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Angularly Correlated Two-Electron Repulsion Operators*

I. One- and Two-Center Integrals

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The Bohr model for two-electron atoms is modified to include angular correlation effects in an empirical fashion. An extension of the model to two-centers is given. Simple expressions for one- and two-center Coulomb repulsion integrals are derived and compared with semi-empirical approximations.

Die Bohrsche Modellvorstellung für ein Atom mit zwei Elektronen wird so modifiziert, daß die Winkelkorrelation empirisch berücksichtigt wird. Die Erweiterung dieses Modells auf zwei Zentren wird angegeben. Einfache Ausdrücke für Ein- und Zweizentren-Coulombintegrale werden abgeleitet und mit semiempirischen Näherungen verglichen.

Introduction

In a previous paper in this journal [1] one of us (AFS) proposed a simple electrostatic model to be used in approximating one-center electron repulsion integrals. The technique in that paper was to replace the repulsion operator, r_{12}^{-1}, in the integrand by the operator $(r_{1\alpha}+r_{2\alpha})^{-1}$ [1]. Since then this model has been extended [2] to include two-center Coulomb integrals by using $(r_{1\alpha}+r_{2\beta}+R)^{-1}$ as the repulsion operator. The repulsion energies calculated using these prescriptions have been found to be somewhat lower than semi-empirical values.

The rationale for choosing these operators is that since wave functions constructed from a basis set of one-electron atomic-orbitals cannot include electron-correlation effects then perhaps they can be included, in some average fashion, in the repulsion operator. For the one-center operator above, this correlation effect is present as a constraint requiring the electrons to be 180° apart with respect to the orbital center. In this paper we assume that the low values of the resulting electron repulsion energies are due to an over-estimation of the angular correlation and an appropriate correction term is applied.

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[1] Greek subscripts refer to nuclei while numerical subscripts refer to electrons. R is an internuclear distance whereas r is either an electron-electron or an electron-nuclear distance. The units are in atomic units (a.u.) where 1 a.u. of energy = 27.2 eV).

The Electron Repulsion Operators

The distance between two electrons in concentric orbits is given by the Law of Cosines as

$$r_{12}=[r_{1\alpha}^2+r_{2\alpha}^2-2r_{1\alpha}r_{2\alpha}\cos\theta]^{\frac{1}{2}}\,, \tag{1}$$

where θ is the minimum angle made by $r_{1\alpha}$ and $r_{2\alpha}$. The repulsion operator may be obtained from the above expression as

$$r_{12}^{-1}=(r_{1\alpha}+r_{2\alpha})^{-1}+\sum_{n=1}^{\infty}\frac{(2n-1)!!}{n!}\,\frac{[r_{1\alpha}r_{2\alpha}(1+\cos\theta)]^n}{(r_{1\alpha}+r_{2\alpha})^{2n+1}}\,. \tag{2}$$

Truncation of the right hand side of Eq. (2) after the first term (equivalent to setting $\theta=\pi$) yields the simple electrostatic model discussed earlier. By fixing θ at some average angle, additional terms may be included in the repulsion operator which correspond to a decrease in the average angular correlation. A three term expression for r_{12}^{-1} appears to be sufficient for one-center repulsion integrals while only two terms are required for two-center Coulomb integrals. For one-center integrals the repulsion operator is taken to be

$$r_{12}^{-1}=(r_{1\alpha}+r_{2\alpha})^{-1}+\xi r_{1\alpha}r_{2\alpha}(r_{1\alpha}+r_{2\alpha})^{-3}+\tfrac{3}{2}(\xi r_{1\alpha}r_{2\alpha})^2\,(r_{1\alpha}+r_{2\alpha})^{-5}\,, \tag{3}$$

where $\xi\equiv 1+\cos\theta$.

In addition to overestimating the angular correlation, the two-center operator $(r_{1\alpha}+r_{2\alpha}+R)^{-1}$ also overestimates the interelectronic distance except when the electrons lie on the locus of the internuclear axis. When R is on the order of a bond length there may be considerable electron density between the nuclei and r_{12} would be grossly overestimated by using this operator.

