

The Screened Hydrogenic Model: Analytical and Empirical Expressions for Effective Charges

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A Screened Hydrogenic Model (SHM) is formulated in closed form. Analytical effective charges for wave functions, radial integrals for arbitrary multipole order, and a new method for semiempirical calculations are presented. The algorithm for the obtention of screening constants is derived for hydrogenic orbitals, based on the splitting of the two body potential energy operators by the sum of effective one body operators. As an example, relevant coefficients for different electron pairs are presented. Further, a general formula for calculating hydrogenic radial integrals for arbitrary multipole order is found. The result is valid when initial and final effective charges are different. It is also valid when the principal and/or orbital quantum numbers are not equal. A new expression for effective charges calculated from experimentally established levels is derived which, for non penetrating orbits, approaches the classic definition $Z_{\text{eff}} = n[(E_{\infty} - E_{n_i})/R]^{1/2}$. In general the results are very close to effective charges given by MCDF calculations and to the closed expressions also developed in this paper. Therefore, our formulation permits: (a) to calculate analytic screening parameters in closed form; (b) to calculate a new type of empirical effective charges from experimental levels; (c) to calculate transition integrals to any multipole order; (d) to calculate diagonal or off-diagonal matrix elements $\langle n_i, \ell_i | r^{\gamma} | n_f, \ell_f \rangle$; for the special cases $n_i = n_f$ and $\ell_i = \ell_f$, mean values are obtained, and when $\ell_i = \ell_f \pm 2$ anisotropies of the core polarizability can also be calculated. Furthermore, when $\gamma = 0$, overlap integrals are automatically performed. Comparison with experiments and numerical self-consistent calculations are presented, and the reliability and degrees of generality of our methods are discussed.

I. Introduction

Hydrogenic radial wave functions and matrix elements have been considered for a long time. For the former, rules for the estimation of the screening from empirical and/or SCF calculations were given by different authors and still such orbitals are particularly useful when preliminary computations are required. Analogously, the study of hydrogenic radial matrix elements $\langle n' \ell' | r^{\gamma} | n \ell \rangle$ using non relativistic radial wave functions have been widely considered^{1,2}, in general using the nuclear charge Z to describe both the initial and the final states of the atomic electron.

There is a wide literature about effective charges, but for our purposes we distinguish between screened Slater type and screened hydrogenic type orbitals. For Slater orbitals, empirical rules³ or direct minimization of the energies^{4,5} can be used for the estimation of screening parameters. A simple rule for the calculation of analytic atomic shielding parameters as functions of the quantum number (n, ℓ) of each orbital, was given

by Bessis and Bessis⁶ and the results follow the trends given by Slater and Burns rules⁷, and Clementi SCF calculations^{4,5}.

In the Section II of this paper, we treat Screened Hydrogenic Type Orbitals following the approach given by Kregar^{8,9}. In these works, the author arrived to a method for the obtention of analytic effective charges but, from these articles, it is not possible to derive screening parameters for other configurations although the results can be repeated by brute force calculations. Here we present a derivation of the algorithm for an easy obtention of screening constants and an explicit example to show how to design a simple computation program for automatic calculations.

For the matrix elements, we remember that Gordon¹⁰ found a general formula in terms of integrals containing confluent hypergeometric functions¹¹ and the solution of $\langle n', \ell - 1 | r | n \ell \rangle$ for $n \neq n'$ can be found in advanced textbooks in terms of two hypergeometric functions^{1,12}, always for $Z_i = Z_f = 1$. In a recent paper, Shertzer¹³ obtained diagonal and off-diagonal matrix elements $\langle n, \ell | r^{\gamma} | n, \ell' \rangle$ generalizing the results of Bockasten¹⁴ and Drake and Swainson¹⁵,

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which calculated expectation values for $-16 \leq \gamma \leq 13$. It must be noted that all results are valid for equal Z 's and n 's. Except for the most simple cases, the reported expressions are long and tedious. A more recent article¹⁶ presents an algebraic approach to matrix elements; recurrence relations and closed formulas for hydrogenlike wave functions were presented for equal Z 's.

On the other hand, the screened hydrogenic model (SHM) describes the atom by single-particle hydrogenic wave functions using two different effective charge parameters Z_i and Z_f , for the initial and the final states, respectively.

Whereas Khandelwal² writes about the usefulness of the SHM for isoelectronic sequences *if and when the numerical values of the parameters Z_i and Z_f become available*, Kregar^{8,9} gives an analytical approach (generalized in the first part of the present paper) to find the effective charges; the validity of the SHM approach and the surprisingly close relation with the Hartree-Fock model, were analyzed by Kregar in the above mentioned articles.

Few authors^{17,18} have given general formulas for the discrete-discrete (and discrete-continuum) transitions within the SHM. Menzel¹⁷ expressed the bound-bound formulas in terms of *two* hypergeometric functions, whereas Fitchard¹⁸ used only *one* hypergeometric function. Unfortunately, the two published versions of this work^{2,19} are not in mutual accordance, and do not give the correct results.

