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A simple and effective approach to calculate the energy of complex atoms

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It is shown in this paper that, using only common concepts of well known modern physics and quantum mechanics textbooks (as one- and two-electron atoms, perturbation theory), we can develop a simple and powerful method to calculate the binding energies of complex electron configurations, as well as ionization energies, X-ray levels, etc.

Keywords: Atomic structure; Z-expansion; relativistic corrections

En este artículo se muestra que usando solamente conceptos comunes bien conocidos que aparecen en los libros de física moderna y de mecánica cuántica (átomos con uno y dos electrones, teoría de perturbaciones), podemos desarrollar un método simple y poderoso para calcular las energías de ligadura de configuraciones electrónicas complejas, energías de ionización, niveles de rayos X, etc.

Descriptores: Estructura átomica; desarrollo en Z; correcciones relativistas

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1. Introduction

It is well known that exact solutions of the Schrödinger equation can be found in a few cases [1–5]. With relation to atomic physics, are treated in general hydrogenic atoms and the ground configuration of He but, in this case, not all necessary calculations are presented in detail [6–8].

In this work it is showed that, provided only with the knowledge about atoms with one and two electrons, we can treat a general theory that permit us to obtain the energy for electron configurations of arbitrary complexity. The method is based on the Z^{-1} expansion due to Layzer [9] and originated in works of Hylleraas on the ground state of He.

On one hand, this is an interesting exercise for non-graduate students. We show as to attain data even for complex atoms that are well compared with the experiment in diverse cases: binding energies, energy of internal (sub) shells and ionization energies of atoms when three or more of the valence electrons are missing. For neutral or few times ionized atoms the results are encouraging (better than 75% for neutrals, in the more stringent case).

In this work we will use only common concepts appearing in quantum mechanics books: one- and two-electron atoms and the Rayleigh-Schrödinger perturbation theory [1–5]. But, in order to give an idea of the usefulness of this approach, we gives modern references to research papers. In the first part of this paper, we use a non-relativistic approach whereas in the second part we use an approximate relativistic treatment. In order to simplify the notation, we indicates with m (not m_l) the component of the orbital angular momentum whereas we use μ (not m_s) the component of the spin momentum.

2. Atomic units

In atomic physics it is useful to use the so called *atomic units* (a.u.), based in the elementary electron charge ($e \approx 4.8 \times 10^{-10}$ esu), the electron rest mass ($m \approx 9.1 \times 10^{-28}$ g) and the reduced Planck constant ($\hbar \equiv h/2\pi \approx 1 \times 10^{-27}$ erg s). In this system the a.u. of length is the radius of the first Bohr orbit

$$a_0 = \frac{\hbar^2}{me^2} \approx 5.29 \times 10^{-9}\ \mathrm{cm},$$

the time unit is

$$\tau_0 = \frac{\hbar^3}{me^4} \approx 2.42 \times 10^{-17}\ \mathrm{s},$$

and the energy unit can be, indistinctly, the Rydberg or the Hartree:

$$\begin{aligned} 1\ \mathrm{Ry} =& \frac{me^4}{2\hbar^2} = \frac{e^2}{2a_0} \equiv 13.6058\ \mathrm{eV} \\ 1\ \mathrm{Ht} =& 2\mathrm{Ry}. \end{aligned}$$

In the following paragraphs $r_i = |\mathbf{r}_i|$ the distance of the i-th electron from the nucleus, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the i-th and the j-th electrons, $\mathbf{l}_i$ and $\mathbf{s}_i$ are the orbital and spin angular-momentum operators, in units of $\hbar$ and $\xi_i(r_i)$ is the spin-orbit operator, measured in energy units. In this units system, the hamiltonian for N electrons moving in the field of a nucleus of charge Z looks as

$$H = -\sum_i \nabla_i^2 - \sum_i \frac{2Z}{r_i} + \sum_{i>j}\sum \frac{2}{r_{ij}} + \sum_i \xi_i(r_i)(\mathbf{l}_i \cdot \mathbf{s}_i), \quad (1)$$

if energies [and $\xi_i(r_i)$] are measured in Ry or

$$H = -\frac{1}{2}\sum_{i=1}^{n} \left(\nabla_i^2 + \frac{2Z}{r_i}\right) + \sum_{i>j} \frac{1}{r_{ij}} + \sum_i \xi_i(r_i)(\mathbf{l}_i \cdot \mathbf{s}_i), \quad (2)$$

if energies [and $\xi_i(r_i)$] are measured in Ht.

3. A brief refreshment about electron configurations and coupling schemes

To each electron of a complex atom we can assign a pair of quantum numbers $(n_i l_i)$ in the non-relativistic approach or a triplet of quantum numbers $(n_i l_i j_i)$ in the relativistic one. A complex electron configuration is denoted, respectively, as

$$(n_1 l_1)^{w_1}(n_2 l_2)^{w_2}\dots(n_q l_q)^{w_q}$$

or

$$(n_1 l_1 j_1)^{w_1}(n_2 l_2 j_2)^{w_2}\dots(n_q l_q j_q)^{w_q},$$

where w_q denote the occupation number of the electron subshell. For example, for neutral Ne, the electron configuration can be written as:

$$(1s)^2(2s)^2(2p)^6$$

or

$$(1s_{1/2})^2(2s_{1/2})^2(2p_{1/2})^2(2p_{3/2})^4,$$

respectively, when using the non-relativistic or the relativistic solutions of the central field problem.

When we consider the *non-relativistic* Hamiltonian [Eqs. (1) or (2)], the LS (or Rusell-Saunders) coupling is valid when the electrostatic interactions are stronger than the spin-orbit whereas jj coupling is applied in the reverse case [4]. When considering the *approximate, relativistic* Hamiltonian, the notion of jj coupling is the natural one (remember that the spin-orbit interaction is relativistic in origin).