A logical extension of the present one-center model to the two-center case would be to require the two electrons to always be on opposite sides of some point on the internuclear axis. We have chosen the location of this point to be a distance

$$R_\alpha=\frac{\langle r\rangle_\alpha}{\langle r\rangle_\alpha+\langle r\rangle_\beta}R \tag{4}$$

from α on the internuclear axis. This point is the center-of-charge for the corresponding Bohr orbitals. Here $\langle r\rangle_\alpha$ is the expectation of r for the atomic orbital centered on α. For Slater Type Orbitals (STO),

$$\chi\equiv[(2\zeta)^{2n+1}/(2n)!]^{\frac{1}{2}}\,r^{n-1}\,e^{-\zeta r}\,Y_{lm}(\theta,\phi)\,, \tag{5}$$

this expectation value is simply

$$\langle r\rangle=\frac{2n+1}{2\zeta}\,. \tag{6}$$

In order to simplify the mathematics and to provide for adjustment of the two-center repulsion operator we have decided to use Coulson's operator with the inclusion of a damping factor;

$$r_{12}^{-1}=(r_{1\alpha}+r_{2\alpha}+\lambda R)^{-1}\,.$$

For the reasons mentioned above, we desire that λ be small when R is on the order of a bond length and that λ approach unity as R tends to infinity. The correlation effect is expected to vary as the two-center overlap and since overlaps fall off exponentially with distance, an exponential form for the damping factor was chosen. Because the overlap depends on the size of the orbitals as well as the distance between then, we have picked as the exponent in the damping factor the ratio

$$\varrho \equiv \frac{\langle r \rangle_\alpha}{R_\alpha} = \frac{\langle r \rangle_\beta}{R_\beta}. \tag{7}$$

The distance between the two electrons for the two-center distribution is then

$$\begin{aligned} r_{12} &= r_{1\alpha} + r_{2\beta} + e^{-\gamma\varrho} R \\ &= (r_{1\alpha} + e^{-\gamma\varrho} R_\alpha) + (r_{2\beta} + e^{-\gamma\varrho} R_\beta). \end{aligned} \tag{8}$$

The terms in parenthesis in the right hand side of Eq. (8) are interpreted as average values of the distances from the charge-center to the respective electrons.

At present there are two widely used semi-empirical methods for determining two-center Coulomb integrals. The Mataga-Nishimoto [3] (MN) approximation has been found to be preferable for calculating singlet state energies while the method of Ohno [4] works best for triplet states [5]. Coulomb integrals calculated using Ohno's formula are larger than those computed by the MN expression. The theoretical explanation for the superiority of Ohno's formula for calculating triplet energies is that the Pauli Principle is operating to keep the electrons apart. By empirically assigning values of γ for singlet and triplet states, the present model will encompass both of these semi-emirical methods.

As would be expected, the angular correction term for two-center integrals is much smaller than that for one-center integrals. The two-center repulsion operator is then approximated by the first two terms of an expansion similar to Eq. (2), i.e.,

$$r_{12}^{-1} = (r_{1\alpha} + r_{2\beta} + e^{-\beta\varrho} R)^{-1} + (r_{1\alpha} + e^{-\gamma\varrho} R)(r_{2\beta} + e^{-\gamma\varrho} R)(r_{1\alpha} + r_{2\beta} + e^{-\gamma\varrho} R)^{-3}. \tag{9}$$

We arbitrarily assume that θ approaches π as R tends to infinity according to

$$\theta = \theta^0 + (\pi - \theta^0)\, e^{-\gamma\varrho}, \tag{10}$$

where θ^0 is the appropriate one-center angle.

Evaluation of the Repulsion Integrals

The electron repulsion integrals are given below for Slater-type atomic orbitals. The requisite integrations are expedited by means of the Laplace transform

$$\frac{1}{y^{n+1}} = \frac{1}{n!} \int_0^\infty x^n e^{-xy}\, dx \tag{11}$$

as suggested by Coulson [2].

