

Chapter 2

Typical Atoms

Topics

Effects on the Outer Electron from the Inner Core
Helium Atom and the Electron-Electron Interaction
Exchange Interaction
Pauli Principle and Antisymmetry
Slater Determinantal Eigenfunctions

2.1 Alkali Atoms

Li, Na, K, Rb, Cs and Fr are a particular group of atoms characterized by one electron (often called *optical* being the one involved in optical spectra) with expectation value of the distance from the nucleus $\langle r \rangle$ considerably larger than the one of the remaining $(N - 1)$ electrons, forming the internal “core”. The alkali atoms are suited for analyzing the role of the core charge in modifying the Coulomb potential $(-Ze^2/r)$ pertaining to Hydrogenic atoms (Sect. 1.4), as well as to illustrate the effect of the spin-orbit interaction (Sect. 1.6).

From spectroscopy one deduces the diagram of the energy levels for Li atom reported in Fig. 2.1, in comparison to the one for Hydrogen.

In Fig. 2.2 the analogous level scheme for Na atom is shown, with the main electric-dipole transitions yielding the emission spectrum.

The quantum numbers for the energy levels in Fig. 2.1 are the ones pertaining to the outer electron. At first we shall neglect the fine structure related to the spin-orbit interaction, which causes the splitting in doublets of the states at $l \neq 0$, as indicated for Na in Fig. 2.2.

A summarizing collection of the energy levels for alkali atoms is reported in Fig. 2.3. It should be remarked that because of the different extent of penetration in

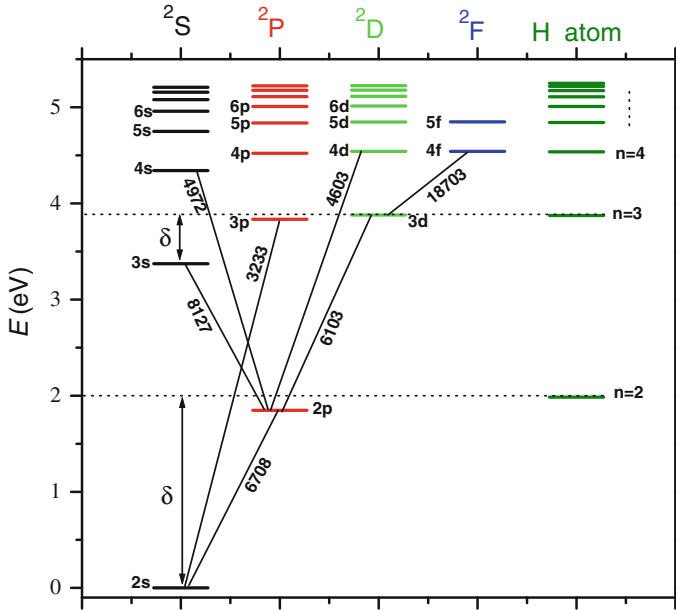


Fig. 2.1 Energy level diagram (*Grotrian diagram*) of Li atom, in term of the quantum numbers nl of the optical electron and comparison with the correspondent levels ($n > 1$) for H atom. The *quantum defect* δ (or *Rydberg defect*) indicated for $2s$ and $3s$ states, is a measure of the additional (negative) energy of the state in comparison to the correspondent state in Hydrogen. The wavelengths (in Å) for some transitions are reported

the core (as explained in the following) an inversion of the order of the energy levels in terms of the quantum number n (namely $|E_n| > |E_{n-1}|$) can occur.

From the Grotrian diagrams one deduces the following:

- (i) the sequence of the energy levels is similar to the one for H, with more bound and no more l -degenerate states;
- (ii) the *quantum defect* δ for a given n -state (see Fig. 2.1) increases on decreasing the quantum number l ;
- (iii) the ground state for Li is $2s$ ($3s$ for Na, etc.), with $L = l$ (and not the $1s$ state);
- (iv) the transitions yielding the spectral lines obey the selection rule $\Delta l = \pm 1$.

These remarkable differences with respect to Hydrogen are related to an effective charge $Z_{eff}(r)$ for the optical electron (see Sect. 1.2) different from unit over a sizeable range of distance r from the nucleus.

In order to give a simple description of these effects we shall assume an *ad hoc* effective charge, of the form $Z_{eff} = (1 + b/r)$, depicted in Fig. 2.4. The characteristic length b depends from the particular atom, it can be assumed constant over a large range of distance while for $r \rightarrow 0$ it must be such that $Z_{eff}(r) \rightarrow Z$.

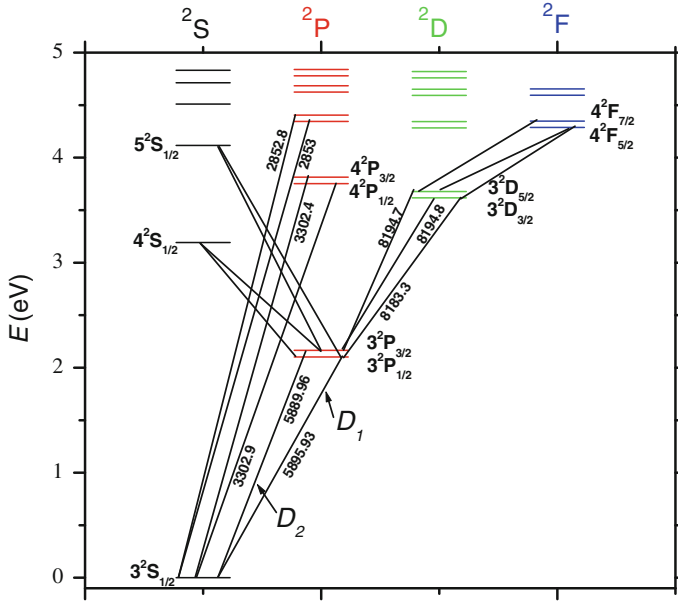


Fig. 2.2 Energy levels for Na atom with the electric dipole transitions ($\Delta l = \pm 1$) generating some spectral lines and correspondent wavelengths (in Å). The doublets related to spin-orbit interaction and resulting in states at different $j \equiv J$, are indicated (not in scale). The yellow emission line (a doublet) is due to the transition from the $^2P_{3/2}$ and $^2P_{1/2}$ states to the ground state $^2S_{1/2}$ with the optical electron in the $3s$ state

As a consequence of that choice for $Z_{eff}(r)$ the radial part of the Schrodinger equation for the optical electron takes a form strictly similar to the one in Hydrogen (see Sect. 1.4):

$$\frac{-\hbar^2}{2mr^2} \frac{d}{dr} r^2 \frac{dR}{dr} + \left[\frac{l(l+1)\hbar^2 - 2me^2b}{2mr^2} - \frac{e^2}{r} \right] R = ER. \quad (2.1)$$

It is remarked that for $b = 0$ the eigenvalues associated with Eq.(2.1) are $E_n = -R_H hc/n^2$ (Eq.(1.13), for $Z = 1$).