We denote the LS coupling by the sequence

$$\big\{\big[\{(L_1,L_2)\mathfrak{L}_2\}\mathfrak{L}_3,\dots\big]\mathfrak{L}_q,\ \big[\{(S_1,S_2)\mathfrak{S}_2,S_3\}\mathfrak{S}_3,\dots\big]\mathfrak{S}_q\big\}\mathfrak{J}_q\mathfrak{M}_q, \quad (3)$$

where the script letters indicates the various intermediate and final quantum numbers. Analogously, the jj coupling implies the sequence

$$\big\{[(l_1,s_1)j_1,(l_2,s_2)j_2]J_2,\dots\big\}JM. \quad (4)$$

There are a biunivocal correspondence between the coupled LS and jj states. For example:

$$\begin{aligned}
s^2\ {}^1S_0 &\longleftrightarrow (s^2)0,\\
2p^2\ {}^3P_0 &\longleftrightarrow (2p_{1/2})^2 0,\\
2p^2\ {}^1S_0 &\longleftrightarrow (2p_{3/2})^2 0,\\
2p^2\ {}^3P_1 &\longleftrightarrow (2p_{1/2}2p_{3/2})1,\\
2p^2\ {}^3P_2 &\longleftrightarrow (2p_{1/2}2p_{3/2})2,\\
2p^2\ {}^1D_2 &\longleftrightarrow (2p_{3/2})^2 2,\\
&\vdots
\end{aligned} \quad (5)$$

The subtle questions of the fundamental importance of these schemes are out of the scope of this paper (see the book by Messiah [4]). An specialized although elementary account can be found in the books by Eisberg [11] and Woodgate [12]; a text about the importance of jj coupling in nuclear structure is the one by Talmi and de-Shalit [13].

As well as the numbers n, l (or n, l, j) indicates an electron configuration, the numbers L, S give the so called *terms*. Denonting by $E_{\rm av}$ the *configuration-average energy*

$$E_{\rm av} = \frac{\sum_{\rm states} E_k}{\text{number of states}},$$

it is important to know that the energy of the *terms*, relative to $E_{\rm av}$ can be found using the vector model of the atom [6,11] and can be calculated in terms of the so called Slater integrals (see below). Although the deduction is not trivial and it is apt for advanced courses, they can be obtained using a computer program presented in Ref. 14. For example, for the configuration p^2 (or p^4) the followings terms appear:

$$\begin{aligned}
E({}^3P) &= E_{\rm av} - \frac{3}{25}F^2(pp),\\
E({}^1D) &= E_{\rm av} + \frac{3}{25}F^2(pp),\\
E({}^1S) &= E_{\rm av} + \frac{12}{25}F^2(pp).
\end{aligned} \quad (6)$$

4. One- and two-electron atoms

4.1. One-electron atoms

Few things are necessary to remind from the non-relativistic hydrogenic atoms:

i) The discrete state energies, relative to the ionization limit (taken as zero), are given by

$$E_n = -\frac{Z^2}{n^2}.$$

ii) The non-relativistic wavefunction for one-electron atoms is of the form called *spin-orbital*

$$\Psi(r,\theta,\varphi,\mu) = r^{-1}P_{nl}(r)Y_{lm}(\theta,\varphi)\chi(\mu), \quad (7)$$

where $P(r)$ and $Y_{lm}(\theta,\varphi)$ are normalized according to the relations

$$\int_0^\infty |P_{nl}(r)|^2\,dr = 1;$$
$$\iint |Y_{lm}(\theta,\varphi)|^2 \sin\theta\,d\theta d\varphi = 1. \quad (8)$$

Explicitly, when r is measured in units of a_0

$$P_{nl}(r) = C_{nl} r^{l+1} \mathrm{e}^{-Zr/n} \sum_{k=0}^{n-l-1} a_k r^k, \quad (9)$$

with

$$a_k = \frac{(-2Z/n)^k}{k!(2l+1+k)!(n-l-1-k)!}, \tag{10}$$

and

$$C_{nl} = \left\{ \frac{2^{2l+2} Z^{2l+3} (n-l-1)!(n+l)!}{n^{2l+4}} \right\}^{1/2}. \tag{11}$$

Abundant theoretical material about the spherical harmonics can be found in quantum mechanics as well as in electromagnetism books (see the above mentioned references, for example the book by Jackson [15].

4.2. Two-electron atoms

This topic is included in some texts about modern physics [6], therefore we will be shyntetic in this section. A more explicit treatment can be found in the book by de la Peña [5] as well as in the one by Borowitz [1]. More detailed treatments are presented in some books about quantum chemistry (See Refs. 7 or 8).

We must evaluate $\langle \Psi | H | \Psi \rangle$ where $|\Psi\rangle$ is a determinantal (antisymmetric) wavefunction and H is the Hamiltonian operator.

The difficulty in the treatment of many-electron atoms is in the term $2/r_{ij}$ of the Hamiltonian (1 or 2) that, without the spin-orbit term, can be re-written using conventional symbols as

$$H(\text{in Ht}) = -\left(\frac{\nabla_i^2}{2} + \frac{\nabla_j^2}{2} + \frac{Z}{r_i} + \frac{Z}{r_j} \right) + \frac{1}{r_{ij}}$$
$$\equiv \sum_{i=1}^{2} H_0(i) + H_{12}(i,j). \tag{12}$$

To proceed with such term, that impedes the variable separation, we introduce the normalized spherical harmonics, according to [15]

$$C_q^{(k)} = \left(\frac{4\pi}{2k+1} \right)^{1/2} Y_{kq}, \tag{13}$$

such that the matrix element, denoted $\langle lm | C_q^{(k)} | l'm' \rangle$, results

$$\langle lm | C_q^{(k)} | l'm' \rangle \equiv \iint Y_{lm}^* Y_{kq} Y_{l'm'} \sin\theta \, d\theta d\phi; \tag{14}$$

and can be calculated directly, although it is laborious. The result can be expressed in terms of the $3j$ symbols due to Wigner, that can be calculated in closed form in terms of factorials (this material can be found in the books of Landau-Lifshitz or Messiah [3,4]:

$$\iint Y_{lm}^* Y_{kq} Y_{l'm'} \sin\theta \, d\theta d\phi = (-1)^{-m} \left[(2l+1)(2l'+1) \right]^{1/2} S_{3j}(l,k,l';0,0,0) S_{3j}(l,k,l';-m,q,m')$$
$$= \delta(q, m-m') c^k(lm, l'm'). \tag{15}$$

The above equation also defines the coefficients $c^k(lm, l'm')$.

It is known from the courses about electrostatics that the following expansion is valid [15]:

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{k} (-1)^q C_{-q}^{(k)}(\theta_1, \phi_1) C_q^{(k)}(\theta_2, \phi_2). \tag{16}$$

It can be shown [7] that, if each spin-orbital is written as in Eq. (7), the average value $\langle 1/r_{12} \rangle \equiv \langle \Psi | 1/r_{12} | \Psi \rangle$ is evaluated as

$$\left\langle i(1)j(2) \left| \frac{1}{r_{12}} \right| t(1)u(2) \right\rangle = \delta(\mu_i, \mu_t) \delta(\mu_j, \mu_u) \sum_k R^k(ij, tu)$$
$$\times \sum_q \delta(q, m_t - m_i) \delta(q, m_j - m_u) (-1)^q c^k(l_i m_i, l_t m_t) c^k(l_j m_j, l_u m_u), \tag{17}$$

where the $R^k(ij, tu)$ are the generalized Slater integrals (see below in this same paragraph). The summation over k involve only a small number of non-zero terms [see below Eqs. (18) and (19)]. Using the fundamental property of de Dirac δ function, we note that the matrix elements 17 are zero unless $q = m_t - m_i = m_j - m_u$, therefore $m_i + m_j = m_t + m_u$.

