

Electronic Structure: Electronic Structure of atoms (theory)

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I. Introduction

The analysis of the spectrum of the hydrogen atom has been the starting point of the development of Quantum Mechanics at the beginning of the last century. The calculation of the energy eigenvalues and of the corresponding eigenfunctions of this one-electron system is simple enough both in non-relativistic and in relativistic quantum mechanics. When the number of the electrons in the atom increases, an exact solution, such as for the hydrogen atom, is no more possible. A multielectron atom is a many body system in which the electron-electron interactions together with the fermionic nature of the electrons as identical particles play a fundamental role. It is necessary to introduce some approximations. The majority of these approximations use a spherical self-consistent mean field $V_c(r)$ that includes, in an average way, all the interactions (mainly the electron-electron and electron-nucleus interactions) and in which the electrons move as independent particles. The electrons, being fermions of spin $\hbar/2$, obey to the Pauli principle and this circumstance, as it will be shown later, allows one to justify the structure of the periodic table of the elements, that is the most important regularity property of the electronic structure of atoms.

The study of the helium atom, which has only two electrons, demonstrates the goodness of the mean field approach because it provides a very good agreement with experiments from both a qualitative and a quantitative point of view. The choice of a suitable central mean potential depending on the atomic number Z provides a description of the periodic table of the elements. The most important ways to achieve $V_c(r)$ are the Thomas-Fermi, the Hartree, and the Hartree-Fock methods.

To improve this approximation, the non-spherical part of the electron-electron interaction has to be taken into account. The effect of this residual electrostatic interaction can be estimated as a perturbation on the Slater determinants containing the single particle states of $V_c(r)$. The residual electrostatic interaction mixes these determinants giving states with a total angular momentum L and with a total spin S (the orbital angular momentum l and the spin s of the single electrons are no more good quantum numbers).

The spin-orbit coupling gives the fine structure of the levels (multiplets) that are characterized also with the total angular momentum $\vec{J} = \vec{L} + \vec{S}$, so that the stationary states of the atom are eigenstates of $\vec{J}^2, \vec{L}^2, \vec{S}^2, J_z$. The knowledge of the multiplets structure allows the interpretation of the complex spectra of many electrons atoms also in presence of electrical and magnetical fields.

II. The Helium Atom

The Hamiltonian of the two electrons that includes only the electrostatic interactions, after the center-of-mass motion separation, is

$$H = \sum_{i=1}^2 \left(-\frac{\hbar^2 \nabla_{\vec{r}_i}^2}{2\mu} - \frac{Ze^2}{r_i} \right) + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} - \frac{\hbar^2}{M} \nabla_{\vec{r}_1} \cdot \nabla_{\vec{r}_2}. \quad (1)$$

The nucleus, in the origin, has mass M and charge $+Ze$, the electrons have the reduced mass $\mu = Mm/(m+M)$ (m is the electronic mass), positions \vec{r}_1, \vec{r}_2 and charge $-e$. In Eq.(1) the terms $\hbar^2 \nabla^2/2\mu$ are the kinetic energies of the relative electronic motion; the electron-electron interaction $e^2/|\vec{r}_1 - \vec{r}_2|$ screens the external coulombian nuclear potential $-Ze^2/r$. The last term in Eq.(1) represents the mass polarization term which, in first approximation, will be neglected.

A mean spherical field $V_c(r)$ can be obtained by substituting Z with an effective charge Z_{eff} . This charge is estimated within a variational approach using, for the ground state, the trial wave function

$$\psi(r_1, r_2) = \frac{1}{\pi a^3} e^{-(r_1+r_2)/a} \chi_{00}(1, 2)$$

where the single particle ground state of the potential $-Z_{eff}e^2/r$ appears $a = \hbar^2/Z_{eff}me^2$. Here $\chi_{00}(1, 2)$ is the singlet spin wave function of the total spin \vec{S} . The addition of two $1/2$ spins gives a singlet state $S = 0, M_s = 0$ and a triplet state $S = 1, M_s = 0, \pm 1$

$$\begin{aligned} \chi_{00}(1, 2) &= \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\ \chi_{10}(1, 2) &= \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) + \beta(1)\alpha(2)) \\ \chi_{11}(1, 2) &= \alpha(1)\alpha(2) \quad , \quad \chi_{1-1}(1, 2) = \beta(1)\beta(2) \end{aligned} \quad (2)$$

where α is the spin-up state, β the spin-down state, while the numbers 1 and 2 distinguish the electrons. The fermionic wave function is totally antisymmetric having a spatial part symmetric (exchanging the coordinates) and a spin part antisymmetric (exchanging the spins). The minimization of the energy provides the following effective charge:

$$Z_{eff} = Z - \frac{5}{16} \quad (3)$$

In **Table 1**, the ground state energies calculated with the variational method are compared with those estimated from experiments for three different two-electron systems (He, Li^+ and Be^{++}). As it can be seen the central field approximation overestimates the electron-electron repulsion.

