) e^{-Zr/2} \quad (1.23b)$$

$$F_{21} = \left(\frac{Z}{2} \right)^{3/2} \frac{Zr^2}{\sqrt{3}} e^{-Zr/2} \quad (1.23c)$$

Figure 1.2 shows the radial probability distribution F_{nl}^2 for the lowest states of hydrogen. Notice the stronger radial dependence near the origin for the p orbital.

Once the wavefunction is known, the mean or “expectation” value of any operator A can be calculated by

$$\langle A \rangle = \langle \psi | A | \psi \rangle = \int \psi^* A \psi d\tau , \quad (1.24)$$

where the integration in (1.24) is over all coordinates of the electron. In particular, the mean values of r^k are

$$\langle r^k \rangle = \int R_{nl}^2 r^{k+2} dr = \int F_{nl}^2 r^k dr . \quad (1.25)$$

For example

$$\begin{aligned} \langle r^{-1} \rangle &= \frac{1}{n^2} Z \\ \langle r^{-2} \rangle &= \frac{1}{n^3(l + \frac{1}{2})} Z^2 \\ \langle r^{-3} \rangle &= \frac{1}{n^3(l + 1)(l + \frac{1}{2})l} Z^3 \end{aligned}$$

3. Spin

The wavefunction (1.19) is still not complete, since the electron also possesses an intrinsic angular momentum s , called spin, with $|s| = \pm 1/2$, for the spin. To incorporate spin into the theory in a satisfactory way, one should use the relativistic Dirac equation. However, for non-relativistic cases, there is no coupling between the spin and the spatial coordinates of the electron, and it is usually sufficient to treat the spin in

terms of an additional wave function with two components, which are usually denoted as $\alpha = \xi(m_s = +1/2) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\beta = \xi(m_s = -1/2) = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Thus, the total wave function is:

$$\Phi(r, \theta, \phi, m_s) = \psi(r, \theta, \phi) \xi(m_s) . \quad (1.26)$$

Φ is still an eigenfunction of the original \mathcal{H} and the eigenvalues remain the same, but another factor of 2 has been introduced, so that the total degeneracy is $2n^2$.

In equation (1.26), the angular part of the wave function is expanded in terms of eigenfunctions of the operators \vec{L}^2 , L_z , \vec{S}^2 , and S_z . If $Y_{lm}(\theta, \phi) \equiv |l, m_l\rangle$, then $\vec{L}^2 |l, m_l\rangle = l(l+1) |l, m_l\rangle$; $L_z |l, m_l\rangle = m_l |l, m_l\rangle$ etc.... The wave function can alternatively be written in terms of the total angular momentum J with

$$\vec{J} = \vec{L} + \vec{S}; \quad J_z = L_z + S_z . \quad (1.27)$$

Then:

$$\vec{J}^2 |jm\rangle = j(j+1) |jm\rangle \quad (1.28)$$

$$J_z |jm\rangle = m |jm\rangle \quad (1.29)$$

where $j = l + s, l + s - 1, \dots, |l - s|$, and $m = m_l + m_s$.

The wave function $|jm\rangle$ can be obtained as linear combinations of the original functions $|lsm_l m_s\rangle$:

$$|jm\rangle = \sum_{m_l} \sum_{m_s} (lsm_l m_s | lsm_l m_s \rangle |jm\rangle , \quad (1.30)$$

where the coefficients (...|...) are called the Clebsch-Gordon coefficients. The CG coefficients are directly related to the so-called Racah-V coefficients and the Wigner $3 - j$ symbols $\begin{pmatrix} l & s & j \\ m_l & m_s & m \end{pmatrix}$. See standard textbooks on angular momentum coupling for more details, and how to compute the CG coefficients (e.g. Sobelman §4.2).

The spectroscopic notation for the hydrogen states now becomes

$$n^{2S+1} l_j \leftrightarrow |nlsjm\rangle , \quad (1.31)$$

where $l = 0, 1, 2, 3, 4, \dots$ correspond to S, P, D, F, G, ... and $j = l \pm 1/2$. For example, $3^2D_{3/2} m = -1/2$ designates a state of principle quantum number $n=3$; it is the $j=3/2$ level of the 2D term, and the $m = -1/2$ (magnetic) sublevel has been singled out.

4. Hydrogen-like atoms

For hydrogen-like atoms such as He^+ , Li^{++} , ..., the energy spectrum is similar to that of hydrogen, with a slightly different Rydberg constant, depending on the mass M :

$$R_M = R_\infty / (1 + m_e/M) . \quad (1.32)$$

Note that $E_n \sim Z^2$, so that the wavelength of a transition $n \rightarrow n'$ is Z^2 times smaller. For example, the Ly α transitions of the various hydrogen-like ions lie at:

Z	Spectrum	$\lambda_{Ly\alpha}$ (Å)
1	H I	1215.68
2	He II	303.78
3	Li III	135.02
4	Be IV	75.94
5	B V	48.58
6	C VI	33.74

Here we have used the spectroscopic system of notation: spectra of neutral atoms are denoted by the Roman numeral I, spectra of singly charged ions by the numeral II, etc....

5. Higher-order terms

For light atoms like hydrogen, the relativistic effects are small and can be taken in to account within the limits of perturbation theory. If the Dirac equation is expanded in terms of v/c , we obtain:

$$\begin{aligned}
H = m_e c^2 + \underbrace{\frac{\vec{p}^2}{2m_e} + V(r)}_{H_o} - \underbrace{\frac{\vec{p}^4}{8m_e^3 c^2}}_{W_{mv}} + \underbrace{\frac{\hbar^2}{2m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \vec{L} \cdot \vec{S}}_{W_{SO}} + \underbrace{\frac{\hbar^2 \Delta V(r)}{8m_e^2 c^2}}_{W_{Darwin}} + \dots
\end{aligned} \tag{1.33}$$

H_o
 W_{mv}
 W_{SO}
 W_{Darwin}

(a) Spin-orbit term

This term arises due to the interaction of the magnetic moment μ of the electron with the magnetic field H , associated with the electron moving in the electrostatic field E created by the proton. Here $\vec{\mu} = -2\mu_0 \vec{s}$, with $\mu_0 = e\hbar/2m_e c$, the Bohr magneton, and $\vec{H} = -\vec{E} \times \vec{v}/c$, with $\vec{E} = (\partial V/\partial r)\vec{r}/r$ and $m\vec{r} \times \vec{v} = \hbar\vec{l}$. Thus, the interaction $W_{SO} = \vec{\mu} \cdot \vec{H}$ becomes

$$W_{SO} = \frac{\hbar^2}{2m_e^2 c^2} \frac{dV}{dr} \frac{1}{r} \vec{l} \cdot \vec{s} . \tag{1.34}$$

This can be rewritten using $\vec{j}^2 = \vec{l}^2 + \vec{s}^2 + 2\vec{l} \cdot \vec{s} \Rightarrow \vec{l} \cdot \vec{s} = (\vec{j}^2 - \vec{l}^2 - \vec{s}^2)/2$, and remembering that $V = -Ze^2/r \Rightarrow$

$$W_{SO} = \frac{Ze^2 \hbar^2}{2m_e^2 c^2} \frac{1}{2r^3} (\vec{j}^2 - \vec{l}^2 - \vec{s}^2) . \tag{1.35}$$

According to perturbation theory, the first order correction to the energy E_{nlj} due to the spin-orbit interaction is:

$$\begin{aligned}
E_{nlj}^{SO} &= \langle nlsjm | W_{SO} | nlsjm \rangle \\
&= \frac{Ze^2 \hbar^2}{2m_e^2 c^2} \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)] \langle \frac{1}{r^3} \rangle_{nl} \\
&= \frac{\alpha^2 [j(j+1) - l(l+1) - s(s+1)]}{2l(l+1)(l + \frac{1}{2})} \frac{Z^4}{4n^3} \quad (\text{a.u.})
\end{aligned} \tag{1.36}$$

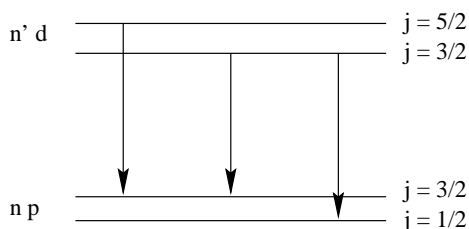
where eq. 1.25 is used to generate the final expression, and where $\alpha = e^2/\hbar c \approx 1/137$ is the fine-structure constant. In particular, for $s = 1/2, j = l \pm 1/2$, the energy difference for the doublet of $l \neq 0$ is:

$$\Delta E^{SO} = \frac{Z^4 \alpha^2}{2n^3} \frac{1}{l(l+1)} \quad (\text{a.u.}) \quad , \quad (1.37)$$

compared with the energy of the unperturbed level $E_n = -Z^2/2n$.

Note that the spin-orbit interaction is largest for small l , and increases as Z^4 ! For example, for hydrogen the splitting of the $j = 1/2$ and $j = 3/2$ levels for $n = 2, 3, 4$ is 0.36, 0.12 and 0.044 cm^{-1} , respectively. For Na, the splitting between the lowest $J = 1/2$ and $J = 3/2$ levels is approximately 20 cm^{-1} . The set of lines arising from transitions between the fine-structure components of the levels nlj and $n'l'j'$ is called a ‘‘multiplet.’’ The selection rule with respect to j is: $\Delta j = 0, \pm 1$.