This is a reflection of the conservation of angular momentum: the electrostatic interaction betweeen two electrons cannot change the total orbital angular momentum of the two electrons, nor the z-component. The situation for the spins is even more restrictive, the δ-factors giving

$$\mu_i = \mu_t, \qquad \mu_j = \mu_u,$$

indicates that since the electrostatic interaction does not operate on the electrons spins, not only is the *total* spin conserved, but so also is the spin of each electron separately.

In particular, from Eq. (17), it is introduced the *Coulomb or direct* integral $J(ij)$:

$$J(ij) \equiv \left\langle ij \left| \frac{1}{r_{12}} \right| ij \right\rangle$$
$$= \sum_k c^k(l_i m_i, l_i m_i) c^k(l_j m_j, l_j m_j) F^k(ij), \tag{18}$$

TABLE I. Electron-pair interaction energies for a non-relativistic system.

$\langle ss \rangle$	$F^0(ss)$
$\langle pp \rangle$	$F^0(pp) - 2F^2(pp)/25$
$\langle dd \rangle$	$F^0(dd) - 2F^2(dd)/63 - 2F^4(dd)/63$
$\langle ss' \rangle$	$F^0(ss') - G^0(ss')/2$
$\langle sp \rangle$	$F^0(sp) - G^1(sp)/6$
$\langle sd \rangle$	$F^0(sd) - G^2(sd)/10$
$\langle pp' \rangle$	$F^0(pp') - G^0(pp')/6 - G^2(pp')/15$
$\langle pd \rangle$	$F^0(pd) - G^1(pd)/15 - 3G^3(pd)/70$
$\langle dd' \rangle$	$F^0(dd') - G^0(dd')/10 - G^2(dd')/35 - G^4(dd')/35$

and the *exchange integral* $K(ij)$:

$$K(ij) \equiv \left\langle ij \left| \frac{1}{r_{12}} \right| ji \right\rangle = \delta(\mu_i, \mu_j) \sum_k [c^k(l_i m_i, l_j m_j)]^2 G^k(ij). \qquad (19)$$

We can see, using the properties of the $3j$ symbols [3] (and therefore of the c^k coefficients, both derived from the integral over spherical harmonics) that:

i) $l + k + l'$ must be even.

ii) The triangle relation of the classical vector model must be satisfied: $|l - l'| \leq k \leq l + l'$.

In Eq. (19) $F^k(i,j)$ and $G^k(i,j)$ are [6,14]

$$F^k(ij) \equiv R^k(ij, ij) = \iint \frac{r_<^k}{r_>^{k+1}} |P_i(r_1)|^2 |P_j(r_2)|^2 \, dr_1 dr_2, \qquad (20)$$

$$G_k(ij) \equiv R^k(ij, ji) = \iint \frac{r_<^k}{r_>^{k+1}} P_i(r_1) P_j(r_1) P_i(r_2) P_j(r_2) \, dr_1 dr_2. \qquad (21)$$

Now it is necessary to average over the magnetic quantum numbers. For non-equivalent orbitals:

$$E(ij) = \langle ij | 1/r_{12} | ij \rangle_{\text{av}} - \langle ij | 1/r_{12} | ji \rangle_{\text{av}} = F^0(ij) - \frac{1}{2} \sum_k \begin{pmatrix} l_i & k & l_j \\ 0 & 0 & 0 \end{pmatrix}^2 G^k(ij), \qquad (22)$$

whereas for the equivalent ones:

$$E(ii) = F^0(ii) - \frac{2l_i + 1}{4l_i + 1} \sum_{k>0} \begin{pmatrix} l_i & k & l_j \\ 0 & 0 & 0 \end{pmatrix}^2 F^k(ii). \qquad (23)$$

Slater integrals can be calculated in closed form if hydrogenic orbitals are used, but the final result is long and complicate. Electron-pair interaction energies for a non-relativistic system are in Table I.

5. Average energies for complex configurations

In the non-relativistic approach, a complex configuration is denoted as

$$(n_1 l_1)^{w_1} (n_2 l_2)^{w_2} \ldots (n_q l_q)^{w_q}, \qquad (24)$$

where $N = \sum_{j=1}^{q} w_q$ is the total number of electrons of the atom or ion.

For the Hamiltonian [Eq. (2)], without the spin-orbit term, the energy

$$E = \langle \Psi | H | \Psi \rangle$$

can be written as the sum of kinetic, electron-nuclear and electron-electron Coulomb energies:

$$E_{\text{av}} = \sum_i E_k(i) + \sum_i E_n(i) + \sum_{i>j} E(i,j) = \sum_i I(i) + \sum_{i>j} E(i,j). \qquad (25)$$

For example, for the neutral Be

$$E_{\text{av}} = 2I(1s) + 2I(2s) + E(1s,1s) + E(2s,2s) + 4E(1s,2s).$$

This very complex many-body problem can be solved using the Hartree-Fock approach (a numerical one), as can be briefly viewed in the books by Eisberg [11], Landau [3] or Messiah [4]. Instead, in this paper we use the following approach.