	Z	E_0	E_{var}	E_{exper}
He	2	-108	-76.6	-78.6
Li^+	3	-243.5	-195.6	-197.1
Be^{++}	4	-433	-368.1	-370.0

Table 1 -Values of the ground state energy of two electrons He atom and ions in eV. Z is the atomic number. E_0 is the energy without electron-electron interaction (with only the coulombian field of the nucleus), E_{var} is the variational estimate (with $Z_{\text{eff}} = Z - 5/16$) and E_{exper} is the experimental value.

An improvement was been obtained by Hylleraas and Kinoshita using trial wave functions (depending on $r_1 + r_2, r_1 - r_2$ and $|\vec{r}_1 - \vec{r}_2|$), that take into account the correlation between the electrons . The density probability of such wave functions is no more the product of two independent functions of r_1 and r_2 . When the mass polarization, the relativistic and the radiative effects are included the agreement between theory and experiment is within the experimental error as the **Table 2** shows.

	H ⁻	He	Li ⁺
I_p^∞ non rel. ion. pot	6090.644298	198344.58014348	610120.4882
+reduced mass corr.	-3.315791	-27.192711	-47.7689
+mass pol.corr.	-3.928	-4.785	-4.960
+relativistic corr.	-0.304	-0.562	19.69
+ radiative corr.	-0.0037	-1.341	-7.83
$=I_0^{\text{th}}$	6083.092	198310.699	610079.62
I_0^{exp}	6100±100	198310.82±0.15	610079±25

Table 2 - I_p^∞ is the ionisation potential (in cm^{-1} , $1\text{cm}^{-1} = 1.24 \times 10^{-4}\text{eV}$) calculated including the correlation effects of the two electron interaction without the relativistic corrections. The complete theoretical estimate I_0^{th} is obtained adding the correction due the reduced mass, the mass polarization, the relativistic corrections and the radiative Quantum Electrodynamics corrections. It coincides with the measured value I_0^{exp} within the experimental error.

The independent particles scheme applies to the excited states too. The lowest-lying excited states correspond to the couple of single particle states:

$$\psi_{100}(\vec{r}), \psi_{nlm}(\vec{r}) \quad (4)$$

where n is the principal quantum number, $l(l+1)\hbar^2$ is the eigenvalue of the orbital angular momentum operator \vec{l}^2 , $m\hbar$ the eigenvalue of the operator l_z . Now a two independent particle state (totally antisymmetric) can have either the singlet or the triplet spin part

$$\begin{aligned} \Phi_{nlm}^+ &= \frac{1}{\sqrt{2}} (\psi_{100}(\vec{r}_1)\psi_{nlm}(\vec{r}_2) + \psi_{100}(\vec{r}_2)\psi_{nlm}(\vec{r}_1)) \chi_{00} \\ \Phi_{nlmM_S}^- &= \frac{1}{\sqrt{2}} (\psi_{100}(\vec{r}_1)\psi_{nlm}(\vec{r}_2) - \psi_{100}(\vec{r}_2)\psi_{nlm}(\vec{r}_1)) \chi_{1M_S} \end{aligned} \quad (5)$$

Starting from the coulombian nuclear potential $-Ze^2/r$ these states have the energy eigenvalues

$$E_n = -\frac{Z^2 e^2}{2a_0} \left(1 + \frac{1}{n^2}\right) \quad a_0 = \frac{\hbar^2}{me^2} \quad (6)$$

on which the electron-electron interaction e^2/r_{12} has to be included. The degeneracy with respect to l and between triplet and singlet states is removed with the energy shifts

$$\begin{aligned} \varepsilon_{nl}^\pm &= \int d^3r_1 \int d^3r_2 |\psi_{100}(\vec{r}_1)|^2 |\psi_{nlm}(\vec{r}_2)|^2 \frac{e^2}{r_{12}} \\ &\pm \int d^3r_1 \int d^3r_2 \psi_{100}^*(\vec{r}_1) \psi_{nlm}^*(\vec{r}_2) \psi_{100}(\vec{r}_2) \psi_{nlm}(\vec{r}_1) \frac{e^2}{r_{12}} \\ &= I_{nl} \pm K_{nl}. \end{aligned} \quad (7)$$

where the signs $+$ and $-$ are relative to singlet and triplet states, respectively.