Example:



(b) Velocity dependence of electron mass

This term arises from the relativistic variation of the mass with velocity. Using similar arguments as above, one can show

$$E_{nlj}^{mv} = -\frac{Z^4}{2n^3} \alpha^2 \left[-\frac{3}{4n} + \frac{1}{l + \frac{1}{2}} \right] \quad (\text{a.u.}) \quad (1.38)$$

For example, for the ground state of hydrogen, $Z = 1, n = 1, l = 0$:

$$E_{nlj}^{mv} = -7.3 \text{ cm}^{-1} \quad .$$

(c) Darwin term

$$E_{nl=0}^D = \frac{Z^4 \alpha^2}{2n^3} \quad \text{a.u., } l = 0 \text{ only.} \quad (1.39)$$

The Darwin term is non-zero for $l = 0$ only.

If all of the above expressions are combined, we obtain:

$$E = -\frac{Z^2}{2n^2} - \frac{Z^4 \alpha^2}{2n^3} \left[\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right] \quad \text{a.u.} \quad (1.40)$$

Figure 1.3 illustrates the fine-structure levels for $n = 1, 2, 3$ of hydrogen.

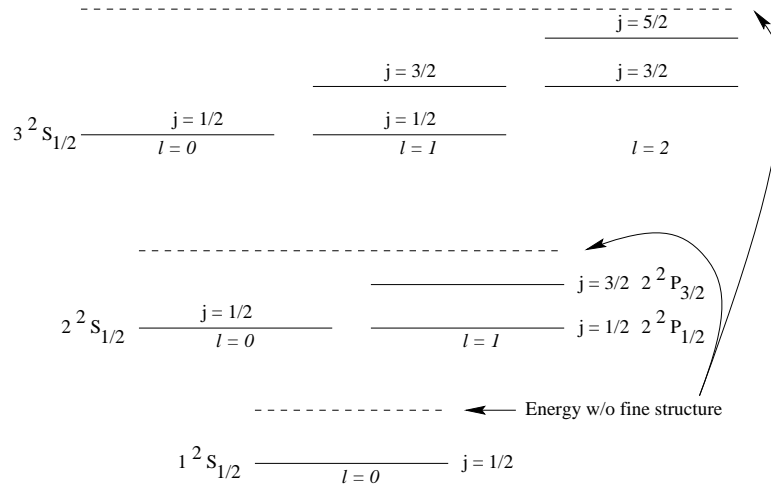


Figure 1.3– A schematic diagram of the lowest energy levels of the H atom, including various fine structure effects (not to scale).

(d) Lamb shift

Note that at this level, the $2^2S_{1/2}$ and $2^2P_{1/2}$ levels have the same energy. Higher-order radiative corrections (the Lamb shift) cause these levels to have slightly different energies. For hydrogen, the splitting of these two levels equals 0.034 cm^{-1} . For the exact energy levels of hydrogenic atoms, see Erickson, G. W. 1977, *J. Phys. Chem. Ref. Data* **6**, 831.

(e) Hyperfine structure

So far, we have assumed that the nucleus (1) has infinite mass; (2) is a point particle; (3) interacts with electrons only through the Coulomb field. Actually, the proton, like the electron, is a spin 1/2 particle. The nuclear spin is denoted as I . With the spin I , is associated a magnetic moment

$$\vec{\mu}_I = g_N \mu_N \vec{I} \quad (1.41)$$

with the nuclear Bohr magneton

$$\mu_N = q_p \hbar / 2M_p c \text{ ,} \quad (1.42)$$

where q_p = charge of proton, M_p = mass of proton, and the factor g_N is equal to $g \approx 5.585$. For electrons, $g_e \approx 2$ (which was used earlier in part (a).) Values of I and g_N for other important nuclei are given below. Since $M_p/m_e \approx 1840$, μ_N is much smaller than μ_0 so that nuclear magnetism is much less important than electronic magnetism. Typically, hyperfine splittings are a factor 2000 times smaller than spin-orbit splittings.

Nucleus	I	g_N
^1H	1/2	5.526
$^2\text{H}=\text{D}$	1	0.857
^{12}C	0	—
^{13}C	1/2	1.404
^{14}N	1	0.404
^{15}N	1/2	-0.566
^{16}O	0	—

The Hamiltonian due to the interaction of the electron with the magnetic field created by μ_I is:

$$W_{hf} = 2\mu_0 g_N \mu_N \left[\frac{\vec{I} \cdot \vec{L}}{r^3} + \frac{3(\vec{I} \cdot \vec{r})(\vec{S} \cdot \vec{r})}{r^5} - \frac{2}{3} \Delta \left(\frac{1}{r} \right) \vec{I} \cdot \vec{S} \right] \quad (1.43)$$

The first term in the brackets represents the interaction of the nuclear magnetic moment with the magnetic field created at the proton by the rotation of electronic charge. The second term represents the dipole-dipole interaction between the electronic and nuclear magnetic moments: the interaction of the magnetic moment of the electron spin with the magnetic field created by μ_I or vice versa. The third term, also called Fermi's "contact term", arises from the singularity at $r = 0$ of the field created by the magnetic moment of the proton. This can be seen by realizing that the expectation value of $\Delta(1/r)$ is equal to $-4\pi\delta(\vec{r})$, with $\delta(\vec{r})$ being the Dirac delta function. In reality, the proton is not a point. It can be shown that the magnetic field inside the proton does not have the same form as the one created outside by μ_I (and which enters into the dipole-dipole interaction). The contact term describes the interaction of the magnetic moment of the electron spin with the magnetic field inside the proton (the contact term exists, as its name indicates, only when the wave functions of the electron and proton overlap).

Consider the specific case of an ns -level. Because $l = 0$, the first term in (1.43) vanishes. Similarly, it can be shown that term (2) is zero because of spherical symmetry of the ns state. Thus only the contact term remains, which can be written as $A\vec{I} \cdot \vec{S}$, where A is a constant. If we define the total angular momentum quantum number including spin:

$$\vec{F} = \vec{I} + \vec{J} \quad , \quad (1.44)$$

then $\vec{F} = \vec{I} + \vec{J}$ for $\vec{L} = 0 \Rightarrow \vec{I} \cdot \vec{S} = (\vec{F}^2 - \vec{I}^2 - \vec{S}^2)/2$.

The corrections due to hyperfine interaction can thus be computed in the same way as those due to spin orbit coupling. Using the fact that $\langle \psi | \delta(\mathbf{r}) | \psi \rangle = |\psi_{nl}(0)|^2$, we find for the hyperfine states in the $1^2S_{1/2}$ ground state:

$$\begin{aligned} E^{hf} &= \frac{4}{3} \pi \mu_0 g_N \mu_N |\psi_{nl}(0)|^2 \quad , \quad F = 1 \\ E^{hf} &= -4\pi \mu_0 g_N \mu_N |\psi_{nl}(0)|^2 \quad , \quad F = 0 \end{aligned} \quad (1.45)$$

Since $|\psi_{10}(0)|^2 = Z^3/\pi n^3 a_0^3$, the energy splitting in the H $1^2S_{1/2}$ state is:

$$\Delta E^{hf} = \frac{16}{3} \frac{\mu_0 g_N \mu_N}{a_0^3} = 0.04738 \text{ cm}^{-1} = 5.9 \times 10^{-6} \text{ eV} \quad . \quad (1.46)$$

A magnetic dipole radiative transition is possible between these two hyperfine structure levels at a frequency of $1420405751.7667 \pm 0.001$ Hz (see Essen et al, Nature **229**, 110). This is, of course, the famous 21 cm wavelength transition of H, which is widely observed in astronomy.

These radiative transitions are extremely rare for any given atom, about one every 10^7 years, but because of the enormous abundance of neutral hydrogen this nonetheless gives rise to observable 21 cm lines. The actual value for the transition probability $A = 2.876 \times 10^{-15} \text{ s}^{-1}$, corresponding to an oscillator strength $f = 5.761 \times 10^{-12}$ (see Lecture III, §4 for formulae).

That the 21 cm H transition might be observable astronomically was first suggested by H. C. van de Hulst (1945, *Nederlandsch Tydschrift voor Natuurkunde* **11**, 210). It was 1951 before developments in receivers made it feasible to attempt the observations, but by then there were three independent groups in Holland, the U.S. and Australia, on the verge of success. According to the (Dutch side of the) story, the Dutch would almost certainly have been first, but their receiver was destroyed in a lab fire just prior to the first test. As it was, Ewen and Purcell (1951, *Nature* **168**, 356) at Harvard made the first measurement, and this was confirmed almost immediately by the other two groups.

For states with $l \neq 0$ in H, the third term vanishes, whereas the first two terms give (using 1.25)

$$E^{hf} = \mu_0 g_N \mu_N \frac{Z^3}{a_0^3 n^3 j(j+1)(l+\frac{1}{2})} [F(F+1) - j(j+1) - I(I+1)] \quad (1.47)$$

Examples: H $2^2P_{1/2}$, $Z = 1$, $j = 1/2$, $I = 1/2$, $n = 2$, $l = 1$

$$\begin{aligned} E^{hf} &= \frac{1}{18} (\mu_0 g_N \mu_N / a_0^3) \quad , \quad F = 1 \\ E^{hf} &= -\frac{1}{6} (\mu_0 g_N \mu_N / a_0^3) \quad , \quad F = 0 \end{aligned} \quad (1.48)$$

Thus, the hyperfine splitting is $\Delta E^{hf} = -2(\mu_0 g_N \mu_N / 9a_0^3)$, which is very much smaller than the ground-state splitting.

