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AN ALTERNATIVE PARAMETERIZATION OF ELECTRON REPULSION TERMS IN MNDO AND AM1

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Abstract

An alternative method of parameterizing the two electron coulomb integrals in MNDO and AM1 is described. Although the method is used to closely approximate the Dewar and Thiel integrals, the formalism and the resulting formulas are much simpler and computationally more efficient. The method strictly obeys rotational invariance, gives integrals and their derivatives directly in space fixed cartesian coordinates, can be used with arbitrary basis sets and gives the correct behavior both at the large and small (united atom) limits of the interatomic distance. The integrals are numerically compared with those of Dewar and Thiel.

I. Introduction

The great success of the MNDO[1] and AM1[2] methods is largely due to the way the original NDDO[3] theory was parameterized by Dewar and co-workers. A key feature of this parameterization is the treatment of the two-electron two-center coulomb integrals. Dewar and Thiel (DT) found that simply calculating these integrals using Slater type orbitals of the appropriate orbital exponent and atomic quantum numbers gave unsatisfactory results[4]. Instead, they replaced these integrals with empirical formulas designed to have the same overall shape and long range behavior as the Slater integral, yet be attenuated in the intermediate range and go to the correct (as determined from atomic spectroscopic parameters) united atom limit. The parameterized integrals should display the same symmetry properties as the original Slater integrals.

The DT formulas are derived from the multipole expansion, valid at large internuclear separations, of the coulomb repulsion integral over the Slater charge distributions. The various multipoles are then represented as discrete arrangements of point charges adjusted so as to agree with the respective multipole moments of the charge distributions. The repulsion integral is then calculated by summing the contributions arising from the discrete charges, the interaction calculated with the Ohno-Klopman(OK)[5] formula

$$\gamma_0 = [r^2 + a^2]^{-\frac{1}{2}} \tag{1}$$

instead of the coulomb potential r^{-1}. The constants a are adjusted to give the desired united atom limits of the integrals. The integrals are first calculated in a local diatomic coordinate system in such a way as to ensure rotational invariance[6,7]. They are then rotated into the molecular frame

using trigonometric transformations. The DT procedure is obviously viable and in principle can be extended to arbitrary basis sets and derivative integrals. In practice, however, it is very awkward to do either.

These problems were recently addressed by Hoggan and Rinaldi[8] (HR) who used a method of parameterizing the integrals that avoids the troublesome discrete charge representations. Their procedure also begins with the multipole expansion of the Slater coulomb integral. The coulomb potential is then everywhere replaced by the OK potential. The resulting formula is then multiplied by a polynomial designed to give the correct united atom limit for each multipole contribution to the integral. Finally, in order to enforce the special symmetry at the united atom limit integrals involving charge distributions with different L and M quantum numbers are multiplied by a switch of the form $(1 - e^{-\alpha r})$ which forces these integrals to go to zero (as r goes to zero) in a way that agrees with the analytically calculated integral.

Although the procedures of DT and HR are different, their approaches are essentially the same. Both parameterize the integrals by replacing the coulomb potential with the OK potential in the multipole expansion. In this paper we report results obtained by a parameterization scheme closely related to DT and HR. Like the HR method, the scheme can be easily extended to arbitrary basis sets and formulas for derivative integrals can be readily obtained. Our integrals are not more "accurate" than DT or HR since an obvious immediate goal is to use the formulas in existing MNDO and AM1 programs without disturbing the numerical results. The main advantages of our method are its simplicity, computational efficiency, and the fact that it readily allows for a more general type of parameterization, should this be desired. In the following section the underlying theory is reviewed and the symmetry requirements are discussed using an example. This is followed by a section in which the integrals are numerically compared to the DT integrals. A few concluding remarks are given in the final section.

II. Theory

The key feature of our approach is the recognition that all two center coulomb integrals can be obtained by applying operators to a single generating function which depends only on the interatomic distance (and adjustable parameters)[9]. The rotational symmetry properties are reflected in the Cartesian derivative operators. If the operators are chosen to represent Slater charge distributions obtained from the $1s^2$ distribution and the generating function is chosen to be the analytically calculated $(1s^2|1s^2)$ integral then formulas for all the analytically calculated integrals result from application of the operators to the generating function. If instead the generating function is chosen to be $1/r$, the large distance or multipole limit value of $(1s^2|1s^2)$, then the correct limiting formulas for the integrals result. Here we use the OK potential as the generating function. The resulting integrals exhibit the rotational symmetry properties and long range behavior of the Slater integrals, yet can be made to match united atom values in much the same way as the DT integrals.