The first integral is called the Coulomb (or direct) integral. It represents the Coulomb interaction between the charge distributions of the two electrons. The integral K is known as the exchange integral and does not have a classical analogue. Since the Coulomb integral is positive and being in the general case $K_{nl} > 0$, it turns out that a spin triplet state has a lower energy than the corresponding spin singlet state with the same n and l quantum numbers. Though the Hamiltonian does not contain spin-dependent terms the purely electrostatic electron-electron interaction removes the spin degeneracy. The exchange term is much stronger than the spin-dependent terms arising from relativistic effects, such as the spin-orbit interaction. In fact, as Heisenberg first observed, the exchange term is strong enough to keep the electron spins aligned in certain solids, giving rise to the phenomenon of ferromagnetism.

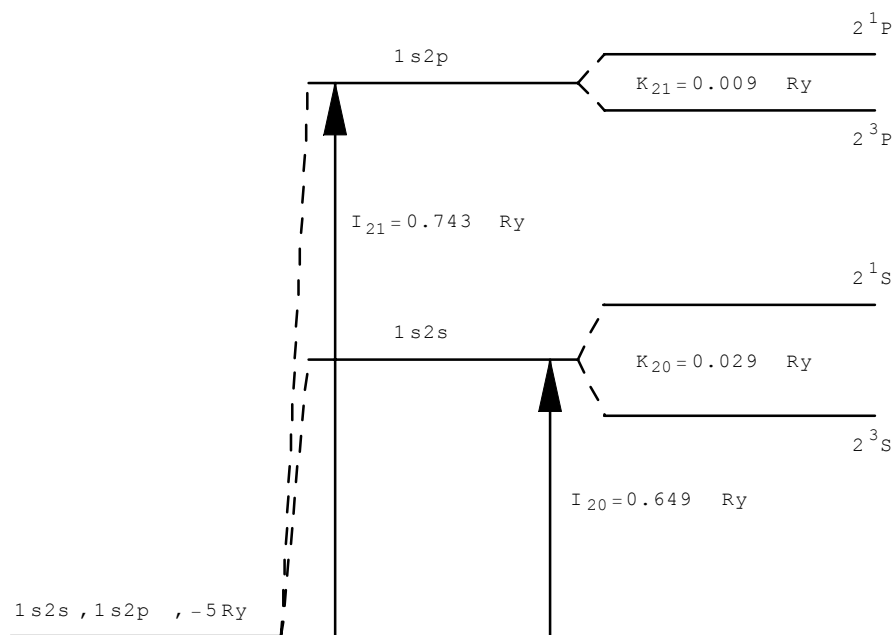


Figure 1 - Splitting of the first unperturbed excited state $n = 2$ of the He by the electron-electron interaction. The Coulomb and exchange integrals are given in Rydberg ($1\text{Ry}=27.2116\text{ eV}$).

Figure 1 shows the splitting of the unperturbed helium level for $n = 2$. In the electric dipole approximation the transitions between the singlet states and the triplet states are forbidden and the most intense helium spectral lines belong to two independent families and apparently two different kinds of helium exist: the orthohelium (with $S = 1$) and parahelium (with $S = 0$).

When $n \rightarrow \infty$ then I_{nl} and K_{nl} go to zero and the first ionisation limit of two-electrons atoms (ions) is reached on the energy $E_\infty = -Z^2e^2/2a_0$ (see Eq.(6)). The crude approximation of non interacting electrons gives for higher energy excited bound states with $n, n' > 1$ the levels

$$E_{nn'} = -\frac{Z^2e^2}{2a_0} \left(\frac{1}{n'^2} + \frac{1}{n^2} \right) > E_\infty. \quad (8)$$

These levels are degenerate with the continuous energy spectrum of the ion starting from E_∞ . The electron-electron interaction induces radiationless transition between the bound

state and the scattering state. These doubly excited states are called autoionising states because they can de-excite losing one of the electrons. The phenomenon of autoionisation is known as Auger effect. Not only helium-like (ions) but all atoms or ions with two or more electrons have such autoionising states.