The equations for the splitting of the hyperfine lines due to an external magnetic field (rather than an internal one generated, for example, by the electrons) are similar to (1.48), but with terms proportional to $\vec{H} \cdot \vec{S}$ and $\vec{H} \cdot \vec{I}$, where H is the external field. Measurements of the splitting of the H 21 cm line due to an external field in astronomy are extremely difficult, because the splitting due to weak fields (at most a few milliGauss) is usually small compared to other sources of broadening. For a recent overview, see C. Heiles, 1987, in *Interstellar Processes*, ed. D. J. Hollenbach and H. A. Thronson (Reidel), p.171.

The ground state of the deuterium atom (D) also has hyperfine structure and an analogous transition, but now $I=1$, and $F=3/2 \rightarrow 1/2$. Its frequency is $\nu = 327.384 \text{ MHz} \Leftrightarrow 91.6 \text{ cm}$, and its transition probability is $A = 4.695 \times 10^{-17} \text{ s}^{-1}$. The abundance of D relative to that of H is of considerable astronomical interest; it is thought that all normal nuclear reactions occurring inside stars tend to destroy D on average, so that the only D currently observable in our galaxy is that left over from processes that occurred at the beginning of the cosmic expansion in the Big Bang. The current D/H ratio is thus a limit on the primordial D/H ratio, which in turn is sensitive to the mean baryon density of the Universe and is related to the properties of the cosmic expansion. Searches have been

made for the D 92 cm line (see e. g. the latest attempt by Blitz and Heiles 1987, *Ap. J.* **313**, L95) without success.

B. Classical Atoms

It is instructive to end the discussion of the hydrogen atom with a classical treatment of the problem. For very large $n \rightarrow \infty$, the classical description of the energy levels becomes exact (according to the correspondence principle), and various other atomic properties can be calculated accurately according to semi-classical models. Very highly-excited atoms (large n) appear in several important astronomical contexts. For example, radio frequency transitions between states $n=732-733$ of interstellar carbon atoms have been observed.

Bohr's postulates:

- (1) electrons in atoms have certain allowed orbits about the nucleus for which angular momentum is an integral multiple of $\hbar = h/2\pi$.
- (2) electromagnetic radiation of frequency ν can be emitted or absorbed in a discontinuous jump from one orbit to another.

If a_n is the radius of the n^{th} orbit, then the angular momentum of the system is:

$$\mu v a_n = n\hbar \quad , \quad n = 1, 2, \dots \quad (1.49)$$

with $\mu = m_e/(1 + m_e/M_p)$.

The force equation

$$\frac{\mu v^2}{a_n} = \frac{Z e^2}{a_n^2} \quad (1.50)$$

implies

$$a_n = \frac{n^2 \hbar^2}{Z e^2 \mu} \sim \frac{n^2}{Z} a_0 \quad , \quad (1.51)$$

where $a_0 = \hbar^2/e^2 m_e = 0.529177 \text{ \AA} = 1 \text{ bohr}$. The classical speed of the electron is:

$$v = Z e^2 / (n\hbar) \quad (1.52)$$

so that the energy of the system in state n is

$$\begin{aligned} E_n &= \frac{\mu v^2}{2} - \frac{Z e^2}{a_n} \\ E_n &= -\frac{\mu e^4}{2\hbar^2} \cdot \frac{Z^2}{n^2} = -\frac{Z^2 E_0}{n^2} \left(\frac{1}{1 + m_e/M_p} \right) \end{aligned} \quad (1.53)$$

where $E_0 = 219474.63 \text{ cm}^{-1} = 1 \text{ hartree} = 2 \text{ Rydbergs}$. The transition frequency is very accurate for $n \gg 1$:

$$\begin{aligned} \nu_{n'n''} &= \frac{Z^2 E_0}{2h} \left(\frac{1}{1 + m_e/M_p} \right) \left[\left(\frac{1}{n''} \right)^2 - \left(\frac{1}{n'} \right)^2 \right] \\ &= \frac{3.289841949 \times 10^{15} Z^2}{1 + m_e/M_p} \left[(n'')^{-2} - (n')^{-2} \right] \end{aligned} \quad (1.54)$$

II. N ELECTRON ATOMS

1. Wave functions

For an N -electron atom, the non-relativistic Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^N \left[\frac{\vec{p}_i^2}{2m_e} - \frac{Ze^2}{r_i} \right] + \sum_{i>j} \frac{e^2}{r_{ij}} . \quad (2.1)$$

For $N \geq 2$, the Schrödinger equation can no longer be solved directly, either analytically or by perturbation methods. Thus, some approximate model has to be used. The simplest assumption is that each electron can be considered separately to move in an effective, centrally symmetric field created by the nucleus and all other electrons, (the “self-consistent field” approximation.)

We therefore assume that the N -electron wave function $\Psi(1, \dots, N)$ can be written as the product of a set of one-electron functions, called “orbitals”. The one-electron functions are solutions of the eigenvalue equation:

$$\left[\frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2} [E - V(r)] - \frac{l(l+1)}{r^2} \right] f(r) = 0 , \quad (2.2)$$

and are thus hydrogen-like functions, specified by quantum numbers n, l, m_l , and m_s . In the simplest approximation, they differ from the hydrogen atom functions only by the replacement of the nuclear charge Z by $(Z - s)$, where s is the “screening charge” due to the inner electrons.

As a first step, one can write

$$\Psi(1, \dots, N) = u_a(1)u_b(2)\dots u_k(N) \quad (2.3)$$

where each subscript a, b, \dots, k represents the set of values (n, l, m_l, m_s) and the numbers $1, 2, \dots, N$ represent the space and spin coordinates of the $1^{st}, 2^{nd}, \dots, N^{th}$ particle. The functions u are the orbitals with a spatial part ψ_{nlm} , multiplied by a spin part α or β . The wave function (2.3) does not, however, satisfy the Pauli principle, which states that the wave function should be antisymmetric with respect to the permutation of any two electrons. The correct form of the wave function is obtained by taking linear combinations of all $N!$ permutations with the appropriate sign $\epsilon_p = -1$ if it is odd with respect to the standard ordering. Thus:

$$\begin{aligned} \Psi(1, \dots, N) &= (N!)^{-1/2} \sum \epsilon_p P[u_a(1)u_b(2)\dots u_k(N)] \\ &= \sqrt{\frac{1}{N!}} \begin{vmatrix} u_a(1) & u_a(2) & \dots & u_a(N) \\ u_b(1) & u_b(2) & \dots & u_b(N) \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ u_k(1) & u_k(2) & \dots & u_k(N) \end{vmatrix} \end{aligned} \quad (2.4)$$

Where the determinant is used to generate the antisymmetrized product and is called the Slater determinant. For example, for $N = 2$: $\Psi = \sqrt{\frac{1}{2}}[u_a(1)u_b(2) - u_a(2)u_b(1)]$.

Note that the Hamiltonian (2.1) is invariant under inversion \equiv reflection through the origin ($x, y, z \rightarrow -x, -y, -z$). This implies that the total wavefunction must have a *definite* parity. The parity of each one-electron function is determined by l . If l is even, the parity is even (or +); if l is odd, the parity is odd (or -). The total parity of the N -electron wave function (2.4) is (-1) raised to the power $\sum_i^N (l_i)$, determined by the arithmetic sum of the individual quantum numbers, not the vector sum.

The “best” orbitals u_j can be found by applying the variational principle for the expectation value of the energy:

$$\delta \langle H \rangle = \delta \int \Psi^* H \Psi d(1)d(2)\dots d(N) = 0 \quad , \quad (2.5)$$

where δ is an arbitrary variation of the normalized trial wave function Ψ . This leads, after some manipulations, to the so-called Hartree-Fock equations for each orbital.

In practice, one chooses a set of one-electron orbitals u with a number of parameters (e.g. the screening charges). One computes the matrix elements (or “mean fields”) entering the Hartree-Fock equations, and solves variationally for a new set of orbitals and energies. This procedure is repeated until the orbitals and energies change little from one iteration to the next; hence the name “self-consistent field”.

Note that the Hartree-Fock procedure is still an approximate theory, since the wave function contains only a *single* Slater determinant. This means that the “correlation” between the electrons is neglected, i.e., electron 1 moves in the average field due to the other electrons, but does not react instantaneously to the actual position of electrons 2, ... N . A higher level of approximation is called “configuration-interaction” (CI), in which the total wave function is expanded in a sum of Slater determinants Φ_i :

$$\Psi(1, 2, \dots N) = \sum_i^N c_i \Phi_i(1, \dots N) \quad . \quad (2.6)$$

With an arbitrarily large expansion, one should get arbitrarily close to the exact wave function. However, computers are still finite, convergence is slow, and the numerical effort increases as a fairly high power of the number of one-electron orbitals and configurations. Thus a certain amount of intuition and experience in choosing configurations is valuable.

2. Configurations

The distribution of electrons in an atom over the orbitals with different values of n and l is called the “electron configuration”. If there are several (k , say) electrons with the same values of n and l , this is denoted $(nl)^k$, for example, $(3s)^2$, $(3p)^3$ etc... or simply $3s^2$ and $3p^3$.

Note that for a general, centrally symmetric potential $V(r)$, the energy of the orbital u will depend on both n and l , in contrast with the case of the Coulomb potential, for which the energy depends only on n . Thus, the $3s$ and $3p$ orbitals can have different energies; as a rule, the greater the sum $n + l$, the greater the electron energy.