The most general one-center electron repulsion integral over STO's is

$$(\alpha_1 \alpha_2 | \alpha_3 \alpha_4) = \int_{v_1} \int_{v_2} \chi_1^*(1)\, \chi_2(1)\, \tilde{r}_{12}^{-1}\, \chi_3^*(2)\, \chi_4(2)\, dv_1\, dv_2, \tag{12}$$

where $\tilde{r}_{12}^{-1}$ is given by the right hand side of Eq. (3) and the subscripts denote possibly different orbitals on the same center. Utilizing Eq. (11) and the binomial expansion

$$(x-c)^{-n}=\sum_{k=0}^{\infty}\frac{(n-1+k)!}{(n-1)!k!}\frac{c^k}{x^{n+k}} \tag{13}$$

the integral in Eq. (12) becomes

$$\begin{aligned}(\alpha_1\alpha_2|\alpha_3\alpha_4)=N'\,&\frac{(n_1+n_2)!(n_3+n_4)!}{(\zeta_1+\zeta_2)^{n_1+n_2+n_3+n_4+1}}\sum_{m=0}^{\infty}\left[1-\frac{\zeta_3+\zeta_4}{\zeta_1+\zeta_2}\right]^m P_m^{n_3+n_4+1}\\ &\cdot\left\{A_1+\frac{\xi}{2}(n_1+n_2+1)(n_3+n_4+1+m)\left[A_1-2A_2+A_3\right]\right.\\ &+\frac{\xi^2}{16}(n_1+n_2+2)(n_1+n_2+1)(n_3+n_4+1+m)(n_3+n_4+1+m)\\ &\left.\cdot\left[A_1-4A_2+6A_3-4A_4+A_5\right]\right\},\end{aligned} \tag{14}$$

where $N'=N_1N_2N_3N_4$,

$$P_m^n=\frac{(n-1+m)!}{(n-1)!m!}, \tag{15}$$

and $A_k=(n_1+n_2+n_3+n_4+k+m)^{-1}$. In the preceeding it has been assumed that $(\alpha_1\alpha_2|\alpha_3\alpha_4)$ is not zero owing to the orthogonality of the spherical harmonics.

For $\chi_1=\chi_2=\chi_3=\chi_4$ Eq. (14) is simplified to

$$\begin{aligned}n=1,\quad&(\alpha\alpha|\alpha\alpha)=(0.4000+0.0857\xi+0.0286\xi^2)\zeta\\ n=2,\quad&(\alpha\alpha|\alpha\alpha)=(0.2222+0.0505\xi+0.0175\xi^2)\zeta\\ n=3,\quad&(\alpha\alpha|\alpha\alpha)=(0.1538+0.0359\xi+0.0127\xi^2)\zeta\,.\end{aligned} \tag{16}$$

Using the repulsion operator given in Eq. (9), the two-center Coulomb integral is computed in similar fashion as

$$\begin{aligned}(\alpha_1\alpha_2|\beta_3\beta_4)=N'\,&\frac{(n_1+n_2)!(n_3+n_4)!}{(\zeta_1+\zeta_2)^{n_1+n_2+n_3+n_4+1}}\sum_{m=0}^{\infty}\left[1-\frac{\zeta_3+\zeta_4}{\zeta_1+\zeta_2}\right]^m P_m^{n_3+n_4+1}\\ &\cdot\left\{F_2+\frac{\xi}{2}(n_1+n_2+1)(n_3+n_4+1+m)\left[F_2-2F_3+F_4\right]\right.\\ &+\frac{\xi}{2}\lambda(\zeta_1-\zeta_2)\left[R_\alpha(n_3+n_4+1+m)+R_\beta(n_1+n_2+1)\right]\\ &\cdot\left[F_1-2F_2+F_3\right]\\ &\left.+\frac{\xi}{2}(\lambda(\zeta_1+\zeta_2))^2R_\alpha R_\beta\left[F_0-2F_1+F_2\right]\right\},\end{aligned} \tag{17}$$

where $\lambda=e^{-\gamma\varrho}$,

$$F_k\equiv e^{\lambda R(\zeta_1+\zeta_2)}E_{n_1+n_2+n_3+n_4+k+m}(\lambda R(\zeta_1+\zeta_2))\,, \tag{18}$$

and $E_n(x)$ is the well-known exponential integral [6]