III. The Periodic Table of the Elements

The Hamiltonian of an atom with Z electrons without relativistic spin-dependent terms and external fields is

$$H = \sum_{i=1}^Z \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \frac{1}{2} \sum_{i=1}^Z \sum_{j(\neq i)=1}^Z \frac{e^2}{|\vec{r}_i - \vec{r}_j|}. \quad (9)$$

The ground state and the first excited states can be described using a mean central field $V_c(r)$ in which the electrons move as independent particles. In this approximation

$$H \simeq H_c = \sum_{i=1}^Z \left(\frac{p_i^2}{2m} - V_c(r_i) \right) \quad (10)$$

and the overall effect of the electrons is to screen the coulombian nuclear field more and more increasing the distance from the nucleus: near the nucleus $V_c(r)$ is of the form $-Ze^2/r$ and very far from it $V_c(r) \simeq -e^2/r$. The screening can be represented by an effective charge depending on the distance r and the spherical mean field is no more coulombian

$$V_c(r) = -Z_{eff}(r) e^2/r. \quad (11)$$

The eigenstates of H_c are the Slater determinants $Z \times Z$ that can be formed with the single particle states $|nlm_l m_s\rangle$ which are eigenstates of $p^2/2m + V_c(r)$, of the orbital momentum operators \vec{l}^2 , l_z , and of spin z component σ_z . The single particle energy levels e_{nl} have a $2(2l+1)$ degeneracy ($-l < m_l < l$, $m_s = \pm 1/2$). The central potential V_c changes with the atomic number Z but the order in the levels sequence e_{nl} is nearly the same for all the atoms and it is shown in the **Table 3**.

The total energy is the sum of the individual energy levels and the Pauli principle allows the occupancy with only one electron of the state $|nlm_l m_s\rangle$. The distribution of the electrons with respect to the quantum numbers n and l is called the electron configuration. The states with the same n and l form a subshell, the subshells with the same n form a shell. The ground state of an atom has a configuration with filled (closed) subshells each containing $n_i = 2(2l+1)$ electrons and an open subshell with $n < n_i$ electrons (called equivalent). A subshell has a degeneracy

$$d_i = \frac{n_i!}{n!(n_i - n)!}$$

the closed subshells have $d_i = 1$. As an example, the ground state of the carbon atom $Z = 6$ has the configuration $1s^2 2s^2 2p^2$. The subshells $1s, 2s$ are non degenerate while the subshell $2p$ has a degeneracy:

$$\frac{6!}{2!4!} = 15$$

the total degeneracy of the ground state is $1 \times 1 \times 15 = 15$.

Quantum numbers n, l	Spectroscopic notation for subshell (n, l)	Maximum number of electrons allowed in the subshell $= 2(2l + 1)$
6,2	6d	10
5,3	5f	14
7,0	7s	2
6,1	6p	6
[5,2	[5d	10
[4,3	[4f	14
[6,0	[6s	2
5,1	5p	6
[4,2	[4d	10
[5,0	[5s	2
4,1	4p	6
[3,2	[3d	10
[4,0	[4s	2
3,1	3p	6
3,0	3s	2
2,1	2p	6
2,0	2s	2
1,0	1s	2

Table 3- The ordering of the single particle energies of each subshell. The energy increases from bottom to top. The levels enclosed in the square brackets have very near energies and their order can change varying the atomic number Z .

The last tightly bound electrons, which are in the subshell of highest energy, and are in an insufficient number to form another closed subshell, are called valence electrons. They are responsible of the bondings between the atoms in the molecules.

All the information that is needed to discuss the electronic structure and the ‘building up’ (aufbau) of atoms is on hand now.