If an effective quantum number l^* such that

$$l^*(l^* + 1) = l(l + 1) - \frac{2me^2b}{\hbar^2} \equiv l(l + 1) - \frac{2b}{a_0}$$

is introduced, then in the light of the formal treatment for Hydrogen, from Eq.(2.1) one derives the eigenvalues

$$E_n = -\frac{R_H hc}{(n^*)^2}, \quad (2.2)$$

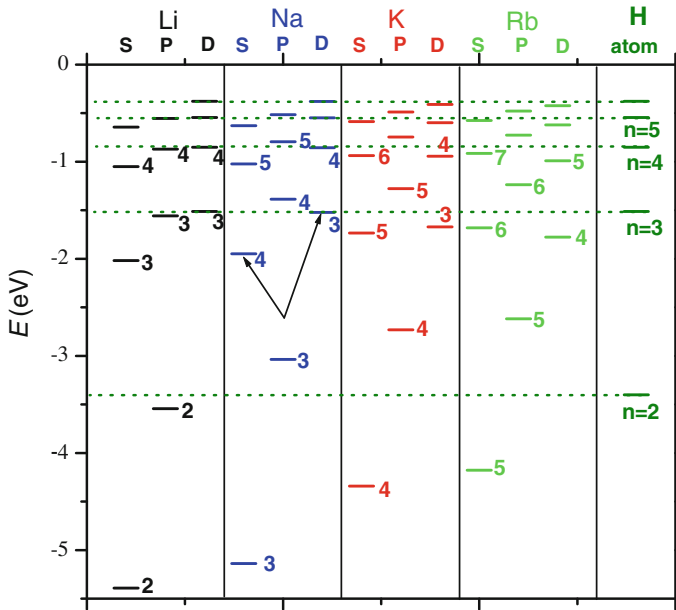


Fig. 2.3 Energy levels (neglecting the fine structure) for some alkali atoms, again compared with the states for Hydrogen at $n > 1$. The $4s$ state is more bound than the $3d$ state (see arrows), typical inversion of the order of the energies due to the extent of penetration of the s -electrons in the core, where the screening is not fully effective (see text and Fig. 2.6)

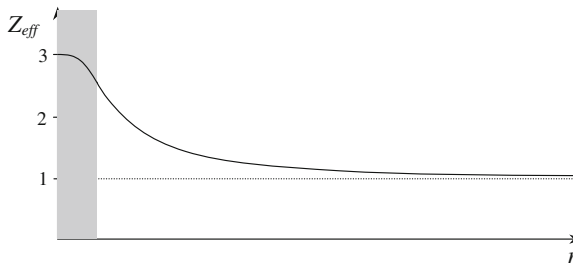


Fig. 2.4 Sketchy behavior of a plausible effective charge for the optical electron in Li atom. The dashed part of the Figure (not in scale) corresponds to the region of r not taken into account in the derivation of the energy levels. For Na, K, etc. atoms $Z_{eff}(r \rightarrow 0) \rightarrow Z$. A similar form of effective charge experienced by one electron because of the partial screening of the nuclear charge by the second electron is derived in Problem 2.7 for He atom

with n^* not integer. To evidence in these energy levels the numbers n and l pertaining to Hydrogen atom, we write $n^* = n - \delta l$, with $\delta l = l - l^*$, thus obtaining

$$E_{n,l} = -\frac{R_H hc}{(n - \delta l)^2}.$$

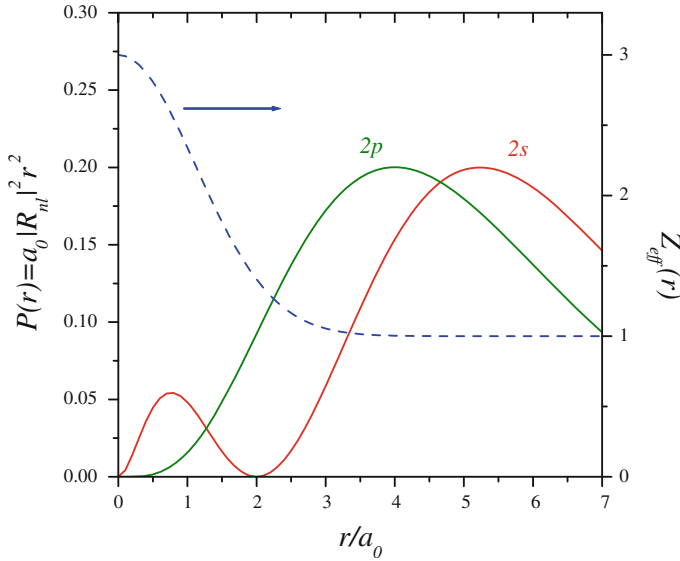


Fig. 2.5 Radial probability of presence for $2s$ and $2p$ electrons in Hydrogen and sketchy behavior of the effective charge for Li (see Fig. 2.4)

By neglecting the term in δl^2

$$E_{n,l} = -\frac{R_H h c}{(n - 2b/[a_0(2l + 1)])^2} \equiv -\frac{R_H h c}{(n - \delta_{n,l})^2}. \quad (2.3)$$

The eigenvalues are l -dependent, through a term that is atom-dependent (via b) and that decreases on increasing l , in agreement with the phenomenological findings.

The physical interpretation of the result described by Eq. (2.3) involves the amount of penetration of the optical electron within the core. In Fig. 2.5 it is shown that for $r \leq a_0$ the electron described by the $2s$ orbital has a radial probability of presence sizeably larger than the one for the $2p$ electron. This implies a reduced screening of the nuclear charge and then more bound state.

As a general rule one can state that the penetration within the core increases on decreasing l . In Fig. 2.6 it is shown how it is possible to have a more penetrating state for $n = 4$ rather than for $n = 3$, in spite of the fact that on the average the $3d$ electron is closer to the nucleus than the $4s$ electron. This effect is responsible of the inversion of the energy levels, with $|E_{4s}| > |E_{3d}|$, as already mentioned.

At the sake of illustration we give some quantum defects $\delta_{n,l}$ to be included in Eq. (2.3), for Na atom:

$\delta_{3s} = 1.373$	$\delta_{3p} = 0.883$	$\delta_{3d} = 0.01$
$\delta_{4s} = 1.357$	$\delta_{4p} = 0.867$	$\delta_{4d} = 0.011$
...	...	$\delta_{4f} \simeq 0$

These values for the quantum defects can be evaluated from the energy levels reported in Fig. 2.2 (see also Problem 2.1).

Finally a comment on the selection rule $\Delta l = \pm 1$ is in order. This rule is consistent with the statement that each electron makes the transition independently from the others, with the one-electron selection rule given in Appendix 1.3. In fact, the total wavefunction for the alkali atom, within the central field approximation, can be written

$$\phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_{core}\phi_{optical}.$$

The electric dipole matrix element associated to a given $1 \leftrightarrow 2$ transition becomes

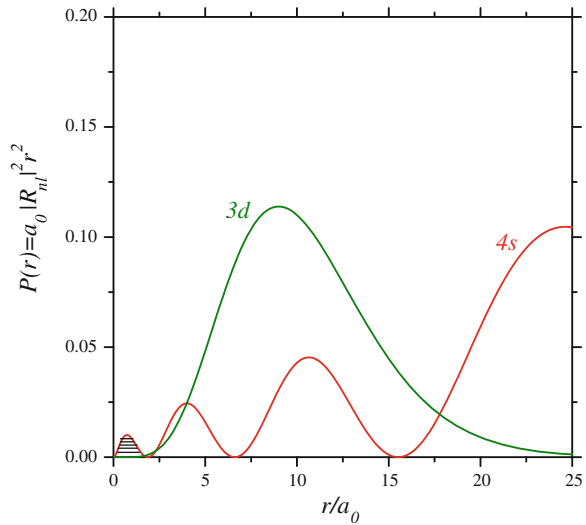
$$\begin{aligned} \mathbf{R}_{1 \leftrightarrow 2} = & -e \int (\phi_{core}^{(2)})^*(\mathbf{r}_1, \mathbf{r}_2, \dots) (\phi^{(2)}(\mathbf{r}_n))^* [\mathbf{r}_1 + \mathbf{r}_2 + \dots + \mathbf{r}_n + \dots + \mathbf{r}_N] \\ & \times \phi_{core}^{(1)}(\mathbf{r}_1, \mathbf{r}_2, \dots) \phi^{(1)}(\mathbf{r}_n) d\tau_1 d\tau_2 \dots d\tau_N \end{aligned}$$

Because of the orthogonality conditions the above integral is different from zero in correspondence to a given term involving \mathbf{r}_n only when $\phi_{core}^{(2)} = \phi_{core}^{(1)}$, while

$$\int (\phi^{(2)}(\mathbf{r}_n))^* [\mathbf{r}_n] \phi^{(1)}(\mathbf{r}_n) d\tau_n$$

yields the selection rule $(\Delta l)_n = \pm 1$ and $(\Delta m)_n = 0, \pm 1$.