II. For high Z , $H_{so} \gg H_{es}$.

In this case, the individual \vec{l}_i and \vec{s}_i are coupled to form $\vec{j}_i = \vec{l}_i + \vec{s}_i$, and $\vec{J} = \sum \vec{j}_i$. This is called the “ jj -coupling” scheme.

Consider first case I:

(a) LS coupling

If the configuration consists entirely of closed shells, there is only one possible determinantal function. For example, with six 2p electrons, the wave function must be

$$\Psi(1, \dots, 6) = \frac{1}{\sqrt{N!}} \sum_p \epsilon_p [p_1\alpha(1)p_1\beta(2)p_0\alpha(3)p_0\beta(4)p_{-1}\alpha(5)p_{-1}\beta(6)] \quad (2.9)$$

If a shell is not full, there are many possibilities belonging to the same configuration. For example, if there are two inequivalent p electrons such as 2p3p, 36 possible determinants can be formed, and even for two equivalent p electrons, there are still 15 possible determinants. All these determinants have the same energy in the purely central-field approximation. They will split if H_{es} is taken into account as a perturbation. Since the various determinants are degenerate in zeroth order, we have to consider the perturbation theory for degenerate states, i.e., we must solve the secular equation:

$$\det|(H_0 + H_{es})_{ij} - E\delta_{ij}| = 0 \quad (2.10)$$

with

$$(H_0 + H_{es})_{ij} = \langle \Psi_i | H_0 + H_{es} | \Psi_j \rangle \quad (2.11)$$

The computation of the matrix elements $\langle \Psi_i | H_{es} | \Psi_j \rangle$ is not a simple task, because of the occurrence of the “two-electron” terms with the operator $1/r_{kl}$. The secular equation (2.10) can, however, be factorized into a set of smaller equations using the group theoretical properties of the angular momentum operators. As mentioned above, the Hamiltonians H_0 and H_{es} commute with \vec{L} and \vec{S} , so that we can form linear combinations of determinants that represent states of total spin and angular momentum \vec{S} and \vec{L} . For details on the actual computation of the LS term energies, see, for example, Sobelman, Ch. 5. Here we simply argue that such a splitting occurs, and give some general rules.

From a physical point of view, it is easy to see that configurations will split into “terms” with particular values of L and S . Remember that the electrons repel each other, so that their mutual electrostatic energy is positive. The farther away the electrons get, the lower will be their contribution to the total energy, and the lower the state will lie in energy. First, note that a large spin implies that the individual spins are aligned in the same direction. Thus, the electrons will be farther apart on the average, by virtue of the Pauli principle. This leads to “Hund’s rule number 1”: **Terms with larger spin tend to lie lower in energy.** There is a similar effect regarding the orbital angular momentum L . A larger L implies that the individual l_i are aligned so that the sense of orbiting around the atom is the same for more electrons. In such a pattern, the electrons will keep farther apart on average than when they orbit in opposite directions. This effect is usually smaller than the first one, leading to “Hund’s rule number 2”: **Of those terms**

of a given configuration with a given spin, those with the largest L tend to lie lower in energy. Note that Hund's rules apply strictly only to the ground configuration.

What spectroscopic LS terms arise from a given configuration? This is mostly an exercise in bookkeeping of the possible values of m_l and m_s , and determining what values of S and L can be constructed within the Pauli principle. Note that only the electrons in the "open" shells need to be considered, since the closed shells have $L = S = 0$.

Examples:

(i) non-equivalent electrons

The terms in this case are fairly easy to find by simple addition of the angular momenta.

$$* 1s2s \Rightarrow l_1 = 0; l_2 = 0 \Rightarrow L = 0$$

$$m_{s_1} = \pm 1/2; m_{s_2} = \pm 1/2 \Rightarrow S = 0 \text{ or } S = 1.$$

The possible terms are thus 1S and 3S , where the superscript is the "spin multiplicity" $2S + 1$, or the number of m_s values.

$$* 2p3p \Rightarrow m_{l_1} = 0, \pm 1; m_{l_2} = 0, \pm 1; m_l = 0, \pm 1, \pm 2 \Rightarrow L = 0, 1, 2$$

$$m_{s_1} = \pm 1/2; m_{s_2} = \pm 1/2 \Rightarrow S = 0 \text{ or } S = 1.$$

The possible terms are thus: $^1S, ^1P, ^1D, ^3S, ^3P, ^3D$.

(ii) equivalent electrons

In the case of equivalent electrons, some of the terms found for non-equivalent electrons are ruled out by the Pauli exclusion principle. For example, for the case of $2p^2$, only the terms $^1S, ^3P$ and 1D are possible. The 3D term does *not* occur because it would require both electrons to have $m_{l_1} = m_{l_2} = 1$ and $m_{s_1} = m_{s_2} = 1/2$. Similarly, we can rule out the other two terms: see Figure 2.1.

The table below gives the terms arising from non-equivalent electrons. The numbers in parentheses in this table denote the number of terms with the same L and S values that arise from the configuration.

Note that the terms for a shell more than half filled will be the same as for the complementary number of electrons needed to fill the shell. For example, the terms arising from a p^4 configuration are $^1S, ^3P, ^1D$, the same as for a p^2 configuration. This rule is proved simply by noting that the total spin and orbital angular momentum of a closed shell are zero. Since only the sums $\sum m_{l_i}$ and $\sum m_{s_i}$ are relevant, it does not matter whether we use those of the missing electrons or those of the actual electrons (the "electron-hole equivalence").

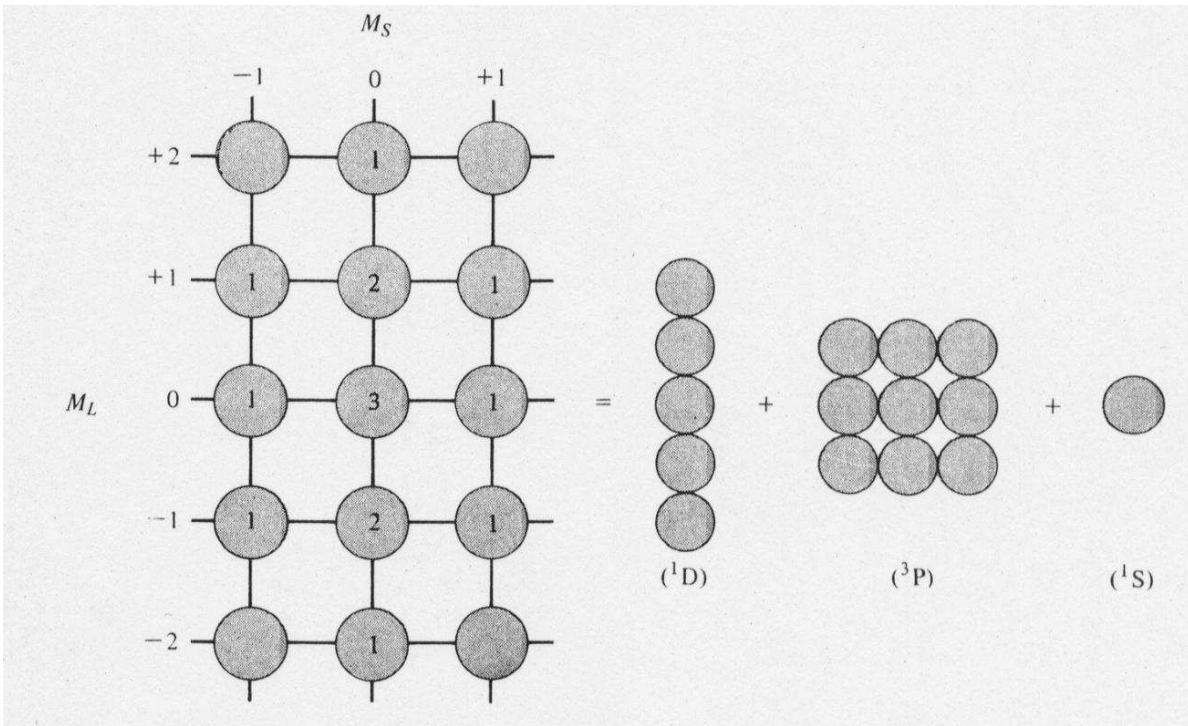
Spin-orbit coupling

In the LS -coupling scheme, spin-orbit interaction can be treated as a small perturbation. In analogy with the one-electron case, the spin-orbit hamiltonian can be written as:

$$H_{so} = \xi \vec{L} \cdot \vec{S} = \frac{1}{2} \xi \left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2 \right) \quad (2.12)$$

where $\vec{J} = \vec{L} + \vec{S}$. The first order correction for the energy of a state with definite L , S and J is then:

$$E^{so} = \langle LSJm_J | H_{so} | LSJm_J \rangle$$



m_{l_1}	m_{l_2}	m_{s_1}	m_{s_2}	M_L	M_S
1	1	+	+	No good (Pauli principle)	
1	1	+	-	2	0
1	1	-	+	Same as preceding state (Pauli principle)	
1	0	+	+	1	1
0	1	+	+	Same as preceding state (Pauli principle)	
1	0	+	-	1	0
1	0	-	+	1	0
1	0	-	-	1	-1
1	-1	+	+	0	1
1	-1	+	-	0	0
1	-1	-	+	0	0
0	0	+	-	0	0
1	-1	-	-	0	-1
0	-1	+	+	-1	1
0	-1	+	-	-1	0
0	-1	-	+	-1	0
0	-1	-	-	-1	-1
-1	-1	+	-	-2	0

Figure 2.1 – Slater diagram for a p^2 electron configuration into 1D , 3P , and 1S terms (top). The table at bottom presents a detailed accounting of the Pauli principle calculations.