In Section III, we give a general closed expression for the screened hydrogenic radial integrals for arbitrary multipole order, effective charges, and principal and orbital quantum numbers without using the hypergeometric functions at all. Finally, in Section IV we consider different definitions of effective charges and their mutual relation. Effective charges Z_i and Z_f can be found from experimentally established energy levels or extrapolated along isoelectronic sequences. As a consequence of practical interest, a new semiempirical method for routine calculation of radial multipole matrix elements can be implemented, analogous to the well known Coulomb approximation²⁰.

II. Closed expressions for obtaining analytic screening parameters

IIa. Theory

Using the virial

$$w = \sum r_i F_i = -(1/2) \sum r_i \nabla_i W_p(r_0, \dots, r_i, \dots, r_N) \quad (1)$$

as the atomic model potential energy operator, the atomic Hamiltonian describing strongly, interacting electrons in a central nuclear field

$$H = \sum (p_i^2/2m - Z/r_i) + \sum \sum 1/r_{ij} \quad (2a)$$

is transformed into the Hamiltonian

$$H^0 = \sum H_i^0 = \sum (p_i^2/2m - Z_i/r_i) \quad (2b)$$

that can be interpreted as describing quasi-electrons with effective charges $q_i^{\text{eff}} = -Z_i/Z$, moving independently in the non-reduced central Coulomb field Z/r_i ^{8,9}.

The validity of this scaled hydrogenic description is explained in the above mentioned papers, but for our purposes it is sufficient to say that the solutions of eq. (2) the hydrogen-like single particle wave functions

$$\psi(i) = R_{nl}(Z_i r_i) Y_l^m(\theta_i, \phi_i) \quad (3)$$

are equal (within the central field approximation and neglecting relativistic and exchange effects) to the corresponding Hartree-Fock wave functions⁸.

In this approach, the interaction energy of the electron pair s and t (the s^{th} electron being equally or more strongly bound than the t^{th} electron) is written

$$\langle st | 1/r_{st} | st \rangle = \langle s | g_{st}/r_s | s \rangle + \langle t | f_{ts}/r_t | t \rangle \quad (4)$$

so that the two-body potential energy operator $1/r_{st}$ is replaced by the sum of effective one-body operators

$$1/r_{st} = g_{st}/r_s + f_{ts}/r_t. \quad (5)$$

In eqs. (4) and (5) g_{st} and f_{ts} are, respectively, the external and internal screening parameters, to be determined from

$$g_{st} = (n_s^2/Z_s) \int_0^{r_t \rightarrow \infty} dq_t \int_{r_t}^{\infty} dq_s/r_s, \quad (6a)$$

and

$$f_{ts} = (n_t^2/Z_t) \int_0^{r_s \rightarrow \infty} dq_s \int_{r_s}^{\infty} dq_t/r_t, \quad (6b)$$

After neglecting the exchange interaction and subshell effects, the effective charges are given by

$$(6c)$$

where q_i, q_j are the occupation number of the respective (sub)shells.

Since screening parameters are determined in terms of effective charges an iterative procedure must be used for their determination. This procedure is short and simple if initial values of g_{st} and f_{ts} are determined according to Slater³ Bessis⁶ or Kregar²¹ rules.

Introducing the parameter

$$y = Z_s n_t / Z_t n_s, \tag{7}$$

and using the hydrogen-like wave functions given by eq. (3) to express dq in eqs. (6a) and (6b), the screening parameters g_s and f_t can be expressed in polynomial form as a function of variables $[y/(1+y)]$ and $[1/(1+y)]$ ⁹.

From the previous works^{8,9} it is not possible to derive screening parameters for more complex configurations and the published results can be repeated only by laborious direct integration of the above mentioned equations.

In this paper we arrive to a simple formulation of the Kregar approach that can be programmed in a personal computer.

IIIb. The screening parameters in closed forms

Eqs. (6a) and (6b) are formally similar and can be calculated using the expressions for radial wave functions for hydrogenic atoms²²

$$dq_s/r_s = C_s (Z_s r/n_s)^{2\ell_s+1} \exp(-2Z_s r/n_s) \times [F(-n_s + \ell_s + 1, 2\ell_s + 2, 2Z_s r/n_s)]^2, \tag{8}$$

where

$$C_s = \frac{2^{\ell_s+2} (n_s + \ell_s)! Z_s^2}{n_s^3 [(2\ell_s + 1)!]^2 [(n_s - \ell_s - 1)!]}, \tag{9}$$

and

$$F(\alpha, \gamma, x) = (1 + (\alpha/\gamma)x + [\alpha(\alpha + 1)/\gamma(\gamma + 1)](x^2/2!) + \dots), \tag{10}$$

is the confluent hypergeometric function.