Fig. 2.6 Radial probability of presence for $3d$ and $4s$ electrons in Hydrogen. From the *dashed area* it is noted how the bumps in $P(r)$ for $r \leq 2a_0$ grant the presence of the $4s$ electron in the vicinity of the nucleus larger than the one pertaining to the $3d$ state



Now we take into account the doublet structure of each of the states at $l \neq 0$ (see the illustrative diagram in Fig. 2.2). The doublets result from spin-orbit interaction, as discussed at Sect. 1.6. The splitting of the np states of the optical electron turns out

Li	Na	K	Rb	Cs	
$2p$	$3p$	$4p$	$5p$	$6p$	
0.337	17.2	57.7	238	554	cm^{-1}
0.042	2.1	7.2	29.5	68.7	meV

supporting the energy corrections derived in terms of the spin-orbit constant ξ_{nl} (see for instance Problem 2.2). It can be observed that because of the selection rule $\Delta j = 0, \pm 1$ ($0 \leftrightarrow 0$ forbidden) (see Appendix 1.3) the spectral lines involving transitions between two non-S states in alkali atoms can display a fine structure in the form of three components (*compound doublets*).

Problems

Problem 2.1 The empirical values of the quantum defects $\delta_{n,l}$ (see Eq. (2.3)) for the optical electron in the Na atom are

	Term	$n = 3$	$n = 4$	$n = 5$	$n = 6$
$l = 0$	s	1.373	1.357	1.352	1.349
$l = 1$	p	0.883	0.867	0.862	0.859
$l = 2$	d	0.010	0.011	0.013	0.011
$l = 3$	f	—	0.000	−0.001	−0.008

By neglecting the spin-orbit fine structure, write the wavenumbers of the main spectral series (see Fig. 2.2).

Solution: The spectral series are

principal (transitions from p to s terms), at wave numbers

$$\bar{\nu}_p = R_H \left[\frac{1}{[n_0 - \delta(n_0, 0)]^2} - \frac{1}{[n - \delta(n, 1)]^2} \right], \quad n \geq n_0, \quad n_0 = 3;$$

sharp (transitions from s to p electron terms)

$$\bar{\nu}_s = R_H \left[\frac{1}{[n_0 - \delta(n_0, 1)]^2} - \frac{1}{[n - \delta(n, 0)]^2} \right], \quad n \geq n_0 + 1;$$

diffuse (transitions from d to p electron terms)

$$\bar{\nu}_d = R_H \left[\frac{1}{[n_0 - \delta(n_0, 1)]^2} - \frac{1}{[n - \delta(n, 2)]^2} \right], \quad n \geq n_0;$$

fundamental (transitions from f to d terms):

$$\bar{\nu}_f = R_H \left[\frac{1}{[n_0 - \delta(n_0, 2)]^2} - \frac{1}{[n - \delta(n, 3)]^2} \right], \quad n \geq n_0 + 1.$$

Problem 2.2 The spin-orbit splitting of the $6^2P_{1/2}$ and $6^2P_{3/2}$ states in Cesium atom causes a separation of the correspondent spectral line (transition to the $^2S_{1/2}$ ground-state) of 422 \AA , at wavelength around 8520 \AA . Evaluate the spin-orbit constant ξ_{6p} and the effective magnetic field acting on the electron in the $6p$ state.

Solution: From $\lambda'' - \lambda' = \Delta\lambda = 422 \text{ \AA}$ and $\nu d\lambda = -\lambda d\nu$ one writes

$$\Delta E = h\Delta\nu \simeq h \cdot \frac{c}{\lambda'^2} \cdot \Delta\lambda \simeq 0.07 \text{ eV}.$$

From

$$\Delta E_{SO} = \frac{\xi_{6p}}{2} \{j(j+1) - l(l+1) - s(s+1)\}$$

one has

$$\Delta E = \frac{\xi_{6p}}{2} \left[\frac{15}{4} - \frac{3}{4} \right] = \frac{3}{2} \xi_{6p}$$

and then

$$\xi_{6p} = \frac{2}{3} \Delta E = 0.045 \text{ eV}.$$

The field (operator, Eq. (1.33)) is

$$\mathbf{H} = \frac{\hbar}{2emc} \frac{1}{r} \frac{dV}{dr} \mathbf{l}$$

with the spin-orbit Hamiltonian

$$\mathcal{H}_{spin-orbit} = -\boldsymbol{\mu}_s \cdot \mathbf{H}_{nl} = \xi_{6p} \mathbf{l} \cdot \mathbf{s}.$$

Thus

$$|\mathbf{H}_{6p}| = \frac{0.045 \text{ eV}}{2\mu_B} \frac{|\mathbf{l}|}{|\mathbf{l}|} \simeq 5.6 \cdot 10^6 \text{ Oe} = 560 \text{ Tesla}$$

Problem 2.3 In a maser ^{85}Rb atoms in the $6^3P_{3/2}$ state are driven to the transition at the $6^1D_{5/2}$ state. The quantum defects $\delta_{n,l}$ for the states are 2.64 and 1.34 respectively. Evaluate the transition frequency and compare it to the one deduced from the classical analogy for Rydberg atoms (Sect. 1.5). Estimate the isotopic shift for ^{87}Rb .

Solution:

From

$$E_{nl} = -R^*hc \frac{1}{n^{*2}}$$

where R^* is the Rydberg constant and $n^* = n - \delta_{n,l}$, the transition frequency turns out

$$\nu = -R^*c \left[\frac{1}{[n_i - \delta(n_i, l_i)]^2} - \frac{1}{[n_f - \delta(n_f, l_f)]^2} \right] \simeq 21.3 \text{ GHz}$$

The classical analogy (see Problem 1.12) yields

$$\nu \approx -R^*c \frac{2\Delta n^*}{(\bar{n}^*)^3} = 27.6 \text{ GHz}.$$

The wavelengths are inversely proportional to the Rydberg constant:

$$\frac{\lambda_{87}}{\lambda_{85}} = \frac{R_{85}^*}{R_{87}^*} \approx 1 - 1.47 \cdot 10^{-7}.$$

Therefore the isotopic shift is $\Delta\nu \approx 3.16 \text{ kHz}$ or $\Delta\lambda \approx -20.6 \text{ \AA}$.

Problem 2.4 By considering Li as a Hydrogenic atom estimate the ionization energy. Discuss the result in the light of the real value (5.39 eV) in terms of percent of penetration of the optical electron in the $(1s)^2$ core.

Solution: By neglecting the core charge one would have $E_{2s} = -13.56 Z^2/n^2 = -30.6 \text{ eV}$, while for total screening (i.e. zero penetration and $Z = 1$) $E_{2s} = -13.56 \text{ eV}/4 = -3.4 \text{ eV}$.

Then the effective charge experimented by the $2s$ electron can be considered $Z_{eff} \sim 1.27$, corresponding to about 15 % of penetration.

2.2 Helium Atom

2.2.1 Generalities and Ground State

The Helium atom represents a fruitful prototype to enlighten the effects due to the inter-electron interaction and then the arise of the central field potential $V(r)$, (see Sect. 1.1), the effects related to the exchange symmetry for indistinguishable electrons and to discuss the role of the spins and the *antisymmetry* of the total wavefunction.

First we shall start with the phenomenological examination of the energy levels diagram *vis-a-vis* to the one pertaining to Hydrogen atom (Fig. 2.7). A variety of comments is in order. It is noted that in He the state corresponding to the electronic

In the assumption of infinite nuclear mass and by taking into account the Coulomb interactions only, the Schrodinger equation is

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \right] \phi(\mathbf{r}_1, \mathbf{r}_2) = E\phi(\mathbf{r}_1, \mathbf{r}_2) \quad (2.4)$$

and it can be the starting point to explain the energy diagram. In Eq. (2.4) $Z = 2$ for the neutral atom.

Let us first assume that the inter-electron term e^2/r_{12} can be consider a perturbation of the hydrogenic-like Hamiltonian for two independent electrons (*independent electron approximation*). Then the unperturbed eigenfunction is

$$\phi_{n'l', n''l''}(\mathbf{r}_1, \mathbf{r}_2) = \phi_{n'l'}(\mathbf{r}_1)\phi_{n''l''}(\mathbf{r}_2) \quad (2.5)$$

and

$$(E^0)_{n'l', n''l''} = Z^2 E_{n'l'}^H + Z^2 E_{n''l''}^H \quad (2.6)$$

E_{nl}^H being the eigenvalues for Hydrogen (degenerate in l).