The list of the elements begin with the hydrogen that has a ionisation potential of 13.6 eV. The next element is helium that has the largest ionisation potential (24.59 eV). The configuration $1s^2$ corresponds to the closed shell $n = 1$. There are no valence electrons and helium is the first inert rare gas. The third element is lithium (the first *alkali* atom) with the ground state configuration $1s^2 2s^1$. If the screening of the closed $n = 1$ shell were perfect, the ionisation potential would be $13.6/4 = 3.4\text{eV}$ ($Z_{eff} = 1$); but the electron-electron potential reduces Z_{eff} and rises the ionisation potential to 5.39eV. Berillium has a configuration $1s^2 2s^2$. The ionisation potential is larger (9.32eV) because of the increase of the nuclear charge. The subshell $2p$ is progressively filled starting from Boron ($Z=5$) up to Neon ($Z=10$) for which the shell $n = 2$ is full. Neon is the second inert rare gas for which the ionisation potential is increased up to 21.56eV. From $Z=11$ (Sodium, the second alkali atom) to $Z=18$ (Argon, the second rare gas) the subshells $3s$ and $3p$ are progressively filled. The filling of the shell $n = 3$ is interrupted at $Z=19$ (Potassium, third alkali element) because the level $4s$ is lower of $3d$ level that starts to be filled from Scandium ($Z=21$) to Zinc ($Z=30$). There is a competition between the levels $4s$ and $3d$ that are very close in energy and the filling is not so regular as for the elements with lower atomic number. The elements with an incomplete $3d$ subshell belong to first transition or iron *group*. The higher incomplete subshells of the chromium ($Z=24$) correspond to the state $[Ar]4s^1 3d^5$

($[Ar]$ stands for the noble gas argon configuration $1s^2 2s^2 3s^2 3p^6$) that is energetically more favourable of $[Ar]4s^2 3d^4$ configuration. The high number of valence electrons allows the very rich class of molecules that can be formed with the chromium. The filling competition of the subshells $5s$ and $4d$ characterizes the second transition or palladium group (from $Z=39$ (yttrium) to $Z=48$ (cadmium)) and the third transition or platinum group (from $Z=71$ to $Z=80$ (mercury)) corresponds to the irregular filling of the states $6s$ and $5d$. The list of elements ends with the actinides beginning from $Z=89$ (actinium) in which a competition occurs between $5f$ and $6d$ states. The $Z=103$ (lawrencium) is the element with the largest atomic number because the actinides are radioactive elements with highly instable nuclei that decay by spontaneous fission in lighter elements.

The list of the elements can be organized in a table putting in columns the elements with similar outer subshell. All the alkali metals have a single weakly bound electron in a subshell s ($2s$ Li, $3s$ Na, $4s$ K and so on). All the halogens (F, Cl, Br, I) have a subshell p^5 lacking of only one electron. The alkalis and the halogens have high chemical reactivities because they can reach more stable energetic arrangements losing or acquiring one electron in such a way to form completely filled subshells. The last column of the table contains the rare gases (He, Ne, Ar, Kr, Xe, Rn).

The recurrences of similar chemical properties led Mendeleev in 1869, long time before the existence of the electrons and of the nuclei were known, to classify the elements in the periodic table. He put elements with similar chemical properties in the same column. The chemical properties change progressively along the rows that are called periods. There are seven periods and each of the periods begins with an alkali element and ends with a noble gas atom, except for the seventh period which is incomplete.

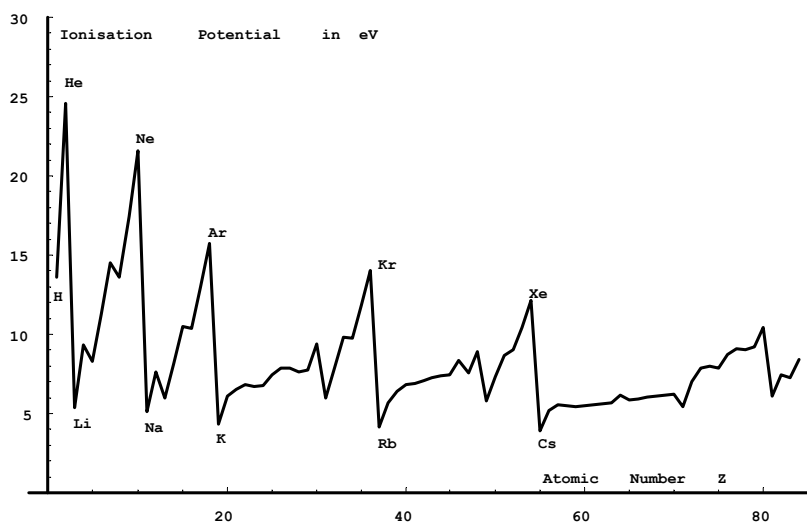


Figure 2 - The first ionisation potential against the atomic number.

The ionisation potential increases along a period and has a sudden drop passing from a noble gas to the alkali of the next period (**Figure 2**).