6. The Z^{-1} expansion

Layzer's formulation of the Z-dependent theory of the many-electron atom can be regarded as the starting point [9]. From the approximate Hamiltonian in atomic units ($e = m_e = \hbar = 1$ and energies measured in Hartrees) given by Eq. (2):

$$H(N,Z) = -\frac{1}{2} \sum_{i=1}^{n} \left(\nabla_i^2 + \frac{2Z}{r_i} \right) + \sum_{i>j} \frac{1}{r_{ij}}, \qquad (26)$$

and introducing the new variable $\rho = Zr$, Eq. (26) becomes (the parameter λ is commonly used in place of Z^{-1})

$$H(N,Z) \rightarrow Z^2 H(N,\lambda) = Z^2(H_0 + \lambda V), \qquad (27)$$

where

$$H(N,\lambda) = -\frac{1}{2} \sum_{i=1}^{n} \left(\nabla_i^2 + \frac{2}{\rho_i} \right) + \lambda \sum_{i>j} \frac{1}{\rho_{ij}}.$$

The first term of the right hand side,

$$H_0 = -\frac{1}{2} \sum_{i=1}^{n} \left(\nabla_i^2 + \frac{2}{\rho_i} \right) \qquad (28)$$

is a sum over non-interacting hydrogenic Hamiltonians, and

$$V \equiv H_1 = \sum_{i>j} \frac{1}{\rho_{ij}}. \qquad (29)$$

If $Z^{-1}(=\lambda)$ is a small parameter, the Rayleigh-Schrödinger perturbation theory (RSPT) can be applied [4,11]. Layzer showed that, within the framework of the Z^{-1}-dependent theory, the wave function and the total energy can be written as the expansions

$$\Psi(N,\lambda)=\Psi_0+\lambda\Psi_1+\lambda^2\Psi_2+\ldots \tag{30}$$

and

$$E(N,\lambda)=E_0+\lambda E_1+\lambda^2E_2+\ldots \tag{31}$$

Then

$$E(N,Z)=Z^2E_0+ZE_1-E_2+\ldots \tag{32}$$

where, *exactly*

$$E_0=\langle\psi_0|H_0|\psi_0\rangle=-\frac{1}{2}\sum_{i=1}^{n}\frac{1}{n_i^2} \tag{33}$$

and

$$E_1=\langle\psi_0|H_1|\psi_0\rangle. \tag{34}$$

According to the Eqs. (22) and (23), E_1 is given in terms of Slater's integrals F^k and G^k evaluated with hydrogenic wavefunctions with $Z=1$. In Table II we display these average Coulomb energies for the ground configurations of He to Ne, in order to explain our following results. More values are exposed in the works of Safronova *et al.* [16] and the present author [17]. We remark the recent publication of these last cited works in order to indicate how a simple approach can give valuable theoretical data apt to interpret complex experiments.

TABLE II. Some Average Coulomb energies E_1 calculated in terms of Slater integrals with $Z=1$. More results can be found in the Refs. 16 and 17.

He	0.62500
Li	1.02281
Be	1.57100
B	2.33445
C	3.27251
N	4.38518
O	5.67245
F	7.13433
Ne	8.77083

If we restrict the expansion (32) up to E_2, the energy can be written as

$$E=-\sum_{n,l}\frac{w_{nl}(Z-\sigma_{nl})^2}{2n^2}, \tag{35}$$

where w_{nl} is the number of electrons in the n,l shell and σ_{nl} is the corresponding screening parameter. Comparing Eqs. (32) and (35), we find that the σ_{nl} satisfy

$$E_1=\sum_{n,l}\frac{w_{nl}}{n^2}\sigma_{nl}, \tag{36}$$

and

$$E_2=\sum_{n,l}\frac{w_{nl}}{2n^2}\sigma_{nl}^2. \tag{37}$$

Then, to second-order approximation in the non-relativistic context, the average energy of a configuration is given by

$$E_{\text{av}}=-\frac{Z^2}{2}\left(w_{1s}+\frac{w_{2s}+w_{2p}}{4}+\frac{w_{3s}+w_{3p}+w_{3d}}{9}+\cdots\right)+Z\left[\frac{1}{2}\sum_i w_i(w_i-1)E_1(ii)+\sum_{i,j}w_iw_jE_1(ij)\right]-E_2, \tag{38}$$

where w_i is a short notation for $w_{n_il_i}$, the number of electrons in the n_i,l_i shell.

6.1. About the concept of screening

The concept of screening (and screened orbitals) is of old data and it is impossible to give a short account in this paper. In the past, screening parameters were obtained using spectroscopic data, numerical calculations and theoretical approaches. A short review can be found in the paper from the author [17].

In more refined approachs the screening parameters all have Z expansions of the form

$$s=s_0+s_1Z^{-1}+s_2Z^{-2}+\ldots,$$

whereas other authors used electrostatic considerations and deduced parameters dependent of both $Z,N:\sigma(Z,N)$ [17]. Looking for simplicity, in this work, we will use only the concept of *external* screening, as shown below and in the Appendix B.

7. Firsts examples of applications

7.1. Binding energies and relativistic contributions

For the He atom, $E_1=F^0(1s,1s)=0.625$, therefore from Eq. (36), $\sigma_{1s}=0.3125$, a result known from variational calculations (see Appendix A). With $Z_{1s}=1.6875$, $E(\text{He})=-2.8477$ Ht; better results could be obtained if relativistic corrections are employed. In this case, $\sigma_{1s}=0.2961$ and $E=-2.9033$ Ht; almost the experimental value.

For Li I: $1s^22s$, we have $E_1=1.0228=2\sigma_{1s}+\sigma_{2s}/4$. Assuming that $\sigma_{1s}=0.3125$ (neglecting the external screening), $\sigma_{2s}=1.5912$ and $E(\text{Li I})=-7.4707$ Ht. Introducing the concept of external screening, we write $\sigma_{1s}=0.3125+g(1s,2s)$, estimate $g(1s,2s)$ according to Appendix B and calculate σ_{2s}. For the Li I case, $g(1s,2s)=0.0143$, therefore $\sigma_{2s}=1.4771$ and $E(\text{Li I})=-7.4361$ Ht, instead of the previous value

TABLE III. Center of gravity binding energies in *Rydbergs* for ground configurations [including relativistic corrections according to Eq. (39)]. The values with a $(^*)$ were calculated using Hartree-Fock methods because no experimental values are available.

Atom	This method	Sucher [24]	Experiment
He	5.695	6.0	5.807
Be	29.245	29.50	29.337
C	75.580	75.50	75.712
Ne	257.460	269.60	258.102
Mg	400.960	414.20	400.621
Si	580.060	593.80	579.732
Ar	1058.040	1072.80	1058.23
Zn	3585.28	3626.00	3588.46^*
Kr	5573.66	5570.00	5575.30^*

of -7.4707 Ht. The experimental one is -7.4344 Ht. The IP is obtained after calculating $E(\text{Li II})$. The He-like Li II has $\sigma_{1s} = 0.3125$, therefore $E(\text{Li II}) = -7.2227$ Ht implying that neglecting $g(1s, 2s)$, $\text{I} = 0.248$ Ht $\equiv 6.75$ eV, whereas $\text{I}_{\text{exp}} = 5.39$ eV. Considering now the external screening, $\text{I} = 0.2134$ Ht $\equiv 5.807$ eV.