$$E_n(x)\equiv\int_1^{\infty}t^{-n}e^{-xt}\,\mathrm{d}t\,. \tag{19}$$

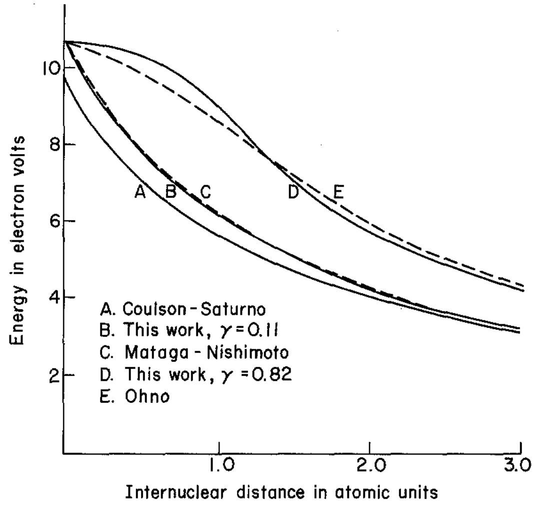

Fig. 1. $(\alpha\alpha|\beta\beta)$ for carbon as a function of internuclear distance

For $\chi_1 = \chi_2 = \chi_3 = \chi_4$ and $n = 2$, Eq. (17) reduces to

$$\begin{aligned}(\alpha\alpha|\beta\beta) = 2\zeta e^{2\zeta R}\Big\{&E_{10} + \frac{\xi}{2}\,[25(E_{10} - 2E_{11} + E_{12})\\ &+ 10\zeta\lambda R(E_9 - 2E_{10} + E_{11}) + (\lambda\xi R)^2\,(E_8 - 2E_9 + E_{10})]\Big\},\end{aligned} \tag{20}$$

where $E_n \equiv E_n(2\zeta\lambda R)$. A plot of the right hand side of Eq. (20) against R is shown in Fig. 1 for two different values of λ.

Results and Discussion

According to Pariser [7], experimental values of one-center electron repulsion integrals may be approximated as the difference between the ionization potential and the electron affinity of a particular valence state. Using these values for $(\alpha\alpha/\alpha\alpha)$ and orbital exponents from Clementi's [8] SCF procedure, values of the angular correlation parameter, θ, may be computed by means of Eq. (12). These values are given in the Table for $1s$, $2s$, $2p$, and $3s$ atomic orbitals.

In the series $1s \to 2s \to 3s$ a decrease in θ would be expected owing to an increase in the size of the orbital. Comparison of s orbitals with p orbitals should show a larger value of θ for the latter due to the spatial orientation of p orbitals. Both of these trends are borne out by the data in the Table. An angle of 90° would correspond to no correlation of the electron pair and angles less than 90° have no physical basis. Indeed we found some angles slightly less than 90° but these occurred for orbitals with $n \geqq 4$ and particularly with inner orbitals of these large atoms. The explanation for this behavior is simply that the ionization potentials and electron affinities are less well-known in these cases.

Table. *Values of θ for ground state atoms*

Atom	Orbital	ζ^a	$I-A(\text{eV})^b$	$\theta(°)$
H	1*s*	1.0000	12.85[c]	108
Li	2*s*	0.6396	4.71	105
B	2*p*	1.2107	8.95[c]	103
C	2*p*	1.5679	10.66[c]	122
N	2*p*	1.9170	13.04	122
O	2*p*	2.2266	14.93	126
F	2*p*	2.5500	17.35	121
Na	3*s*	0.8358	4.54	93

[a] Ref. [8].
[b] Average values from Ref. [10] and Ref. [9] except where noted.
[c] Ref. [10].

Values of some two-center Coulomb integrals are compared in Fig. 1. For the case of carbon $2p_\pi$ atomic orbitals, the present model with $\gamma = 0.11$ agrees almost exactly with the MN formula while good agreement with Ohno's semi-empirical expression is obtained by setting $\gamma = 0.82$.

Conclusion

Electron correlation has been used as a rationale for constructing electron operators which yield results that agree with semi-empirical calculations. The extension of this method to multi-center electron repulsion integrals and the treatment of some representative systems will be given in later papers.

We note that since the repulsion operators contain only radial terms, the repulsion integrals have the rotational invariance [11] necessary for application of the ZDO approximation to systems transcending the π-electron approximation.

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