IV. Beyond the Central-Field Approximation

There are two main corrections to the approximate hamiltonian H_c . The first one is the correlation due to the electron-electron interaction

$$H_1 = H - H_c = - \sum_i \frac{(Z - Z_{eff}(r_i)) e^2}{r_i} + \frac{1}{2} \sum_{i,j(j \neq i)} \frac{e^2}{r_{ij}} \quad (12)$$

$$r_{ij} = |\vec{r}_i - \vec{r}_j|$$

that is called the residual electrostatic interaction and is no more spherically symmetric. The second correction is the spin-orbit term that, within the central field approximation, is

$$H_2 = \sum_i \xi(r_i) \vec{l}_i \cdot \vec{s}_i \quad (13)$$

$$\xi(r_i) = \frac{1}{2mc^2} \frac{1}{r_i} \frac{dV_c(r_i)}{dr_i}.$$

If we neglect the spin-orbit coupling terms the effect of the residual electrostatic interaction can be evaluated treating H_1 as a perturbation on H_c . The ground state and the first excited states of H_c are strongly degenerate and the levels of H can be obtained by diagonalizing H_1 in the subspace \mathcal{S}_o of the lowest eigenvalue E_0 of H_c . As an example, the subspace \mathcal{S}_o of the ground state of the carbon atom contains 15 Slater 6×6 determinants formed with the 4 states of the two closed subshell $1s^2$ and $2s^2$ and two states of the incomplete $2p$ subshell, namely:

$$|-1, \frac{1}{2}\rangle, |-1, -\frac{1}{2}\rangle, |0, \frac{1}{2}\rangle, |0, -\frac{1}{2}\rangle, |1, \frac{1}{2}\rangle, |1, -\frac{1}{2}\rangle$$

where the first number is the eigenvalue of l_z , the second one that of s_z (in units \hbar). The subspace \mathcal{S}_o is called a multiplet. The multiplet is spanned by the eigenvalues of the angular orbital momenta \vec{l}_i and of the spins \vec{s}_i of the single particle levels of the central potential $V_c(r)$. If the overall electron-electron interaction is taken into account only the total angular momentum $\vec{L} = \sum \vec{l}_i$ commutes with H , while the single angular orbital momenta are not conserved (H is invariant only under overall rotations). The perturbation H_1 is diagonal in the multiplet basis $\{\vec{L}^2, L_z, \vec{S}^2, S_z\}$ whose vectors $|\alpha L S M_L M_S\rangle$ are eigenvectors of the total orbital momentum, of the total spin and the quantum number α labels the different vectors having the same total angular momentum and total spin. The use of this basis, that has the symmetries of the total hamiltonian H , greatly simplifies the diagonalization of H_1

$$\begin{aligned} & \langle \alpha' L' S' M'_L M'_S | H_1 | \alpha L S M_L M_S \rangle \\ & = \delta_{LL'} \delta_{SS'} \delta_{M_L M'_L} \delta_{M_S M'_S} V_{\alpha\alpha'}^{(LS)} \end{aligned} \quad (14)$$

and we need only to diagonalize the matrices $V_{\alpha\alpha'}^{(LS)}$ corresponding to each pair of quantum numbers LS . The complete electron-electron interaction does not remove the degeneracy with respect to M_L and M_S because H_1 has an overall spherical symmetry and it does not have a preferential direction. The levels LS (usually denoted as ^{2S+1}C , C being the capital letter S for $L = 0$, P for $L = 1$, D for $L = 2 \dots$) are left by the residual electrostatic interaction with a $(2L + 1)(2S + 1)$ degeneracy.

The vectors $|\gamma L S M_L M_S\rangle$ can be constructed by summing up the single orbital momenta \vec{l}_i , and the single spins \vec{s}_i . The Slater determinants spanning the subspace \mathcal{S}_0 have to be mixed each other to form the eigenstates of the basis $\{\vec{L}^2, L_z, \vec{S}^2, S_z\}$. The antisymmetry of the wave function forbids some values of L and S compatible with the single particle angular momenta addition. Returning to the example of the carbon atom ground state and putting apart the Pauli principle, the addition of the single particle angular momenta of two $2p$ electrons gives the following spectral terms:

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

that have an overall degeneracy of $3 \times 1 + 3 \times 3 + 3 \times 5 + 1 \times 1 + 1 \times 3 + 1 \times 5 = 36 = 6 \times 6$, while only 15 states are available. It turns out that the terms of this list satisfying the Pauli principle are

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

As the triplet- and the singlet-spin states are, respectively, symmetrical and antisymmetrical in the exchange of the spins, and as the states S and D on the one hand and P on the other hand, are respectively symmetrical and antisymmetrical in the interchange of the orbital variables. The number of linearly independent antisymmetrical states is $9 + 1 + 5 = 15$ just the number of the Slater determinants in \mathcal{S}_0 .