We had previously advised against using the OK integral as a generating function.[9] The reason for this was that our operator for the $2s^2$ charge distribution gave results equivalent to that of the sum of the operators for the $2p_x^2$, $2p_y^2$ and $2p_z^2$ charge distributions when applied to the analytical $(1s^2|1s^2)$ integral (or its large r limit) but not when applied to the OK integral. This violates a symmetry condition and can lead to ambiguities. The problem is unimportant for charge distributions made up of s and p orbitals as long as one avoids using the symmetry relation, Eq (3) of reference [9], in computing the integrals. For higher angular quantum number orbitals (d, f, etc), one must recognize that a set of six cartesian d orbitals, eg, will give different results than the equivalent set of 5 spherical harmonic type d functions and their companion s orbital. Thus, there is a caveat in extending the parameterization scheme to d, f etc. functions. One must choose the best representation of the orbitals and use it consistently everywhere. The problem does not lie in the properties of the operators. The DT and HR integrals also violate the symmetry condition. Rather the problem lies with the OK function itself. We will consider here only integrals involving s and p orbitals. Formulas for all of the integrals (and their first and second derivatives) involving 1s, 2s and 2p orbitals are obtained by using the OK potential in place of the analytical $(1s^2\ 1s^2)$ integral in Eqs (7) - (21) of [9]. Semiempirical or analytical integrals over arbitrary orbitals can be obtained by straightforward extensions of this theory.[10]

We illustrate the features of our approach by considering the example of two interacting $2p^2$ charge distributions. The 36 distinct integrals in space fixed cartesian coordinates depend only on the three functions of interatomic distance, f_0 , f_2 and f_4 as seen in Eqs (35)-(37) of reference [9]. These primitive integrals are obtained from the generating function using Eqs (19)-(21) of [9]. When the normalized generating function γ_0 is chosen to be independent of orbital exponents, the primitive integrals have the particularly simple forms,

$$f_0 = \gamma_0 \tag{2}$$

$$f_2 = \frac{3}{2\zeta_b^2}\gamma_0 \tag{3}$$

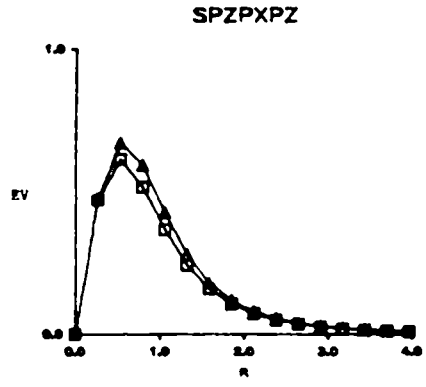
$$f_4 = \frac{9}{4\zeta_a^2\zeta_b^2}\gamma_0 \tag{4}$$

where ζ_a and ζ_b are the orbital exponents for atoms a and b. In the present case, γ_0 is chosen to be the OK potential, Eq (1). When Eqs (2), (3) and (4) are substituted into Eqs (35)-(37) of [9] or in Eqs (5)-(9) below, the resulting formulas are simple polynomials in γ_0 . The computational efficiency is due to the fact that γ_0 need be calculated only once for each a.

The rotational symmetry is illustrated by considering the integrals,

$$(2p_x^2\ 2p_x^2) = f_0 + \frac{\partial^2}{\partial x^2}f_2 + \frac{\partial^2}{\partial x^2}f_2' + \frac{\partial^4}{\partial x^4}f_4 \tag{5}$$