Terms of Non-Equivalent Electrons

Electron Configuration	Terms
<i>s s</i>	¹ S, ³ S
<i>s p</i>	¹ P, ³ P
<i>s d</i>	¹ D, ³ D
<i>p p</i>	¹ S, ¹ P, ¹ D, ³ S, ³ P, ³ D
<i>p d</i>	¹ P, ¹ D, ¹ F, ³ P, ³ D, ³ F
<i>d d</i>	¹ S, ¹ P, ¹ D, ¹ F, ¹ G, ³ S, ³ P, ³ D, ³ F, ³ G
<i>s s s</i>	² S, ² S, ⁴ S
<i>s s p</i>	² P, ² P, ⁴ P
<i>s s d</i>	² D, ² D, ⁴ D
<i>s p p</i>	² S, ² P, ² D, ² S, ² P, ² D, ⁴ S, ⁴ P, ⁴ D
<i>s p d</i>	² P, ² D, ² F, ² P, ² D, ² F, ⁴ P, ⁴ D, ⁴ F
<i>p p p</i>	² S(2), ² P(6), ² D(4), ² F(2), ⁴ S(1), ⁴ P(3), ⁴ D(2), ⁴ F(1)
<i>p p d</i>	² S(2), ² P(4), ² D(6), ² F(4), ² G(2), ⁴ S(1), ⁴ P(2), ⁴ D(3), ⁴ F(2), ⁴ G(1)
<i>p d f</i>	² S(2), ² P(4), ² D(6), ² F(6), ² G(6), ² H(4), ² I(2) ⁴ S(1), ⁴ P(2), ⁴ D(3), ⁴ F(3), ⁴ G(3), ⁴ H(2), ⁴ I(1)

$$= \frac{1}{2}C[J(J+1) - L(L+1) - S(S+1)] \quad , \quad (2.13)$$

where C is a constant related to the average of $\xi(r)$ over the spatial part of the wave function. Note that for fixed L and S , the energy shift is proportional to $J(J+1)$ and that:

$$E_{J+1} - E_J = \frac{1}{2}C(J+1) \quad (2.14)$$

This is the ‘‘Landé interval rule’’: the spacing between two consecutive levels of a term is proportional to the larger of the two J values. As an example of how well this rule holds, the table below shows the actual data on the $3d^6 4s^2 \ ^5D$ term of iron. If the rule were rigorously true, the entries in the last column would all be equal. The deviations represent the effect of smaller interaction terms, which we have omitted.

Multiplet intervals in the 5D term of iron

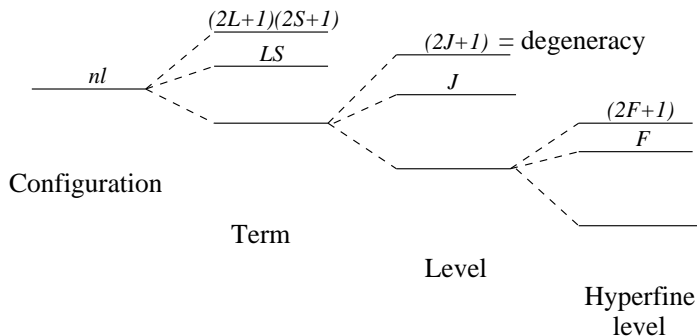
Level	Energy(cm ⁻¹)	Interval	$\zeta \equiv \text{interval}/J$
⁵ D ₄	0.0	-415.9	-103.9
⁵ D ₃	415.9	-288.1	-96.1
⁵ D ₂	704.0	-184.1	-92.1
⁵ D ₁	888.1	-89.9	-89.9
⁵ D ₀	978.1		

Notation: $^{2S+1}\mathbf{L}_J^{\text{parity}}$ e.g. $^3P_2^0, ^2S_{1/2}$ (2.15)

The parity is given as a superscript when the parity is odd; when the parity is even, no superscript appears. (Note: the absence of a superscript does not necessarily mean that the term is even!) The allowed values of J are usually separated by commas, for example

${}^3F_{2,3,4}; {}^2P_{1/2,3/2}$. The number of J values in any term is equal to the *smaller* of $(2L + 1)$ and $(2S + 1)$.

For shells less than half full, C is positive, so that the level with the lowest J lies lowest in energy. For example, in the 3P term of carbon, the 3P_0 state is the lowest one. This is called a “normal” term. For shells more than half full, C is negative, so that the level with the highest J lies lowest in energy, for example for O, the 3P_2 state lies lowest. This is called an “inverted” term. Each of the J levels can, of course, be further split by hyperfine interaction, similar to the one electron case.



(b) jj-coupling

In the jj -coupling scheme, the spin-orbit interaction is assumed to be much larger than the electrostatic interaction. Thus, \vec{l}_1 and \vec{s}_1 are first coupled to form \vec{j}_1 ; \vec{l}_2 and \vec{s}_2 to form \vec{j}_2 ; and finally \vec{j}_1 and \vec{j}_2 to form \vec{J} . Finding the possible values of J is carried out in exactly the same way as finding possible terms in LS coupling. Consider, for example, the configuration $np\ nd$. For a p electron, $j_1=1/2, 3/2$; for a d electron, $j_2=3/2, 5/2$. The resulting states, denoted by $(j_1, j_2)_J$ or $(J\ j_1j_2)$ are:

j_1	j_2	J	Terms
1/2	3/2	1,2	$(1/2, 3/2)_{1,2}$
1/2	5/2	2,3	$(1/2, 5/2)_{2,3}$
3/2	3/2	0,1,2,3	$(3/2, 3/2)_{0,1,2,3}$
3/2	5/2	1,2,3,4	$(3/2, 5/2)_{1,2,3,4}$

In the case of equivalent electrons, it is necessary again to take into account the Pauli principle. Note, however, that for equivalent electrons, the electrostatic interaction is almost always larger than the spin-orbit coupling. Thus, the non-equivalent electrons are of greatest interest for jj -coupling.

Neither the LS nor the jj -coupling scheme is, in itself completely adequate; rather, they are two limits that blend smoothly from one to another as a function of Z . Such a connection of two limiting cases is known as a “correlation diagram”, and is very extensively used in spectroscopy. The figure below illustrates the correlation diagram for the p^2 configuration.

The total number of levels for a specific electron configuration must be the same, both in the LS and jj coupling cases. For LS coupling, the number of terms for a 2-electron configuration equals $2(2l_{min}+1)$, where l_{min} is the minimum of the numbers l_1, l_2 ; when

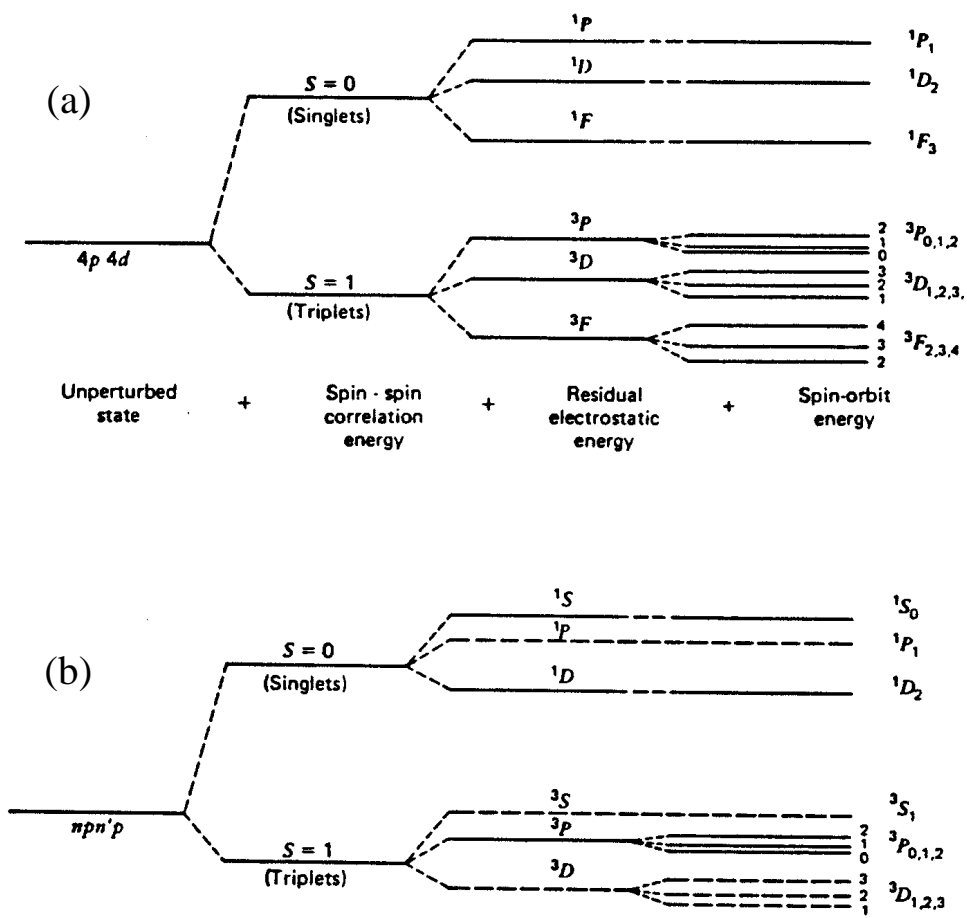


Figure 2.2– (a) Schematic diagram illustrating the terms generated by a $4p - 4d$ configuration in LS coupling. (b) Same as for diagram (a), but for two p electrons. For equivalent p electrons ($n = n'$), the dashed levels are missing due to the Pauli principle.