It is straightforward to show that we must solve $2(n_s - \ell_s) - 1$ integrals of the type

$$e^{-2kr} \int_r^\infty (kr)^a e^{-2kr} dr. \tag{11}$$

Explicitly, we obtain

$$\int_r^\infty (Z_s r/n_s)^a \exp(-2Z_s r/n_s) dr = (n_s/2^{\alpha+1} Z_s) \exp(-2Z_s r/n_s) \sum_{j=0}^{\alpha} \frac{a!}{j!} \left[\frac{2Z_s r}{n_s} \right]^j \tag{12}$$

where $a = 2\ell_s + 1, 2\ell_s + 2, \dots, 2n_s - 1$.
Therefore

$$\int_r^\infty dq_s/r_s = (C_s n_s / 2Z_s) \exp(-2Z_s r/n_s) \times \sum_a \sum_{j=0}^{\alpha} \frac{a!}{2^a j!} (2Z_s r/n_s)^j. \tag{13}$$

Now we must solve $2(n_t - \ell_t) - 1$ definite integrals of the type

$$C_t \int_0^\infty (Z_t r/n_t)^b \exp(-2Z_t r/n_t) \left\{ \int_r^\infty dq_s/r_s \right\} dr, \tag{14}$$

where

$$C_t = \frac{2^{\ell_t+2} (n_t + \ell_t)! Z_t}{n_t^2 [(2\ell_t + 1)!]^2 (n_t - \ell_t - 1)!}, \tag{15}$$

and $b = 2\ell_t + 2, 2\ell_t + 3, \dots, 2n_t$.

Multiplying by (n_s^2/Z_s) , the final result obtained for g_{st} is

$$g_{st} = \frac{n_s^3 n_t}{2Z_s^2 Z_t} \sum_a \sum_{j=0}^{\alpha} \sum_{i=0}^{\beta} \frac{C_s^a C_t^b a! b!}{2^{a+b}} \binom{1}{1+y}^{b+1} \frac{(b+j)!}{b! j!} \left(\frac{y}{1+y} \right)^j \tag{16}$$

where the successive values of C_s^a are: $C_s, 4C_s(\alpha/\gamma), 4C_s \{ \alpha(\alpha + 1)/[\gamma(\gamma + 1)] + \alpha^2/\gamma^2 \}$, etc. (See eqs. (8), (9) and (10)) and similar results are obtained for the C_t^b s.

A straightforward analysis shows that: (a) $[1/(1+y)]^{(2\ell_t+3)}$ is a common factor; (b) the maximum exponent of y is $(2n_s - 1)$ and (c) the remanent exponent of $[1/(1+y)]$ is $[2(n_s + n_t - \ell_t) - 3]$.

On the other hand, we can write the previous expression as

$$g_{st} = \sum_k A_k [y/(1+y)]^k, \tag{17}$$

where $k = 0, 1, \dots, 2(n_s + n_t - \ell_t) - 3$ and the parameters A_k s are calculated after comparison between expressions (16) and (17) as it is shown in the following example for the configurations $2s - 3s$.

IIc. An example: 2s - 3s pair

For the pair 2s - 3s, $a = 1, 2, 3$, $b = 2, 3, 4, 5, 6$; $C_s^a = 1, -2, 1$ and $C_t^b = 4/3, -16/3, 64/9, -32/9, 16/27$. For the successive values of b , evaluation of eq. (16) gives

$$\begin{aligned} b = 2 & : 1 + 3y/(1+y) - 6y^2/(1+y)^2 \\ & \quad + 30y^3/(1+y)^3 \\ b = 3 & : -6/(1+y) - 24y/(1+y)^2 + \\ & \quad 60y^2/(1+y)^3 - 360y^3/(1+y)^4 \\ b = 4 & : 16/(1+y)^2 + 80y/(1+y)^3 \\ & \quad - 240y^2/(1+y)^4 + 1680y^3/(1+y)^5 \\ b = 5 & : -20/(1+y)^3 - 120y/(1+y)^4 \\ & \quad + 420y^2/(1+y)^5 - 3360y^3/(1+y)^6 \\ b = 6 & : 10/(1+y)^4 + 70y/(1+y)^5 \\ & \quad - 280y^2/(1+y)^6 + 2520y^3/(1+y)^7 \end{aligned}$$

where the common factor $[1/(1+y)]^3$ was dropped.

Taking $(1+y)^7$ as the common denominator, we have

$$\begin{aligned} g_{st} & = \{[1/(1+y)]^3[(1+y)^7 \\ & \quad + (3y-6)(1+y)^6 + \dots + 2520y^3]\}/(1+y)^7 \\ & = \{[1/(1+y)]^3[1 + 10y - 47y^2 + 560y^3 - 953y^4 \\ & \quad + 726y^5 - 215y^6 + 28y^7]\}/(1+y)^7. \end{aligned} \quad (18)$$

On the other hand, evaluation of eq. (17) gives

$$\begin{aligned} g_{st} & = \{[1/(1+y)]^3[A_0 + y(7A_0 + A_1) \\ & \quad + y^2(21A_0 + 6A_1 + A_2) + \dots \\ & \quad \dots + y^7(A_0 + A_1 + \dots + A_7)]\}/(1+y)^7. \end{aligned} \quad (19)$$

Comparison between eqs. (18) and (19) gives the final evaluation of eq. (16) which is given by

$$g_{2s-3s} = [1/(1+y)]^3 \sum_0^7 a_k [y/(1+y)]^k \quad (20)$$

where a_k assumes the values 1, 3, -86, 910, -3810, 7490, -7000, 2520 which coincides with the results previously published⁶.

