

Extension of the MNDO formalism to *d* orbitals: Integral approximations and preliminary numerical results

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Received May 21, 1991/Accepted July 15, 1991

Summary. The point charge model for calculating the two-center two-electron integrals in MNDO and related methods is extended to *d* orbitals. It is suggested to expand these integrals in terms of semiempirical multipole-multipole interactions where all monopoles, dipoles and quadrupoles are included, and all higher multipoles are neglected. The proposed scheme has been implemented, and numerical results for the integrals are reported. A preliminary MNDO parametrization for chlorine indicates that the inclusion of *d* orbitals improves the results significantly, compared with the original MNDO and related methods.

Key words: MNDO – *d* orbitals

1 Introduction

MNDO [1], AM1 [2], and PM3 [3] are widely used in theoretical studies of molecular structure and reactivity [4–6]. These semiempirical methods employ an *sp* basis set and do not include *d* orbitals in their present implementation. Therefore they cannot be applied to most transition metal compounds. The lack of *d* orbitals may also explain that MNDO and AM1 normally predict hypervalent compounds of main-group elements much too unstable [3]. It has been claimed that this deficiency has been largely overcome by the PM3 parametrization [3] but, on the other hand, there is ample evidence for the importance of *d* orbitals in hypervalent compounds, both at the *ab initio* [7] and semiempirical [8] level. Thus an extension of the MNDO formalism to *d* orbitals appears to be desirable for semiempirical investigations of transition metals and heavier main-group elements.

The treatment of the two-center two-electron integrals is the most difficult problem in such an extension. A semiempirical scheme for evaluating these integrals in an *spd* basis has been suggested [9] which is based on a spherical tensor approach and involves polynomials of interpolation for small interatomic distances. The present paper proposes a generalization of the original point charge model [10] which is currently used in MNDO, AM1, and PM3 to calculate the two-center two-electron integrals. Numerical tests and a preliminary

MNDO parametrization for chlorine are reported to demonstrate the validity of our new approach for introducing d orbitals into the MNDO formalism.

2 Theoretical derivations

Unless noted otherwise we adopt the same conventions as in the original paper [10]. The two-electron integral $(\mu\nu, \lambda\sigma)$ is defined by:

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

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 electron 1 and 2, respectively. The functions φ are the atomic orbitals (AOs) of our basis, the Greek subscripts denoting the particular AOs involved. They are chosen to be Slater–Zener orbitals with quantum numbers n, l, m :

$$\varphi_{nlm} = R_n(r)S_{lm}(\Theta, \varphi) \quad (2)$$

where the radial functions $R_n(r)$ and the normalized real spherical harmonics $S_{lm}(\Theta, \varphi)$ are defined in the usual manner [10, 11]. The two-center two-electron integrals $(\mu^A\nu^A, \lambda^B\sigma^B)$ represent the electrostatic interactions between the charge distributions $\mu^A\nu^A = \varrho^{\mu\nu}(1)$ at atom A and $\lambda^B\sigma^B = \varrho^{\lambda\sigma}(2)$ at atom B. For Slater–Zener orbitals these charge distributions can be expressed [11] in terms of a finite linear combination of normalized real spherical harmonics:

$$\varrho^{\mu\nu} = e\varphi_\mu\varphi_\nu = eR_{n_\mu l_\mu}(r)R_{n_\nu l_\nu}(r) \sum_{LM} a_{LM}^{\mu\nu} S_{LM}(\Theta, \varphi) \quad (3)$$

with an analogous formula for $\varrho^{\lambda\sigma}$. The coefficients $a_{LM}^{\mu\nu}$ are closely related to Clebsch–Gordan coefficients, and a complete list of their values is available for an spd basis [12]. The multipole moments of a given charge distribution can be defined either in cartesian tensor form [13] or using spherical tensors [14, 15], with well-known relationships between the two representations [15, 16]. For our purposes it is most convenient to introduce real spherical multipole components [10, 15]:

$$M_{lm}^{\mu\nu} = \int d_{lm} r^l S_{lm}(\Theta, \varphi) \varrho^{\mu\nu}(r, \Theta, \varphi) d\tau \quad (4)$$

$$d_{lm} = [4\pi/(2l+1)]^{1/2} \quad (5)$$

Explicit expressions for $d_{lm} r^l S_{lm}(\Theta, \varphi)$ up to $l = 4$ are given in Table 1 of Ref. [15] (denoted as R_{l0} for $m = 0$, R_{lmc} for $m > 0$, and $R_{l|m|s}$ for $m < 0$). After inserting Eq. (3) into Eq. (4), only the terms with $l = L$ and $m = M$ survive in the angular integration due to the orthogonality of the spherical harmonics, and we obtain:

$$M_{lm}^{\mu\nu} = ea_{lm}^{\mu\nu} d_{lm} \int R_{n_\mu l_\mu}(r)R_{n_\nu l_\nu}(r)r^{l+2} dr = ea_{lm}^{\mu\nu} d_{lm} A_l^{\mu\nu} \quad (6)$$

$$A_l^{\mu\nu} = (2\zeta_\mu)^{n_\mu+1/2}(2\zeta_\nu)^{n_\nu+1/2}(\zeta_\mu + \zeta_\nu)^{-n_\mu-n_\nu-l-1}[(2n_\mu)!(2n_\nu)!]^{-1/2}(n_\mu+n_\nu+l)! \quad (7)$$

where ζ is the orbital exponent appearing in the explicit formulas [10, 11] for the radial functions $R_n(r)$. An expression analogous to Eq. (6) holds for $M_{lm}^{\lambda\sigma}$.

Under the assumption that the two interacting charge distributions $\varrho^{\mu\nu}(1)$ at atom A and $\varrho^{\lambda\sigma}(2)$ at atom B do not overlap, the two-center two-electron integral

can be calculated exactly as a sum over classical multipole interactions [10]:

$$(\mu\nu, \lambda\sigma) = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m=-l_{\min}}^{l_{\min}} f_{l_1 l_2 m} R_{AB}^{-l_1-l_2-1} M_{l_1 m}^{\mu\nu}(1) M_{l_2 m}^{\lambda\sigma}(2) \quad (8)$$

$$f_{l_1 l_2 m} = (-1)^{l_2+|m|} (l_1+l_2)! [(l_1+|m|)! (l_2+|m|)! (l_1-|m|)! (l_2-|m|)!]^{1/2} \quad (9)$$

where l_{\min} is the smaller of l_1 and l_2 , and R_{AB} the internuclear distance. It should be noted that our current definitions for d_{lm} , see Eq. (5), and $f_{l_1 l_2 m}$, see Eq. (9), deviate from the previous ones [10] in the case $l=2$, $m \neq 0$ (by a constant factor) in order to be consistent with spherical tensor conventions [14, 15]. This does not affect any physically relevant results, e.g. for $(\mu\nu, \lambda\sigma)$.

The classical expression for $(\mu\nu, \lambda\sigma)$, see Eq. (8), shows the correct asymptotic behaviour for $R_{AB} \rightarrow \infty$, but breaks down for small internuclear distances since the assumption of zero diatomic overlap is then no longer valid. It 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 semiempirical one-center two-electron integrals. In order to satisfy these objectives it has been suggested [10] to represent the nonvanishing multipoles of the two interacting charge distributions by suitable configurations of point charges. The interactions $[M_{l_1 m}^{\mu\nu}, M_{l_2 m}^{\lambda\sigma}]$ between the multipoles are then calculated by applying the Klopman formula [17] 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 two-electron integrals are given as the sum over these semiempirical multipole-multipole interactions:

$$(\mu\nu, \lambda\sigma) = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m=-l_{\min}}^{l_{\min}} [M_{l_1 m}^{\mu\nu}, M_{l_2 m}^{\lambda\sigma}] \quad (10)$$

The essential step in this scheme is obviously the definition of suitable point charge configurations for all relevant multipoles. Table 1 specifies the quantum numbers l and m of all 96 multipole moments $M_{lm}^{\mu\nu}$ which turn out to be nonzero in a minimal spd basis with 45 unique charge distributions $\mu\nu$.