For the ground state $(1s)^2$ one has

$$\phi_{1s, 1s}(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi a_0^3} e^{-\frac{Z(r_1+r_2)}{a_0}} \quad (2.7)$$

and

$$E_{1s, 1s}^0 = 2Z^2 E_{1s}^H = -8 \frac{e^2}{2a_0} \simeq -108.80 \text{ eV} \quad (2.8)$$

In this oversimplified picture the first ionization energy would be 54.4 eV, evidently far from the experimental datum (see Fig. 2.7). This discrepancy had to be expected since the effect of the electron-electron repulsion had not yet been evaluated.

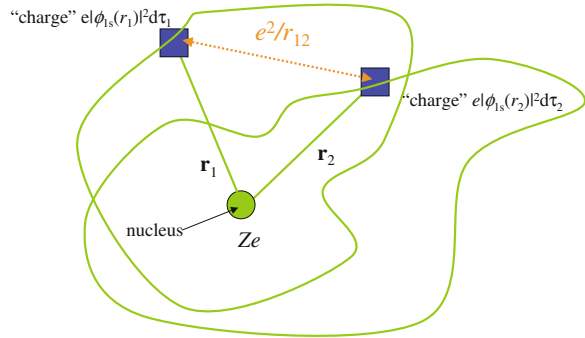
At the first order in the perturbative approach the repulsion reads

$$\begin{aligned} E_{1s, 1s}^{(1)} &= \int \int \phi_{1s, 1s}^*(\mathbf{r}_1, \mathbf{r}_2) \frac{e^2}{r_{12}} \phi_{1s, 1s}(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2 \equiv \\ &\equiv \langle 1s, 1s | \frac{e^2}{r_{12}} | 1s, 1s \rangle \equiv I_{1s, 1s} \end{aligned} \quad (2.9)$$

$I_{1s, 1s}$ is called *Coulomb integral* in view of its classical counterpart, depicted in Fig. 2.8.

The estimate of the Coulomb integral can be carried out by expanding r_{12}^{-1} in term of the associated Legendre polynomials (see Problem 2.5). For the particular case of $1s$ electrons, the Coulomb integral $I_{1s, 1s}$ can be worked out in a straightforward way on the basis of the classical analogy for the electrostatic repulsion. The result is

Fig. 2.8 Illustrative plot sketching the classical analogy of the first order perturbation term $\langle e^2/r_{12} \rangle$ for the ground-state, in terms of electrostatic repulsion of two electronic clouds



$$I_{1s,1s} = \frac{5}{4}Z(-E_{1s}^H) = \frac{5}{8}\frac{e^2}{a_0}Z \quad (2.10)$$

The ground state energy corrected to the first order turns out

$$E_{1s,1s} = E_{1s,1s}^{(0)} + I_{1s,1s} = \left(2Z^2 - \frac{5}{4}Z\right) E_{1s}^H \simeq -74.8 \text{ eV} \quad (2.11)$$

to be compared with the experimental value -78.62 eV .

The energy required to remove one electron is

$$\left[\left(2Z^2 - \frac{5}{4}Z\right) - Z^2 \right] 13.6\text{eV} \simeq 20.4 \text{ eV}$$

This estimate is not far from the value indicated in Fig. 2.7, in spite of the crudeness of the assumption for the unperturbed one-electron wavefunctions. An immediate refinement could be achieved by adjusting the hydrogen-like wave functions: in this way a good agreement with the experimental ionization energy would be obtained.

Another way to improve the description is to derive variationally an *effective nuclear charge* Z^* , which in indirect way takes into account the mutual screening of one electron by the other and the related correction in the wavefunctions. As shown in Problem 2.6, this procedure yields $Z^* = Z - (5/16)$, implying for the ground state

$$E_{1s,1s} = 2 \left(Z - \frac{5}{16} \right)^2 \left(\frac{-e^2}{2a_0} \right) = -77.5 \text{ eV}$$

One can remark how the perturbative approach, without modification of the eigenfunctions, is rather satisfactory, in spite of the relatively large value of the first order energy correction.

The ground state energy for He turns out about 94.6% of the “exact” one (numerically obtained via elaborate trial functions, see Sect. 3.4) with the first-order

perturbative correction and 98 % with the variationally-derived effective charge. The agreement is even better for atoms with $Z \geq 3$, as Li^+ or Be^{2+} . At variance the analogous procedure fails for H^- (see Problem 2.8).

2.2.2 Excited States and the Exchange Interaction

The perturbative approach used for the ground state could be naively attempted for the excited states with an electron on a given nl state. For a trial wavefunction of the form

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1)\phi_{nl}(\mathbf{r}_2) \quad (2.12)$$

the energy

$$E_{1s,nl} = E_{1s,nl}^0 + \langle 1s, nl | \frac{e^2}{r_{12}} | 1s, nl \rangle$$

would not account for the experimental data, numerically falling approximately in the middle of the singlet and triplet ($1s, nl$) energy levels. The striking discrepancy is evidently the impossibility to infer two energy levels in correspondence to the same electronic configuration from the wavefunction in Eq. (2.12). The obvious inadequacy of the tentative wavefunction is that it disregards the *exchange symmetry* (discussed at Sect. 1.3). At variance with Eq. (2.12) one has to write the functions

$$\phi_{1s,nl}^{sym}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_{1s}(\mathbf{r}_1)\phi_{nl}(\mathbf{r}_2) + \phi_{nl}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2) \right] \quad (2.13)$$

$$\phi_{1s,nl}^{ant}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_{1s}(\mathbf{r}_1)\phi_{nl}(\mathbf{r}_2) - \phi_{nl}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2) \right] \quad (2.14)$$

granting indistinguishable electrons, the same weights being attributed to the configurations $1s(1)nl(2)$ and $1s(2)nl(1)$. The labels *sym* and *ant* correspond to the *symmetrical* and *antisymmetrical character* of the wavefunctions upon exchange of the electrons.

On the basis of the functions (2.13) and (2.14), along the same perturbative procedure used for the ground state, instead of Eq. (2.11) one obtains

$$E_+^{sym} = Z^2 E_{1s}^H + Z^2 E_{nl}^H + I_{1s,nl} + K_{1s,nl} \quad (2.15)$$

and

$$E_-^{ant} = Z^2 E_{1s}^H + Z^2 E_{nl}^H + I_{1s,nl} - K_{1s,nl} \quad (2.16)$$

where

$$K_{1s,nl} = \int \int \phi_{1s}^*(\mathbf{r}_1)\phi_{nl}^*(\mathbf{r}_2) \frac{e^2}{r_{12}} \phi_{1s}(\mathbf{r}_2)\phi_{nl}(\mathbf{r}_1) d\tau_1 d\tau_2 \quad (2.17)$$

is the *exchange integral*, essentially positive and without any classical interpretation, at variance with the Coulomb integral $I_{1s,nl}$. Thus double series of levels is justified by the quantum effect of *exchange symmetry*.¹

The wavefunctions (2.13) and (2.14) are not complete, spin variables having not yet been considered. In view of the weakness of the spin-orbit interaction, as already stated (Sect. 1.6), one can factorize the spatial and spin parts. Then, again by taking into account indistinguishable electrons, the spin functions are

$$\begin{aligned} \alpha(1)\alpha(2), \quad \beta(1)\beta(2), \quad & \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad \text{for } S = 1 \\ & \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad \text{for } S = 0 \end{aligned} \quad (2.18)$$

The first group can be labelled $\chi_{S=1}^{sym}$ and it includes the three eigenfunctions corresponding to $S = 1$. The fourth eigenfunction is the one pertaining to $S = 0$. $\chi_{S=0}^{ant}$ is antisymmetrical upon the exchange of the electrons, while $\chi_{S=1}^{sym}$ are symmetrical.

