An Efficient Screening Approach to be Used in Plasma Modeling and Ion-Surface Collision Experiments

J. Pomarico, D. I. Iriarte, and H. O. Di Rocco

Instituto de Física Arroyo Seco

Facultad de Ciencias Exactas, UNCPBA

Pinto 399, (7000) Tandil, Buenos Aires, Argentina

In this work we show that the Layzer theory for atomic calculations provides a theoretical framework and also a powerful computational approach if correct rules for the calculation of the screening parameters are given. Using the virial as a model for potential energy and splitting of two-body operators as sum of one-body operators, a neat definition of screening is given, satisfying diverse physically indispensable properties. Many different experimental and theoretical results are reproduced with high accuracy, with no fitting procedure involving energy levels or numerical potentials. A $C++$ code and an executable file are available upon request.

1 Introduction

The use of screened hydrogenic models (SHM) for modeling plasmas and surface ion collision experiments has been well documented in recent works [1], [2]. Different methods are available for systematic numerical calculations of atomic parameters, based on the self-consistent Hartree-Fock procedure [3] [4]. However, it is important to have an efficient analytical approach, suitable for the calculation of energies of a large number of excited states. The purpose of this article is to give explicit formulas for the average energies of arbitrary complex configurations, specially of medium to highly ionized atoms. However, also good results for neutral and almost neutral atoms are obtained.

The starting point is the Layzer's formulation of the Z-dependent theory of the many-electron atom truncated to second order [4][5] [6]. Many authors pointed out in the past that the screening approximation is not very useful; however, that statement is not right provided that correct rules are given for calculating the screening. Moreover, relativistic corrections to the energy can be easily made and configuration interaction effects can be properly considered. It is important to point out that several published screening rules produce negative ionization potentials (IP) for neutral or few ionized systems [2] [7]. Other authors obtain the screening parameters either in order to reproduce the IP's calculated by Hartree-Fock [9] [10] or by adjusting analytical potentials with numerical results [11].

In this work, no empirical adjustments are made nor negative IP's emerge from our calculations. For the screening parameters, we use the approach due to Kregar [12] generalized by one of us [13], based on the splitting of the two-body potential energy operators into the sum of effective one-body operators. Total binding energies, ionization potentials and energies of complex excited configurations are

in good or very good agreement with both, theoretical and experimental values.

In the following, we use the atomic units, where the electron charge and mass and the Dirac constant are equal to one ($e = m_e = \hbar = 1$) and the energies are measured in Hartrees: $1\ Ht \equiv 27.21\ eV$. A numerical code written in $C++$ and an executable file are available upon request.

2 A Brief Summary of the Theory

2.1 The Z^{-1} expansion

Layzer's formulation of the Z-dependent theory of the many-electron atom is the starting point of our work [4], [5] [6]. The approximate non-relativistic Hamiltonian in atomic units given by

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

Introducing the new variable $\rho = Zr$, it can be shown that the total *non-relativistic* energy can be written as the expansion [4]

$$E(N, Z) = Z^2 E_0 + Z E_1 - E_2 + Z^{-1} E_3... \quad (2)$$

where, *exactly*

$$E_0 = \langle \psi_0 | H_0 | \psi_0 \rangle = -\frac{1}{2} \sum_{i=1}^{N} \frac{1}{n_i^2} \quad (3)$$

and

$$E_1 = \langle \psi_0 | H_1 | \psi_0 \rangle. \quad (4)$$

E_1 is given by the sum of the average Coulomb energy for electron pairs $\{ij\}$ (see below, Equation 10), and therefore in terms of the Slater's integrals F^k and G^k, evaluated with hydrogenic wavefunctions with $Z = 1$ [3][14]. For non-equivalent orbitals:

$$\{ij\} = F^0(ij) - \sum_k g_k G^k(ij) \tag{5}$$

whereas for the equivalent ones:

$$\{ii\} = F^0(ii) - \sum_{k>0} f_k F^k(ii); \tag{6}$$

the coefficients g_k and f_k can be found in the above cited references.

