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Simple Electrostatic Model for the $I - A$ Approximation

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Employing the approximation which replaces r_{ij}^{-1} by $(r_i + r_j)^{-1}$ we derive the relation

$$\frac{2\zeta}{4l+5} = I - A$$

where ζ is the orbital exponent of a Slater AO. This semiempirical relation appears to agree with experiment for the cases compared.

Introduction

One of the basic assumptions of the Parr-Pariser-Pople method is that which prescribes the evaluation of the one-center Coulomb integrals $(pp|pp)$ by the following formula:

$$(pp|pp) = I_p - A_p \tag{1}$$

where I_p and A_p are the ionization potential and electron affinity respectively, of the orbital χ_p, when the atom p is in some valence state. Its origin lies in the fact that on one hand the energy difference for the reaction $2A(g) \rightarrow A^+(g) + A^-(g)$ is experimentally given by $I - A$, while on the other hand if this same difference is calculated assuming no change in the AO's of both neutral and ionic species the result is $\Delta e = (pp|pp)$. Furthermore it is well-known that the theoretical value is much larger than the $I - A$ value. It is the purpose of this paper to examine the following simple prescription in evaluating the one-center Coulomb integral: assume that a pair of electrons about a single attracting center are always 180° to one another, i.e., replace the operator r_{12}^{-1} by the operator $(r_1 + r_2)^{-1}$. The result of this procedure will be to drastically lower the value of $(pp|pp)$.

Evaluation of the Basic Integral

Since to the author's knowledge the integral to be evaluated has not appeared in the literature a detailed derivation of the results follows. The integral to be evaluated is (in a.u.)

$$V_{pp} = \int\int \chi_p^{-2}(1)\, \chi_p^2(2)\, (r_1 + r_2)^{-1}\, dv_1\, dv_2 \tag{2}$$

where χ_p is a normalized Slater atomic orbital of the form

$$\chi_p = \left[\frac{(2\zeta)^{2l+3}}{(2l+2)!}\right]^{\frac{1}{2}} r^l e^{-\zeta r}\, Y_{lm}(\theta, \phi)\,. \tag{3}$$

Substitution of (3) into (2) and subsequent integration over the angle variables gives

$$V_{pp}=\frac{(2\zeta)^{4l+6}}{[(2l+2)!]^2}\int_0^\infty\int_0^\infty r_1^{2l+2}\,e^{-2\zeta r_1}\,r_2^{2l+2}\,e^{-2\zeta r_2}\,\frac{dr_1\,dr_2}{r_1+r_2}. \tag{4}$$

A further change of variables $x=2\zeta r_1$; $y=2\zeta r_2$ gives

$$V_{pp}=\frac{2\zeta}{[(2l+2)!]^2}\int_0^\infty\int_0^\infty x^{2l+2}\,e^{-x}\,y^{2l+2}\,e^{-y}\,\frac{dx\,dy}{x+y}. \tag{5}$$

We now define the integral

$$\int_0^\infty y^{2l+2}\,\frac{e^{-y}}{x+y}\,dy=\left[\left(\frac{d}{da}\right)^{2l+2}\int_0^\infty\frac{e^{-ay}}{x+y}\,dy\right]_{a=1} \tag{6}$$

where

$$\int_0^\infty\frac{e^{-ay}}{x+y}\,dy=-e^{ax}\,\mathrm{Ei}(-ax) \tag{7}$$

where $\mathrm{Ei}(-ax)$ is the usual exponential integral. Substituting (6) and (7) into (5) we now obtain

$$V_{pp}=\frac{-2\zeta}{[(2l+2)!]^2}\left[\left(\frac{d}{da}\right)^{2l+2}\int_0^\infty x^{2l+2}\,e^{-(1-a)x}\,\mathrm{Ei}(-ax)\,dx\right]_{a=1}. \tag{8}$$