Figure 1 shows the point charge configurations used for multipoles up to $l=2$. The monopole $[q]$ of any charge distribution is represented by a single point charge of magnitude e at the respective nucleus (multipole M_{00}). The dipole $[\mu_x]$ of an sp or pd charge distribution is represented by two equal but opposite point charges, $\pm e/2$, located on the α -axis on opposite sides of the nucleus (multipole M_{10} for $\alpha = z$, M_{11} for $\alpha = x$, and M_{1-1} for $\alpha = y$). While the preceding definitions are obvious and unique there are several feasible point charge configurations for quadrupoles. In the original paper [10] a linear configuration $[Q_{\alpha\alpha}]$ is suggested for the charge distributions $p_\alpha p_\alpha$, and a square configuration $[Q_{\alpha\beta}]$ for $p_\alpha p_\beta$. Each linear configuration $[Q_{\alpha\alpha}]$ correctly reproduces the quadrupole moments M_{20} and M_{22} of the corresponding distribution $p_\alpha p_\alpha$ ($\alpha = x, y, z$), and each square configuration $[Q_{\alpha\beta}]$ generates the only nonzero quadrupole moment of the distribution $p_\alpha p_\beta$ (M_{21} for $\alpha\beta = xz$, M_{2-1} for $\alpha\beta = yz$, and M_{2-2} for $\alpha\beta = xy$). However, the symmetry relation $[Q_{xx}, Q_{xx}] - [Q_{xx}, Q_{yy}] = 2[Q_{xy}, Q_{xy}]$ is not satisfied for the original choice [10] of equal charge separations in $[Q_{\alpha\alpha}]$ and $[Q_{\alpha\beta}]$. Therefore small numerical deviations from rotational invariance occur with the original point charge model [10]. Rotational invariance can be restored [18] by imposing the condition:

$$(p_x p_y, p_x p_y) = [(p_\pi p_\pi, p_\pi p_\pi) - (p_x p_x, p_y p_y)]/2 \quad (11)$$

Table 1. Nonzero multipole moments $M_{lm}^{\mu\nu}$ for charge distributions $\mu\nu^a$

μ	ν	lm	μ	ν	lm
s	s	0 0	p_π	d_δ	1 1, 3 1, 3 3
s	p_σ	1 0	p_π	$d_{\bar{\delta}}$	1 -1, 3 -1, 3 -3
s	p_π	1 1	$p_{\bar{\pi}}$	d_σ	1 -1, 3 -1
s	$p_{\bar{\pi}}$	1 -1	$p_{\bar{\pi}}$	d_π	3 -2
p_σ	p_σ	0 0, 2 0	$p_{\bar{\pi}}$	$d_{\bar{\pi}}$	1 0, 3 0, 3 2
p_σ	p_π	2 1	$p_{\bar{\pi}}$	d_δ	1 -1, 3 -1, 3 -3
p_σ	$p_{\bar{\pi}}$	2 -1	$p_{\bar{\pi}}$	$d_{\bar{\delta}}$	1 1, 3 1, 3 3
p_π	p_π	0 0, 2 0, 2 2	d_σ	d_σ	0 0, 2 0, 4 0
p_π	$p_{\bar{\pi}}$	2 -2	d_σ	d_π	2 1, 4 1
$p_{\bar{\pi}}$	$p_{\bar{\pi}}$	0 0, 2 0, 2 2	d_σ	$d_{\bar{\pi}}$	2 -1, 4 -1
s	d_σ	2 0	d_σ	d_δ	2 2, 4 2
s	d_π	2 1	d_σ	$d_{\bar{\delta}}$	2 -2, 4 -2
s	$d_{\bar{\pi}}$	2 -1	d_π	d_π	0 0, 2 0, 4 0, 2 2, 4 2
s	d_δ	2 2	d_π	$d_{\bar{\pi}}$	2 -2, 4 -2
s	$d_{\bar{\delta}}$	2 -2	d_π	d_δ	2 1, 4 1, 4 3
p_σ	d_σ	1 0, 3 0	d_π	$d_{\bar{\delta}}$	2 -1, 4 -1, 4 -3
p_σ	d_π	1 1, 3 1	$d_{\bar{\pi}}$	$d_{\bar{\pi}}$	0 0, 2 0, 4 0, 2 2, 4 2
p_σ	$d_{\bar{\pi}}$	1 -1, 3 -1	$d_{\bar{\pi}}$	d_δ	2 -1, 4 -1, 4 -3
p_σ	d_δ	3 2	$d_{\bar{\pi}}$	$d_{\bar{\delta}}$	2 1, 4 1, 4 3
p_σ	$d_{\bar{\delta}}$	3 -2	d_δ	d_δ	0 0, 2 0, 4 0, 4 4
p_π	d_σ	1 1, 3 1	d_δ	$d_{\bar{\delta}}$	4 -4
p_π	d_π	1 0, 3 0, 3 2	$d_{\bar{\delta}}$	$d_{\bar{\delta}}$	0 0, 2 0, 4 0, 4 4
p_π	$d_{\bar{\pi}}$	3 -2			