If we restrict the expansion (2) up to E_2, the energy can be written as

$$E = -\sum_{n,l} \frac{w_{nl}(Z - \sigma_{nl})^2}{2n^2} \tag{7}$$

where w_{nl} is the number of electrons in the n, l shell and σ_{nl} is the corresponding screening parameter. Comparing Equations (2) and (7), we find that the σ_{nl}'s satisfy

$$E_1 = \sum_{n,l} \frac{w_{nl}}{n^2} \sigma_{nl} \tag{8}$$

and

$$E_2 = \sum_{n,l} \frac{w_{nl}}{2n^2} \sigma_{nl}^2. \tag{9}$$

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

$$
\begin{aligned}
E_{av} = \;& -\frac{Z^2}{2}\left\{ w_{1s} + \frac{w_{2s} + w_{2p}}{4} + \frac{w_{3s} + w_{3p} + w_{3d}}{9} + ... \right\} \\
& +Z\left\{ \frac{1}{2}\sum_i w_i(w_i - 1)\{ii\} + \sum_{i,j} w_i w_j \{ij\} \right\} - E_2
\end{aligned}
\tag{10}
$$

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

Comparing Equation 8 with Equation 10, we see that E_1 can be calculated by two ways: in terms of the Slater integrals F^k and G^k or in terms of the σ's. Indeed, if we are capable of select a good method for $\sigma's$ calculations, the two values must be nearly equal. One of the merits of this work is the algorithm used for this calculus.

2.2 The calculation and desirable properties of the screening parameters

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 one of the authors [6].

Screening parameters must have several indispensable properties: i) it must be derived theoretically in a neat form, ii) it must be dependent on Z and N, accounting for the contraction of the orbitals, iii) the sum given by Equation 8 must be *very* nearly to the value $\frac{1}{2}\sum_i w_i(w_i - 1)\{ii\} + \sum_{i,j} w_i w_j \{ij\}$; this property is verified and it is exact for $Z \rightarrow \infty$, when $\sigma \rightarrow \sigma_0$ (see below, Eq. 11), iv) the corresponding values of E_2 must follow a law of the type $E_2 \sim a + b/Z$ in order to reproduce the non-relativistic calculations using the Cowan ´s code (see below, section Results), v) it must satisfy the Z expansion

$$\sigma(Z) = \sigma_0 + \sigma_1 Z^{-1} + ... \tag{11}$$

We use the point of view introduced by Kregar generalized by one of us, based on the virial as potential energy and the splitting of the two-body potential energy operators into the sum of effective one-body operators (see below Equation 12) [12][13]. Briefly, in the zero approximation, disregarding for a moment the exchange and sub-shell corrections, as can be viewed in Equations 5 and 6, the average Coulomb energy of electron pairs is (the $i - th$ electron is equally or more strongly bound that the $j - th$ one)

$$\left\langle ij \left| \frac{1}{r_{ij}} \right| ij \right\rangle = F^0(ij) = \left\langle i \left| \frac{g_{ij}}{r_i} \right| i \right\rangle + \left\langle j \left| \frac{f_{ji}}{r_j} \right| j \right\rangle$$

so that the operator $1/r_{ij}$ can be written as

$$1/r_{ij} = g_{ij}/r_i + f_{ji}/r_j; \tag{12}$$

where g_{ij} and f_{ji} are the external and internal screening parameters, respectively. When $i = j$, $f_{ii} = g_{ii} \equiv k_{ii}$. For a given value of r, inner screening is associated with electrons at $r' \leq r$, outer screening is due to a shell of charge located at $r' > r$, adding a constant to the potential $V(r)$. As it was shown in the References [12] and [13], the two parameters can be expressed in simple form in terms of $y = Z_i n_j/Z_j n_i$; Z_i and Z_j are the screened charge seen by each electron. A neat demonstration of this result can be found in reference [13].

To add the exchange and sub-shell corrections implies the changes

$$g_{ij} \rightarrow g_{ij}(1 - \varepsilon_{ij}), \qquad f_{ji} \rightarrow f_{ji}(1 - \varepsilon_{ij})$$

and can be accounted for as the ratio between the second term of the r.h.s. of Equations 5 and 6 and F^0.