IIId. Results

According to the above analysis for g_{st} (and for f_{ts}) the external and internal screening parameters are given, as a function of $y = Z_s n_t / Z_t n_s$, by

$$g_{st} = [1/(1+y)]^{3+2\ell_t} \sum_{k=0}^{2(n_s+n_t-\ell_t)-3} a_k [y/(1+y)]^k, \quad (21a)$$

and

$$f_{ts} = [y/(1+y)]^{3+2\ell_t} \sum_{k=0}^{2(n_s+n_t-\ell_t)-3} b_k [1/(1+y)]^k. \quad (21b)$$

Calculated coefficients a_k and b_k for electron pairs beyond those reported by Kregar⁵ are given in Tables 1 and 2. If both electrons belong to the same subshell we have $y = 1$ and then $g_{ii} = f_{ii}$ and they are denoted by k_{ii} . Screening parameters k_{ii} for ns^2 , np^2 and nd^2 configurations are given in Table 3.

III. Screened Hydrogenic radial integrals for arbitrary multipole order

As it is well known²³, the normalized hydrogenic radial functions can be written as a polynomial of degree $(n - \ell - 1)$ as

$$P_{n\ell}(r) = C_{n\ell} e^{-Zr/n} r^{\ell+1} \sum_{k=0}^{n-\ell-1} \frac{(-2Z/n)^k r^k}{k!(2\ell+1+k)!(n-\ell-1-k)!}, \quad (22)$$

where

$$C_{n\ell} = \{[2^{2\ell+2} Z^{2\ell+3} (n-\ell-1)!(n+\ell)!/n^{2\ell+4}]^{1/2}\}. \quad (22')$$

As we must solve $\langle n_1 \ell_1 | r^\gamma | n_2 \ell_2 \rangle$, γ being the multipole order ($y = 1$ for dipole, 2 for quadrupole, etc.), it is straightforward to show that the product of the two radial functions and r^γ is of the form

$$\begin{aligned} P_1(r) r^\gamma P_2(r) & = C_1 C_2 r^{\ell_1 + \ell_2 + 2 + \gamma} \\ & \quad \sum_{t=0}^{NL} \left\{ \sum_{j=0}^{n_2 - \ell_2 - 1} b_j a_{t-j} r^t \right\} \\ & \quad \exp\{-[n_2 Z_1 + n_1 Z_2]/n_1 n_2 r\}, \end{aligned} \quad (23)$$

Table I - Coefficients a_k in equation (21a).

| | k=0 | k=1 | k=2 | k=3 | k=4 | k=5 | k=6 | k=7 | k=8 | k=9 | k=10 | k=11 |
|------|-----|-----|------|------|---------|---------|----------|---------------------|---------------------|--------------------|---------------------|-----------|
| 1s4s | 1 | 3 | -75 | 385 | -975 | 1365 | -1015 | 315 | | | | |
| 1s4p | 1 | 5 | -60 | 210 | -315 | 189 | | | | | | |
| 2s4s | 1 | 3 | -156 | 2320 | -14880 | 50400 | -98140 | 110880 | -67725 | 17325 | | |
| 2s4p | 1 | 5 | -135 | 1785 | -8925 | 20979 | -23625 | 10395 | | | | |
| 2p4s | 1 | 3 | 6 | 10 | -1470 | 8610 | -22050 | 29610 | -20475 | 5775 | | |
| 2p4p | 1 | 5 | 15 | 35 | -1225 | 4599 | -6615 | 3465 | | | | |
| 3s4s | 1 | 3 | -237 | 5815 | -63975 | 389865 | -1432096 | 3295216 | -4781701 | 4250401 | -2113651 | 450450 |
| 3s4p | 1 | 5 | -210 | 4760 | -45185 | 226359 | -633150 | 990990 | -810810 | 270270 | | |
| 3p4s | 1 | 3 | 6 | 10 | -5925 | 72345 | -380205 | 1090846 | -1839601 | 1824901 | -987525 | 225225 |
| 3p4p | 1 | 5 | 15 | 35 | -5110 | 50274 | -198765 | 384615 | -363825 | 135135 | | |
| 3d4s | 1 | 3 | 6 | 10 | 15 | 21 | -13209 | 79569 | -200340 | 258720 | -169785 | 45045 |
| 3d4p | 1 | 5 | 15 | 35 | 70 | 126 | -10773 | 40887 | -56133 | 27027 | | |
| 4s4p | 1 | 5 | -285 | 9135 | -128520 | 1005984 | -4746000 | 1.399×10^7 | -2.58×10^7 | 2.90×10^7 | -1.80×10^7 | 4729724 |

Table II - Coefficients b_k in equation (21b).