Using Z-independent screening parameters we have for the Be atom $\sigma_{1s} = 0.3125 + 2 \times 0.0143$. Then, $\sigma_{1s} = 0.3125 + 2 \times 0.0143 = 0.3410$ and according to Eq. (36) and Table II, $\sigma_{2s} = 1.8349$ and thus $E(\text{Be I}) = -14.56$ Ht. The experimental value is found to be -14.6685 Ht. The difference between these values lies within 0.7%.

Proceeding in this form, in Table III we show binding energies for a number of elements in order to compare with the values reported by the experiment [18]. The most important relativistic contribution is due to the more internal electrons and can be estimated as a simple sum over terms of the form

$$E_{\text{rel}} = -\frac{\alpha^2 Z_{\text{ef}}^4}{8n^4}\left(\frac{4n}{j+1/2} - 3\right) w_{nl} \text{ Ht}. \qquad (39)$$

7.2. The isoelectronic sequences of neon and argon

In Ref. 17 we exhibit, as examples, the ionization potentials for the Ne I and Ar I isoelectronic sequences calculated by means of our approach. A comparison with the experiment indicates that agreement is within 76% for Ne I and better than 3% for the third member of the serie. Our IP's can be fitted by the adjusted empirical curve $\text{IP(eV)} = 128.29 - 45.42Z + 3.4231Z^2$. For the Ar I isoelectronic sequence, the fit function is $\text{IP} = 285.16 - 43.06Z + 1.5861Z^2$. Now, the IP's are better than 7% for the 4-th member of the serie. Also the experimental ionization potentials follow an empirical law of the type

$$I = aZ^2 + bZ + c;$$

TABLE IV. K-shell binding energies in eV for some representative neutral atoms.

Atom	Ours	Experiment
Be	123.8	119.30
C	297.6	283.8
Ne	876.0	870.10
Mg	1316.3	1311.20
Si	1856.2	1846.00
Ar	3211.6	3202.90
Zn	10392.8	10367.1
32	11131.9	11103.1
33	11897.6	11866.7
34	12690.1	12657.8
35	13509.6	13473.7
Kr	14356.2	14325.6

this behaviour is easy to understand from Eq. (32). In particular, it is a simple exercise to show that

$$a = \frac{Z^2}{2n_k^2},$$

where n_k is the principal quantum number of the removed electron [19].

7.3. K-shell binding energies

In Table IV we present the K-shell binding energies for some neutral atoms from Be to Kr. We establish a comparison with experimental results tabulated in the *Handbook of Chemistry and Physics* [20]. In general, we can see that our simple approach gives an agreement of the order of 0.2%.

8. Now, the relativity, why?

We see that the most important relativistic contribution to the total energy is due to the more internal electrons and can be well estimated as a simple sum over terms of the form given by the Eq. (39).

However, we know from the modern physics courses that in the X-ray spectra appear a fine structure such that, for example, the $2p_{1/2}$ electrons have a notorious different energy than the $2p_{3/2}$ ones [6,11,21]. We will show that, although the energy of the valence electrons do not differ appreciably between relativistic or non-relativistic treatments, we can easily calculate the different subshell energies.

8.1. Approximate relativistic wave functions and some of their properties

The relativistic theory of the H atom is briefly presented in the books by Merzbacher [2] and also in the one by Messiah [4]. Also brief are the expressions for the hydrogen relativistic radial wave functions that can be found in these classic texts.

They have a large and a small component, denoted respectively by $F_{nlj}(r)$ and $G_{nlj}(r)$ (other authors use the reverse notation!), with the general property that, when $(Z\alpha)^2 \to 0$, $F_{nlj}(r) \to R_{nl}(r)$, and $G_{nlj} \to 0$. The normalization condition is

$$\int_0^\infty \left(F_{nlj}^2 + G_{nlj}^2\right) r^2 dr = 1. \tag{40}$$

In our case, we introduce one heuristic approach apt to the purpose of this paper and also to diverse applications, therefore we take $G_{nlj} = 0$ and normalize $F_{nlj}(r)$ according to Eq. (40). Heuristic approachs are very common when modelling complex physical situations, for example when atomic and fluid equations are coupled or when plasmas in non-thermal equilibrium exists [22]. In this form we have a wave function for each sub-shell defined by the individual quantum numbers (nlj) and we can calculate the corresponding energies for each subshell.

Taking into account that diverse notations exists for the relativistic functions, we shall summarize the symbols to be used. Given the quantum numbers n, l, we construct the following quantities, with $\alpha = 1/137.037$:

$$\begin{aligned}
j_+ &= l + \frac{1}{2}, \\
j_- &= \left| l - \frac{1}{2} \right|, \\
\lambda_+ &= \left[\left(j_+ + \frac{1}{2} \right)^2 - \alpha^2 \right]^{1/2} \\
&= \left[(l+1)^2 - \alpha^2 \right]^{1/2} \to (l+1), \\
\lambda_- &= \left[\left(j_- + \frac{1}{2} \right)^2 - \alpha^2 \right]^{1/2} \\
&= (l^2 - \alpha^2)^{1/2} \to l, \\
n'_+ &= n - j_+ - 1/2 = n - l - 1, \\
n'_- &= n - j_- - 1/2 = n - l, \\
N_+ &= \left[n^2 - 2n'_+ \left(j_+ + \frac{1}{2} - \lambda_+ \right) \right]^{1/2} \to n, \\
N_- &= \left[n^2 - 2n'_- \left(j_- + \frac{1}{2} - \lambda_- \right) \right]^{1/2} \to n, \\
\kappa_+ &= -\left(j_+ + \frac{1}{2} \right) = -(l+1), \\
\kappa_- &= +\left(j_- + \frac{1}{2} \right) = +l.
\end{aligned}$$

With these quantities, and calling for brevity $rF_{nlj} \equiv P_{nlj}$, our hydrogen radial wave-function has the form [2]

$$P_{nlj}(r) = C_{nj} \left(\sum_{v=0}^{n'} f_v r^{v+\lambda} \right) \mathrm{e}^{-Zr/N}. \tag{41}$$