Therefore the complete eigenfunctions describing the excited states of the Helium atom are of the form $\phi_{tot} = \phi_{1s,nl} \chi_S$ and in principle in this way one would obtain 8 spin-orbitals. However, from the comparison with the experimental findings (such as the spectral lines from which the diagram in Fig. 2.7 is derived) one is lead to conclude that only four states are actually found in reality. These states are the ones for which the total (spatial and spin) wavefunctions are *antisymmetrical* upon the exchange of the two electrons.

This requirement of antisymmetry is also known as *Pauli principle* and we shall see that it corresponds to require that the electrons differ at least in one of the four quantum numbers n, l, m and m_s . For instance, the lack of the triplet $(1s)^2$ is evidently related to the fact that in this hypothetical state the two electrons would have the same quantum numbers, meantime having a wavefunction of symmetric character $\phi_{tot} = \phi_{1s}\phi_{1s}\chi_{S=1}^{sym}$. Thus $\phi^{sym}\chi_{S=0}^{ant}$ describes the singlet states, while $\phi^{ant}\chi_{S=1}^{sym}$ describes the triplet states. Accordingly, one can give the following pictorial description

When	S	χ	$\phi(\mathbf{r})$	ϕ_{tot}	Energy
$\uparrow\downarrow$	0	ant	sym	ant	E_+
$\uparrow\uparrow$	1	sym	ant	ant	E_-

In other words, because of the exchange symmetry a kind of relationship, arising from electron-electron repulsion, between the mutual “direction” of the spin momenta and the energy correction does occur. For “parallel spins” one has $E_- < E_+$, the repulsion is decreased as the electron should move, on the average, more apart.

¹Order of magnitude estimates yield $I_{1s,2s} \simeq 9$ eV, $I_{1s,2p} \simeq 10$ eV, $K_{1s,2s} \simeq 0.4$ eV and $K_{1s,2p} \simeq 0.1$ eV (see Problem 2.9).

The dependence of the energy from the spin orientation can be related to an exchange *pseudo-spin interaction*, in other words to an Hamiltonian operator of the form²

$$H = -2K \mathbf{s}_1 \cdot \mathbf{s}_2 \quad (2.19)$$

In fact if we extend the vectorial picture to spin operators (in a way analogous to the definition of the \mathbf{j} angular momentum for the electron (see Sect. 1.6)) and write

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2, \quad (2.20)$$

by “squaring” this sum one deduces $\mathbf{s}_1 \cdot \mathbf{s}_2 = (1/2)[\mathbf{S}^2 - \mathbf{s}_1^2 - \mathbf{s}_2^2]$. Thus, from the Heisenberg Hamiltonian (2.19) the two energy values

$$E' = -2K(1/2)[S(S+1) - 2(1/2)(1+1/2)] = -K/2$$

for $S = 1$ and

$$E'' = 3K/2$$

for $S = 0$ are obtained. In other words, from the Hamiltonian (2.19), for a given $1snl$ configuration, the singlet and the triplet states with energy separation and classification consistent with Eqs. (2.15) and (2.16), are deduced.

Now it is possible to justify the weak singlet \leftrightarrow triplet transition probability indicated by the optical spectra. The electric dipole transition element connecting parahelium to orthohelium states can be written

$$\mathbf{R}_{S=0 \leftrightarrow S=1} \propto \langle \chi_{ant} | \chi_{sym} \rangle \int \int \phi_{sym}^*[\mathbf{r}_1 + \mathbf{r}_2] \phi_{ant} d\tau_1 d\tau_2. \quad (2.21)$$

This matrix element is zero, both for the orthogonality of the spin states and because the function in the integral changes sign upon exchange of the indexes 1 and 2, then requiring zero as physically acceptable result. Thus one understands why orthohelium cannot be converted to parahelium and *vice-versa*. This selection rule would seem to prevent any transitions (including the ones related to magnetic dipole or electric quadrupole mechanisms) and then do not admit any violation. The weak singlet-triplet transitions actually observed in the spectrum are related to the non-total validity of the factorization in the form $\phi_{tot} = \phi(\mathbf{r}_1, \mathbf{r}_2)\chi_{spin}$. The spin-orbit interaction, by coupling spin and positional variables, partially invalidates that form of the wavefunctions. This consideration is supported by looking at the transitions in an atom similar to Helium, with two electrons outside the core. Calcium has the ground state electronic configuration $(1s)^2 \dots (4s)^2$ and the diagram of the energy levels is strictly similar to the one in Fig. 2.7. At variance with Helium, because of the

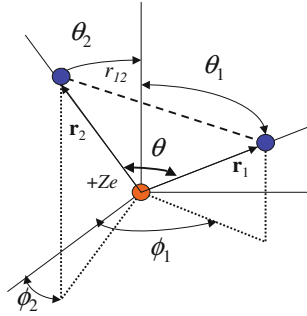
²This Hamiltonian, known as *Heisenberg Hamiltonian*, is often assumed as starting point for quantum magnetism in bulk matter. Below a given temperature, in a three-dimensional array of atoms, this Hamiltonian implies a spontaneous ordered state, with magnetic moments cooperatively aligned along a common direction (see Sect. 4.4 for comments and Chap. 17).

increased strength of the spin-orbit interaction, the lines related to $S = 0 \leftrightarrow S = 1$ transitions are rather strong. Analogous case is Hg atom (see Fig. 3.9).

Problems

Problem 2.5 Evaluate the Coulomb integral for the ground state of the Helium atom.

Solution:



In the expectation value (for $e = a_0 = 1$)

$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{Z^6}{\pi^2} \int e^{-2Z(r_1+r_2)} \frac{1}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2.$$

$1/r_{12}$ is expanded in Legendre polynomials

$$\begin{aligned} \frac{1}{r_{12}} &= \frac{1}{r_1} \sum_{l=0}^{\infty} \left(\frac{r_2}{r_1} \right)^l P_l(\cos \theta), & r_1 > r_2 \\ &= \frac{1}{r_2} \sum_{l=0}^{\infty} \left(\frac{r_1}{r_2} \right)^l P_l(\cos \theta), & r_1 < r_2 \end{aligned}$$

where θ is the angle between the vectors \mathbf{r}_1 and \mathbf{r}_2 and

$$\cos \theta = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)$$

In compact form

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{(r_{<})^l}{(r_{>})^{l+1}} P_l(\cos \theta)$$

where $r_{<}$ is the smallest and $r_{>}$ the largest between r_1 and r_2 . From the *addition theorem* one writes

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{(2l+1)} \frac{(r_{<})^l}{(r_{>})^{l+1}} Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2).$$

The function $\exp[-2Z(r_1 + r_2)]$ is spherically symmetric and $Y_{00} = (4\pi)^{-\frac{1}{2}}$. By integrating over the polar angles one has

$$I'_{1s,1s} = \frac{Z^6}{\pi^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{(4\pi)^2}{(2l+1)} \int_0^{\infty} dr_1 r_1^2 \int_0^{\infty} dr_2 r_2^2 e^{-2Z(r_1+r_2)} \frac{(r_<)^l}{(r_>)^{l+1}} \cdot \delta_{l,0} \delta_{m,0}.$$

All terms in the sum vanish, except the one for $l = m = 0$. Then

$$\begin{aligned} I'_{1s,1s} &= 16Z^6 \int_0^{\infty} dr_1 r_1^2 \int_0^{\infty} dr_2 r_2^2 e^{-2Z(r_1+r_2)} \frac{1}{r_>} \\ &= 16Z^6 \int_0^{\infty} dr_1 r_1^2 e^{-2Zr_1} \left[\frac{1}{r_1} \int_0^{r_1} dr_2 r_2^2 e^{-2Zr_2} + \int_{r_1}^{\infty} dr_2 r_2 e^{-2Zr_2} \right] = \frac{5}{8} Z \end{aligned}$$

and properly including a_0 and e , $I_{1s,1s} = \frac{5}{4} Ze^2 / 2a_0$.

