

## A Semiempirical Model for the Two-Center Repulsion Integrals in the NDDO Approximation

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A self-consistent formalism is proposed for the two-center electron repulsion integrals in the NDDO approximation, based on their expansion in terms of multipole-multipole interactions and free from adjustable parameters.

**Key words:** Two-center repulsion integrals, NDDO approximation

### 1. Introduction

While a number of semiempirical treatments have been based on the CNDO and INDO formalisms [1–4], little attention has as yet been paid to the more rigorous [2] NDDO approximation [1]. The reason for this neglect clearly lies in the problem of evaluating the bicentric electron repulsion integrals. In CNDO and INDO, most of these are neglected while the rest are assumed to have a common value ( $\gamma_{AB}$ ) for a given pair of atoms, A and B. In NDDO, on the other hand, there are twenty-two nonvanishing integrals between each pair of dissimilar first-row atoms, all of which have to be evaluated separately. It is not easy to see how this can be done in a self-consistent manner.

Published NDDO studies [5, 6] have met this difficulty by using theoretical values for the integrals [7], evaluated from Slater-Zener AOs. This procedure is acceptable if the objective is merely an approximation to the results that would be given by Roothaan[8]-Hall[9] (RH) calculations, as in the original CNDO/2 and INDO versions of Pople *et al.* [1]. If, however, one wishes to reproduce the observed properties of molecules, in particular their heats of atomization, the integrals must [2] be modified to allow for the effects of electron correlation, following some procedure analogous to that suggested by Pariser and Parr[10].

A scheme of this kind was developed [11] in these laboratories but subsequent study showed it to suffer from certain inconsistencies. Here we suggest a general

and self-consistent formalism for the NDDO electron repulsion integrals, based on their expansion in terms of multipole-multipole interactions. While this approach has been suggested before [12, 13], it has not, as far as we know, been implemented in a specific semiempirical model.

## 2. Definitions and Notation

The two-electron repulsion integral  $(\mu\nu, \lambda\sigma)$  is defined by:

$$(\mu\nu, \lambda\sigma) = \iint \phi_\mu(1)\phi_\nu(1)(e^2/r_{12})\phi_\lambda(2)\phi_\sigma(2) d\tau_1 d\tau_2 \quad (1)$$

where  $e$  is the electronic charge,  $r_{12}$  is the interelectronic distance, and  $d\tau_1$  and  $d\tau_2$  are the volume elements for integration over the coordinates of electrons 1 and 2, respectively. The functions  $\phi$  are the atomic orbitals (AOs) of our basis, the Greek subscripts denoting the particular AOs involved. As our basis functions, we choose Slater-Zener orbitals which are products of a radial function  $R_{nl}(r)$  and a normalized real spherical harmonic  $y_{lm}(\theta, \phi)$ , with quantum numbers  $n, l, m$ .

$$\phi_{nlm} = R_{nl}(r)y_{lm}(\theta, \phi) \quad (2)$$

$$R_{nl}(r) = (2\zeta_{nl})^{n+1/2} [(2n)!]^{-1/2} r^{n-1} e^{-\zeta_{nl}r} \quad (3)$$

$$y_{l0}(\theta, \phi) = [(2l+1)/4\pi]^{1/2} P_l(\cos \theta) \quad (4)$$

$$y_{lm}(\theta, \phi) = \left[ \frac{2l+1}{2\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta) \begin{cases} \cos |m|\phi & \text{for } m > 0 \\ \sin |m|\phi & \text{for } m < 0 \end{cases} \quad (5)$$

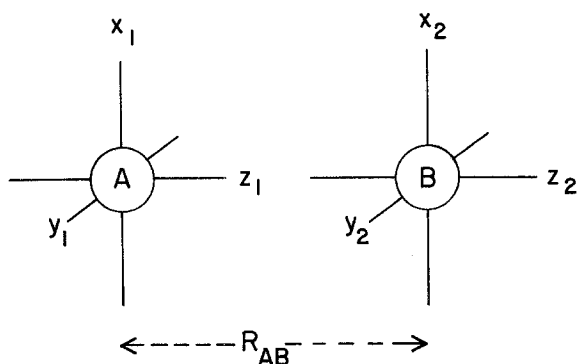
Here  $\zeta_{nl}$  is the orbital exponent of the Slater AO, and  $P_l^{|m|}(\cos \theta)$  an associated Legendre function. In the present study, we shall consider  $s$ - and  $p$ -basis AOs only ( $l=0, 1$ ).

In the NDDO approximation (neglect of diatomic differential overlap), the integrals  $(\mu\nu, \lambda\sigma)$  vanish unless  $\phi_\mu$  and  $\phi_\nu$  are both AOs of the same atom (A), and  $\phi_\lambda, \phi_\sigma$  are both AOs of the same atom (B). The non-zero NDDO repulsion integrals thus are either one-center ( $A=B$ ) or two-center ( $A \neq B$ ) integrals. The one-center integrals can be determined from experimental atomic data by well-known procedures [14, 15] which do not concern us here. The two-center integrals represent the electrostatic interactions between the charge distributions  $\rho(1)$  at atom A and  $\rho(2)$  at atom B.

$$\rho(1) = e\phi_\mu(1)\phi_\nu(1) \quad (6)$$

$$\rho(2) = e\phi_\lambda(2)\phi_\sigma(2) \quad (7)$$

For the calculation of the two-center repulsion integrals, we use the coordinate system indicated in Fig. 1. Atoms A and B (interatomic distance  $R_{AB}$ ) are the origins of two local Cartesian coordinate systems  $(x, y, z)$ , with the  $z$ -axes aligned along the internuclear axis and pointing in the same direction. The  $x$ -axes in both systems are parallel to each other, as are the  $y$ -axes. For general references to any of the Cartesian coordinates, the symbols  $\alpha$  and  $\beta$  will be used ( $\alpha, \beta = x, y, \text{ or } z$ ). Atoms A and B are also taken as the origin of local spherical coordinate systems  $(r, \theta, \phi)$ , with the usual relations between Cartesian and spherical coordinates.