^a $p_\pi = p_x, p_{\bar{\pi}} = p_y, p_\sigma = p_z, d_\sigma = d_{z^2}, d_\pi = d_{xz}, d_{\bar{\pi}} = d_{yz}, d_\delta = d_{x^2-y^2}, d_{\bar{\delta}} = d_{xy}$ in the standard local coordinate system [10]

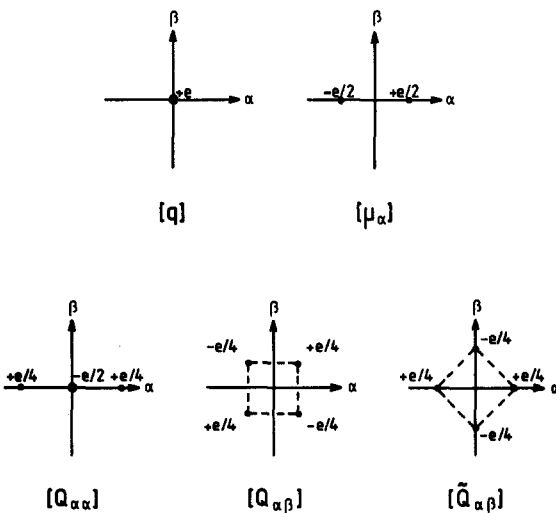


Fig. 1. Point charge configurations for multipoles up to $l = 2$ ($\alpha, \beta = x, y, z$). The separation between two adjacent point charges of opposite sign is $2D_1$ in $[\mu_x]$, and $2D_2$ in $[Q_{xx}]$, $[Q_{y\beta}]$, and $[\tilde{Q}_{\alpha\beta}]$

which has been adopted in all standard semiempirical computer programs for MNDO, AM1, and PM3 [19–21].

For practical reasons we have decided to retain the original point charge model [10] with the above modification, Eq. (11), for all two-center two-electron integrals which do not involve *d* orbitals, so that the established MNDO formalism and parameters remain unchanged for all elements without *d* orbitals. In the case of two-center two-electron integrals involving *d* orbitals, we do use the square configuration $[Q_{\alpha\beta}]$ for representing the quadrupoles M_{21} , M_{2-1} , and M_{2-2} , but abandon the linear configuration $[Q_{\alpha\alpha}]$ in order to avoid problems such as those discussed above. Instead we introduce a second square configuration $[\tilde{Q}_{\alpha\beta}]$ of four equal point charges with alternating signs which are located on the α and β axes (see Fig. 1). The quadrupole M_{22} is then represented by $[\tilde{Q}_{xy}]$, and M_{20} by $[\tilde{Q}_{zx}] - \frac{1}{2}[\tilde{Q}_{xy}]$. Hence, for two-electron interactions involving *d* orbitals, the multipoles up to $l = 2$ are described by the point charge configurations $[q]$, $[\mu_\alpha]$, $[Q_{\alpha\beta}]$, and $[\tilde{Q}_{\alpha\beta}]$.