Although the perturbation H_1 does not depend on the spin S the perturbed levels depends on S via the exchange integrals introduced by the two-body operator H_1 , like those that appear in the excited levels of the helium. The repulsive electron-electron interaction decreases with the mutual distance of the electrons, that is, when the orbital part of the wave function becomes more antisymmetrical. The spin part of the wave function is more symmetrical for larger S and therefore the orbital part is more antisymmetrical for larger S . The levels of a given configuration are in order of decreasing total spin (Hund's rule). In the ground state of the carbon atom the lowest level is the triplet one 3P , followed first by the singlet 1D and then by 1S . These two levels have the same spin multiplicity, but 1D has an higher orbital momentum and in this state the electrons are farther away and the repulsive effect of electron-electron interaction on it is less.

Subshells that contain the same number of occupied or empty states (holes in the filled subshell) are equivalent each other. It can be seen that the two subshells with k and $4l + 2 - k$ equivalent electrons have the same LS terms, so the perturbative corrections due to H_1 are the same.

The addition of the spin-orbit coupling H_2 to the electrostatic correction H_1 gives a less symmetric perturbative correction to H_c : $H_1 + H_2$ commutes with $\vec{J} = \vec{L} + \vec{S}$, but neither with \vec{L} nor with \vec{S} . The relative importance of H_2 increases rapidly with Z . In the light and medium atoms $|H_1| \gg |H_2|$; in heavier atoms (starting from Pb) $|H_1|$ and $|H_2|$ are of the same order of magnitude. In the first case H_2 is treated as a small perturbation on LS levels. This scheme is called Russel-Saunders coupling or LS coupling. First, H_1 removes the degeneracy of the linear combinations of Slater determinants corresponding to the values of $\vec{L} = \sum \vec{l}_i$ and of $\vec{S} = \sum \vec{s}_i$ allowed by the Pauli principle. Then H_2 gives a different energy eigenvalue to each possible value of J ($J = L + S, L + S - 1, \dots, |L - S|$) with a residual degeneracy of order $(2J + 1)$.

The other scheme relatively simple is the jj coupling in which $|H_2| \gg |H_1|$. The Slater determinants are formed using single particle states perturbed by spin-orbit interaction on V_c : first the orbital angular momentum \vec{l}_i is coupled with the spin \vec{s}_i as $\vec{j}_i = \vec{l}_i + \vec{s}_i$ by H_2 , then H_1 removes the degeneracy between the allowed values of $\vec{J} = \sum \vec{j}_i$. The level structure of the ground state of the heavier atoms is intermediate between those given by LS and jj coupling.

It turns out that the matrix elements in the subspace of a level (αLS) with a degeneracy of the order $(2L+1)(2S+1)$ are the same as those of the operator $\gamma(\alpha, L, S) \vec{L} \cdot \vec{S}$, where $\gamma(\alpha, L, S)$ is a constant characteristic of the unperturbed level:

$$\begin{aligned} & \langle \alpha LSM_L M_S | H_2 | \alpha LSM'_L M'_S \rangle \\ &= \gamma \langle \alpha LSM_L M_S | \vec{L} \cdot \vec{S} | \alpha LSM'_L M'_S \rangle \end{aligned} \quad (15)$$

This relationship between the matrix elements of $\sum_i \vec{l}_i \cdot \vec{s}_i$ and $\vec{L} \cdot \vec{S}$ is proved in the quantum mechanics theory of angular momentum by the theorem of Wigner-Eckart. The constant γ is proportional to the average value of $\xi(r)$ on the radial orbital part common to all the single particle states spanning the subspace of the level. The spin-orbit correction on a closed subshell is null (for it $L = S = M_L = M_S = 0$).