Then, taking into account the exchange interaction and subshell effects, effective charges are given by

$$Z_i = Z - \left[\sum_{j<i} q_i q_j f_{ji} + \sum_{j>i} q_i q_j g_{ij} + (q_i - 1) k_{ii} \right] \quad (13)$$

where q_i, q_j are the occupation number of the respective subshells. As (see details in [13]), in terms of $y = Z_i n_j / Z_j n_i$

$$g_{ij} = \left[\frac{1}{1+y} \right]^{3+2l_j} \sum_k a_k \left[\frac{y}{1+y} \right]^k,$$

$$f_{ji} = \left[\frac{y}{1+y} \right]^{3+2l_i} \sum_k b_k \left[\frac{1}{1+y} \right]^k, \quad (14)$$

a short and simple iterative procedure must be used for their determination. The iteration can be reduced to one or two steps if, as zero approximation, Slater-like rules are used as starting point for Z_i (see below, section 3). Explicit expressions for the coefficients a_k and b_k can be found in reference [13].

Both the Layzer and the Kregar formulations ensures exact energy levels for H-like ions in the non-relativistic regime; for He-like ions, $\sigma_0 = 5/16$, as deduced for the variational principle.

2.3 Relativistic corrections

From the Breit-Pauli Hamiltonian the relativistic shift operator H_{RS} has five terms [4]:

$$H_{RS} = H_{MC} + H_{D1} + H_{D2} + H_{OO} + H_{SSC}$$

that signifies respectively: mass correction, one- and two-body Darwin, spin-spin contact and orbit-orbit terms. Far, the more important are the two first ones, that scale as Z^4.

These energy shifts can be estimated very simple and correctly as the sum of contributions

$$E_{rel} = -\frac{\alpha^2}{2} \sum_i \frac{Z^4}{n_i^3} \left(\frac{1}{l_i + 0.5} - \frac{0.75}{n_i} - \delta(l_i, 0) \right). \quad (15)$$

The remaining terms scale as Z^3 and will be ignored in this work. An analysis is presented in the work by Safronova et al [2].

3 Results and comparison with experiments and other calculations

The comparison with experiment, in order to see the $Z-$dependence of experimental binding energies it is difficult, because there are relativistic effects dependent of Z^4 and Z^3 [8] and higher powers of Z. Therefore, we compare in first place our expansion with non-relativistic calculations. We verified that the non-relativistic values from the Cowan's code follow a dependence of the type

$$E(N, Z) = Z^2 E_0 + Z E_1 - E_2 (1 + a/Z);$$

moreover, the Cowan values with relativistic corrections are very similar to the results from the Dirac-Hartree-Fock values from Huang et al. [15]

In Table 1, we show the center-of-gravity binding energies, including relativistic corrections for ground configurations, for atoms with closed (sub)shells. As we can see, our values are in very good agreement both with Hartree-Fock ([3], [15]) and experimental ones (up to $Z = 20$, because there are not experimental results for all elements and ionization degrees).

In Fig. 1 we show the first ionization potential for the above cited elements, jointly with experimental values. The relation is of the order of two and better values can not be expected. In fact, the Layzer theory is valid, in principle, for large Z. Therefore this, the most rigorous test for our choice of the screening evaluation, is very promissory.

TABLE 1: Center of gravity binding energies (in *Ht*) including relativistic corrections for ground configurations.

Element	This Work	Theory ([15])	Experiment	$\frac{\text{This work}}{\text{Theory}}$	$\frac{\text{This work}}{\text{Experiment}}$
He	$2, 85$	$2, 86$	$2, 90$	$0, 99$	$0, 99$
Be	$14, 59$	$14, 57$	$14, 67$	$1, 00$	$0, 99$
Ne	$128, 44$	$128, 65$	$129, 05$	$0, 99$	$1, 00$
Mg	$200, 06$	$199, 89$	$200, 31$	$1, 00$	$1, 00$
Ar	$528, 78$	$528, 53$	$529, 12$	$1, 00$	$1, 00$
Ca	$680, 24$	$679, 51$	680.14	$1, 00$	$1, 00$
Zn	$1793, 04$	$1793, 84$	NA^*	$0, 99$	—
Kr	$2787, 80$	$2787, 50$	NA	$1, 00$	—
Sr	$3177, 06$	$3176, 46$	NA	$1, 00$	—
Cd	$5580, 65$	$5589, 78$	NA	$0, 99$	—
Xe	$7423, 77$	$7441, 68$	NA	$0, 99$	—