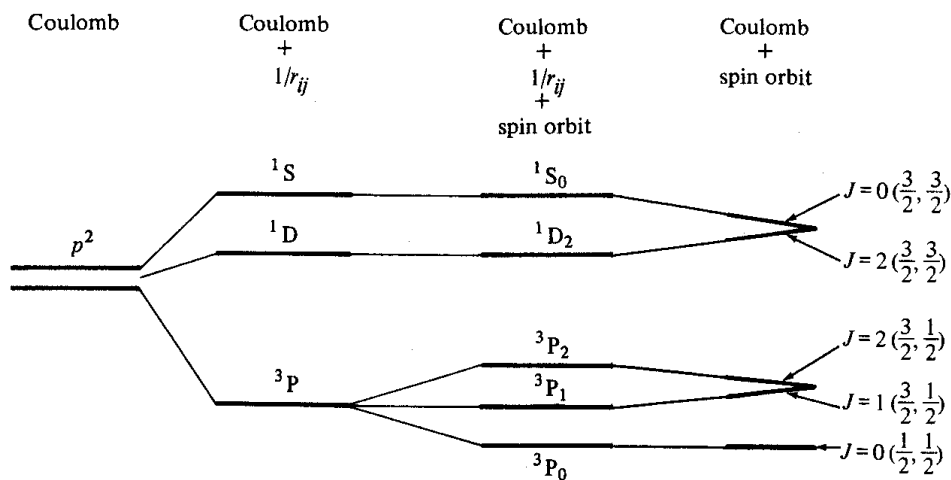


Figure 2.3– Correlation diagram for the p^2 configuration. From left: The first effect shown is that of electron-electron repulsion, which splits the configuration into multiplets; spin-orbit coupling then splits nonsinglet states into different J levels. As spin-orbit dominates the electron repulsion, with high Z , levels labeled by equal j values tend to cluster together.

$l_{min} = 1, 2, 3, 4, \dots$, there are 6, 10, 14, 18 ... terms. But for jj -coupling, only four different combinations of j_1, j_2 are possible, since $j_1 = l_1 \pm 1/2$ and $j_2 = l_2 \pm 1/2$. Thus, at low spectral resolution, a spectrum in the jj -coupling limit will be considerably less rich in lines than an LS -type spectrum.

(c) Examples

(i) Helium

The helium atom has two electrons, with spins s_1 and s_2 . The possible spin combinations with the corresponding spin functions are:

$$\begin{array}{lll}
 s_1=1/2 & s_2=1/2 & \alpha(1)\alpha(2) \\
 s_1=-1/2 & s_2=-1/2 & \beta(1)\beta(2) \\
 s_1=1/2 & s_2=-1/2 & \alpha(1)\beta(2) \\
 s_1=-1/2 & s_2=1/2 & \alpha(2)\beta(1)
 \end{array} \tag{2.16}$$

The last two spin functions do not satisfy the Pauli principle, so that appropriate combinations have to be taken. The results are:

$$\left. \begin{array}{l}
 s_+ = \alpha(1)\alpha(2) \\
 s_- = \beta(1)\beta(2) \\
 s_o = \sqrt{\frac{1}{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]
 \end{array} \right\} S = 1 \tag{2.17}$$

These spin functions describe the triplet, symmetric spin states with $S = 1$, that is, $(2S + 1) = 3$. These spin functions need to be combined with antisymmetric spatial functions, so that the total wave function is antisymmetric. Spin-orbit effects split these states into triplets for $L > 0$. These are called the “ortho” states of helium.

The other spin function is:

$$s_p = \sqrt{\frac{1}{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad S = 0 \tag{2.18}$$

which describes a singlet, antisymmetric spin state with $S = 0$. These combine with symmetric spatial functions to form states called “para”.

In the He ground state, both electrons have $n = 1$. The state is denoted as $1s^2 \ ^1S_0$ $n = 1, 2S + 1 = 1, L = 0, J = 0$. As a first guess, we might expect that the He ground state has twice the binding energy of the H ground state evaluated for $Z = 2$; that is, in the independent particle approximation: $E \approx 2(-Z^2/2n^2)$ a.u. or $E \approx -4$ a.u. with $Z = 2, n = 1$. In fact, the He ($1s^2$) binding energy is $637219.4 \text{ cm}^{-1} = 2.90$ a.u., somewhat smaller than 4 a.u. (due to the e-e interaction), but of the same order. Note that this is the (absolute value of the) energy required to remove both electrons to infinity. The first ionization potential of He (=binding energy of one electron) is much smaller, of course, being $198310 \text{ cm}^{-1} = 0.904$ a.u.

The lowest excited states of He have configurations $1s \ ns, 1s \ np, \dots$, in which one electron remains in the $1s$ orbital. The overall wave function (including both spatial and spin parts) must be antisymmetric and must have definite parity. The accompanying Figure (2.4) illustrates the He I (neutral He) term diagram. Note that for each singlet state,

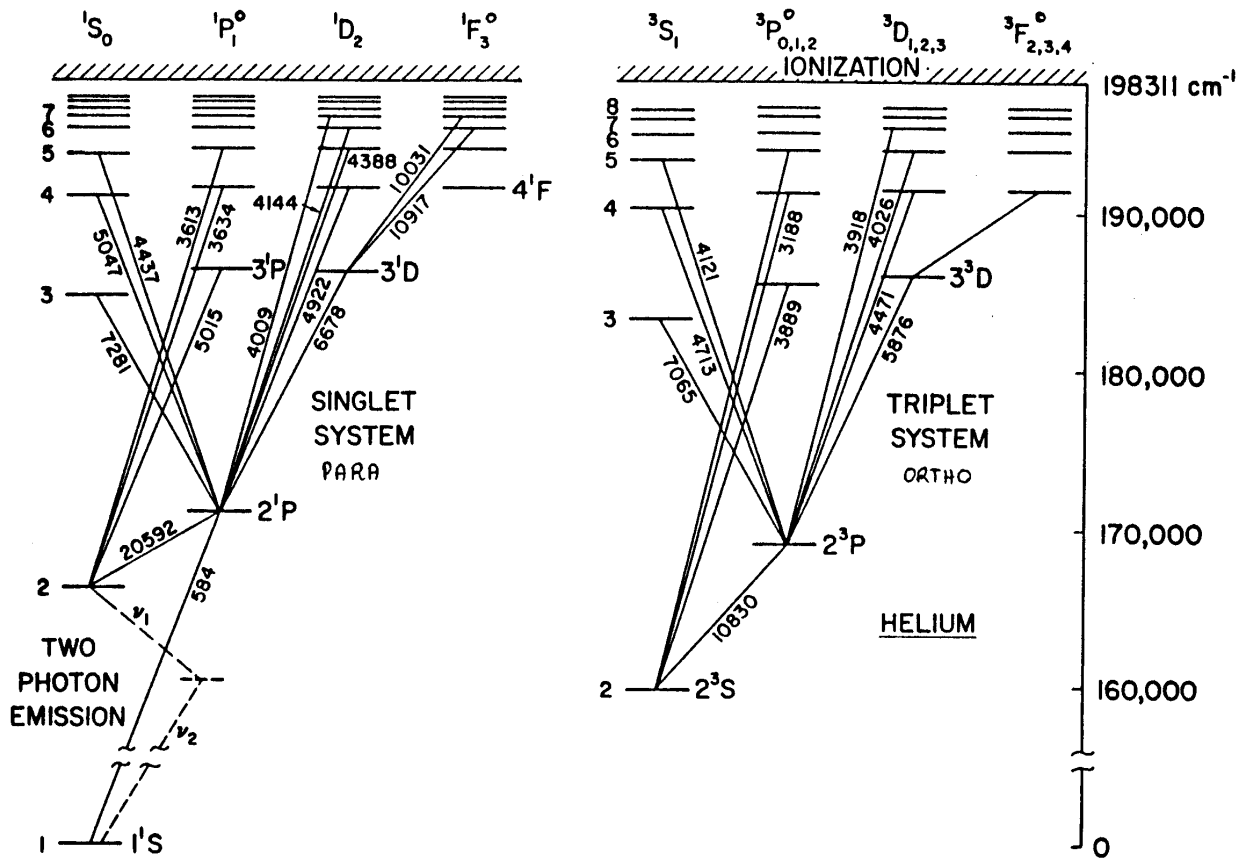


Figure 2.4— Helium energy levels, with transition wavelengths shown in Å.

there is only one level, with $J = L$; in the triplets, there is one level with $J = S = 1$ in the 3S states (since $L = 0$), but 3 levels having $J = L - 1, L, L + 1$ when $L \neq 0$. The triplet state terms lie below their singlet counterparts, although the separations diminish with increasing n . Only in the lowest 3P terms is the fine structure relatively easily resolved.