**Fig. 1.** Local Cartesian coordinate system used in the calculation of two-center electron repulsion integrals involving atoms A and B

The coordinates of electron 1 (subscript 1, e.g.  $x_1$ ) always refer to a coordinate system centered at A, and, correspondingly, the coordinates of electron 2 (subscript 2) to a system centered at B. As a general rule, superscripts A or B assign a particular symbol to atom A or B, while the electron is denoted by a number in parentheses ((1) or (2)). Thus  $\zeta_{2s}^A$  is the orbital exponent of the  $2s$  orbital of atom A. We define the multipole moments  $M_{lm}$  of a charge distribution  $\rho(r, \theta, \phi)$  by:

$$M_{lm} = \int d_{lm} r^l y_{lm}(\theta, \phi) \rho(r, \theta, \phi) d\tau \quad (8)$$

This definition in terms of normalized real spherical harmonics will be useful in the following derivations, it is equivalent to the commonly accepted definition [16] of the multipole moments (e.g. of the quadrupole moment as a traceless tensor). For charge distributions arising from an  $sp^3$  basis set, we only have to consider the multipole moments  $M_{lm}$  up to  $l=2$ , since all higher moments vanish by symmetry. Table 1 contains the values for the coefficients  $d_{lm}$  in (8), up to  $l=2$ , along with an alternative, more familiar notation [16] for the multipole moments (monopole  $q$ , dipoles  $\mu_\alpha$ , quadrupoles  $Q_{\alpha\beta}$ ). Both notations ( $M_{lm}$  and  $q, \mu_\alpha, Q_{\alpha\beta}$ ) will be used interchangeably.

**Table 1.** Coefficients  $d_{lm}$  and notation for the multipole moments  $M_{lm}$

$l$	$m$	$d_{lm}$	notation
0	0	$(4\pi)^{1/2}$	$q$
1	0	$(4\pi/3)^{1/2}$	$\mu_z$
1	1	$(4\pi/3)^{1/2}$	$\mu_x$
1	-1	$(4\pi/3)^{1/2}$	$\mu_y$
2	0	$(4\pi/5)^{1/2}$	$Q_{zz}$
2	1	$(3\pi/5)^{1/2}$	$Q_{xz}$
2	-1	$(3\pi/5)^{1/2}$	$Q_{yz}$
2	2	$(3\pi/5)^{1/2}$	$\frac{1}{2}(Q_{xx} - Q_{yy})$
2	-2	$(3\pi/5)^{1/2}$	$Q_{xy}$

### 3. Derivation of the Semiempirical Formalism

We first calculate the two-center NDDO repulsion integrals under the assumption that the two interacting charge distributions do not overlap:

$$(\mu\nu, \lambda\sigma) = \iint \rho(1, r_1, \theta_1, \phi_1) r_{12}^{-1} \rho(2, r_2, \theta_2, \phi_2) d\tau_1 d\tau_2 \quad (9)$$

The solution of this problem is well-known. For non-overlapping charge distributions, the Neumann expansion for the inverse interelectronic distance  $r_{12}^{-1}$  can be simplified to a bipolar expansion [17]. After introduction of normalized real spherical harmonics, we obtain:

$$r_{12}^{-1} = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m=-l_{\min}}^{l_{\min}} 4\pi (-1)^{l_2+|m|} (l_1+l_2)! \\ \times [(2l_1+1)(2l_2+1)(l_1+|m|)(l_2+|m|)(l_1-|m|)(l_2-|m|)]^{-1/2} \\ \times r_1^{l_1} r_2^{l_2} R_{AB}^{-l_1-l_2-1} Y_{l_1 m}(\theta_1, \phi_1) Y_{l_2 m}(\theta_2, \phi_2) \quad (10)$$

where  $l_{\min}$  is the smaller of  $l_1$  and  $l_2$ . Introducing (10) into (9), the repulsion integral  $(\mu\nu, \lambda\sigma)$  can be separated into a product of two integrals, each of which depends on the coordinates of one electron only. Comparison with (8) shows that these two integrals are related to the multipole moments of the two interacting charge distributions:

$$(\mu\nu, \lambda\sigma) = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m=-l_{\min}}^{l_{\min}} f_{l_1 l_2 m} R_{AB}^{-l_1-l_2-1} M_{l_1 m}(1) M_{l_2 m}(2) \quad (11)$$

$$f_{l_1 l_2 m} = 4\pi (-1)^{l_2+|m|} (l_1+l_2)! \\ \times [(2l_1+1)(2l_2+1)(l_1+|m|)(l_2+|m|)(l_1-|m|)(l_2-|m|)]^{-1/2} d_{l_1 m}^{-1} d_{l_2 m}^{-1} \quad (12)$$

Values of the coefficients  $f_{l_1 l_2 m}$  are listed in Table 2, for all relevant combinations of  $l_1$ ,  $l_2$ , and  $m$ .

$l_1$	$l_2$	$m$	$f_{l_1 l_2 m}$
0	0	0	1
0	1	0	-1
0	2	0	1
1	0	0	1
1	1	0	-2
1	2	0	3
2	0	0	1
2	1	0	-3
2	2	0	6
1	1	$\pm 1$	1
1	2	$\pm 1$	-2
2	1	$\pm 1$	2
2	2	$\pm 1$	-16/3
2	2	$\pm 2$	4/3

Table 2. Coefficients  $f_{l_1 l_2 m}$  (12)

The previous derivation provides us with a physical representation of the NDDO repulsion integrals as a sum of multipole-multipole interactions. Eq. (11) has the correct asymptotic behaviour for large interatomic distances ( $R_{AB} \rightarrow \infty$ ). For some specific integrals it also [12] leads to reasonable results even for medium distances ( $R_{AB} > 1.5 \text{ \AA}$ ). For small interatomic distances, however, Eq. (11) breaks down since the assumption of zero diatomic overlap is no longer valid. The classical expression (11) must therefore be modified semiempirically to ensure proper behaviour at small distances. For the limit  $R_{AB} = 0$ , in particular, the modified expression should reproduce the values of the corresponding one-center repulsion integrals which are obtained from experimental atomic data.