**NA: not available data.*

In Fig. 2 shows the binding energies of the internal sub-shells for Xe; our values are compared with those from the theory and the experiment [15]; as can be seen, the agreement is very good.
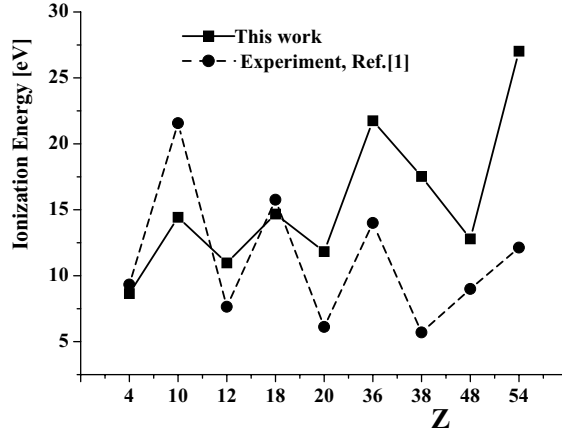

Figure 1. First ionization potentials for the elements with closed (sub)shells with Z between 1 and 54.

TABLE 2: Ionization energies (in eV) for Ar isonuclear sequence.

Z-N+1	This work	Experimental [3]	$\frac{\text{This work}}{\text{Experimental}}$
1	14, 72	15, 76	0, 93
2	27, 34	27, 63	0, 99
3	41, 20	40, 74	1, 01
4	56, 22	59, 81	0, 94
5	72, 34	75, 02	0, 96
6	89, 55	91, 01	0, 98
7	127, 75	124, 32	1, 03
8	147, 15	143, 46	1, 03
9	418, 49	422, 45	0, 99
10	480, 70	478, 69	1, 01
11	545, 47	538, 96	1, 01
12	612, 81	618, 26	0, 99
13	682, 70	686, 11	0, 99
14	755, 17	755, 75	0, 99
15	850, 34	854, 78	0, 99
16	918, 27	918, 00	1, 00
17	4121, 25	4120, 00	1, 00
18	4427, 30	4426, 00	1, 00

In Table 2 are shown the ionization energies for the Ar isonuclear sequence; the relative values are near one.

In Table 3, are shown the ionization energies of the Ar isoelectronic sequence; as it is expected, the relation between our values and the Cowan values are in excellent agreement.

TABLE 3: Ionization potentials (in eV) for the isoelectronic sequence of Ar I.

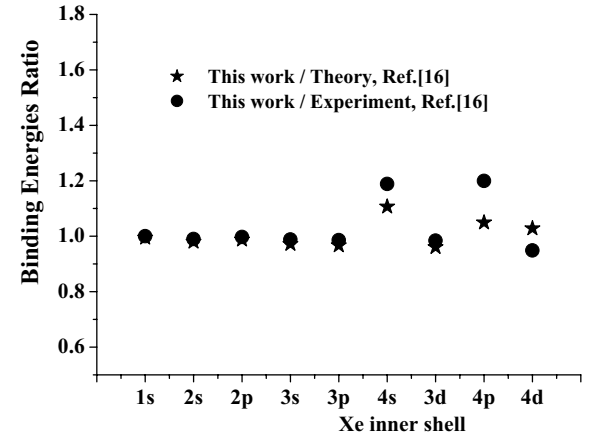| Z	This work	Experimental[3]	$\frac{\text{This work}}{\text{Experimental}}$
18	14, 73	15, 76	0, 93
19	30, 74	31, 62	0, 92
20	50, 16	50, 91	0, 99
21	72, 86	73, 47	0, 99
24	159, 93	161, 10	0, 99
25	195, 16	196, 46	0, 99
26	233, 52	235, 04	0, 99

Figure 2. Binding energies ratio for the internal subshells of Xe.