$$(2p_y^2\ 2p_y^2) = f_0 + \frac{\partial^2}{\partial y^2}f_2 + \frac{\partial^2}{\partial y^2}f_2' + \frac{\partial^4}{\partial y^4}f_4 \tag{6}$$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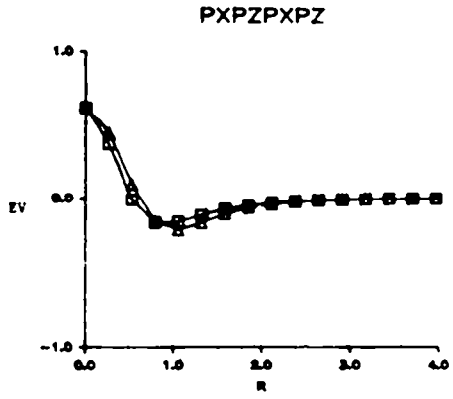
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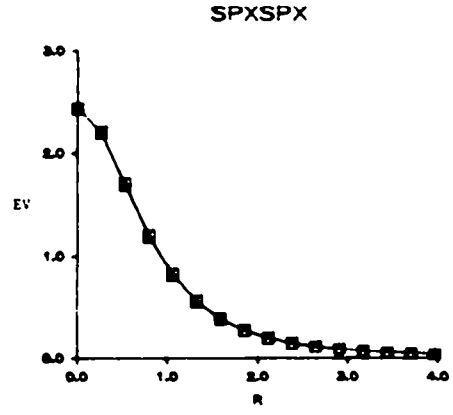
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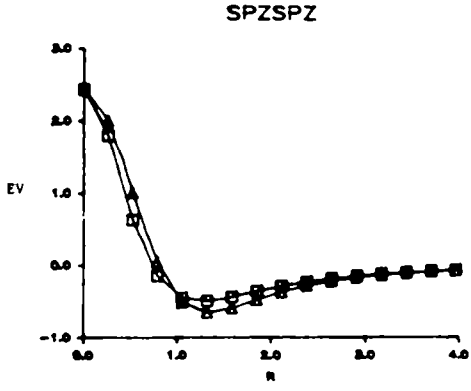
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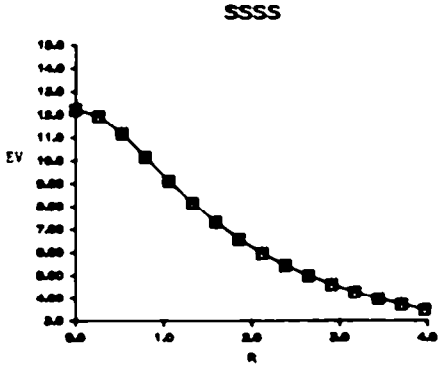
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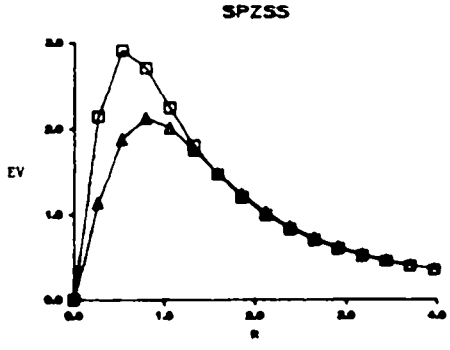
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$$(2p_x^2|2p_y^2) = f_0 + \frac{\partial^2}{\partial x^2} f_2 + \frac{\partial^2}{\partial y^2} f_2' + \frac{\partial^4}{\partial x^2 \partial y^2} f_4 \tag{7}$$

$$(2p_y^2|2p_z^2) = f_0 + \frac{\partial^2}{\partial y^2} f_2 + \frac{\partial^2}{\partial z^2} f_2' + \frac{\partial^4}{\partial x^2 \partial y^2} f_4 \tag{8}$$

$$(2p_x 2p_y|2p_z 2p_y) = \frac{\partial^4}{\partial x^2 \partial y^2} f_4 \tag{9}$$

which are the translationally invariant forms of Eqs (35)-(37) of [9]. Here x, y and z are components of the interatomic vector along the space fixed x, y and z axes. The function f_2' is identical to f_2 except that atomic parameters for atoms a and b, such as ζ_a and ζ_b, are interchanged. Using the properties of the differential operators, eqs (5)-(8) can be combined into the invariant form,

$$(2p_x^2|2p_z^2) + (2p_y^2|2p_y^2) - (2p_x^2|2p_y^2) - (2p_y^2\,2p_z^2) = 4(2p_x 2p_y\,2p_x 2p_y)' \tag{10}$$

where $(2p_x 2p_y\,2p_x 2p_y)'$ is given by Eq (9) after a 45 degree rotation about the space fixed z axis. If the two atoms lie on the z axis then we have $(2p_x^2|2p_z^2) = (2p_y^2\,2p_y^2)$, $(2p_x^2\,2p_z^2) = (2p_y^2|2p_z^2)$ and $(2p_x 2p_y\,2p_x 2p_y)' = (2p_x 2p_y\,2p_x 2p_y)$. Using these in Eq (10) leads to,

