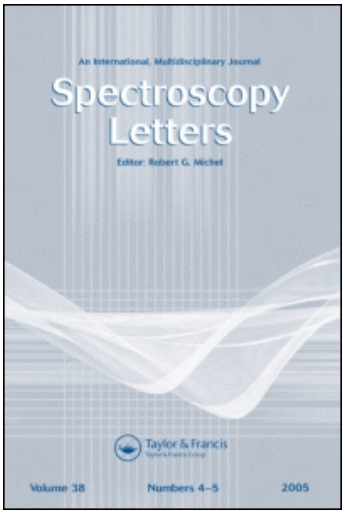

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ANALYTIC ATOMIC SCREENING PARAMETERS FOR SLATER TYPE ORBITALS

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ABSTRACT

Screening parameters to be used in Slater Type Orbitals were obtained in analytic form. The values compared well with the numerical results given by Clementi and Roetti (after a laborious process of optimization) and with the phenomenological values of Jung and Gould. The analytic formulation is based on the splitting of the two-body operator $1/r_{st}$ as the sum of effective one-body operators.

1.- INTRODUCTION

The accurate description of many-electron atoms can be made after simplifying approximations, such as the Independent Particle and the Central Field Approximations. If wave functions are expressed in

numerical form, we have the Self- Consistent Field Hartree-Fock method [1,2]. On the other hand, Roothaan-Hartree-Fock (RHF) or Analytic SCF wavefunctions are approximations to conventional HF's ones in which the radial atomic orbitals are expanded as a finite superposition of primitive radial functions [3]. In general, RHF functions have been expanded in terms of nodeless Slater Type Orbitals (STO).

Sometimes highly accurate wave functions are not required and an approximate wave function can be useful. For such approximate description of many-electron atoms in analytic rather than numerical form, Screened Hydrogenic Orbitals [1-3] and STO's [7-10] can be used.

There is a copious literature about the STO's. Several rules were proposed to compute the screening parameters either from spectroscopical fittings [7], phenomenologically [10], or from SCF calculations [8]. The calculation of good screening constants and then, energies and wave functions can be very useful because the treatment is analytical rather than numerical; on the other hand, the analytical STO's can also be used as starting wave functions in the HF calculations.

Slater [7] and Jung and Gould [10] assume that the energy levels (measured in Rydbergs) are related to the screening constants by the relations

$$E \approx \sum E_i \qquad (1)$$

and

$$E_i = -(Z-S_i)^2/n_i^2 \qquad (2)$$

but this is not what Clementi and coworkers [8] assumed; in their work, the corresponding screening parameters are the best exponents to be used in nodeless basis set functions. Roughly speaking, all

these screening constants have been obtained from numerical fittings.

An analytic approach was used by Bessis and Bessis [9] where, using simple mathematics and without any fitting considerations, derived expressions for the screening constants that reproduced the trend of Clementi and Roetti for Single Z functions [8].

Developing $1/r_{st}$ in Taylor's series to the first order in $1/r_s$ and $1/r_t$ around mean values $(1/r_s)_o$ and $(1/r_t)_o$, Bessis and Bessis obtained (in our notation)

$$1/r_{st} = g_{st}/r_s + f_{ts}/r_t \qquad (3)$$

In order to take into account the ℓ dependence of the radial part of the orbitals, the authors introduced the parameter

$$x_{st} = [3n_t^2 - \ell_t(\ell_t+1)]/[3n_s^2 - \ell_s(\ell_s+1)] \qquad (4)$$

which is a measure of $\langle r_t\rangle/\langle r_s\rangle$ between unscreened hydrogenic functions. Finally, for the orbital s, the screening constant results

$$S_s = \sum_{t\neq s} (1+x_{st}^2)^{-3/2} \qquad (5)$$

obtaining in particular a contribution to S_s originating from an electron t of the same subshell equal to $\sqrt{2}/4$ irrespective of the configuration.

In our work we arrive to an analytic formulation for $S_{n\ell}$ based on the splitting of the two-body operator $1/r_{st}$ as the sum of effective one-body operators. This turns out from the assumption that the virial can be used as a potential energy operator for closed many particle systems governed by Coulomb forces [4,5].

We remark the fact that, as in the Bessis-Bessis or the Clementi-Roetti rules, our screening constants are not related to the energy levels through eqs. (1-2) and an orthonormalization procedure must be carried out.

Making some considerations, the values from Jung and Gould (that are related to the energy levels through eqs. (1-2)) are reproduced within a few percent.