As other example of complex transitions, we show in Table 4 transitions of the type $\Phi_0\Phi_1 - 2p^{-1}3d\Phi_0\Phi_1$ as defined in Reference [2]: $\Phi_0 = 1s^22s^22p^6$, $\Phi_1 = 3d^n \ \Phi_0$. Both values are within 1%, but it must be mentioned that the approach of Safronova et al. produces very bad values (negatives!) of the ionization energies for neutral and almost-neutral elements.

TABLE 4: Transitions of the type $\Phi_0\Phi_1 - 2p^{-1}3d\Phi_0\Phi_1$ for the Xe atom compared with the values of reference[2].

N^*	This work	[2]	$\frac{\text{This work}}{[2]}$
10	4607, 80	4647	0, 992
11	4583, 12	4621	0, 992
12	4559, 12	4595	0, 992
13	4535, 80	4568	0, 993
14	4513, 20	4542	0, 994
15	4491, 31	4516	0, 995
16	4470, 13	4490	0.996
17	4449, 67	4464	0, 997
18	4429, 96	4438	0, 998
19	4411, 00	4412	1, 000

*$N=10+n$, being n the number of 3d electrons.

TABLE 5. Scaled Slater integral $G^1(4s4p)$ for the Zn isoelectronic sequence, in cm^{-1}.

Z	$Element$	$G^1(4s4p)_{our}$	$G^1(4s4p)_{HFR}$ [3]	$Ratio$
35	*Br 5+*	69636	86463	0.80
40	*Zr 10+*	101611	121566	0.83
45	*Rh 15+*	131118	153698	0.85
50	*Sn 20+*	159552	184778	0.86
55	*Cs 25+*	187504	215526	0.87
60	*Nd 30+*	215079	246241	0.87
65	*Tb 35+*	242547	277162	0.87
70	*Yb 40+*	269801	308436	0.87
74	*W 44+*	291636	333775	0.87

TABLE 6. Iteratively determined screening parameters f_{ji} (values above diagonal) and g_{ij} (values below diagonal) for electron pairs for Kr-like ions, with $Z \to \infty$. Diagonal elements (bold characters) are k_{ii}.

	1s	2s	2p	3s	3p	3d	4s	4p
1s	**0.3125**	0.6924	0.8776	0.8095	0.9299	0.9967	0.8636	0.9539
2s	0.0258	**0.3008**	0.2230	0.6055	0.6466	0.7756	0.7290	0.7630
2p	0.0149	0.3668	**0.3492**	0.6617	0.6821	0.8452	0.7650	0.7887
3s	0.0068	0.0528	0.0471	**0.2988**	0.2435	0.2164	0.5512	0.5737
3p	0.0034	0.0674	0.0635	0.3121	**0.3104**	0.2561	0.5861	0.5914
3d	0.0002	0.0562	0.0368	0.4213	0.4066	**0.3765**	0.6281	0.6391
4s	0.0026	0.0189	0.0167	0.0776	0.0746	0.0678	**0.2982**	0.2545
4p	0.0011	0.0238	0.0223	0.0900	0.0855	0.0784	0.2889	**0.2987**

3.1 Calculation of terms and energy levels

The results shown up to this point allow the calculation of the configurations average energies [3]. This may be enough for calculating, for example, the array oscillator strength, which is frequently used for statistical treatments of dielectronic recombination and collisional excitation, in plasma physics and astrophysical applications. For the calculation of the multiplet oscillator strength, the *terms* are needed and, consequently, the Slater integrals, $F^k(ij)$ and $G^k(ij)$, which scale with Z_{eff}. Thus, $F^k(ij;Z) = (Z - \sigma_{nl}) \times F^k(ij;Z=1)$, $G^k(ij;Z) = (Z - \sigma_{nl}) \times G^k(ij;Z=1)$. Values of these integrals for $Z = 1$ can be found in the book by Condon-Odabasi [14]. In particular, and as an example, $G^1(4s4p;Z=1) = 0.02444565\ Ry$.

Table 5 shows the values of $G^1(4s4p;Z) = 0.02444565(Z - \sigma_{nl})$ for the configuration $4s4p$ of $Zn - like$ with $Z = 30 - 74$. These results are compared with the relativistic Hartree-Fock approximation (HXR). It is very important take into account that in practice, in order to give a better accordance with experimental spectroscopy, the theoretical Slater integrals must be multiplied by "fudge" factors lesser than 1 [3].