A guide to the necessary modifications is provided by those used in previous semiempirical methods at the CNDO and INDO levels. Here the nonvanishing two-center repulsion integrals ( $\mu\mu, \lambda\lambda$ ) are treated as pure monopole-monopole interactions between the charge distributions  $\mu\mu$  and  $\lambda\lambda$ . The MINDO-method [4, 18, 19], for example, approximates these integrals by Klopman's [20] generalization of the Dewar-Sabelli[21a]-Ohno[21b] formula:

$$(\mu\mu, \lambda\lambda)_{\text{MINDO}} = e^2 [R_{AB}^2 + (\rho_0^A + \rho_0^B)^2]^{-1/2} \quad (13)$$

This expression has the correct asymptotic form ( $e^2 R_{AB}^{-1}$ ) for large internuclear distances and also for  $R_{AB} = 0$ , the additive terms  $\rho_0^A$  and  $\rho_0^B$  being chosen so that (13) gives the correct average of one-center repulsion integrals when  $R_{AB}$  vanishes. Following this lead, we have developed an analogous treatment of multipole-multipole interactions.

The nonvanishing multipoles  $M_{lm}$  of the two charge distributions are represented by configurations  $[M_{lm}]$  of  $2^l$  point charges of magnitude  $e/2^l$ . The interactions  $[M_{l_1 m_1}, M_{l_2 m_2}]$  between the multipoles are then calculated by applying the Klopman formula to each of the repulsions and attractions between the point charges representing the two interacting multipoles, and by summing over all these repulsions and attractions. The two-center NDDO repulsion integrals are given as the sum over these semiempirical multipole-multipole interactions:

$$(\mu\nu, \lambda\sigma) = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m=-l_{\min}}^{l_{\min}} [M_{l_1 m}(1), M_{l_2 m}(2)] \quad (14)$$

We now have to specify the relevant point charge configurations.

The monopole  $[q]$  of a charge distribution  $ss$  or  $p_\alpha p_\alpha$  is naturally represented by a single point charge of magnitude  $e$  at the respective nucleus.

The dipole  $[\mu_\alpha]$  of the charge distribution  $sp_\alpha$  is represented by two equal but opposite point charges,  $\pm e/2$ , located on the  $\alpha$ -axis on opposite sides of the nucleus.

Quadrupole fields are generated by sets of four equal point charges, of magnitude  $e/4$  and alternating signs, at the corners of a rhomboid, i.e. two equal but opposite dipoles. A linear configuration  $[Q_{\alpha\alpha}]$  is used for the charge distributions  $p_\alpha p_\alpha$ , and a square configuration  $[Q_{\alpha\beta}]$  for  $p_\alpha p_\beta$ .

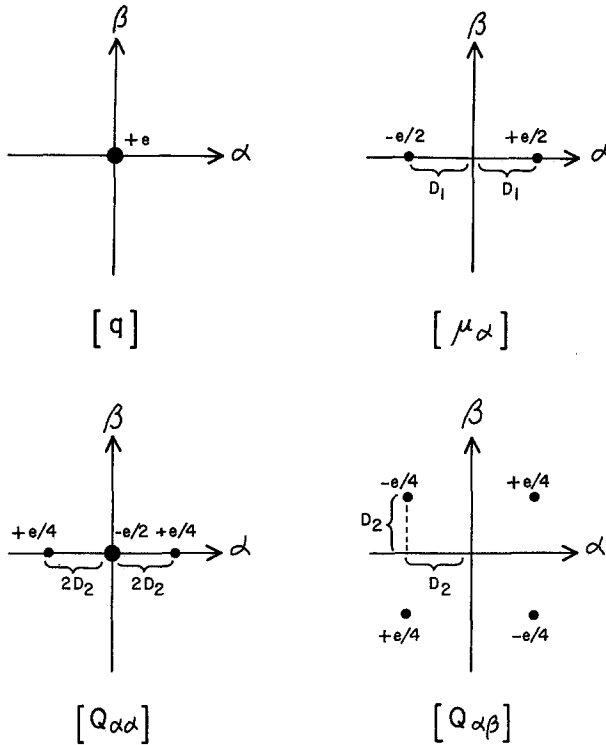


Fig. 2. Point charge configurations corresponding to various multipoles

Figure 2 shows the various point charge configurations. In each case, the origin of the coordinate system corresponds to the nucleus of the atom at which the configuration is centered. Note that two point charges of magnitude  $e/4$  coincide at the origin in the case of the linear configuration  $[Q_{\alpha\alpha}]$ , leading to a net charge of magnitude  $e/2$ .

In order to determine the charge separations  $D_1$  in the dipole and quadrupole configurations (see Fig. 2), we require the multipole moment of each point charge configuration to be equal to that of the corresponding charge distribution. Explicit formulae for the multipole moments are easily derived from the definitions in the literature [16] and in the present paper (cf. Eq. (8) and Table 1). Table 3 contains the resulting expressions for the multipole moments of the relevant charge distributions (I) and of the corresponding point charge configurations (II). The formulae (I) refer to charge distributions (6), (7) in which both basis AOs share the same quantum number  $n$ . Comparing Eq. (I) and (II), we obtain for the charge separations  $D_1$

$$D_1 = \frac{2n+1}{\sqrt{3}} \frac{(4\zeta_{ns}\zeta_{np})^{n+1/2}}{(\zeta_{ns} + \zeta_{np})^{2n+2}} \quad (15)$$

$$D_2 = \sqrt{\frac{(2n+1)(2n+2)}{20}} \zeta_{np}^{-1} \quad (16)$$

Note that the charge separation  $D_2$  turns out to be the same for the linear and square quadrupole configurations,  $[Q_{\alpha\alpha}]$  and  $[Q_{\alpha\beta}]$ , and that the linear configuration  $[Q_{\alpha\alpha}]$  correctly reproduces the quadrupole moment of the distribution  $p_\alpha p_\alpha$  along the  $\alpha$ -axis as well as perpendicular to it.