| | k=0 | k=1 | k=2 | k=3 | k=4 | k=5 | k=6 | k=7 | k=8 | k=9 | k=10 | k=11 | k=12 |
|------|-----|-----|------|------|--------|--------|----------|---------------------|---------------------|--------------------|---------------------|--------------------|---------------------|
| 4s1s | 1 | 3 | -18 | 210 | -855 | 1995 | -2380 | 1260 | | | | | |
| 4s2s | 1 | 5 | -450 | 7350 | -3990 | 11970 | -17850 | 11550 | | | | | |
| 4s2p | 1 | 5 | -45 | 735 | -3990 | 11970 | -17850 | 11550 | | | | | |
| 4s3s | 1 | 3 | -178 | 4530 | -51915 | 334495 | -1314460 | 3262140 | -5121901 | 4920300 | -2633399 | 600600 | |
| 4s3p | 1 | 5 | -145 | 3395 | -32830 | 172410 | -517650 | 889350 | -808500 | 300300 | | | |
| 4s3d | 1 | 7 | -84 | 1764 | -11970 | 43890 | -78540 | 60060 | | | | | |
| 4p1s | 1 | 3 | 6 | 10 | -135 | 651 | -1092 | 756 | | | | | |
| 4p2s | 1 | 3 | 6 | 10 | -1185 | 10101 | -35952 | 65016 | -58590 | 20790 | | | |
| 4p2p | 1 | 5 | 15 | 35 | -630 | 3906 | -8190 | 6930 | | | | | |
| 4p3s | 1 | 3 | 6 | 10 | -5035 | 67151 | -388612 | 1233877 | -2297821 | 2499421 | -1469161 | 360360 | |
| 4p3p | 1 | 5 | 15 | 35 | -3897 | 41706 | -182490 | 399630 | -429660 | 180180 | | | |
| 4p3d | 1 | 7 | 28 | 84 | -1890 | 14322 | -36036 | 36036 | | | | | |
| 4p4s | 1 | 3 | 5 | 10 | -14835 | 275751 | -2276022 | 1.072×10^7 | -3.15×10^7 | 6.07×10^7 | -7.40×10^7 | 5.69×10^7 | -2.49×10^7 |

Table III - Screening parameters $k_{nl,nl}$ for hydrogenic wavefunctions

| n | 1 | 2 | 3 | 4 | 5 |
|-------------|--------|--------|--------|--------|--------|
| $k_{ns,ns}$ | 0.3125 | 0.3010 | 0.2988 | 0.2982 | 0.2979 |
| $k_{np,np}$ | | 0.3633 | 0.3234 | 0.3114 | 0.2532 |
| $k_{nd,nd}$ | | | 0.3872 | 0.3414 | |

where $NL \equiv n_1 + n_2 - (\ell_1 + \ell_2 + 2)$, the b_j 's and the a_{t-j} 's are the appropriate coefficients of $P_2(r)$ and $P_1(r)$ respectively. The integrals can be calculated using elementary methods and the result is given by

$$\int_0^\infty P_1(r)r^\gamma P_2(r)dr = \left\{ \frac{2^{2(\ell_1 + \ell_2 + 2)} Z_1^{2\ell_1 + 3} Z_2^{2\ell_2 + 3} (n_1 - \ell_1 - 1)!(n_2 - \ell_2 - 1)!(n_1 + \ell_1)!(n_2 + \ell_2)!}{n_1^{2\ell_1 + 4} n_2^{2\ell_2 + 4}} \right\}^{1/2} \times [n_1 n_2 / (n_2 Z_1 + n_1 Z_2)]^{\ell_1 + \ell_2 + 3 + \gamma} \times \sum_t \left\{ \sum_j \frac{(-2)^t Z_2^j Z_1^{t-j} (\ell_1 + \ell_2 + t + 2 + \gamma)!}{n_2^j n_1^{t-j} j!(t-j)!} \right. \\ \left. \times \frac{[n_1 n_2 / (n_2 Z_1 + n_1 Z_2)]^t}{(2\ell_2 + 1 + j)!(n_2 - \ell_2 - 1 - j)!(2\ell_1 + 1 + t - j)!(2\ell_1 + t - j)!(n_1 - \ell_1 - 1 - t + j)!} \right\}, \quad (24)$$

where $0 \leq t \leq [n_1 + n_2 - (\ell_1 + \ell_2 + 2)]$ and $\max(0; t + 1 + \ell_1 - n_1) \leq j \leq \min(t; n_2 - \ell_2 - 1)$.

We remark some merits of using Eq. (24): first, we need no hypergeometric function; second, ℓ_1 (or ℓ_2) indicates indistinctly the lesser or the greater angular momentum. Furthermore, unlike other formulas [12] Eq. (3) is valid for $Z_1 = Z_2 = Z$ and $n_1 = n_2$, reproducing the well known result

$$\int_0^\infty P_{n,\ell}(r)r P_{n,\ell-1}(r)dr = (-1)^{\ell-1} (3n/2Z) [\ell(n^2 - \ell^2)]^{1/2}, \quad (24')$$

and also reproduces the results of Shertzer¹³, Misuzhima²⁴ and Morales¹⁶ for diagonal and off-diagonal matrix elements.

IV. Empirical effective charge; a new definition

Screening constants for many electron atoms are important for the calculation of energy eigenvalues, diamagnetic susceptibilities, Born cross sections for elastic scattering of fast charged particles²⁵, inner-shell ionization²⁶, etc.