In Eq. (41)

$$f_v = (-1)^v \frac{(2\lambda)!(2Z/N)^{v+\lambda-1} n'!}{v!(2\lambda+v)!(n'-v)!} (v - n' + N - \kappa), \tag{42}$$

for $v = 0$ up to $v = n' - 1$ and

$$f_v = (-1)^v \frac{(N-\kappa)(2\lambda)!(2Z/N)^{v+\lambda-1}}{(2\lambda+v)!}, \tag{43}$$

for $v = n'$. The normalization constant is found by performing the integral given by the Eq. (40) with the appropriate values of f_v. In such manner, we find in place of Eq. (11),

$$C_{nj} = \left[\frac{(2Z/N)^{2\lambda+1}}{\sum_{\alpha=0}^{2n'} A_\alpha \Gamma(\alpha + 2\lambda + 1)(N/2Z)^\alpha} \right]^{1/2}, \tag{44}$$

with

$$A_\alpha = \sum_{\beta=0}^{\alpha} f_\beta f_{\alpha-\beta}. \tag{45}$$

A general property of these wave functions is that, denoting by P_{nl} the non-relativistic functions, P_{nlj}^+ the relativistic functions with $j = j_+$ and by P_{nlj}^- when $j = j_-$

$$P_{nlj}^+ \simeq P_{nl},$$

and

$$P_{nlj}^- \simeq cr^l \mathrm{e}^{-Zr/N} + P_{nl}.$$

8.2. *jj* coupling and the calculation of the Slater integrals

We give here an heuristic point of view, indicating that a correct relativistic Hamiltonian for many-electron atoms was derived by Breit. The *electrostatic* part of the relativistic energy of an atom is the straightforward generalization of the nonrelativistic energy

$$E = \sum_i I(i) + \sum_{i,j} [J(i,j) - K(i,j)], \tag{46}$$

where the energies must be calculated using*relativistic* wave-functions.

In a analogous way to the non-relativistic theory, the energy of an atomic configuration may be expressed in terms of Slater integrals, now*in the jj coupling scheme*. For a two-electron system and from Eq. (46), the electron-electron Coulomb energy can be written (neglecting here magnetic and retardation effects) as

$$\left\langle n_a l_a j_a, n_b l_b j_b \left| \frac{1}{r_{12}} \right| n_a l_a j_a, n_b l_b j_b \right\rangle = \sum_k \left[f_k(a,b) F^k(a,b) - (-1)^{j_a + j_b + J} g_k(a,b) G^k(a,b) \right]. \tag{47}$$

Now the diverse summations, corresponding $3 - nj$ symbols and coefficients f_k and g_k depend on quantum numbers $l's$ and $j's$ and not on $l's, L's$ and $S's$. In the Appendix, we give explicit expressions for these coefficients and the calculated ones

TABLE V. Electron-pair interaction energies for a relativistic system.

$\langle s_+s_+\rangle$	$F^0(s_+s_+)$
$\langle p_-p_-\rangle$	$F^0(p_-p_-)$
$\langle p_+p_+\rangle$	$F^0(p_+p_+) - F^2(p_+p_+)/15$
$\langle d_-d_-\rangle$	$F^0(d_-d_-) - F^2(d_-d_-)/15$
$\langle d_+d_+\rangle$	$F^0(d_+d_+) - 24F^2(d_+d_+)/525 - 10F^4(d_+d_+)/525$
$\langle s_+s'_+\rangle$	$F^0(s_+s'_+) - G^0(s_+s'_+)/2$
$\langle s_+p_\mp\rangle$	$F^0(s_+p_\mp) - G^1(s_+p_\mp)/6$
$\langle s_+d_\mp\rangle$	$F^0(s_+d_\mp) - G^2(s_+d_\mp)/10$
$\langle p_-p'_-\rangle$	$F^0(p_-p'_-) - G^0(p_-p'_-)/2$
$\langle p_-p_+\rangle$	$F^0(p_-p_+) - G^2(p_-p_+)/10$
$\langle p_-d_-\rangle$	$F^0(p_-d_-) - G^1(p_-d_-)/6$
$\langle p_-d_+\rangle$	$F^0(p_-d_+) - G^3(p_-d_+)/14$
$\langle p_+p_+\ '\rangle$	$F^0(p_+p'_+) - G^0(p_+p'_+)/4 - G^2(p_+p'_+)/20$
$\langle p_+d_-\rangle$	$F^0(p_+d_-) - G^1(p_+d_-)/60 - 9G^3(p_+d_-)/140$
$\langle p_+d_+\rangle$	$F^0(p_+d_+) - G^1(p_+d_+)/10 - G^3(p_+d_+)/35$
$\langle d_-d'_-\rangle$	$F^0(d_-d'_-) - G^0(d_-d'_-)/4 - G^2(d_-d'_-)/20$
$\langle d_-d_+\rangle$	$F^0(d_-d_+) - G^2(d_-d_+)/70 - G^4(d_-d_+)/21$
$\langle d_+d'_+\rangle$	$F^0(d_+d'_+) - G^0(d_+d'_+)/6 - 4G^2(d_+d'_+)/105 - G^4(d_+d'_+)/63$

ones are presented in Table V. For some examples,

$$\langle s_+s_+\rangle = F^0(s_+s_+);$$

$$\langle p_+p_+\rangle = F^0(p_+p_+) - \frac{F^2(p_+p_+)}{15}.$$

The Slater parameters F^k, G^k for *hydrogenic* wavefunctions can be calculated analytically, but the expressions are tedious and not very illuminating as to be presented here. The results shown small differences with the non-relativistic ones but the jj approach permit us to calculate the subshell binding energies (and X-ray ones, if we like). Some examples can be viewed in Table VI and compared with the numbers of Asaad [23]. So, the term energies E_0 and E_1 of a given configuration can be calculated. For the neutral Ne, for example,

$$E_0(\text{Ne I}) = 2I(1s) + 2I(2s) + 2I(2p_-) + 4I(2p_+),$$

where

$$I(nl_\pm) \equiv I_{nj}$$
$$= -\frac{1}{2n^2}\left[1 + \frac{(Z\alpha)^2}{4n^2}\left(\frac{4n}{j_i + 1/2} - 3\right)\right], \qquad (48)$$

and

$$E_1(\text{Ne I}) = \langle 1s1s\rangle + \langle 2s2s\rangle + 4\langle 1s2s\rangle + 4\langle 1s2p_-\rangle$$
$$+8\langle 1s2p_+\rangle + 4\langle 2s2p_-\rangle + 8\langle 2s2p_+\rangle + \langle 2p_-2p_-\rangle$$
$$+6\langle 2p_+2p_+\rangle + 8\langle 2p_-2p_+\rangle.$$

TABLE VI. Relativistic Slater's integrals (in Ht).