2.- THE SCREENED SLATER ORBITALS

Analytic wave functions for many electron atoms are constructed from single term basis functions of the form [10]

$$\chi_\alpha(r,\theta,\phi) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^n e^{-\zeta r} Y_{lm}(\theta,\phi)$$

$$= \lambda_n(r) Y_{lm}(\theta,\phi) \qquad (6)$$

where α designates the quantum numbers (n,ℓ,m) which have the same meaning as in hydrogenic functions and ζ is a parameter which, in terms of the screened Z, is given by

$$\zeta=(Z-S_{nl})/n. \qquad (7)$$

The function (6) is normalized, that is,

$$\int|\chi_\alpha|^2 \, dr = 1 \qquad (8)$$

but the functions are orthogonal only in the sense

$$\int\chi^*_\alpha \chi_{\alpha'} dr = I_{\alpha\alpha'}\delta_{ll'}\delta_{mm'} \qquad (9)$$

where, after elementary integration

$$I_{\alpha\alpha'} = \frac{(2\zeta)^{n+1/2}(2\zeta')^{n'+1/2}(n+n')!}{(\zeta+\zeta')^{n+n'+1}[(2n)!(2n')!]^{1/2}} \quad (10)$$

To preserve orthogonality, we must construct the wave function from linear combinations of the χ_α's

$$\Psi_\sigma = \sum_\alpha C_{\sigma\alpha}\chi_\alpha \quad (11)$$

using the Gramm-Schmidt procedure; the various C's are fixed by normalization and orthogonalization [11].

3. OUR APPROACH

Using the virial

$$w = \sum r_i F_i = -(1/2)\sum r_i \nabla_i W_p(r_0, \ldots, r_i, \ldots r_N) \quad (12)$$

as the atomic model potential energy operator, the two-body operator $1/r_{st}$ is replaced by the sum of effective one-body operators as in Eq. (3) [4-6]. Hence formally, this approach is equivalent to the first order development made in Ref. [9] but now g_{st} and f_{ts}, the external and internal screening parameters respectively, are defined in terms of $dq_i \equiv |\chi_\alpha(r)|^2 dV_i$ by [4-6]

$$g_{st} \equiv (n_s^2/Z_s) \int_0^{r_t \to \infty} dq_t \int_{r_t}^{\infty} dq_s / r_s \quad (13)$$

and similarly for f_{ts} by interchanging s and t. Using the approach given in Ref.[6] for the hydrogenic orbitals to the STO's given by Eq. (6), it is easy to show, using the well known properties

$$\int_0^\infty r^n \exp(-\alpha r)\, dr = \Gamma(n+1)/\alpha^{n+1} \qquad (14)$$

and

$$\int_r^\infty (Z_s r/n_s)^a \exp(-2Z_s r/n_s)dr = (n_s/2^{a+1}Z_s)\exp(-2Z_s r/n_s) \times \sum_{j=0}^{a} (a!/j!)[2Z_s r/n_s]^j \qquad (15)$$

that g_{st} and f_{ts} are now independent of ℓ_s and ℓ_t and equal respectively to

$$g_{st} = [1/(1+y)]^{2n_t+1} \left\{ \sum_{j=0}^{2n_s-1} \frac{(2n_t+j)!}{j!(2n_t)!} [y/(y+1)]^j \right\} \qquad (16)$$

and

$$f_{ts} = [y/(y+1)]^{2n_s+1} \left\{ \sum_{j=0}^{2n_t-1} \frac{(2n_s+j)!}{j!(2n_s)!} [1/(y+1)]^j \right\} \qquad (17)$$

where $y \equiv Z_s n_t / Z_t n_s$. Screening parameters are given by

$$S_i = \sum_{j<i} q_i q_j f_{ji} + \sum_{j>i} q_i q_j g_{ij} + (q_i - 1) f_{ii} \qquad (18)$$