For spherically symmetric wavefunctions one can evaluate the Coulomb integral from the classical electrostatic energy:

$$I_{1s,1s} = \frac{Ze^2}{32\pi^2 a_0} \int \frac{e^{-\rho_1} e^{-\rho_2}}{\rho_{12}} d\tau_1 d\tau_2$$

where

$$\rho_{1,2} = \frac{2Zr_{1,2}}{a_0}, \quad \rho_{12} = \frac{2Zr_{12}}{a_0}$$

and

$$d\tau_{1,2} = \rho_{1,2}^2 \sin \theta_{1,2} d\rho_{1,2} d\theta_{1,2} d\phi_{1,2}.$$

The electric potential from the shell $d\rho_1$ at ρ_1 is

$$\begin{aligned} d\Phi(r) &= 4\pi \rho_1^2 e^{-\rho_1} d\rho_1 \frac{1}{\rho_1} \text{ for } r < \rho_1, \\ &4\pi \rho_1^2 e^{-\rho_1} d\rho_1 \frac{1}{r} \text{ for } r > \rho_1. \end{aligned}$$

Then the total potential turns out

$$\Phi(r) = \frac{4\pi}{r} \int_0^r e^{-\rho_1} \rho_1^2 d\rho_1 + 4\pi \int_r^{\infty} e^{-\rho_1} \rho_1 d\rho_1 = \frac{4\pi}{r} \{2 - e^{-r}(r+2)\}$$

and therefore

$$I_{1s,1s} = \frac{Ze^2}{32\pi^2 a_0} \int \Phi(\rho_2) e^{-\rho_2} d\tau_2 = \frac{Ze^2}{2a_0} \int_0^{\infty} [2 - e^{-\rho_2}(\rho_2+2)] e^{-\rho_2} \rho_2^2 d\rho_2 = \frac{Ze^2}{2a_0} \frac{5}{4}.$$

Problem 2.6 By resorting to the variational principle, evaluate the effective nuclear charge Z^* for the ground state of the Helium atom.

Solution: The energy functional is

$$E[\phi] = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$

where

$$\phi(r_1, r_2) = \frac{Z^{*3}}{\pi} e^{-Z^*(r_1+r_2)}$$

with Z^* variational parameter ($e = a_0 = 1$).

Then

$$E[\phi] = \left\langle \phi \left| T_1 + T_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right| \phi \right\rangle$$

and

$$\langle \phi | T_1 | \phi \rangle \equiv \langle \psi_{1s}^{Z^*} | T_1 | \psi_{1s}^{Z^*} \rangle = \frac{1}{2} Z^{*2}, \quad \langle \phi | T_2 | \phi \rangle = \langle \phi | T_1 | \phi \rangle,$$

while

$$\left\langle \phi \left| \frac{1}{r_1} \right| \phi \right\rangle = \left\langle \psi_{1s}^{Z^*} \left| \frac{1}{r_1} \right| \psi_{1s}^{Z^*} \right\rangle = Z^* = \left\langle \phi \left| \frac{1}{r_2} \right| \phi \right\rangle$$

Since

$$\left\langle \phi \left| \frac{1}{r_{12}} \right| \phi \right\rangle = \frac{5}{8} Z^* \quad (\text{see Eq. (2.10)})$$

one has

$$E[\phi] \equiv E(Z^*) = Z^{*2} - 2ZZ^* + \frac{5}{8} Z^*.$$

From

$$\frac{\partial E(Z^*)}{\partial Z^*} = 0, \quad Z^* = Z - 5/16.$$

Problem 2.7 In the light of the interpretation of the Coulomb integral in terms of repulsion between two spherically symmetric charge distributions, evaluate the effective potential energy for a given electron in the ground state of He atom and the effective charge $Z_{eff}(r)$.

Solution: The electric potential due to a spherical shell of radius R (thickness dR and density $-e\rho(R)$) at distance r from the center of the sphere is

$$-\frac{1}{4\pi e} d\phi(r) = R^2 \rho(R) \frac{dR}{R} \quad \text{for } r \leq R,$$

$$R^2 \rho(R) \frac{dR}{r} \quad \text{for } r \geq R.$$

By integrating over R and taking into account that

$$\varrho(r) \equiv |\psi_{1s}(r)|^2 = \left(\frac{Z}{a_0}\right)^3 \frac{e^{-\frac{2Zr}{a_0}}}{\pi},$$

one has

$$\begin{aligned} -\frac{\phi(r)}{4\pi e} &= \frac{1}{\pi} \left(\frac{Z}{a_0}\right)^3 \left[\frac{1}{r} \int_0^r dR R^2 e^{-\frac{2ZR}{a_0}} + \int_r^\infty dR R e^{-\frac{2ZR}{a_0}} \right] \\ &= \frac{1}{4\pi} \left(\frac{Z}{a_0}\right) \left[\frac{1}{u} \int_0^u dx x^2 e^{-x} + \int_u^\infty dx x e^{-x} \right] \\ &= \frac{1}{4\pi} \left(\frac{Z}{a_0}\right) \frac{1}{u} [2 - e^{-u}(u+2)], \end{aligned}$$

where $u = \frac{2Zr}{a_0}$. Therefore

$$\phi(r) = -\frac{e}{r} \left[1 - e^{-\frac{2Zr}{a_0}} \left(\frac{Zr}{a_0} + 1 \right) \right]$$

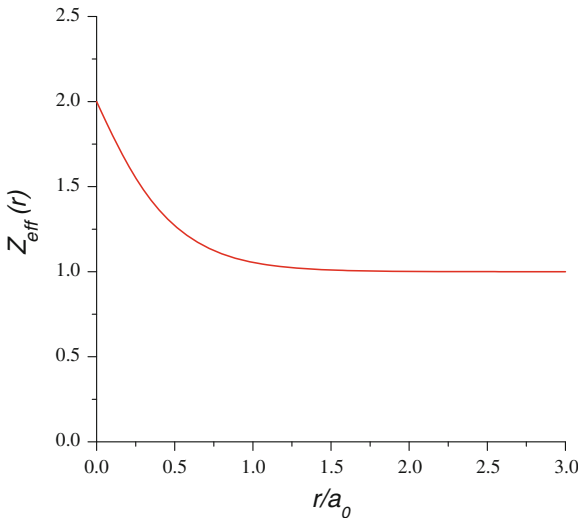
and from

$$-\frac{Z_{eff}(r)e^2}{r} = -\frac{Ze^2}{r} - e\phi(r)$$

for $Z = 2$ one finds

$$Z_{eff}(r) = 1 + e^{-\frac{4r}{a_0}} \left(1 + \frac{2r}{a_0} \right)$$

plotted below.



Problem 2.8 The *electron affinity* (energy gain when an electron is acquired) for Hydrogen atom is 0.76 eV. Try to derive this result in the framework of a perturbative approach for the ground state of H^- , as well as by considering a reduced nuclear charge.

Comment the results in the light of the almost-exact value which, at variance, is obtained only by means of a variational procedure with elaborate trial wavefunctions.

Solution: For H^- , by resorting to the results for He and setting $Z = 1$, in the perturbative approach one would obtain

$$E'_{H^-} = -2Z^2 R_H hc + \frac{5}{4} Z R_H hc = -\frac{3}{4} R_H hc$$

to be compared with $-R_H hc$ for H. With the variational effective charge

$$Z_{eff} = (1 - \frac{5}{16})$$

$$E''_{H^-} = -2Z_{eff}^2 R_H hc = -0.945 R_H hc$$

again less bound than the ground-state for neutral Hydrogen.

Only more elaborate calculations yield the correct value, the reason being that for small Z the perturbation is too large with respect to the unperturbed energy. By repeating the estimate for $Z = 3$ (Li^+), for $Z = 4$ (Be^{2+}) and for $Z = 5$ (B^{3+}) a convergence is noted towards the “exact” values of the ground state energy (namely 198.1, 371.7 and 606.8 eV, respectively) obtained from the variational procedure with elaborate trial functions. It should be remarked that the real experimental eigenvalues cannot be derived simply on the basis of the Hamiltonian in Eq. (2.4) which does not include the finite nuclear mass, the relativistic and the radiative terms (see for the Hydrogen atom the recall in Appendix 5.1).