Integral	This work	Asaad [23]
$F^0(1s,1s)$	0.624926	0.625003
$F^0(1s,2s)$	0.209844	0.209891
$F^0(1s,2p_-)$	0.242852	0.242822
$F^0(1s,2p_+)$	0.242800	0.242817
$F^0(2s,2s)$	0.150367	0.150389
$F^0(2s,2p_-)$	0.162117	0.162113
$F^0(2s,2p_+)$	0.162107	0.162112
$F^0(2p_-,2p_-)$	0.181667	0.181629
$F^0(2p_-,2p_+)$	0.181652	0.181627
$F^0(2p_+,2p_+)$	0.181637	0.181625
$F^2(2p_+,2p_+)$	0.087712	0.087909
$G^0(1s,2s)$	0.021921	0.021942
$G^1(1s,2p_-)$	0.051225	0.051195
$G^1(1s,2p_+)$	0.051180	0.051194
$G^1(2s,2p_-)$	0.087955	0.087910
$G^1(2s,2p_+)$	0.087968	0.087910
$G^2(2p_-,2p_+)$	0.087714	0.087909

Average Coulomb energies E_1 calculated in term of Slater integrals with $Z = 1$ are presented in Table VII.

With respect to the terms, we must consider the relations between the Slater integrals $F^k(ii), G^k(ij)$ and their relativistic counterparts. We develop here one case; other ones

TABLE VII. Electron pair energies (in Ht).

$\langle 1s_+1s_+\rangle$	0.624926
$\langle 1s_+2s_+\rangle$	0.198833
$\langle 1s_+2p_-\rangle$	0.234314
$\langle 1s_+2p_+\rangle$	0.234270
$\langle 2s_+2s_+\rangle$	0.150367
$\langle 2s_+2p_-\rangle$	0.147458
$\langle 2s_+2p_+\rangle$	0.147445
$\langle 2p_-2p_-\rangle$	0.181667
$\langle 2p_-2p_+\rangle$	0.172881
$\langle 2p_+2p_+\rangle$	0.175790

TABLE VIII. Some relationships between the non-relativistic and the relativistic expressions for the Slater integrals.

$F^2(pp)$	$[2G^2(-+)+F^2(++)]/3$
$F^2(dd)$	$[7F^2(--)+6G^2(-+)+12F^2(++)]/25$
$F^4(dd)$	$[4G^4(-+)+F^4(++)]/5$
$G^0(ss)$	$G^0(++)$
$G^1(sp)$	$[G^1(+-)+2G^1(++)]/3$
$G^2(sd)$	$[2G^2(+-)+3G^2(++)]/5$

TABLE IX. $L_{II}-L_{III}$ shell binding energies (in eV) for some representative atoms.

Z	Element	Our values (eV)	Experiment (eV) [20]
18	Ar	247.0	247.3
		245.2	245.2
31	Ga	1135.07	1142.3
		1112.22	1115.4
32	Ge	1239.22	1247.3
		1212.82	1216.7
33	As	1350.06	1358.6
		1319.70	1323.1
34	Se	1464.62	1476.2
		1429.88	1435.8
35	Br	1583.97	1596.0
		1544.40	1549.9
36	Kr	1708.15	1727.2
		1663.27	1674.9

are in Table VIII. From Tables I and V

$$\begin{aligned}\langle pp\rangle &= F^0(pp)-\frac{2}{25}F^2(pp),\\ \langle p_-p_-\rangle &= F^0(p_-p_-),\\ \langle p_+p_+\rangle &= F^0(p_+p_+)-\frac{1}{15}F^2(p_+p_+),\\ \langle p_-p_+\rangle &= F^0(p_-p_+)-\frac{1}{10}F^2(p_-p_+).\end{aligned}$$

In the respective complete shells there are 15 pairs pp, 1 pair p_-p_-, 6 pairs p_+p_+ and 8 pairs p_-p_+. Multiplying adequately and equalizying, results in

$$F^0(pp)=\frac{F^0(--)+6F^0(++)+8F^0(-+)}{15}$$

and

$$F^2(pp)=\frac{F^2(++)+2G^2(-+)}{3}.$$

9. Further applications and results

We base our heuristic approach in the expansion given by Eq. (32) which contains itself a contribution proportional to Z^4, because E_0 is now given by Eq. (49). To second order approximation

$$E_{\text{av}}=-\frac{Z^2}{2}\sum_i\frac{w_i}{n_i^2}\left[1+\frac{(Z\alpha)^2}{4n_i^2}\left(\frac{4n_i}{j_i+1/2}-3\right)\right] +Z\left[\frac{1}{2}\sum_i w_i(w_i-1)E_1(ii)+\sum_{i,j}w_iw_jE_1(ij)\right]-E_2, \quad (49)$$

with E_1 and E_2 satisfying the relations (36) and (37). Ionization energies for the valence electrons do not differ appreciably from the non-relativistic case. As examples, L_{II} and L_{III} shell bindings energies are in Table IX. Agreement with experimental values are better than 1% [20].

10. Comparison with other simple approachs

Some simple approachs for the calculation of atomic structures were published in the last two decades. In 1978, Sucher [24] presented a simplified version of the atomic shell model and calculated the ground-state energy of any atom. The agreement with Hartree-Fock calculations was within 5% for He and Ne and better than 0.5% for $Z>45$. No calculations for ions or for shell binding energies were presented, nor for excited states. On the other hand, based in the use of the virial $\sum \mathbf{r}_i\mathbf{F}_i$ as the model potential energy operator, Kregar [25] calculated screening parameters for any configuration. These works of Kregar were generalized by the present author [26].

When comparing the above mentioned papers with the present approach, we can conclude that

i) Our results for ground configurations binding energies are clearly better than the values presented by Sucher (see Table III).

ii) Our values for binding energies and ionization potentials are very similiar to those calculated by Kregar.

iii) We can calculate sub-shell binding energies (and X-ray spectra) whereas the works of Sucher and Kregar are, essentially, non-relativistic.

11. Conclussions

The heuristic point of view presented in Ref. 17 using the Z-expansion theory supplemented with the inclusion of the external screening concept is generalized to the relativistic case in the jj coupling. We use the normalized large component relativistic wave-function such that we can calculate the binding energies for each orbital indexed by the n, l, j quantum numbers. From the analysis of the tables we can obtain the following conclusions. The center-of-gravity binding energies calculated in the Z^{-1} approach are in very good agreement with experimental values. As can be viewed in Ref. 17 the ionization potentials for the (Ne I) and (Ar I) isoelectronic sequence are within 3% for three times ionized atoms and better for higher ionization degrees: 1% for five times ionized atoms and 0.5% for the 15-th spectra of the sequence. Results are worse for neutrals (within 25%) yet better than other screening approaches; for example, the values of Safronova *et al.* [16] are negative for low ionization degrees. K- and L- shell binding energies are in very good agreement with experiment [20]. An important aspect to be taken into account is that, in our approach there are no adjustable parameters. Better results can be attained with small efforts in the calculation of external screening parameters but extensive use of research papers must be made. We think that the numbers obtained with this simple approach will give to the student a clear idea of the power of the approximation methods applied to complex many-body problems.