At least two different notions of effective charges (and screening constants) can be mentioned in the context of Screened Hydrogenic Models (leaving aside Slater, Thomas-Fermi or similar rules). One of them is related with the experimental energy levels, and the other with the behavior of the wave functions.

In the first case, we denote by $Z_{\text{eff}}^{\text{old}}$ the effective charge as defined by²⁷

$$Z_{\text{eff}}^{\text{old}} = (Z - S_{n\ell} = n[(E_\infty - E_{n\ell})/R]^{1/2} \quad (25a)$$

where Z is the atomic number, $S_{n\ell}$ is the screening constant, E_∞ is the energy ionization limit, and R is the Rydberg constant. This type of effective charges is very useful in the discussion of isoelectronic sequences²⁷.

The second concept of effective charges is concerned with wave functions: these are effective Z 's such that a hydrogen-like wave function using this Z_{eff} , would give as good a fit as possible to the calculated SCF wave function, and have been applied for example in the Z expansion approximation for the calculation of transition probabilities²⁸.

If $R_{n\ell}$ is a typical length, for example $R_{n\ell} \equiv \langle r_{n\ell} \rangle = \int_0^\infty r P_{n\ell}^2(r)dr$, and, if for a given (n, ℓ) the radial wave functions for different atomic numbers Z are similar (a property that can be called the *rigidity* of hydrogenic wave functions) the scaling property $R_{n\ell}^{1/2} P_{n\ell}(r) = f(r/R_{n\ell})$ holds²⁹. Further more if $\langle r_{\text{H}} \rangle$ is the value of $R_{n\ell}$ for the wave function of the hydrogen atom, then in the Coulomb field of a point charge $(Z - S_{n\ell})$ is

$$R_{n\ell} = \langle r_{\text{H}} \rangle / (Z - S_{n\ell}). \quad (25b)$$

Similarly, if I denotes a radial integral, then

$$I = I_{\text{H}} / (Z - S_{n\ell}). \quad (25c)$$

The rigidity of the hydrogenic wave functions is supported, for example, by the calculation of the total binding energy of Argon by Kregar⁸ using the SHM where the difference between the calculated and the experimental values is $\simeq 2 \times 10^{-4}$.

Effective charges can be easily calculated from Eq. (25a) if tables of experimentally established levels are at hand, whereas theoretical screening constants can be available after self-consistent calculations³⁰. The two values are very different, and that is the reason why it is not possible to use effective charges derived from a level scheme for radial integrals calculations within the SH model. As an example, we show in Table 4 effective charges for Xe II and Ne III, where the columns indicates respectively, the configuration, Z_{eff} given by

Eq. (25a), the Z_{eff} 's obtained from MCDF calculations, the effective quantum number, and Z_{eff} as given by Eqs. (27) or (29).

Table IV - Effective charges for Xe II and Ne III average configurations

| Configuration | Z_{eff} (Eq. (25a)) | Z_{eff} MCDF | n^* | Z_{eff} (Eq. (27)) |
|---------------|---------------------------------|--------------------------|-------|--------------------------------|
| Xe II 6s | 4.951 | 11.050 | 2.424 | 12.256 |
| 6p | 4.276 | 8.901 | 2.805 | 9.143 |
| 5d | 3.933 | 8.418 | 2.542 | 7.735 |
| 7s | 4.039 | 7.711 | 3.466 | 8.156 |
| Ne II 3d | 3.047 | 3.184 | 2.954 | 3.095 |

The discrepancy between the effective Z 's given by Eqs. (25a) and (25b) was considered also by Slater³ and explained in terms of inner and outer shielding. These are now related, of course, with the external and internal screening parameters introduced in the Section II. However, a very simple connection between the two values of Z_{eff} can be made, that permits the same usefulness of the concept of effective charge to isoelectronic sequences, and in addition it serves as estimation of wave functions. MCDF calculations using the code of I.P. Grant, indicates that

$$\langle r_{n\ell} \rangle \approx [3n^{*2} - \ell(\ell + 1)]/2Z_0 \quad (26)$$

where n^* is the effective quantum number, and $Z_0 = Z - N + 1$ is the core net charge. In Table 5 we indicate $\langle 1/r \rangle$, $\langle r \rangle$ and $\langle r^2 \rangle$ values for Xe II both from Eq. (26) and from MCDF calculations.

Table V - Expectation values (r^γ) for Xe II

| Configuration | Method | $\langle 1/r \rangle$ | $\langle r \rangle$ | $\langle r^2 \rangle$ |
|---------------|----------|-----------------------|---------------------|-----------------------|
| 5d | Eq. (24) | 0.309 | 4.46 | 22.56 |
| | MCDF* | 0.306 | 4.10 | 19.61 |
| 7s | Eq. (24) | 0.166 | 8.97 | 90.42 |
| | MCDF' | 0.135 | 9.53 | 101.10 |

*From Ref. 40.