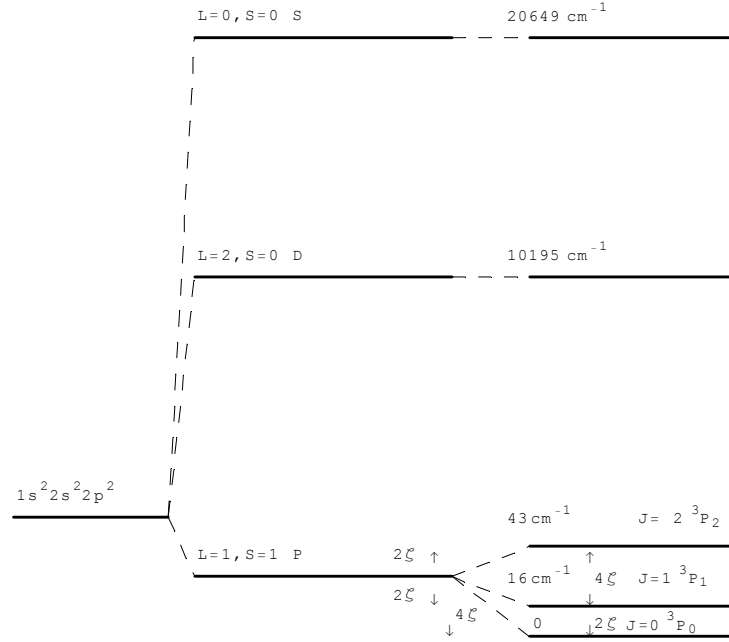


Figure 3 - Splitting of the ground state configuration of the carbon atom due to electrostatic residual interaction and to the spin-orbit coupling. Here $\zeta = \gamma(\alpha, L, S)\hbar^2/2$. The numbers near the levels (in cm^{-1}) are the experimental values of the energy levels. The Landè interval rule is approximatively satisfied. The separation between 3P_0 and 3P_1 gives a value of $\zeta = 8\text{cm}^{-1}$ and the energy of 3P_2 , above the ground state 3P_0 , foreseen by the interval rule is of $6 \times 8 = 48\text{cm}^{-1}$, a little bigger than the measured value of 43cm^{-1} .

While H_2 is not diagonal in the representation $\{\alpha LSM_L M_S\}$, as $L_x S_x + L_y S_y + L_z S_z$ does not commute with L_z and S_z , it becomes diagonal in the equivalent representation $\{\alpha LSJM_J\}$. Since

$$\begin{aligned} \vec{J}^2 &= \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S} \\ &= \frac{1}{2} (\vec{J}^2 - \vec{L}^2 + \vec{S}^2) \end{aligned} \quad (16)$$

one has

$$\langle \alpha LSJM_J | H_2 | \alpha LSJM'_J \rangle \quad (17)$$

$$= \frac{1}{2}\gamma\hbar^2(J(J+1) - L(L+1) - S(S+1)) = E(J)$$

and the unperturbed level αLS splits into as many levels as the possible values of $J(= L + S, \dots, |L - S|)$. The degeneracy of these levels is of order $(2J + 1)$ (**Figure 3**).

The energy separation between adjacent levels $E(J)$ and $E(J - 1)$ is proportional to J :

$$\begin{aligned} & E(J) - E(J - 1) \\ &= \frac{1}{2}\gamma\hbar^2[J(J+1) - L(L+1) - S(S+1) - \\ & \quad J(J-1) + L(L+1) + S(S+1)] \\ &= \gamma\hbar^2 J. \end{aligned} \tag{18}$$

This result is known as the Landè interval rule and is well satisfied experimentally for Z large enough, when among the overall magnetic interactions between the angular momenta

$$a_{ij}\vec{l}_i \cdot \vec{s}_j, \quad b_{ij}\vec{l}_i \cdot \vec{l}_j, \quad c_{ij}\vec{s}_i \cdot \vec{s}_j$$

only the diagonal terms a_{ii} dominate all the others. For a single open subshell that is less than half-filled the constant γ is positive and the lowest energy value has the smallest possible value of J . These multiplets are called regular. On the other hand multiplets more than half-filled have $\gamma < 0$, the order with J is turned upside down and they are called inverted. Regular and inverted multiplets have opposite spin-orbit corrections

$$\begin{aligned} & \left| \sum_{k \in \text{filled states}} \vec{l}_k \cdot \vec{s}_k \right| \\ &= \left| \left(\sum_{k \in \text{all shell}} - \sum_{k \in \text{empty states}} \right) \vec{l}_k \cdot \vec{s}_k \right| = - \left| \sum_{k \in \text{empty states}} \vec{l}_k \cdot \vec{s}_k \right| \end{aligned} \tag{19}$$

being

$$\left| \sum_{k \in \text{all shell}} \vec{l}_k \cdot \vec{s}_k \right| = 0. \tag{20}$$

When the subshell is just half-filled there is no multiplet splitting.

See also: Hartree and Hartree-Fock Methods in Electronic Structure.

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V. Further Reading

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