The separation between two adjacent charges with opposite signs is $2D_1$ in $[\mu_\alpha]$, and $2D_2$ in $[Q_{\alpha\beta}]$ and $[\tilde{Q}_{\alpha\beta}]$. To satisfy the symmetry relations and to ensure rotational invariance, the charge separations must be identical for all charge distributions $\mu\nu$ with the same quantum numbers l_μ and l_ν , respectively, so that there are only five independent charge separations for an *spd* basis, i.e. D_1^{sp} , D_1^{pd} , D_2^{pp} , D_2^{sd} , and D_2^{dd} . They are determined from the requirement [10] that the multipole moment $M_{lm}^{\mu\nu}$ of a reference charge distribution is reproduced by the multipole moment M_{lm}^{PC} of the corresponding point charge configuration which is easily calculated from the definitions in Eqs. (4) and (5): $M_{10}^{PC} = eD_1$, $M_{20}^{PC} = 3eD_2^2/2$, and $M_{2m}^{PC} = 3^{1/2}eD_2^2$ for $m \neq 0$. With our choice of reference distributions (see below, $c_{lm}^{\mu\nu} = 1$ in Table 2) we obtain the following expressions in terms of $A_i^{\mu\nu}$, see Eq. (7):

$$D_1^{sp} = 3^{-1/2}A_1^{sp} \tag{12}$$

$$D_1^{pd} = 5^{-1/2}A_1^{pd} \tag{13}$$

$$D_2^{pp} = 5^{-1/2}(A_2^{pp})^{1/2} \tag{14}$$

$$D_2^{sd} = 15^{-1/4}(A_2^{sd})^{1/2} \tag{15}$$

$$D_2^{dd} = 7^{-1/2}(A_2^{dd})^{1/2} \tag{16}$$

The formulas for D_1^{sp} and D_2^{pp} are equivalent to those given previously [10]. The definition of the charge separations in Eqs. (12)–(16) implies:

$$M_{lm}^{\mu\nu} = c_{lm}^{\mu\nu}M_{lm}^{PC} \tag{17}$$

where the coefficients $c_{lm}^{\mu\nu}$ are listed in Table 2. In the original point charge model [10] for two-center two-electron integrals involving only *s* and *p* orbitals, the charge separations in the configurations $[\mu_\alpha]$, $[Q_{\alpha\alpha}]$, and $[Q_{\alpha\beta}]$ were defined such that all $c_{lm}^{\mu\nu} = 1$, at the expense of problems with rotational invariance (see above). In the present extension to *d* orbitals, our choice for the charge separations in the configurations $[\mu_\alpha]$, $[Q_{\alpha\beta}]$, and $[\tilde{Q}_{\alpha\beta}]$ avoids such invariance problems, at the expense of introducing coefficients $c_{lm}^{\mu\nu} \neq 1$ in Eq. (17). It is obvious from Table 2, however, that $c_{lm}^{\mu\nu}$ always remains close to 1. It should be stressed that our definitions in Eqs. (12)–(16) and Table 2 are, to some extent, arbitrary since a simultaneous scaling [10] of the charge separations $D_i^{\mu\nu}$ by a factor p and of the coefficients $c_{lm}^{\mu\nu}$ by a factor p^{-l} would not affect the internal

Table 2. Coefficients $c_{lm}^{\mu\nu}$ for point charge configurations $[\mu_\alpha]$, $[Q_{\alpha\beta}]$, and $[\tilde{Q}_{\alpha\beta}]^a$