Appendix A

The variational calculation of the He ground configuration energy

This topic can be found in the books by Messiah [4], Karplus-Porter [7] and Levine [8]. If we assign to each electron of the $1s^2$ configuration an hydrogenic radial wave-function with effective charge Z_e

$$P_{1s} = 2Z_e^{3/2} r \mathrm{e}^{-Z_e r}$$

and using the Hamiltonian (2) without the spin-orbit term, then

$$\langle H \rangle = -2Z_e^2 + 4Z_e(Z_e - 2) + 1.25Z_e.$$

The values of $\langle H \rangle$ and Z_e corresponding to the minimum are determined by differentiation; that is, from

$$\frac{d\langle H \rangle}{dZ_e} = -4Z_e + 8Z_e - 8 + 1.25 = 0;$$

therefore $Z_e = 2 - 5/16 = 1.6875$ and $\langle H \rangle = 5.6953$ $\mathrm{Ry} = 77.49$ eV.

Appendix B

A simple approach to the screening

As was said above, there are many works about screening parameters and screened functions. Here, we gives a simple point of view apt to calculate *external* screenings [27]. *Total* screenings are deduced according to Eq. (36) (see the examples given above).

Schrödinger equation is non-separable, due to the term

$$\frac{1}{r_{ij}} = (r_i^2 + r_j^2 - 2r_i r_j \cos\omega_{ij})^{-1/2}.$$

Making $u = 1/r_i$, $v = 1/r_j$, $f = 1/r_{ij}$ and developing a two-variable function in a Taylor series to a first order

$$f(u+h, v+k) \approx f(u,v) + \left[\frac{\partial f}{\partial u} h + \frac{\partial f}{\partial v} k\right],$$

it results

$$\begin{aligned}\frac{1}{r_{ij}} = \left(u_0^{-2} + v_0^{-2}\right)^{-1/2} + \frac{u_0^{-3}\left(u_0^{-2} + v_0^{-2}\right)^{-3/2}}{r_i} \\ -u_0^{-2}\left(u_0^{-2} + v_0^{-2}\right)^{-3/2} + \frac{v_0^{-3}\left(u_0^{-2} + v_0^{-2}\right)^{-3/2}}{r_j} \\ -v_0^{-2}\left(u_0^{-2} + v_0^{-2}\right)^{-3/2}.\end{aligned}$$

Because the sum of the 1st, 3rd and 5th terms are zero, the second one (and mutatis mutandis) the fourth can be put in the form

$$\frac{u_0^{-3}\left\{u_0^{-2}\left[1 + \left(\frac{v_0}{u_0}\right)^{-2}\right]\right\}^{-3/2}}{r_i} = \frac{\left[1 + \left(\frac{v_0}{u_0}\right)^{-2}\right]^{-3/2}}{r_i};$$

therefore

$$\frac{1}{r_{ij}} = \frac{A_{ij}}{r_i} + \frac{A_{ji}}{r_j},$$

with

$$A_{ij} = \left[1 + \left(\frac{v_0}{u_0}\right)^{-2}\right]^{-3/2}.$$

Using for the mean values

$$u_0 = \langle n_i l_i | r | n_i l_i \rangle^{-1} = \frac{2Z}{3n_i^2 - l_i(l_i+1)}$$

we have, calling x_{ij} to

$$x_{ij} = \frac{v_0}{u_0} = \frac{3n_j^2 - l_j(l_j+1)}{3n_i^2 - l_i(l_i+1)}$$

that

$$A_{ij} = \left\{1 + \left[\frac{3n_j^2 - l_j(l_j+1)}{3n_i^2 - l_i(l_i+1)}\right]^2\right\}^{-3/2}.$$

When $j > i$ we are calculating the external screening parameters.

In principle, a best recipe is given below, but the deduction is longer. In the spirit of this paper, the present point of view is sufficient. Since the application of this formula is straightforward, is not necessary to give a table of these parameters.

Observe that for an orbital pair i, j we call $x_{ij} = \langle 1/r_i\rangle / \langle 1/r_j\rangle$, and $y_{ij} = (n_i/n_j)x_{ij}$. We propose the following expression, based in electrostatic considerations [25]:

$$g_{ij} = \left(\frac{1}{1+y_{ij}}\right)^{(2n_j+1)} \left[\sum_{k=0}^{2n_i-1} \frac{(2n_j+1)!}{k!(2n_j)!}\left(\frac{y_{ij}}{y_{ij}+1}\right)^k\right].$$

Appendix C

Calculation of the coefficients f_k and g_k for the relativistic case

In place of the non relativistic expressions presented in Table I, now we have [28]

$$f_k\big(l_a j_a, l_b j_b\big) = \frac{\sum(2J_i+1) f_k\big(l_a j_a, l_b j_b; J\big)}{\sum(2J_i+1)},$$

where

$$f_k\big(l_a j_a, l_b j_b; J\big) = (-1)^{J+l_a+l_b+1}(2j_a+1)(2j_b+1) \times S_{6j}(J, j_a, j_b; k, j_b, j_a) S_{6j}(1/2, j_a, l_a; k, l_a, j_a) S_{6j}(1/2, j_b, l_b; k, l_b, j_b) \big\langle l_a \big\| C^{(k)} \big\| l_a \big\rangle \big\langle l_b \big\| C^{(k)} \big\| l_b \big\rangle$$

and

$$g_k(l_a j_a, l_b j_b) = \frac{\sum(2J_i+1) g_k(l_a j_a, l_b j_b; J)}{\sum(2J_i+1)}$$

where

$$g_k(l_a j_a, l_b j_b; J) = (-1)^{J+j_b-j_a+1+k}(2j_a+1)(2j_b+1) \times S_{6j}(J, j_a, j_b; k, j_a, j_b) S_{6j}^2(1/2, j_a, l_a; k, l_b, j_b) \times \big\langle l_a \big\| C^{(k)} \big\| l_b \big\rangle^2.$$

The so called $6j$ symbols as well as the expressions for the matrix elements can be found in the book by Messiah [4].

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