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

Up to this point, screening parameters for subshells of a given principal quantum number n will be equal, henceforth it is necessary to introduce the ℓ-dependence. For unscreened hydrogenic orbitals, a measure of r_t/r_s is given by

$$x \equiv \langle 1/r_s \rangle / \langle 1/r_t \rangle = n_t^2/n_s^2 = (n_t/n_s)y \qquad (19)$$

and a first attempt to choose a measure of r_t/r_s is to follow the election of Bessis and Bessis (see Eq. (4)) but it is possible to show, using Screened Hydrogenic Orbitals [4-6] that a good measure of r_t/r_s better than eq. (4) is: i) for the orbitals with principal quantum numbers $n_s \leq (n_{max}-2)$ and $n_t \leq (n_{max}-2)$

$$x \equiv [3n_t^2-(Z/30)\ell_t(\ell_t+1)]/[3n_s^2-(Z/30)\ell_s(\ell_s+1)] \qquad (20)$$

and ii) when one or both of the orbitals have $n > (n_{max}-2)$

$$x \equiv [3n_t^2+(Z/30)\ell_t(\ell_t+1)]/[3n_s^2+(Z/30)\ell_s(\ell_s+1)] \qquad (21)$$

Z being the atomic number.

Using these values of x and the relation $y=(n_s/n_t)x$ in Eqs. (16-18) we obtain screening parameters that follows the values of Clementi and Roetti [8] for Single Z Functions and the values of Bessis and Bessis [9]. Furthermore, for orbitals with $n-\ell=1$, we obtain the one parameter variational values ($S_{1s}=5/16$, $S_{2p}=93/256$, etc.).

RESULTS

Since the application of the Eqs. (16-18) and (20-21) is straightforward, we give not here an extensive table of the orbital exponents ζ. As an example, we compare our values of ζ's for neutral Xe with those obtained by using the method of Bessis and Bessis and the Clementi-Roetti SCF ones in Table 1.

In Table 2 we compare our analytic screening constants rounded to two digits to the phenomenological constants of Jung and Gould [10]. Alike that work, we

TABLE 1

Comparison between analytic (A) and numerical (N) screening parameters $\zeta=(Z-S)/n$ for neutral Xe.

Orbital	This work (A)	Ref. 8 (N)	Ref. 9 (A)
1s	53.30	52.92	53.43
2s	22.80	19.90	23.45
2p	24.48	24.92	24.27
3s	11.00	11.86	11.67
3p	11.46	11.89	12.14
3d	12.72	13.31	13.16
4s	6.73	6.54	5.79
4p	6.19	6.24	6.02
4d	5.21	5.47	6.50
5s	2.66	2.84	2.88
5p	2.41	2.48	2.98

TABLE 2

Comparison between our screening constants (upper values) with those from Ref. [10] (lower values). See the text where the obtention of S_{2s} and S_{3s} is explained.

	Screening				
Screened	1s	2s	2p	3s	3p
1s	0.31	0	0	0	0
	0.31	0	0	0	0
2s	0.90	0.27	0.36	0	0
	0.90	0.25	0.34	0	0
2p	0.92	0.27	0.36	0	0
	0.95	0.25	0.34	0	0
3s	1.00	0.83	0.80	0.29	0.39
	1.00	0.90	0.90	0.25	0.34
3p	1.00	0.85	0.81	0.29	0.39
	1.00	0.95	0.95	0.25	0.34

multiply our $S_{ns,ns}$ values by 0.75 taking into account that a measure of the screening by electron j would be the charge interior to r:

$$N_j(r) = \int_0^r P_j^2(r)dr \qquad (22)$$

and for hydrogenic wave functions and $r \approx n^2/(Z-S)$, the ratio N_{ns}/N_{np} is about that value [10].

With the values of Table 2, binding energies of K shell will be in good agreement both with experiments and more refined approaches. Accurate calculations for the L and M shells are more complex, and a same set of screening constants cannot give good results for a large range of elements. When compared with the values of Ref. [10] our binding energies of the M shell for Ar, Cl and S are closer to the experimental ones but this is not the case for lighter elements.

CONCLUSIONS

In conclusion, we have obtained analytic screening parameters to be used in STO's that follows closely the trends given by Clementi and Roetti for Single Zeta Functions after a laborious process of optimization. Our method is very simple and fast: screening constants for neutrals and ions and the constants of the orthonormalization procedure are obtained automaticaly using a small PC. Although it is well known that the Single Zeta Functions are not as accurate as a HF (or RHF) function, the orbital exponents are of physical interest since they provide a simple and quantitative description of the electron screening.

Furthermore, the screening constants derived phenomenologically in Ref [10] can be reproduced whithin a few percent and therefore, binding energies of K, L (specially) and M shells will be in many cases in qualitative agreement both with experiments and more refined calculations.

We finish this paper to stressing again that our screening constants do not imply the existence of eqs. (1) and (2) and the orthonormalization procedure must be carried out.

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