μ	ν	lm	$c_{lm}^{\mu\nu}$	μ	ν	lm	$c_{lm}^{\mu\nu}$
s	p_σ	1 0	1	p_π	d_δ	1 1	1
s	p_π	1 1	1	p_π	d_δ^-	1 -1	1
s	$p_{\bar{\pi}}$	1 -1	1	$p_{\bar{\pi}}$	d_σ	1 -1	$(1/3)^{1/2}$
p_σ	p_σ	2 0	4/3	$p_{\bar{\pi}}$	$d_{\bar{\pi}}$	1 0	1
p_σ	p_π	2 1	1	$p_{\bar{\pi}}$	d_δ	1 -1	1
p_σ	$p_{\bar{\pi}}$	2 -1	1	$p_{\bar{\pi}}$	$d_{\bar{\delta}}$	1 1	1
p_π	p_π	2 0	2/3	d_σ	d_σ	2 0	4/3
p_π	p_π	2 2	1	d_σ	d_π	2 1	$(1/3)^{1/2}$
p_π	$p_{\bar{\pi}}$	2 -2	1	d_σ	$d_{\bar{\pi}}$	2 -1	$(1/3)^{1/2}$
$p_{\bar{\pi}}$	$p_{\bar{\pi}}$	2 0	2/3	d_σ	d_δ	2 2	$(4/3)^{1/2}$
$p_{\bar{\pi}}$	$p_{\bar{\pi}}$	2 2	1	d_σ	$d_{\bar{\delta}}$	2 -2	$(4/3)^{1/2}$
s	d_σ	2 0	$(4/3)^{1/2}$	d_π	d_π	2 0	2/3
s	d_π	2 1	1	d_π	d_π	2 2	1
s	$d_{\bar{\pi}}$	2 -1	1	d_π	$d_{\bar{\pi}}$	2 -2	1
s	d_δ	2 2	1	d_π	d_δ	2 1	1
s	$d_{\bar{\delta}}$	2 -2	1	d_π	$d_{\bar{\delta}}$	2 -1	1
p_σ	d_σ	1 0	$(4/3)^{1/2}$	$d_{\bar{\pi}}$	$d_{\bar{\pi}}$	2 0	2/3
p_σ	d_π	1 1	1	$d_{\bar{\pi}}$	$d_{\bar{\pi}}$	2 2	1
p_σ	$d_{\bar{\pi}}$	1 -1	1	$d_{\bar{\pi}}$	d_δ	2 -1	1
p_π	d_σ	1 1	$(1/3)^{1/2}$	$d_{\bar{\pi}}$	$d_{\bar{\delta}}$	2 1	1
p_π	d_π	1 0	1	d_δ	d_δ	2 0	4/3
				$d_{\bar{\delta}}$	$d_{\bar{\delta}}$	2 0	4/3

^a See footnote a of Table 1

consistency of the proposed model. The final numerical results for the two-electron integrals are, however, quite insensitive to such a scaling, and we thus adopt the definitions in Eqs. (12)–(16) and Table 2.

Having specified the geometry and orientation of the point charge configurations and knowing the internuclear 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 [17], the semiempirical multipole-multipole interactions in Eq. (10) are given by:

$$[M_{l_1 m}^{\mu\nu}(1), M_{l_2 m}^{\lambda\sigma}(2)] = \frac{e^2}{2^{l_1+l_2}} c_{l_1 m}^{\mu\nu} c_{l_2 m}^{\lambda\sigma} \sum_{i=1}^{2l_1} \sum_{j=1}^{2l_2} [R_{ij}^2 + (q_{l_1}^{\mu\nu} + q_{l_2}^{\lambda\sigma})^2]^{-1/2} \quad (18)$$

The factors $c_{l_1 m}^{\mu\nu}$ and $c_{l_2 m}^{\lambda\sigma}$, see Eq. (17), ensure the correct asymptotic behaviour for large internuclear distances ($R_{AB} \rightarrow \infty$) where the multipole-multipole interactions approach their classical limit [10]. The additive terms $q_{l_1}^{\mu\nu}$ and $q_{l_2}^{\lambda\sigma}$ must be chosen such that Eq. (18) yields the correct one-center two-electron integrals in the homonuclear case [10]. To maintain rotational invariance, identical additive terms are required for all charge distributions $\mu\nu$ with the same quantum numbers l_μ and l_ν , respectively, so that there are at most eight independent additive terms, i.e. q_0^{ss} , q_0^{pp} , q_0^{dd} , q_1^{sp} , q_1^{pd} , q_2^{pp} , q_2^{sd} , and q_2^{dd} . They are determined from the following conditions at $R_{AB} = 0$ (given in atomic units):