Defining now $Z_{\text{eff}}^{\text{new}}$ such that

$$\langle r_{n\ell} \rangle = [3n^2 - \ell(\ell + 1)]/2Z_{\text{eff}}^{\text{new}}, \quad (27)$$

means that expressing the energies in Rydberg units we obtain

$$Z_{\text{eff}}^{\text{new}} = \left\{ \frac{[3n^2 - \ell(\ell + 1)](E_\infty - E_{n\ell})}{3Z_0^2 - \ell(\ell + 1)(E_\infty - E_{n\ell})} \right\} Z_0, \quad (28)$$

and taking into account that $\ell(\ell + 1) \ll 3n^2$ and $\ell(\ell + 1)(E_\infty - E_{n\ell}) \ll 3Z_0^2$, then

$$Z_{\text{eff}}^{\text{new}} \cong n^2(E_\infty - E_{n\ell})/Z_0, \quad (29)$$

which leads to

$$Z_{\text{eff}}^{\text{new}} \cong (n/n^*)Z_{\text{eff}}^{\text{old}}. \quad (30)$$

We note that the effective charges, derived from level values, are very close to those from MCDF or Scaled HF calculations; indeed, for non penetrating orbits $n \cong n^*$ and $Z_{\text{eff}}^{\text{new}} \cong Z_{\text{eff}}^{\text{old}}$. Even for the highly penetrating ground orbitals 5p of Xe II, $Z_{\text{eff}}^{\text{new}} \cong Z_{\text{eff}}^{\text{MCDF}}$, the results are relatively close (19.2 vs 17.6) whereas $Z_{\text{eff}}^{\text{old}}$ has a value (= 6.2).

Table VIa - Absolute oscillator strengths for 5s-5p II transitions

| λ (Å) | $f(\text{exp})$ | $f(\text{Coul})$ | $f(\text{presentwork})$ | Ref. |
|---------------|-----------------|------------------|-------------------------|------|
| 4832 | 0.585 | 0.307 | 0.390 | 41 |
| 4739 | 0.546 | 0.250 | 0.318 | 41 |
| 4619 | 0.518 | 0.409 | 0.519 | 41 |
| 4615 | 0.495 | 0.341 | 0.433 | 41 |
| 4431 | 0.577 | 0.345 | 0.438 | 41 |
| 4300 | 0.114 | 0.116 | 0.147 | 41 |
| 4292 | 0.216 | 0.216 | 0.274 | 41 |
| 4154 | 0.095 | 0.071 | 0.090 | 41 |

Table VIb - Absolute transition probabilities for Xe II transitions

| λ (Å) | $A(\text{exp})^*$ | $A(\text{Coul.})$ | $A(\text{IC-HFS})^{**}$ | (Present work) |
|---------------|-------------------|-------------------|-------------------------|----------------|
| 5438 | 0.801 | 0.835 | 1.016 | 0.721 |
| 5419 | 0.406 | 0.888 | 1.018 | 0.766 |
| 5372 | 0.665 | 0.911 | 1.004 | 0.786 |
| 5339 | 0.457 | 0.884 | 0.868 | 0.763 |
| 5292 | 0.561 | 0.905 | 0.460 | 0.777 |
| 5261 | 0.723 | 0.988 | 1.018 | 0.853 |
| 5191 | 0.606 | 0.958 | 1.121 | 0.827 |
| 4921 | 0.981 | 1.102 | 1.399 | 0.950 |
| 4887 | 0.504 | 1.117 | 0.557 | 0.966 |
| 4883 | 0.688 | 1.119 | 1.101 | 0.967 |
| 4844 | 0.607 | 1.154 | 1.475 | 0.996 |
| 4603 | 0.921 | 1.373 | 1.356 | 1.185 |

*From Ref. 42; **From Ref. 34.

Table VII - Summary of measured and calculated values of the lifetimes of the Kr II $5p\ ^4D_{7/2}$ and the Xe II $6p\ ^4D_{7/2}$ levels. IC: intermediate coupling; HFS: Hartree-Fock-Slater; BD: Bates-Damgaard; PP: parametric potential; HFRC: Hartree-Fock with relativistic corrections; BF: beam-foil; PEE: pulsed electron excitation; CPC: cascade-photon coincidence; BL: beam-laser; BG: beam-gas; PLE: pulsed-laser excitation.