Having defined the geometry and orientation of the point charge configurations and knowing the interatomic distance  $R_{AB}$ , we can calculate all the distances  $R_{ij}$  between the point charges  $i$  and  $j$  of two configurations at atoms A and B respectively. Applying the Klopman formula, the semiempirical multipole-multipole interactions are given by:

$$[M_{l_1 m}(1), M_{l_2 m}(2)] = \frac{e^2}{2^{l_1+l_2}} \sum_{i=1}^{2^{l_1}} \sum_{j=1}^{2^{l_2}} [R_{ij}^2 + (\rho_{l_1}^A + \rho_{l_2}^B)^2]^{-1/2} \quad (17)$$

In (17), we still have to specify the additive terms  $\rho_l$ . With an  $sp^3$ -basis set, there are three such terms for each element, characteristic of monopole, dipole, and quadrupole. We choose these terms so that Eq. (17) yields the correct one-center limit for the monopole-monopole, dipole-dipole, and quadrupole-quadrupole interactions. For a homonuclear pair of atoms and  $R_{AB}=0$ , we thus have the conditions:

$$[q^A, q^A] = g_{ss}^A = (s^A s^A, s^A s^A) \quad (18)$$

$$[\mu_x^A, \mu_x^A] = h_{sp}^A = (s^A p_x^A, s^A p_x^A) \quad (19)$$

$$[Q_{\alpha\beta}^A, Q_{\alpha\beta}^A] = h_{pp}^A = (p_x^A p_\beta^A, p_x^A p_\beta^A) \quad (20)$$

In order to calculate  $\rho_0^A$ , for example, we insert the explicit expression for  $[q^A, q^A]$  into (18) and solve for  $\rho_0^A$ :

$$\rho_0^A = \frac{e^2}{2g_{ss}^A} \quad (21)$$

In the case of  $\rho_1^A$  and  $\rho_2^A$ , the resulting explicit expressions obtained from (19) and (20) cannot be solved analytically. Expansions in power series lead to the approximate solutions:

$$\rho_1^A \approx \frac{1}{2} \left[ \frac{e^2 (D_1^A)^2}{h_{sp}^A} \right]^{1/3} \quad (22)$$

**Table 3.** Expressions for the multipole moments of the relevant charge distributions (I) and of the corresponding point charge configurations (II)

Charge distribution	Multipole moment	Formula (I)	Formula (II)
$sp_\alpha$	$\mu_x$	$\frac{2n+1}{\sqrt{3}} \frac{e(4\zeta_{ns} \zeta_{np})^{n+1/2}}{(\zeta_{ns} + \zeta_{np})^{2n+2}}$	$eD_1$
$p_\alpha p_\alpha$	$Q_{\alpha\alpha}$	$(2n+1)(2n+2)e/(10\zeta_{np}^2)$	$2eD_2^2$
$p_\alpha p_\alpha$	$Q_{\beta\beta}$	$-(2n+1)(2n+2)e/(20\zeta_{np}^2)$	$-eD_2^2$
$p_\alpha p_\beta$	$Q_{\alpha\beta}$	$3(2n+1)(2n+2)e/(40\zeta_{np}^2)$	$\frac{3}{2}eD_2^2$

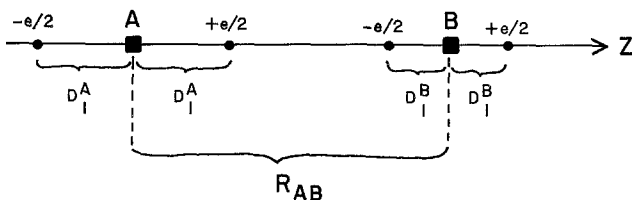


Fig. 3. Interaction between two point charge configurations,  $[\mu_z, \mu_z]$

$$\rho_2^A \approx \frac{1}{2} \left[ \frac{3e^2(D_2^A)^2}{h_{pp}^A} \right]^{1/5}$$

These approximate values are taken as the starting point for an iterative numerical solution, by which  $\rho_1^A$  and  $\rho_2^A$  can be determined to any accuracy desired.

With the preceding definitions for the charge separations  $D_1$  and the additive terms  $\rho_1$ , we are ready to write down explicit semiempirical formulas for the two-center NDDO repulsion integrals.

Consider for example the integral  $(sp_z, sp_z)$ . For a charge distribution  $sp_x$ , the dipole  $\mu_x$  is the only nonvanishing multipole. Thus the expansion (14) reduces to:

$$(sp_z, sp_z) = [\mu_z, \mu_z] \quad (24)$$

Figure 3 shows the interacting point charge configurations. Using Eq. (17), we obtain by inspection:

$$\begin{aligned} [\mu_z, \mu_z] = & (e^2/4)[(R_{AB} + D_1^A - D_1^B)^2 + (\rho_1^A + \rho_1^B)^2]^{-1/2} \\ & - (e^2/4)[(R_{AB} + D_1^A + D_1^B)^2 + (\rho_1^A + \rho_1^B)^2]^{-1/2} \\ & - (e^2/4)[(R_{AB} - D_1^A - D_1^B)^2 + (\rho_1^A + \rho_1^B)^2]^{-1/2} \\ & + (e^2/4)[(R_{AB} - D_1^A + D_1^B)^2 + (\rho_1^A + \rho_1^B)^2]^{-1/2} \quad (25) \end{aligned}$$

Explicit expressions for the other NDDO repulsion integrals are derived analogously. The resulting formulae are collected in the Appendix, which gives the expansions of all nonvanishing NDDO repulsion integrals in terms of multipole-multipole interactions (cf. (14)), and the semiempirical equations for these interactions (cf. (17)).