The strongest transition from the He ground state (also at the longest wavelength) is the $2^1P_1 - 1^1S_0$ transition at 584.4Å (the so-called resonance line). As we will see shortly, transitions between the ground state and the 2^1S_0 and 2^3S_1 states are electric dipole forbidden. Thus, these states cannot decay rapidly back to the ground state, so that they can have relatively large populations. These states are therefore called “metastable”.

(ii) Alkali atoms

Figure 2.5 shows the energy levels for the alkali metal atoms. It is clear, even for Cesium, that spin-orbit coupling is appreciably less than the intermultiplet splitting. The alkali elements have only one electron in the ns state outside the filled shells. This is the $^2S_{1/2}$ ground term. The filled shells are very stable, as they are in, for example, the noble gas atoms. Thus, the spectra of alkali atoms are determined solely by the transitions of the outer, most weakly bound electron. The effective field in which this electron moves is centrally symmetric, and coincides with the Coulomb field of charge e at great distances. Thus, the further the electron is from the filled shell, the more hydrogen-like is the field, so that for large n , the levels lie close to that of hydrogen. It is therefore customary to

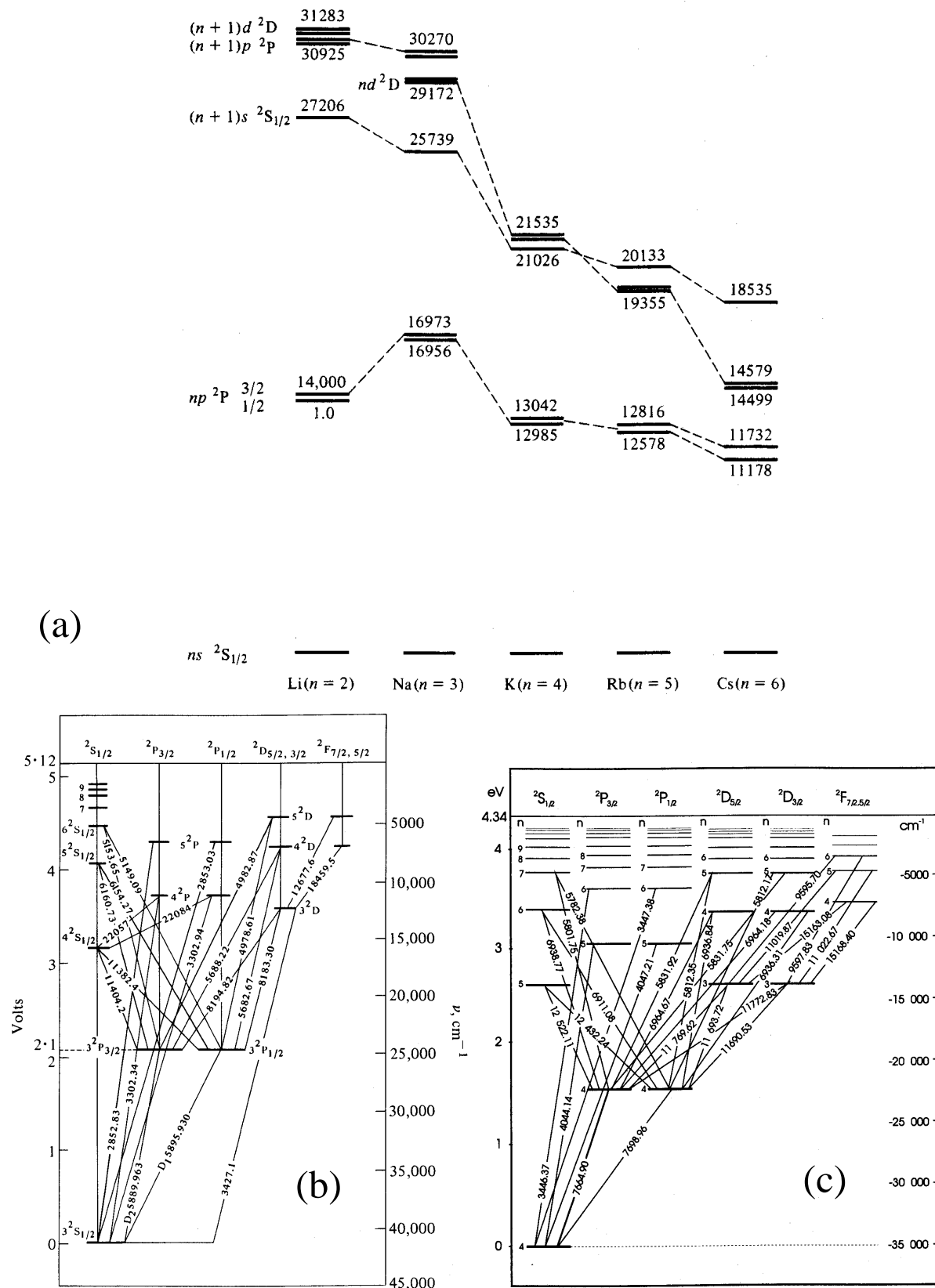


Figure 2.5— a. (Top) Energy levels for various neutral alkali atoms. b. (Bottom) Allowed transitions in the spectrum of K (wavelengths again in Å).

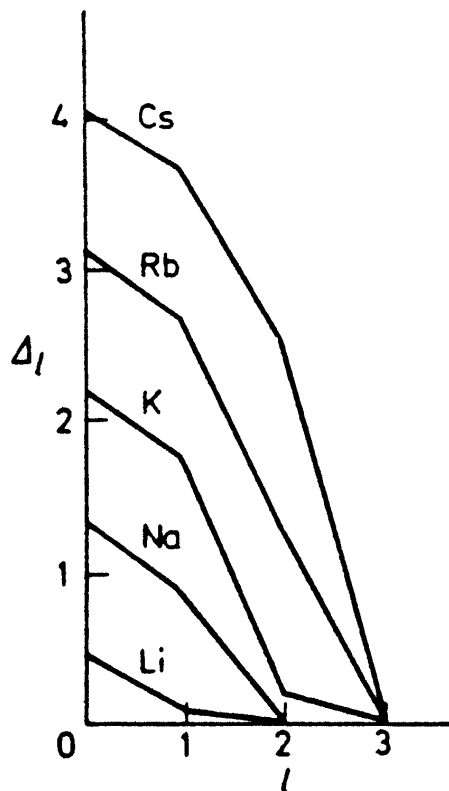


Figure 2.6– Quantum defects for various alkali atoms.

describe the terms of alkali atoms by analogy with hydrogen by the formula:

$$E_{nl} = -R_A/n_*^2, \quad (2.19)$$

where R_A =Rydberg constant for atom A, and n_* is an effective principal quantum number, which is selected so as to satisfy experimental data. To good accuracy:

$$n_* = n - \Delta_l, \quad (2.20)$$

where Δ_l , the so-called “quantum defect”, does not depend on n . The relation of Δ_l to l for the various alkali atoms is shown in Figure 2.6. Because the outer electron is weakly bound, the alkali atoms all have very low ionization potentials.

The spectra of the alkali atoms contain series very similar to those of hydrogen. If n' denotes the upper level of the transition, then the main series are called:

$n s S - n' p P$	Principal series
$n p P - n' s S$	Sharp series
$n p P - n' d D$	Diffuse series
$n d D - n' f F$	Fundamental series

where n and n' can be the same or different.

(iii) Other species

Figure 2.7 illustrates the lowest energy levels of neutral atoms which have a p^2 ground state configuration. Note that in this series, the heaviest member, lead, is still far from being at the pure jj -coupling limit.