We must consider the integral

$$W=-\int_0^\infty x^p\,e^{-bx}\,\mathrm{Ei}(-ax)\,dx=\int_0^\infty x^p e^{-bx}\,dx\int_{ax}^\infty z^{-1}\,e^{-z}\,dz. \tag{9}$$

Application of Dirichlet's theorem [1] gives

$$W=\int_0^\infty z^{-1}\,e^{-z}\,dz\int_0^{z/a} x^p\,e^{-bx}\,dx \tag{10}$$

which upon substitution of $bx=t$ gives

$$W=\frac{1}{b^{p+1}}\int_0^\infty z^{-1}\,e^{-z}\,dz\int_0^{zb/a} t^p e^{-t}\,dt. \tag{11}$$

We note that the integral over t is just the incomplete gamma function, $\gamma(p+1, zb/a)$, given by the series expansion [2]

$$\gamma(p+1,zb/a)=\left(\frac{zb}{a}\right)^{p+1}e^{-zb/a}\sum_{n=0}^{\infty}\frac{(zb/a)^n}{(p+1)(p+2)\dots(p+n)(p+n+1)}. \tag{12}$$

Substitution of (12) into (11) and integration over z gives

$$W=\sum_{n=0}^{\infty}\frac{1}{(a+b)^{p+1}}\left(\frac{b}{a+b}\right)^{n}\frac{\Gamma(p+n+1)}{(p+1)\ldots(p+n)(p+n+1)}. \tag{13}$$

Finally we recall the identity

$$\Gamma(p+1+n)=(p+1)(p+2)\ldots(p+n)\Gamma(p+1) \tag{14}$$

to obtain

$$W=\frac{(p+1)}{(a+b)^{p+1}}\sum_{n=0}^{\infty}\frac{1}{p+n+1}\left(\frac{b}{a+b}\right)^{n}. \tag{15}$$

Identifying $p=2l+2$ and $b=1-a$ and substitution of (15) back into (8) results in

$$V_{pp}=\frac{2\zeta}{[(2l+2)!]^{2}}\Gamma(2l+3)\left[\left(\frac{d}{da}\right)^{2l+2}\left(\sum_{n=0}^{\infty}\frac{1}{2l+3+n}(1-a)^{n}\right)\right]_{a=1}. \tag{16}$$

Performing the indicated differentiation and taking the limit as $a\to 1$ we obtain the surprisingly simple result

$$V_{pp}=\frac{2\zeta}{(2l+2)!}\left[\frac{(2l+2)!}{4l+5}\right]=\frac{2\zeta}{4l+5}. \tag{17}$$

Results and Discussion

For the case of $2p$ AO's the results of the previous section give the simple semi-empirical relation (in a.u.)

$$Z_p/9=(I_p-A_p) \tag{18}$$

where we have defined 2ζ to be equal to the effective nuclear charge. In the table we present some appropriate data with which to make comparisons with the results as calculated from Eq. (18).

Table

Atom	Z_p	I_p[a] (eV)	A_p[a] (eV)	I_p-A_p	$Z_p/9$	$(pp\|pp)_{exact}$
C	3.25[b]	11.42	0.58	10.84	9.82	17.30
N	3.96	14.49	1.58	12.91	11.98	21.08
O	4.55[b]	15.45	1.73	13.72	13.75	24.22

[a] These values except for the $2p$ AO of the oxygen atom are quoted from Pritchard and Skinner's table [Chem. Rev. **55**, 745 (1955)].

[b] Yonezawa, Yamaguchi, and Kato: Bull. chem. Soc. Japan **40**, 536 (1967).

We see that the results are in fairly good agreement with experiment, and it may be that the generalization of equation (18), for atomic orbitals χ_{n_l} to give

$$Z_{\text{eff}}\approx\frac{n(4l+5)}{2}(I-A)$$

may have use as a simple estimate of effective nuclear charges for AO's. It is also possible that replacement of r_{ij}^{-1} by $(r_i + r_j)^{-1}$ may have further application as a semi-empirical procedure.

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References

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