This semiempirical model for the two-center NDDO repulsion integrals involves five parameters for each element, namely the charge separations,  $D_1$  and  $D_2$ , and the additive terms,  $\rho_0$ ,  $\rho_1$ , and  $\rho_2$ . For hydrogen, there is of course only one parameter,  $\rho_0$ . It should be pointed out that these parameters are calculated from quantities (orbital exponents and one-center repulsion integrals) which occur elsewhere in any semiempirical MO treatment. No additional independent parameters are involved in our expressions for the repulsion integrals.

The Hartree-Fock (orbital) approximation neglects Coulombic correlation between the motions of electrons. As a result, the interelectronic repulsions are overestimated. In semiempirical treatments of the MINDO type [2, 18], this error



**Table 4.** Charge separations  $D_i^c$  and additive terms  $\rho_i^c$  for carbon

Parameter	Value (Å)
$D_1^c$	0.427284
$D_2^c$	0.362563
$\rho_0^c$	0.588660
$\rho_1^c$	0.430254
$\rho_2^c$	0.395734

is compensated by adjustment of the electron repulsion integrals. The values found in this way must therefore be smaller than those calculated analytically from the appropriate orbital functions and a similar relationship should hold in the case of the MNDO treatment [22].

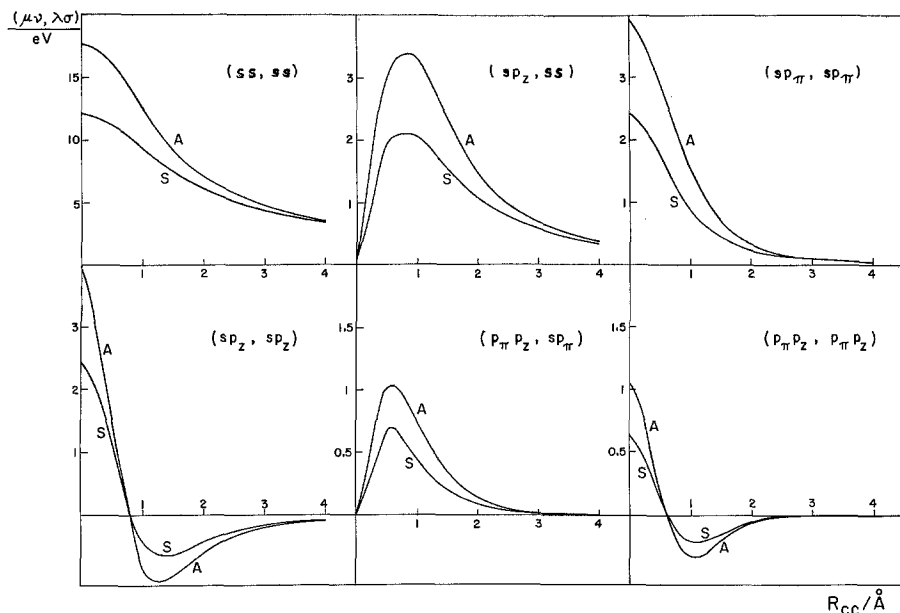
The relationship between the semiempirical and theoretical values for the various integrals is therefore a matter of some interest since it indicates the magnitude of the correction that is being made to allow for the effects of correlation. We have therefore calculated these values for a wide range of orbital exponents, covering combinations of the elements H, C, N, O. Since the trends are similar in all cases, we report numerical results only for carbon, using the orbital exponents found in the final MNDO optimization, [22] i.e.:

$$\zeta_{2s}^C = \zeta_{2p}^C = 1.787537 \quad (26)$$

The values for the one-center integrals are those used in the MINDO/3 method, [4] found by an extension of Oleari's [14] procedure. The calculated charge separations ( $D_i^c$ ) and additive terms ( $\rho_i^c$ ) are listed in Table 4. The semiempirical integrals were computed from the formulae in the Appendix and the analytical integrals from the exact equations.[7]

In Figure 4, semiempirical (S) and analytical (A) values for six of the repulsion integrals are plotted as functions of the interatomic distance  $R_{cc}$ . Several conclusions follow.

- The absolute value of each semiempirical integral is always less than that of the corresponding analytical integral. The difference increases with increasing overlap between the interacting charge distributions (i.e. usually with decreasing interatomic distance).
- For each integral, the semiempirical and analytical curves show a very similar dependence on the interatomic distance. Extrema and zero points, whenever existing, occur at about the same distance.
- At large interatomic distances ( $R_{cc} > 3\text{Å}$ ) the semiempirical and analytical integrals are almost identical, and they converge to the same asymptotic value (11) in the limit  $R_{cc} \rightarrow \infty$ . It can be shown by expansions in power series that the semiempirical formulae (see Appendix) always approach the corresponding classical formulae in the limit  $R_{AB} \rightarrow \infty$ . This of course is due to our requirement that the multipole moments of the charge distributions and of the corresponding point charge configurations should be equal.
- At intermediate interatomic distances ( $R_{cc} \approx$  equilibrium bondlength), the semiempirical integrals are appreciably smaller than the analytical ones.



**Fig. 4.** Semiempirical (S) and analytical (A) NDDO repulsion integrals (in eV) plotted as a function of the interatomic distance  $R_{cc}$  (in Å)

This reduction is rather uniform for different types of integrals; cf. the ratios between the semiempirical and analytical integrals, listed in Table 5 for  $R_{cc} = 1.5$ . Also, if the integrals at medium interatomic distances are arranged in order of magnitude, the same order is obtained for both the semiempirical and the analytical values.