| Ion | Source | Method | Reference | Lifetime (ns) | |
|-------|----------------|--------------------|-------------------|---------------|---------------|
| Kr II | | <u>Theory</u> | | | |
| | | Marantz et al. | IC-HFS | 35 | 6.8 ± 1.4 |
| | | Koozekanani et al. | IC-HFS | 35 | 6.08 |
| | | El Sherbini | IC-BD | 35 | 5.6 |
| | | Spector-Garpman | IC-HFS | 34 | 6.1 |
| | | Helbig | LS-BD | 35 | 7.13 |
| | | Fonseca-Campos | LS-BD | 35 | 6.9 |
| | | Present work | Scaled Hydrogenic | | 7.63 |
| | | | <u>Experiment</u> | | |
| | | Delgado et al. | PEE | 35 | 8.50 |
| | | Donnelly et al. | PEE | 35 | 7.70 |
| | | Mohamed et al. | CPC | 35 | 7.22 |
| | | Blagoev | PEE | 35 | 8.80 |
| | | Fonseca Campos | PEE | 35 | 7.00 |
| | | Ward et al. | BL | 35 | 7.04 |
| | Le Mond et al. | BG | 35 | 8.0 | |
| | Schade et al. | PLE | 35 | 7.2 | |
| | Mitchell et al | CPC | 35 | 7.0 | |
| Xe II | | <u>Theory</u> | | | |
| | | Garpman-Spector | IC-HTS | 33 | 9.3 |
| | | Hansen-Persson | IC-HFRC | 36 | 7.01 |
| | | Present work | Scaled Hydrogenic | | 5.85 |
| | | | <u>Experiment</u> | | |
| | Mohamed et al. | CPC | 37 | 5.8 ± 0.2 | |

V. Result; and discussions on the reliability and generality of the method

It is not the purpose of this paper to present a table of calculated atomic properties, using the newly defined Z_{eff} . Moreover, orthogonalization procedures were not carried out, and this question was eluded using average Z_{eff} 's values given by

$$\langle Z_{\text{eff}} \rangle \cong \langle Z_{\text{eff}}^{(i)} + Z_{\text{eff}}^{(f)} \rangle / 2 \cong \langle Z_{\text{eff}}^{(i)} * Z_{\text{eff}}^{(f)} \rangle^{1/2} \quad (31)$$

In the present form, our method is superior at least to the Coulomb approximation of Bates and Damgaard²⁰, and produces good results when it is compared with Intermediate Coupling-Hartree Fock Slater (IC-HFS) method, as we will see in Tables 6 and 7.

In Table 6, we present transition probabilities using our radial integrals with pure LS coupling, compared with experimental^{31,32} and IC-HFS values^{33,34} for Kr II and Xe II; we note that our method compares very favorably both with theory and experiments.

In Table 7, we show lifetimes calculations for the levels of Kr II 5p ⁴D_{7/2} and Xe II 6p ⁴D_{7/2}. In the first case our value (=7.63 ns) is the same as the mean value obtained from the experiments quoted in ref. 35 and is larger than the results of other theoretical works. In the Xe II case³⁶, our result (=5.85 ns) is exactly the average between the calculations of ref. 33 and 36, and coincides with the experiments of Mohamed³⁷.

We also notice that the SHM is able to reproduce many atomic properties, and compares very well with the more sophisticated calculation techniques and experimental results, within a factor less than 1.5. The discrepancy can be due not only to the radial values, but also to Intermediate Coupling and Configuration Interaction problems.

When the sums of matrix elements are required (e.g., lifetimes, line widths and shifts) the LS-SHM yields surprisingly accurate results, because the sums are more accurate than the individual values; a fortunate circumstance which is connected with the existence of sum rules. This fact is well documented in ref. 35, 36 when Bates-Damgaard values were used for lifetimes and in ref. 38 for broadening calculations.

As it is stated in Ref. 35: "the spread of calculated values for lifetimes, perhaps indicates the increased difficulty of including relativistic effects such as spin-orbit mixing, and the resultant lack of any good approximate coupling scheme for heavy ions. A reasonable estimate of the reliability of the sophisticated calculations would be no better than 15-20%".

For routine calculations as, for example, the collisions of electrons with ions, or when the sum of matrix elements are needed, our method works very well as was showed in the Tables. For more subtle calculations our method must be improved, although it was not thought to compete with refined many body atomic

theories. However, it must be said that codes based in Hartree-Fock methods such as HX²³, use adjustable parameters, and several least square fits between calculated and observed level values are required before other properties are calculated. This procedure is well known for experimental spectroscopists who used these types of codes, and it is also known that good functions for energy levels are not necessarily good to calculate other quantities (e.g., g-factors, A_{ij} 's). Usually fairly small changes in the parameters can lead to large changes in some properties³⁶.

VI. Conclusions

The screened hydrogenic model (SHM) was formulated in closed form for wave functions and radial integrals. Analytic screening parameters generalizing the published results of Kregar, and a new definition of experimental effective charges, were given. A general formula for calculating hydrogenic radial integrals for arbitrary multipole order was found, valid for equal or not equal values of $Z_i, Z_f, n_i, n_f, \ell_i, \ell_f$. From Eq. (24) it is possible to calculate transition integrals, mean values, anisotropies of the core polarizabilities, and overlapping integrals when $\gamma = 0$.

On the other hand, a method to estimate the effective charges from experimentally established levels is proposed that, for nonpenetrating orbits ($n \simeq n'$) is nearly coincident with old definitions, and in general is approximately the same as calculated from Dirac-Fock codes. It can also be verified that for many important transitions, where $(Z_{\text{eff},i} \times Z_{\text{eff},f})^{1/2} \simeq (Z_{\text{eff},i} + Z_{\text{eff},f})/2 = \langle Z \rangle$, the transition integrals are in accordance with the values reported by Shore and Menzel³⁹ divided $\langle Z \rangle$.

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