2.3 Pauli Principle, Determinantal Eigenfunctions and Superselection Rule

In the light of the analysis of the properties of the electronic states in Helium atom, one can state the *Pauli principle*: the total wavefunction (spatial and spin) of electrons, particles at half integer spin, must be antisymmetrical upon exchange of two particles. This statement is equivalent to the one inhibiting a given set of the four quantum numbers ($n l m m_s$) to more than one electron. For instance, this could be realized by considering an hypothetical triplet ground state $(1s)^2$ for orthohe-
 lium, for which the wavefunction would be $\phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\alpha(1)\alpha(2)$ (or $\beta(1)\beta(2)$ or $(1/\sqrt{2})[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$), and the quantum numbers n, l, m, m_s would be the same for both electrons. At variance, one only finds the singlet ground state, for which $m_s = \pm 1/2$.

From the specific case of Helium now we go back to the general properties of multi-electron atoms (see Sects. 1.1 and 1.3). Because of the exchange degeneracy and of the requirement of antisymmetrical wavefunction the total eigenfunction, instead of Eq. (1.10), must be written

$$\varphi_{tot} = \frac{1}{\sqrt{N!}} \sum_P P(-1)^P \varphi_\alpha(1) \varphi_\beta(2) \dots \varphi_\nu(N) \quad (2.22)$$

where α, β, \dots here indicate the group of quantum numbers ($nlmm_s$) and the numbers $1, 2, 3, \dots, N$ include spatial and spin variables. P is an operator exchanging the electron i with the electron j and the wavefunction changes (does not change) sign according to an odd (even) number of permutations. The sum includes all possible permutations.

A total eigenfunction complying with exchange degeneracy and antisymmetry is the *determinantal wavefunction* devised by Slater³

$$\varphi_{tot} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_\alpha(1) & \varphi_\alpha(2) & \dots & \varphi_\alpha(N) \\ \varphi_\beta(1) & \varphi_\beta(2) & \dots & \varphi_\beta(N) \\ \dots & \dots & \dots & \dots \\ \varphi_\nu(1) & \varphi_\nu(2) & \dots & \varphi_\nu(N) \end{vmatrix}$$

accounting for all the possible index permutations with change of sign when two columns are exchanged. On the other hand the determinant goes to zero when two groups of quantum numbers (and then two rows) are the same.

Now it can be proved that no transition, by any mechanism, is possible between globally antisymmetric and symmetric states (in the assumption that they exist), sometimes known as *superselection rule*. In fact such a transition would be controlled by matrix elements of the form

$$\mathbf{R}_{ANT \leftrightarrow SYM} \propto \int \phi_{SYM}^* [\mathbf{O}_1 + \mathbf{O}_2 + \dots] \phi_{ANT} d\tau_{gen} \quad (2.23)$$

that must be zero in order to avoid the unacceptable result of having a change of sign upon exchange of indexes, since the integrand is globally antisymmetric.

In the light of what has been learned from the analysis of alkali atoms and of Helium atom, now we can move to a useful description of multi-electrons atoms which allows us to derive the structure of the eigenvalues and their classification in terms of proper quantum numbers (The *vectorial model*, Chap. 3). Other typical atoms, such as N, C and transition metals (Fe, Co, *etc.*...) shall be discussed in that framework.

³This form is the basis for the multiplet theory in the perturbation approach dealing with operators r_i^{-1} and r_{ij}^{-1} (see Sect. 3.4).

Problems

Problem 2.9 By means of the perturbation approach for independent electrons derive the energy levels for the first excited states of Helium atom, in terms of Coulomb and exchange integrals, writing the eigenfunctions and plotting the energy diagram.

Solution: The first excited $1s2l$ states are

$$\begin{aligned} u_1 &= 1s(1)2s(2) & u_5 &= 1s(1)2p_y(2) \\ u_2 &= 1s(2)2s(1) & u_6 &= 1s(2)2p_y(1) \\ u_3 &= 1s(1)2p_x(2) & u_7 &= 1s(1)2p_z(2) \\ u_4 &= 1s(2)2p_x(1) & u_8 &= 1s(2)2p_z(1) \end{aligned}$$

From the unperturbed Hamiltonian without the electron-electron interaction, by setting $\hbar = 2m = e = 1$, one finds

$$\mathcal{H}^0 u_i(1, 2) = -4 \left(1 + \frac{1}{4} \right) u_i(1, 2) = -5u_i(1, 2)$$

The secular equation involves the integrals

$$\begin{aligned} I_s &= \left\langle 1s(1)2s(2) \left| \frac{1}{r_{12}} \right| 1s(1)2s(2) \right\rangle \\ I_p &= \left\langle 1s(1)2p(2) \left| \frac{1}{r_{12}} \right| 1s(1)2p(2) \right\rangle \\ K_s &= \left\langle 1s(1)2s(2) \left| \frac{1}{r_{12}} \right| 1s(2)2s(1) \right\rangle \\ K_p &= \left\langle 1s(1)2p(2) \left| \frac{1}{r_{12}} \right| 1s(2)2p(1) \right\rangle \end{aligned}$$

(p here represents p_x , p_y or p_z) and it reads

$$\begin{vmatrix} I_s - E' & K_s & 0 & 0 & 0 \\ K_s & I_s - E' & 0 & 0 & 0 \\ 0 & 0 & I_p - E' & K_p & 0 \\ 0 & 0 & K_p & I_p - E' & 0 \\ 0 & 0 & 0 & 0 & I_p - E' \\ 0 & 0 & 0 & 0 & 0 & I_p - E' & K_p \\ & & & & & K_p & I_p - E' \end{vmatrix} = 0$$

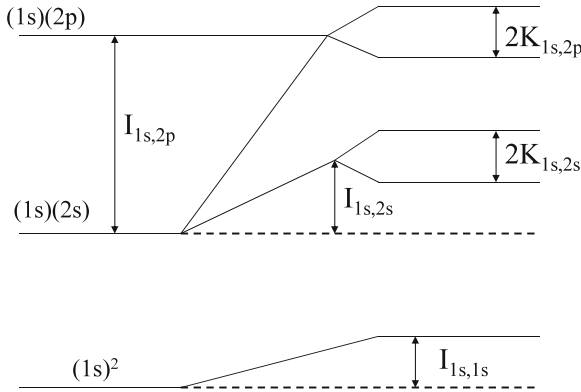
From the first block $E' = I_s \pm K_s$, with the associated eigenfunctions

$$\phi_{1,2} = \frac{1}{\sqrt{2}}[1s(1)2s(2) \pm 1s(2)2s(1)].$$

From the second block $E'' = I_p \pm K_p$, with eigenfunctions

$$\phi_{3,4} = \frac{1}{\sqrt{2}}[1s(1)2p_x(2) \pm 1s(2)2p_x(1)]$$

and the analogous for y and z . Thus the following diagram (not in scale, see Sect. 2.2.2) is derived (I and $K > 0$ and $I_p > I_s$).



Problem 2.10 For the optical electron in Li atom consider the *hybrid orbital*

$$\Phi = (1 + \lambda^2)^{-\frac{1}{2}}[\phi_{2s} + \lambda\phi_{2p_z}]$$

ϕ_{2s} and ϕ_{2p_z} being normalized hydrogen-like wavefunctions, with effective nuclear charge Z . Find the pseudo-dipole moment $\mu = e\langle z \rangle$ and the value of λ yielding the maximum of μ (relevant connections for situations where hybrid orbitals are actually induced are to be found at Sects. 4.2 and 9.2).

Solution: The pseudo-dipole moment turns out

$$\begin{aligned} \mu &= e \int \Phi^* z \Phi d\tau = \\ &= \frac{e}{(1 + \lambda^2)} \left[\int \phi_{2s}^2(r) z d\tau + \lambda^2 \int \phi_{2p_z}^2(r) z d\tau + 2\lambda \int \phi_{2s}(r) \phi_{2p_z}(r) z d\tau \right], \end{aligned}$$

where the first two integrals are 0. From Table 1.3 (with $e = a_0 = 1$)

$$\begin{aligned}\mu &= \frac{2\lambda}{1+\lambda^2} \left(\frac{Z}{2}\right)^3 \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \cos^2\theta \sin\theta d\theta \int_0^\infty Zr^4 (Zr-2)e^{-Zr} dr = \\ &= \frac{\lambda}{1+\lambda^2} \frac{Z^3}{12} \left[\frac{Z^2 5!}{Z^6} - \frac{2Z 4!}{Z^5} \right] = \frac{\lambda}{1+\lambda^2} \frac{6}{Z},\end{aligned}$$

i.e. $\mu = (6ea_0/Z)\lambda/(1+\lambda^2)$ in complete form.