- e) The largest differences between the semiempirical and analytical integrals occur at small interatomic distances ( $R_{cc} < 1\text{Å}$ ) and in the limit  $R_{cc} = 0$ . Table 6 contains the calculated values for the nonvanishing one-center repulsion integrals, along with the values derived [14, 15] from experimental data. Evidently the semiempirical integrals are much closer to Oleari's values than the analytical ones. Due to the definition of the additive terms  $\rho_i$  in our model, the calculated semiempirical values for the integrals  $g_{ss}$ ,  $h_{sp}$ , and  $h_{pp}$  reproduce Oleari's values exactly. Slight differences are found for the remaining integrals  $g_{sp}$ ,  $g_{pp}$ , and  $g_{pp}^*$ ; however the calculated

$(\mu\nu, \lambda\sigma)$	$R_{\mu\nu\lambda\sigma}$
$(ss, ss)$	0.804
$(sp_z, ss)$	0.662
$(sp_\pi, sp_\pi)$	0.625
$(sp_z, sp_z)$	0.632
$(p_\pi p_z, sp_\pi)$	0.595
$(p_\pi p_z, p_\pi p_z)$	0.649

**Table 5.** Ratios  $R_{\mu\nu\lambda\sigma}$  of semiempirical and analytical integrals at  $R_{cc} = 1.5\text{Å}$

**Table 6.** One-center repulsion integrals for carbon

Integral	Value of the integral (eV)		
	Oleari	semiempirical	analytical
$g_{ss}$	12.23	12.23	17.67
$g_{sp}$	11.47	10.80	17.67
$g_{pp}$	11.08	10.58	19.04
$g_{pp^*}$	9.84	10.00	16.99
$h_{sp}$	2.43	2.43	3.91
$h_{pp}$	0.62	0.62	1.03

semiempirical integrals show the same ordering as Oleari's values, whereas the analytical integrals do not.

From the curves in Fig. 4 and the comparisons above, we conclude that the semiempirical and analytical functions for each of the NDDO repulsion integrals show fairly similar general features, e.g. with respect to their dependence on the interatomic distance. The differences between the two functions which occur at smaller interatomic distances seem to be qualitatively consistent with the intended inclusion of correlation effects into the semi-empirical repulsion integrals.

#### 4. Alternative Expressions for the Repulsion Integrals

In our model for the repulsion integrals, there are some details which can be changed without perturbing the internal consistency of the model. We shall discuss a few of these options which we investigated but discarded, for the reasons indicated below.

##### 4.1 Mataga-Nishimoto Approximation

The interaction between the point charges of two point charge configurations can, in principle, be treated by any function which behaves properly in the limits  $R_{AB} \rightarrow 0$  and  $R_{AB} \rightarrow \infty$ . Instead of the Klopman approximation, we can e.g. choose the Mataga-Nishimoto (MN) approximation [23]

$$[q, q]_{\text{MN}} = e^2 \left[ R_{AB} + \frac{1}{\rho_0^A + \rho_0^B} \right]^{-1} \quad (27)$$

In (27), the additive terms  $\rho_0$  are again determined from the one-center repulsion integrals; they are, of course, numerically different from the corresponding terms in the Klopman approximation. Using the MN approximation for monopole-monopole interactions and our formalism for multipole-multipole interactions, explicit formulae can be developed for the NDDO repulsion integrals. We have compared these values with the Klopman and analytical ones, again for a pair of carbon atoms.

$R_{cc}/\text{\AA}$	0.0	0.5	1.0	1.5	2.0
$\Delta_K/eV$	5.44	4.78	3.23	1.81	0.97
$\Delta_{MN}/eV$	5.44	7.45	5.93	3.98	2.64

**Table 7.** Differences  $\Delta$  between semiempirical and analytical integrals ( $ss, ss$ ) in Klopman (K) and Mataga-Nishimoto (MN) approximation

In general, the MN integrals are smaller than the Klopman integrals. This can be seen e.g. from Table 7 which lists the differences between the analytical and semiempirical values for the integral ( $ss, ss$ ) in the Klopman and MN approximations ( $\Delta_K$  and  $\Delta_{MN}$ , respectively) at several internuclear distances  $R_{cc}$ .

Since the differences,  $\Delta_K$  or  $\Delta_{MN}$ , should be measures of the effect of electron correlation, one would expect them to decrease monotonically with increasing  $R_{cc}$ . The  $\Delta_K$  values conform to this but the  $\Delta_{MN}$  values do not,  $\Delta_{MN}$  being smaller for  $R_{cc}=0$  than for  $0.5 < R_{cc} < 1.00\text{\AA}$ . These results seem to suggest that the MN values lead to an overestimate of the effects of electron correlation at medium distances in the case of the integral ( $ss, ss$ ).

Our basic assumptions ensure that the MN integrals show the correct asymptotic behaviour for  $R_{AB} \rightarrow \infty$  and also reproduce exactly the one-center integrals  $g_{ss}$ ,  $h_{sp}$ , and  $h_{pp}$ . The MN values for the remaining one-center integrals,  $g_{sp}$ ,  $g_{pp}$ , and  $g_{pp^*}$ , are, however, less satisfactory than the Klopman ones. At medium distances, the ratios between the semiempirical and analytical values are much less uniform in the MN approximation. Also, extrema and zero points of the MN integrals, whenever they exist, are found at smaller interatomic distances than those of either the Klopman or the analytical integrals.

In view of these inconsistencies, the Mataga-Nishimoto approximation seems less attractive for the present purpose than the Klopman approximation. We therefore used the latter in MNDO [22].

#### 4.2 Scaling of the Point Charge Configurations

In our model, the point charge configurations [ $M_{lm}$ ] consist of  $2^l$  point charges of magnitude  $e/2^l$ , with charge separations  $D_l$ . If both the charges and their separations are scaled by a common factor  $p$ , leading to charges of magnitude  $e/(2p)^l$  and separations  $pD_l$ , the values for the repulsion integrals in the limits  $R_{AB} \rightarrow 0$  and  $R_{AB} \rightarrow \infty$  remain unchanged. We have checked the dependence of the semiempirical integrals on the scaling factor  $p$  and found that the integrals are little affected by moderate changes in it. For example, changing  $p$  from 1 to 0.5 leads to an average change in the repulsion integrals at  $R_{cc} = 1.5\text{\AA}$  of only  $0.04 eV$ .