$$(2p_x^2\,2p_z^2) = (2p_x^2|2p_y^2) + 2(2p_x 2p_y|2p_x 2p_y) \tag{11}$$

which is the relationship used to enforce rotational invariance in the MNDO integrals. Eq (11) must also be satisfied at the united atom limit.[11] When the OK potential is used as γ_0, each integral, Eqs (5)-(9), displays the correct limiting behavior and corresponds, term by term, to the separate multipole-multipole interactions in the DT method. Indeed, the DT integrals can be regarded as finite difference approximations to ours[12]. We note that although f_0, f_2 and f_4 can be obtained from a common "a" parameter, the rotational symmetry is retained if the a's are chosen independent of one another. For the homonuclear case, DT use two atomic parameters (aside from the orbital exponent) to evaluate all of the $(p^2\,p^2)$ integrals. These two parameters, ρ_0^a and ρ_2^a, are adjusted such that the calculated one center integrals match the "spectroscopic" values (see, however, the discussion in [7]). An entirely analogous procedure can be applied in the present parameterization by identifying the a's in f_0, f_2 and f_4 with the DT a_{00}, a_{02} and a_{22} respectively. These are computed as $a_{ij} = \rho_i^a + \rho_j^a, (i, j = 0, 2)$, where ρ_0 and ρ_2 are the two atomic parameters. Results of doing this are reported in the next section. As a practical matter, however, it may be desirable to use the full flexibility in fitting integrals to the DT values for use in the current MNDO and AM1 methods.

III. Results

The figure shows the six integrals for two carbon atoms examined by DT, calculated by their method (triangles) and by the present method (squares). Distances are in angstroms. For our results, the parameters ρ_0^a , ρ_1^a and ρ_2^a were obtained exactly from the united atom formulas as,

$$\rho_0^a = \frac{1}{2g_{ss}} \tag{12}$$

$$\rho_1^a = \frac{1}{2}\left(\frac{25}{12\zeta_a^2 h_{sp}}\right)^{\frac{1}{2}} \tag{13}$$

$$\rho_2^a = \frac{1}{2}\left(\frac{24}{12\zeta_a^4 h_{pp}}\right)^{\frac{1}{2}} \tag{14}$$

using the DT values for ζ_a , g_{ss} , h_{sp} and h_{pp} . The results are in apparently reasonable agreement with DT and we are hopeful these integrals will be useful in MNDO and AM1. If not, then the greater flexibility of our method can be used to obtain a better fit to the DT values, at least in the region ($r > 1\mathring{A}$) beyond the cutoff below which the coded integrals are not evaluated.

IV.Summary and Conclusion

We have presented a much simpler and more efficient method of computing parameterized two electron integrals for MNDO and AM1. The method is readily extended to arbitrary basis sets and easily applied to derivative integrals. The method appears very attractive for future semiempirical theories.

Acknowledgements

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[10] A reviewer of reference [9] suggested that such reporting of formulas for individual integrals can easily get out of hand, particularly when the formulas can be generated by a straightforward algorithm. In the present case we are using machine algebra programs to generate formulas and efficient FORTRAN code for arbitrary Slater basis sets. See M. McCourt and J. McIver, QCPE Bulletin 7, 69 (1987).

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[12] In local coordinates, the DT integrals are finite difference approximations to the cartesian derivatives in Eqs (5) - (9). The formal relationship is established by a limiting procedure. For example, the DT integrals $[q, Q_{zz}]$, $[Q_{zz}, Q_{zz}]$ and $[Q_{xy}, Q_{xy}]$ are related to our $\frac{\partial^2 f_2}{\partial z^2}$, $\frac{\partial^4 f_4}{\partial z^4}$ and $\frac{\partial^4 f_4}{\partial x^2 \partial y^2}$ by,

$$\frac{\partial^2 f_2}{\partial z^2} = (D_z^B)^2 \lim_{D_z^B \to 0} \frac{[q, Q_{zz}]}{(D_z^B)^2}$$

$$\frac{\partial^4 f_4}{\partial z^4} = (D_z^A)^2 (D_z^B)^2 \lim_{D_z^A \to 0 D_z^B \to 0} \frac{[Q_{zz}, Q_{zz}]}{(D_z^A)^2 (D_z^B)^2}$$

$$\frac{\partial^4 f_4}{\partial x^2 \partial y^2} = (D_z^A)^2 (D_z^B)^2 \lim_{D_z^A \to 0 D_z^B \to 0} \frac{[Q_{xy}, Q_{xy}]}{(D_z^A)^2 (D_z^B)^2}$$

where D_z^A and D_z^B are the point charge displacement parameters of DT. Similar relationships exist for all the integrals.