From

$$\frac{d\mu}{d\lambda} = \frac{6}{Z} \frac{(1+\lambda^2-2\lambda^2)}{(1+\lambda^2)^2} = \frac{6}{Z} \frac{(1-\lambda^2)}{(1+\lambda^2)^2} = 0$$

the maximum is found for $\lambda = 1$, as it could be expected.

Problem 2.11 Prove that the two-particles spin-orbital

$$\psi_{ANT} = \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2)[\phi_a(1)\phi_b(2)] - \alpha(2)\beta(1)[\phi_a(2)\phi_b(1)] \}.$$

represents an eigenstate for the z -component of the total spin at zero eigenvalue. Then evaluate the expectation value of \mathbf{S}^2 .

Solution: From

$$S_1^z \psi_{ANT} = \frac{1}{2} \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2)[\phi_a(1)\phi_b(2)] + \alpha(2)\beta(1)[\phi_a(2)\phi_b(1)] \} = \frac{1}{2} \psi_{SYM}.$$

and

$$S_2^z \psi_{ANT} = -\frac{1}{2} \psi_{SYM}$$

Thus

$$S^z \psi_{ANT} = (S_1^z + S_2^z) \psi_{ANT} = 0$$

Since

$$S_1^z S_2^z \psi_{ANT} = -\frac{1}{4} \psi_{ANT}$$

while

$$S_1^x S_2^x \psi_{ANT} = \frac{1}{4} \frac{1}{\sqrt{2}} \{ \beta(1)\alpha(2)[\phi_a(1)\phi_b(2)] - \alpha(1)\beta(2)[\phi_a(1)\phi_b(2)] \} \equiv \frac{1}{4} \psi'_{ANT}$$

and

$$< \psi_{ANT} | \psi'_{ANT} > \equiv - \left| \int \phi_a^*(\mathbf{r}) \phi_b(\mathbf{r}) d\tau \right|^2 \equiv -\mathcal{A}$$

(with the same result for the y component). By taking into account that $(\mathbf{S})^2 = (\mathbf{S}_1)^2 + (\mathbf{S}_2)^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2$, then

$$\langle \psi_{ANT} | (S_1^{x,y} + S_2^{x,y})^2 | \psi_{ANT} \rangle = \frac{1}{2} \{1 - \mathcal{A}\}$$

and

$$\langle \psi_{ANT} | (\mathbf{S})^2 | \psi_{ANT} \rangle = 1 - \mathcal{A}.$$

Problem 2.12 At Chap. 5 it will be shown that between one electron and one proton an hyperfine interaction of the form $A \mathbf{I} \cdot \mathbf{S} \delta(\mathbf{r})$ occurs, where \mathbf{I} is the nuclear spin (*Fermi contact interaction*). An analogous term, i.e. $\mathcal{H}_p = A \mathbf{s}_1 \cdot \mathbf{s}_2 \delta(\mathbf{r}_{12})$ (with $\mathbf{r}_{12} \equiv \mathbf{r}_1 - \mathbf{r}_2$) describes a relativistic interaction between the two electrons in the Helium atom. In this case A turns out $A = -(8\pi/3)(e\hbar/mc)^2$. Discuss the first-order perturbation effect of \mathcal{H}_p on the lowest energy states of orthohelium and parahelium, showing that only a small shift of the ground-state level of the latter occurs (return to Problem 1.38 for similarities).

Solution: For orthohelium the lowest energy states is described by the spin-orbital

$$\phi_{tot}(1, 2) = \chi_{sym}^{S=1} \left[\phi_{1s}(\mathbf{r}_1) \phi_{2s}(\mathbf{r}_2) - \phi_{2s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2) \right].$$

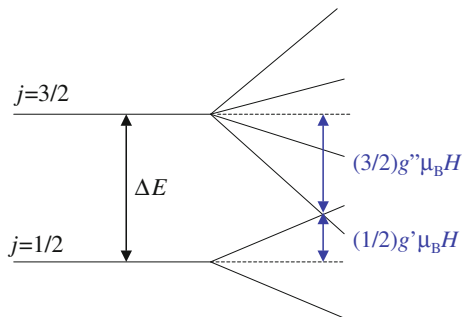
The expectation value of \mathcal{H}_p yields zero since two electrons at parallel spin cannot have the same spatial coordinates. For the ground state of parahelium since $\mathbf{s}_1 \cdot \mathbf{s}_2 = -3/4$ (see Eq. (2.20)), by using hydrogenic wave functions $\phi_{1s}(\mathbf{r}_1)$ and $\phi_{1s}(\mathbf{r}_2)$ one estimates

$$\begin{aligned} \langle 1s, 1s | \mathcal{H}_p | 1s, 1s \rangle &= -\frac{3A}{4} \frac{Z^6}{\pi^2 a_0^6} \int \int e^{-2\frac{Z(r_1+r_2)}{a_0}} \delta(\mathbf{r}_{12}) d\tau_1 d\tau_2 = \\ &= -\frac{3A}{4} \frac{Z^6}{\pi^2 a_0^6} 4\pi \int_0^\infty e^{-4Z\frac{r}{a_0}} r^2 dr = \frac{3}{32} \left(\frac{e\hbar}{mc} \right)^2 \frac{Z^3}{a_0^3} \simeq 10^{-3} \text{ eV}, \end{aligned}$$

a small shift compared to -78.62 eV .

Problem 2.13 The spin-orbit constant ξ_{2p} for the $2p$ electron in Lithium turns out $\xi_{2p} = 0.34 \text{ cm}^{-1}$. Evaluate the magnetic field causing the first crossing between $P_{3/2}$ and $P_{1/2}$ levels, in the assumption that the field does not affect the structure of the doublet (return to Problems 1.23 and 1.17).

Solution: In the assumption that the field linearly affects the two levels, i.e.



the first crossing takes place when

$$\left(\frac{3}{2}g'' + \frac{1}{2}g'\right)\mu_B H = \Delta E$$

Since $g' = 2/3$ and $g'' = 4/3$ the crossing occurs for $H = \Delta E / (7\mu_B/3)$.

The correction associated with the spin-orbit interaction is

$$\frac{\xi_{2p}}{2}[j(j+1) - l(l+1) - s(s+1)]$$

Then $\Delta E = (3/2)\xi_{2p}$ and $H \simeq 4370$ Oe.

When the *weak field* condition (corresponding to $\mu_B H \ll \xi_{2p}$) is released and the full Hamiltonian $\xi_{nl}\mathbf{l} \cdot \mathbf{s} + \mu_B \mathbf{H} \cdot (\mathbf{l} + 2\mathbf{s})$ is diagonalized (as it would be more appropriate), the crossing is found at a slightly different field.

Try to estimate it after having read Chap. 4 (or see Problem 1.1.20, in the book by Balzarotti, Cini and Fanfoni or Problem 7.24 in the book by Johnson and Pedersen). A somewhat similar situation is the one discussed at Problem 5.13 with \mathbf{l} substituted by the nuclear momentum \mathbf{I}

Problem 2.14 Refer to the double-excited electron state $2s4p$ of the Helium atom. In the assumption that the $2s$ electron in practice is not screened by the $4p$ electron, which in turn feels just the residual charge $Z(r) \simeq 1$ (see Sect. 2.1), evaluate the wavelength of the radiation required to promote the transition from the ground state to that double-excited state. After the *autoionization* of the atom, and decay to the ground-state of He^+ , one electron is ejected. Estimate the velocity of this electron.

Solution:

$E(2s, 4p) = -14.5$ eV, then $\lambda = c/\nu = 192$ Å and $v = 3.75 \times 10^8$ cm/s.

Specific References and Further Reading

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