The exact value of  $p$  is therefore not critical. We keep  $p$  equal to unity because the total charge involved in each configuration is then equal to the elementary charge  $e$  and because the distance of the point charges from the nucleus is close to the radial maximum ( $r_{\max}$ ) of the corresponding charge distributions. Thus for carbon, with orbital exponent (26),  $r_{\max} = 0.591\text{\AA}$ , while the distance of the point charges from the nucleus is  $0.427\text{\AA}$  for the dipole,  $0.513\text{\AA}$  for the square quadrupole, and  $0.725\text{\AA}$  for the linear quadrupole.

### 4.3 Equal Additive Terms

Finally, we considered the option of using only one additive term  $\rho^\Lambda = \rho_0^\Lambda$  (cf. Eq. (21)) for all interactions, in order to simplify the formalism. While the numerical values for the integrals are affected only slightly by this modification, all the resulting changes seemed unfavourable, especially for small interatomic distances. Since the simplification does not even significantly reduce the time required to compute the integrals, we decided to retain a separate term  $\rho_l$  for each multipole.

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### Appendix. Explicit formulae for the NDDO repulsion integrals

We first expand the NDDO repulsion integrals ( $\mu\nu, \lambda\sigma$ ) in terms of the multipole-multipole interactions [ $M_{l_1 m}, M_{l_2 m}$ ]. The subscript  $\pi$  stands for either  $x$  or  $y$  (e.g.  $p_\pi$  is the  $p_x$ - or  $p_y$ -AO).

$$(ss, ss) = [q, q] \quad (28)$$

$$(ss, p_\pi p_\pi) = [q, q] + [q, Q_{\pi\pi}] \quad (29)$$

$$(ss, p_z p_z) = [q, q] + [q, Q_{zz}] \quad (30)$$

$$(p_\pi p_\pi, ss) = [q, q] + [Q_{\pi\pi}, q] \quad (31)$$

$$(p_z p_z, ss) = [q, q] + [Q_{zz}, q] \quad (32)$$

$$(p_\pi p_\pi, p_\pi p_\pi) = [q, q] + [q, Q_{\pi\pi}] + [Q_{\pi\pi}, q] + [Q_{\pi\pi}, Q_{\pi\pi}] \quad (33)$$

$$(p_x p_x, p_y p_y) = [q, q] + [q, Q_{\pi\pi}] + [Q_{\pi\pi}, q] + [Q_{xx}, Q_{yy}] \quad (34)$$

$$(p_\pi p_\pi, p_z p_z) = [q, q] + [q, Q_{zz}] + [Q_{\pi\pi}, q] + [Q_{\pi\pi}, Q_{zz}] \quad (35)$$

$$(p_z p_z, p_\pi p_\pi) = [q, q] + [q, Q_{\pi\pi}] + [Q_{zz}, q] + [Q_{zz}, Q_{\pi\pi}] \quad (36)$$

$$(p_z p_z, p_z p_z) = [q, q] + [q, Q_{zz}] + [Q_{zz}, q] + [Q_{zz}, Q_{zz}] \quad (37)$$

$$(sp_z, ss) = [\mu_z, q] \quad (38)$$

$$(sp_z, p_\pi p_\pi) = [\mu_z, q] + [\mu_z, Q_{\pi\pi}] \quad (39)$$

$$(sp_z, p_z p_z) = [\mu_z, q] + [\mu_z, Q_{zz}] \quad (40)$$

$$(ss, sp_z) = [q, \mu_z] \quad (41)$$

$$(p_\pi p_\pi, sp_z) = [q, \mu_z] + [Q_{\pi\pi}, \mu_z] \quad (42)$$

$$(p_z p_z, sp_z) = [q, \mu_z] + [Q_{zz}, \mu_z] \quad (43)$$

$$(sp_\pi, sp_\pi) = [\mu_\pi, \mu_\pi] \quad (44)$$

$$(sp_z, sp_z) = [\mu_z, \mu_z] \quad (45)$$

$$(sp_\pi, p_\pi p_z) = [\mu_\pi, Q_{\pi z}] \quad (46)$$

$$(p_\pi p_z, sp_\pi) = [Q_{\pi z}, \mu_\pi] \quad (47)$$

$$(p_\pi p_z, p_\pi p_z) = [Q_{\pi z}, Q_{\pi z}] \quad (48)$$

$$(p_x p_y, p_x p_y) = [Q_{xy}, Q_{xy}] \quad (49)$$

Using the abbreviations

$$R = R_{AB} \quad (50)$$

$$a_{l_1 l_2} = \rho_{l_1}^A + \rho_{l_2}^B \quad (51)$$

we now give the expressions for the semiempirical multipole-multipole interactions :

$$[q, q] = e^2 [R^2 + a_{00}^2]^{-1/2} \quad (52)$$

$$[q, \mu_z] = (e^2/2) [(R + D_1^B)^2 + a_{01}^2]^{-1/2} - e^2/2 [(R - D_1^B)^2 + a_{01}^2]^{-1/2} \quad (53)$$

$$[q, Q_{\pi\pi}] = (e^2/2) [R^2 + (2D_2^B)^2 + a_{02}^2]^{-1/2} - e^2/2 [(R^2 + a_{02}^2)]^{-1/2} \quad (54)$$

$$[q, Q_{zz}] = (e^2/4) [(R + 2D_2^B)^2 + a_{02}^2]^{-1/2} - e^2/2 [R^2 + a_{02}^2]^{-1/2} \\ + (e^2/4) [(R - 2D_2^B)^2 + a_{02}^2]^{-1/2} \quad (55)$$

$$[\mu^\pi, \mu_\pi] = (e^2/2) [R^2 + (D_1^A - D_1^B)^2 + a_{11}^2]^{-1/2} \\ - (e^2/2) [R^2 + (D_1^A + D_1^B)^2 + a_{11}^2]^{-1/2} \quad (56)$$

$$[\mu_z, \mu_z] = (e^2/4) [(R + D_1^A - D_1^B)^2 + a_{11}^2]^{-1/2} \\ - (e^2/4) [(R + D_1^A + D_1^B)^2 + a_{11}^2]^{-1/2} \\ - (e^2/4) [(R - D_1^A - D_1^B)^2 + a_{11}^2]^{-1/2} \\ + (e^2/4) [(R - D_1^A + a_{11}^2)]^{-1/2} \quad (57)$$