3.2 Slater-like rules and constant values for the g_{ij} 's and the f_{ji} 's for $Z \to \infty$.

As stated above (see equation 11), a desirable property for σ is that for $Z \to \infty$, $\sigma \to \sigma_0$. This is verified by our approach and implies that for $Z \to \infty$, the values of f_{ij} and g_{ij} trend themselves to constant values, which we can denominate f_{ij}^∞ and g_{ij}^∞. An example is given in Table 6 for the particular case of the orbitals of Kr-like ions. These values, once known, can be stored and reliably reused either in calculations for high ionization stages or, as input parameter to reduce the number of iterations needed to achieve convergency in Eq. 14. For example, using Eq. 13, $\sigma_{1s} = 0.4973$, $\sigma_{2s} = 5.0253$, etc.

4 Conclusions

In this work we showed that the Layzer expansion is not only a theoretical framework but also a very convenient quantitative method when a correct approach for screening parameter calculations is given. We select the point of view introduced by Kregar, generalized by one of us, taking into account subshell and exchange corrections. With our approach, we always obtain positive ionization potentials, even for neutral atoms, the most difficult test. This fact is easily understood because the Layzer theory is an expansion valid for large Z. In practice, for slightly ionized atoms (as low as three times), results are very accurate accordingly with the main scope of this work: plasma modelling and collision experiments. It it important to point out that in the present work no fitting procedure is used although, if we want to extend the method for neutral and almost neutral atoms, a correction factor (very close to 1) for the $\sigma's$ could be used. Moreover, it should be mentioned that, although a set of f_{ji} and g_{ij} *constants* could be used (which we have called f_{ij}^∞ and g_{ij}^∞), better results are obtained if the f_{ji} and g_{ij} are handled as *parameters*. Our approach assure this property taking into account the variation with Z and N. However, it is true that for sufficiently ionized atoms, the use of constants provides a very good approximation, useful for plasma modeling and ion-surface collision experiments [2].

References

[1] J.G. Rubiano, R. Rodríguez, J.M. Gil, F. H. Ruano, P. Mare-tel, and E. Mínguez, J. Quant. Spectrosc. Radiat. Transfer, **72**, 575 (2002).

[2] U. I. Safronova et al., Phys. Scripta **47**, 364 (1993); M.W. Clark et al, Phys. Rev. A **47**, 3983 (1993).

[3] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley and Los Angeles, 1981).

[4] C. Froese Fischer, T. Brage, and P. Jonsson, *Computational Atomic Structure* (IoP Publishing, Bristol, 1997).

[5] D. Layzer, Ann. Phys. **8**, 271 (1959); D. Layzer et al., Ann. Phys. **29**, 101 (1964).

[6] H.O. Di Rocco, Il Nuovo Cimento D **20**, 131 (1998).

[7] G. Faussurier, C. Blancard, and A. Decoster, J. Quant. Spectrosc. Radiat. Transfer **58**, 233 (1997).

[8] D. Layzer, Int. J. Quantum Chemistry **1 S**, 45 (1967).

[9] R. M. More, J. Quant. Spectrosc. Radiat. Transfer **27**, 345 (1982).

[10] F. Perrot, Phys. Scripta **39**, 332 (1989).

[11] P. Martel, J.G. Rubiano, J.M. Gil, L. Doreste, and E. Mínguez, J. Quant. Spectrosc. Radiat. Transfer, **60**, 623 (1998).

[12] M. Kregar, Phys. Scripta **29**, 438 (1984), Phys. Scripta **31**, 246 (1985).

[13] H. O. Di Rocco, Braz. J. Phys. **22**, 227 (1992).

[14] E. U. Condon and H. Odabasi, *Atomic Structure* (University Press, Cambridge, 1980).

[15] K.-N. Huang et al., At. Data Nucl. Data Tables **18**, 249 (1976).

[16] H. O. Di Rocco, Revista Mexicana de Física **48**, 76 (2002).