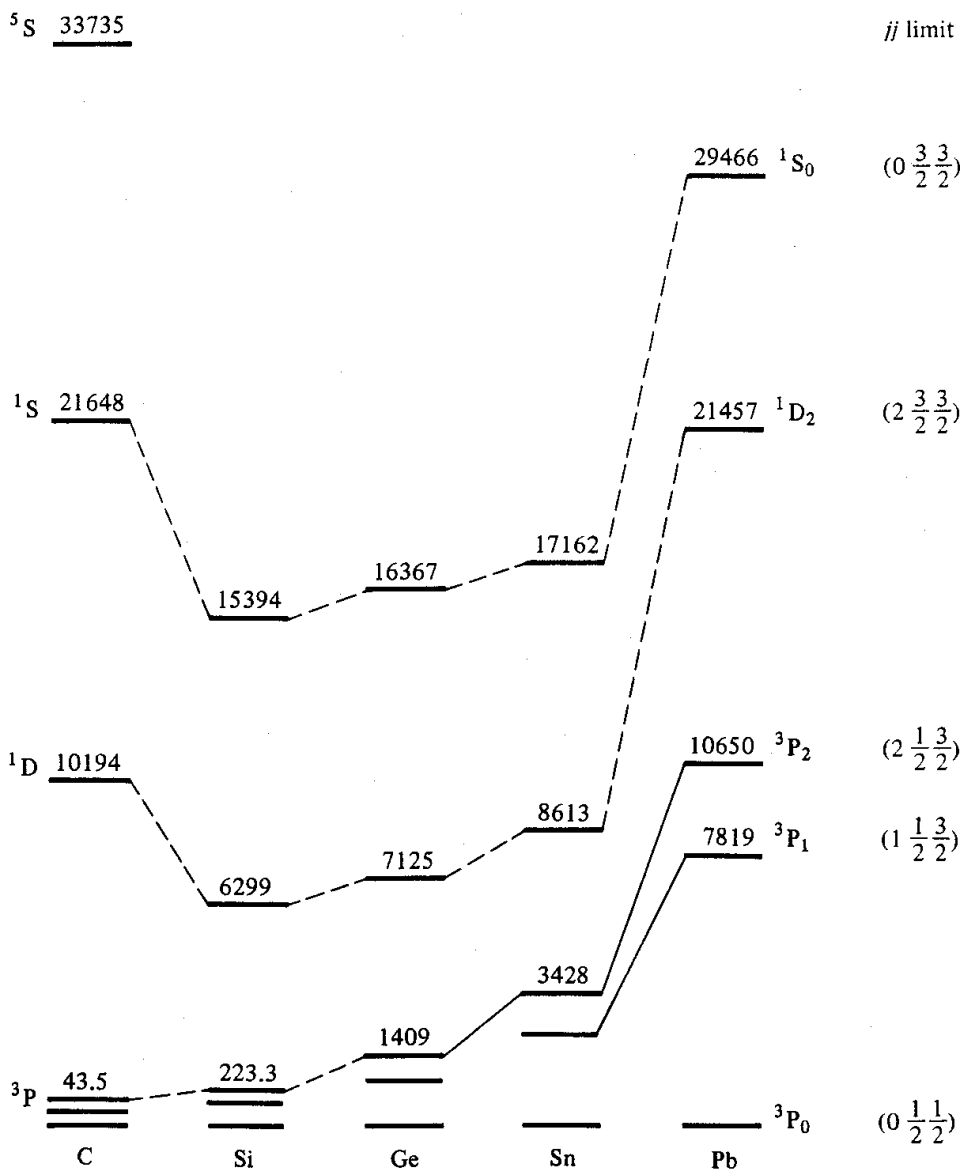


Figure 2.7– Energy levels for neutral atoms of the fourth column of the periodic table. All states arise from the p^2 configuration except for the 5S state, which arises from sp^3 . Energies and splittings in the figure are all in cm^{-1} . The right-hand (high Z) terms are labeled with the jj -limit quantum numbers.

The table on the last page of this chapter summarizes the lowest electronic configurations and the ground terms of the various atoms. The configurations can be found by successive filling of the electron shells in the approximate order:

$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 5d, 4f, \dots$

Also included in the table are the ionization potentials from the ground states. On average, although not monotonically, the ionization potentials increase with the filling of the shells. The greatest ionization potential is reached for the noble gas atoms He, Ne, Ar, Kr, Xe, ... which correspond to entirely filled shells. It drops sharply in passing to the alkali elements.

Table 2.1 – Electron configuration of atoms

Element	Electron configuration	Ground term	E_1 [eV]	Element	Electron configuration	Ground term	E_1 [eV]
1 H	1s	$^2S_{1/2}$	13.598	51 Sb	$5s^2 5p^3$	$^4S_{3/2}$	8.641
2 He	1s ²	1S_0	24.587	52 Te	$5s^2 5p^4$	3P_2	9.009
3 Li	2s	$^2S_{1/2}$	5.392	53 I	$5s^5 5p^5$	$^2P_{3/2}$	10.451
4 Be	2s ²	1S_0	9.322	54 Xe	$5s^2 5p^6$	1S_0	12.130
5 B	2s ² 2p	$^2P_{1/2}$	8.298	55 Cs	6s	$^2S_{1/2}$	3.894
6 C	2s ² 2p ²	3P_0	11.260	56 Ba	6s ²	1S_0	5.212
7 N	2s ² 2p ³	$^4S_{3/2}$	14.534	57 La	5d 6s ²	$^2D_{3/2}$	5.577
8 O	2s ² 2p ⁴	3P_2	13.618	58 Ce	4f 5d 6s ²	$^1G_4?$	5.47
9 F	2s ² 2p ⁵	$^2P_{3/2}$	17.422	59 Pr	4f ³ 6s ²	$^4I_{9/2}?$	5.42
10 Ne	2s ² 2p ⁶	1S_0	21.564	60 Nd	4f ⁴ 6s ²	3I_4	5.49
11 Na	3s	$^2S_{1/2}$	5.139	61 Pm	4f ⁵ 6s ²	$^6H_{5/2}?$	5.55
12 Mg	3s ²	1S_0	7.646	62 Sm	4f ⁶ 6s ²	7F_0	5.63
13 Al	3s ² 3p	$^2P_{1/2}$	5.986	63 Eu	4f ⁷ 6s ²	$^8S_{7/2}$	5.67
14 Si	3s ² 3p ²	3P_0	8.151	64 Gd	4f ⁷ 5d 6s ²	9D_2	6.14
15 P	3s ² 3p ³	$^4S_{3/2}$	10.486	65 Tb	4f ⁹ 6s ²	$^6H_{15/2}$	5.85
16 S	3s ² 3p ⁴	3P_2	10.360	66 Dy	4f ¹⁰ 6s ²	$^5I_6?$	5.93
17 Cl	3s ² 3p ⁵	$^2P_{3/2}$	12.967	67 Ho	4f ¹¹ 6s ²	$^4I_{13/2}?$	6.02
18 Ar	3s ² 3p ⁶	1S_0	15.759	68 Er	4f ¹² 6s ²	$^3H_6?$	6.10
19 K	4s	$^2S_{1/2}$	4.341	69 Tm	4f ¹³ 6s ²	$^2F_{7/2}$	6.18
20 Ca	4s ²	1S_0	6.113	70 Yb	4f ¹⁴ 6s ²	1S_0	6.254
21 Sc	3d 4s ²	$^2D_{3/2}$	6.54	71 Lu	5d 6s ²	$^2D_{3/2}$	5.426
22 Ti	3d ² 4s ²	3F_2	6.82	72 Hf	5d ² 6s ²	3F_2	7.0
23 V	3d ³ 4s ²	$^4F_{3/2}$	6.74	73 Ta	5d ³ 6s ²	$^4F_{3/2}$	7.89
24 Cr	3d ⁵ 4s	7S_3	6.766	74 W	5d ⁴ 6s ²	3D_0	7.98
25 Mn	3d ⁵ 4s ²	$^6S_{5/2}$	7.435	75 Re	5d ⁵ 6s ²	$^6S_{5/2}$	7.88
26 Fe	3d ⁶ 4s ²	5D_4	7.870	76 Os	5d ⁶ 6s ²	3D_4	8.7
27 Co	3d ⁷ 4s ²	$^4F_{9/2}$	7.86	77 Ir	5d ⁷ 6s ²	$^4F_{9/2}?$	9.1
28 Ni	3d ⁸ 4s ²	3F_4	7.635	78 Pt	5d ⁹ 6s	3D_3	9.0
29 Cu	4s	$^2S_{1/2}$	7.726	79 Au	6s	$^2S_{1/2}$	9.225
30 Zn	4s ²	1S_0	9.394	80 Hg	6s ²	1S_0	10.437
31 Ga	4s ² 4p	$^2P_{1/2}$	5.999	81 Tl	6s ² 6p	$^2P_{1/2}$	6.108
32 Ge	4s ² 4p ²	3P_0	7.899	82 Pb	6s ² 6p ²	3P_0	7.416
33 As	4s ² 4p ³	$^4S_{3/2}$	9.81	83 Bi	6s ² 6p ³	$^4S_{3/2}$	7.289
34 Se	4s ² 4p ⁴	3P_2	9.752	84 Po	6s ² 6p ⁴	3P_2	8.42
35 Br	4s ² 4p ⁵	$^2P_{3/2}$	11.814	85 At	6s ² 6p ⁵	$^2P_{3/2}$	9.5
36 Kr	4s ² 4p ⁶	1S_0	13.999	86 Rn	6s ² 6p ⁶	1S_0	10.748
37 Rb	5s	$^2S_{1/2}$	4.177	87 Fr	7s	$^2S_{1/2}$	4.0
38 Sr	5s ²	1S_0	5.695	88 Ra	7s ²	1S_0	5.279
39 Y	4d 5s ²	$^2D_{3/2}$	6.38	89 Ac	6d 7s ²	$^2D_{3/2}$	6.9
40 Zr	4d ² 5s ²	3F_2	6.84	90 Th	6d ² 7s ²	3F_2	
41 Nb	4d ⁴ 5s	$^6D_{1/2}$	6.88	91 Pa	5f ² 6d 7s ²	$^4K_{11/2}?$	
42 Mo	4d ⁵ 5s	7S_3	7.099	92 U	5f ³ 6d 7s ²	3L_6	4
43 Tc	4d ⁵ 5s ²	$^6S_{3/2}$	7.28	93 Np	5f ⁴ 6d 7s ²	$^4L_{11/2}$	
44 Ru	4d ⁷ 5s	3F_5	7.37	94 Pu	5f ⁶ 7s ²	7F_0	5.8
45 Rh	4d ⁸ 5s	$^4F_{9/2}$	7.46	95 Am	5f ⁷ 7s ²	$^8S_{7/2}$	6.0
46 Pd	4d ¹⁰	1S_0	8.34	96 Cm	5f ⁷ 6d 7s ²	9D_2	
47 Ag	5s	$^2S_{1/2}$	7.576	97 Bk	5f ⁸ 6d 7s ²	$^8H_{17/2}$	
48 Cd	5s ²	1S_0	8.993	98 Cf	5f ¹⁰ 7s ²	9I_8	
49 In	5s ² 5p	$^2P_{1/2}$	5.786	99 Es	5f ¹¹ 6s ²	$^4I_{15/2}$	
50 Sn	5s ² 5p ²	3P_0	7.344				