$$[\mu_\pi, Q_{\pi z}] = (-e^2/4) [(R - D_2^B)^2 + (D_1^A - D_2^B)^2 + a_{12}^2]^{-1/2} \\ + (e^2/4) [(R - D_2^B)^2 + (D_1^A + D_2^B)^2 + a_{12}^2]^{-1/2} \\ + (e^2/4) [(R + D_2^B)^2 + (D_1^A - D_2^B)^2 + a_{12}^2]^{-1/2} \\ - (e^2/4) [(R + D_2^B)^2 + (D_1^A + D_2^B)^2 + a_{12}^2]^{-1/2} \quad (58)$$

$$[\mu_z, Q_{\pi\pi}] = (-e^2/4) [(R + D_1^A)^2 + (2D_2^B)^2 + a_{12}^2]^{-1/2} \\ + (e^2/4) [(R - D_1^A)^2 + (2D_2^B)^2 + a_{12}^2]^{-1/2} \\ + (e^2/4) [(R + D_1^A)^2 + a_{12}^2]^{-1/2} \\ - (e^2/4) [(R - D_1^A)^2 + a_{12}^2]^{-1/2} \quad (59)$$

$$[\mu_z, Q_{zz}] = (-e^2/8) [(R + D_1^A - 2D_2^B)^2 + a_{12}^2]^{-1/2} \\ + (e^2/8) [(R - D_1^A - 2D_2^B)^2 + a_{12}^2]^{-1/2} \\ - (e^2/8) [(R + D_1^A + 2D_2^B)^2 + a_{12}^2]^{-1/2} \\ + (e^2/8) [(R - D_1^A + 2D_2^B)^2 + a_{12}^2]^{-1/2} \\ + (e^2/4) [(R + D_1^A)^2 + a_{12}^2]^{-1/2} \\ - (e^2/4) [(R - D_1^A)^2 + a_{12}^2]^{-1/2} \quad (60)$$

$$\begin{aligned}
 [Q_{\pi\pi}, Q_{\pi\pi}] = & (e^2/8)[R^2 + 4(D_2^A - D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/8)[R^2 + 4(D_2^A + D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/4)[R^2 + (2D_2^A)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/4)[R^2 + (2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/4)[R^2 + a_{22}^2]^{-1/2}
 \end{aligned} \tag{61}$$

$$\begin{aligned}
 [Q_{xx}, Q_{yy}] = & (e^2/4)[R^2 + (2D_2^A)^2 + (2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/4)[R^2 + (2D_2^A)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/4)[R^2 + (2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/4)[R^2 + a_{22}^2]^{-1/2}
 \end{aligned} \tag{62}$$

$$\begin{aligned}
 [Q_{\pi\pi}, Q_{zz}] = & (e^2/8)[(R - 2D_2^B)^2 + (2D_2^A)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/8)[(R + 2D_2^B)^2 + (2D_2^A)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/8)[(R - 2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/8)[(R + 2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/4)[R^2 + (2D_2^A)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/4)[R^2 + a_{22}^2]^{-1/2}
 \end{aligned} \tag{63}$$

$$\begin{aligned}
 [Q_{zz}, Q_{zz}] = & (e^2/16)[(R + 2D_2^A - 2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/16)[(R + 2D_2^A + 2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/16)[(R - 2D_2^A - 2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/16)[(R - 2D_2^A + 2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/8)[(R + 2D_2^A)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/8)[(R - 2D_2^A)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/8)[(R + 2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/8)[(R - 2D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/4)[R^2 + a_{22}^2]^{-1/2}
 \end{aligned} \tag{64}$$

$$\begin{aligned}
 [Q_{\pi z}, Q_{\pi z}] = & (e^2/8)[(R + D_2^A - D_2^B)^2 + (D_2^A - D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/8)[(R + D_2^A - D_2^B)^2 + (D_2^A + D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/8)[(R + D_2^A + D_2^B)^2 + (D_2^A - D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/8)[(R + D_2^A + D_2^B)^2 + (D_2^A + D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/8)[(R - D_2^A - D_2^B)^2 + (D_2^A - D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/8)[(R - D_2^A - D_2^B)^2 + (D_2^A + D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/8)[(R - D_2^A + D_2^B)^2 + (D_2^A - D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (-e^2/8)[(R - D_2^A + D_2^B)^2 + (D_2^A + D_2^B)^2 + a_{22}^2]^{-1/2}
 \end{aligned} \tag{65}$$

$$\begin{aligned}
 [Q_{xy}, Q_{xy}] = & (e^2/4)[R^2 + 2(D_2^A - D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & + (e^2/4)[R^2 + 2(D_2^A + D_2^B)^2 + a_{22}^2]^{-1/2} \\
 & - (e^2/2)[R^2 + 2(D_2^A)^2 + 2(D_2^B)^2 + a_{22}^2]^{-1/2}
 \end{aligned} \tag{66}$$

The formulas for  $[\mu_z, q]$ ,  $[Q_{\pi\pi}, q]$ ,  $[Q_{zz}, q]$ ,  $[Q_{\pi z}, \mu_\pi]$ ,  $[Q_{\pi\pi}, \mu_z]$ ,  $[Q_{zz}, \mu_z]$ ,  $[Q_{zz}, Q_{\pi\pi}]$  are obtained from those for  $[q, \mu_z]$ ,  $[q, Q_{\pi\pi}]$ ,  $[q, Q_{zz}]$ ,  $[\mu_\pi, Q_{\pi z}]$ ,  $[\mu_z, Q_{\pi\pi}]$ ,  $[\mu_z, Q_{zz}]$ ,  $[Q_{\pi\pi}, Q_{zz}]$  by exchanging  $D_i^A \leftrightarrow D_i^B$ ,  $a_{i_1 i_2} \leftrightarrow a_{i_2 i_1}$ , and multiplying by  $(-1)^{i_1 + i_2}$ , respectively.

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