$$(q_0^{ss})^{-1} = 2g_{ss} = 2F_{ss}^0 \quad (19)$$

$$q_0^{pp} = q_0^{ss} \quad (20)$$

$$(\varrho_0^{dd})^{-1} = \frac{2}{5}(g_{d_\sigma d_\sigma} + 2g_{d_\sigma d_\pi} + 2g_{d_\sigma d_s}) = 2F_{dd}^0 \quad (21)$$

$$(\varrho_1^{sp})^{-1} - [(\varrho_1^{sp})^2 + (D_1^{sp})^2]^{1/2} = 4h_{sp} = 4G_{sp}^1/3 \quad (22)$$

$$(\varrho_1^{pd})^{-1} - [(\varrho_1^{pd})^2 + (D_1^{pd})^2]^{1/2} = 4h_{p_\sigma d_\pi} = 16G_{pd}^1/15 \quad (23)$$

$$(\varrho_2^{pp})^{-1} - 2[(\varrho_2^{pp})^2 + (D_2^{pp})^2/2]^{1/2} + [(\varrho_2^{pp})^2 + (D_2^{pp})^2]^{1/2} = 8h_{pp} = 4F_{pp}^2/25 \quad (24)$$

$$(\varrho_2^{sd})^{-1} - 2[(\varrho_2^{sd})^2 + (D_2^{sd})^2/2]^{1/2} + [(\varrho_2^{sd})^2 + (D_2^{sd})^2]^{1/2} = 8h_{sd} = 8G_{sd}^2/5 \quad (25)$$

$$(\varrho_2^{dd})^{-1} - 2[(\varrho_2^{dd})^2 + (D_2^{dd})^2/2]^{1/2} + [(\varrho_2^{dd})^2 + (D_2^{dd})^2]^{1/2} = 8h_{d_\sigma d_\pi} = 8F_{dd}^2/49 \quad (26)$$

where $g_{\mu\nu}$ and $h_{\mu\nu}$ denote the usual one-center Coulomb and exchange integrals, respectively, while $F_{\mu\mu}^0$, $F_{\mu\mu}^2$, $G_{\mu\nu}^1$, and $G_{\mu\nu}^2$ are Slater–Condon parameters. Equations (19), (20), (22), and (24) are equivalent to the conditions used in the original model [10]. The implicit expressions for $\varrho_i^{\mu\nu}$ in Eqs. (22)–(26) are solved by iterative numerical techniques [10]. ϱ_1^{pd} and ϱ_2^{sd} may alternatively be determined from conditions involving other one-center exchange integrals which, however, leads to the same numerical results as Eqs. (23) and (26), respectively.

At this point of our derivation, the two-center two-electron integrals involving d orbitals can be calculated from semiempirical multipole-multipole interactions (up to $l=2$). The computational procedure is completely specified by Eqs. (10), (12)–(16), (18)–(26) and the information given in Fig. 1 and Tables 1 and 2. In analogy to previous work [10] explicit expressions for all nonzero integrals can be written easily. Considering the large number of such integrals in an spd basis, however, these explicit formulas will not be given here. We only note one simplification concerning the quadrupole M_{20} which is represented by $[\tilde{Q}_{zx}] - \frac{1}{2}[\tilde{Q}_{xy}]$: Its interactions with M_{00} , M_{10} , and M_{20} can be evaluated from $[q, \tilde{Q}_{zx}]$, $[\mu_z, \tilde{Q}_{zx}]$, and $[\tilde{Q}_{zx}, \tilde{Q}_{zx}] - \frac{1}{4}[\tilde{Q}_{xy}, \tilde{Q}_{xy}]$, respectively, since $[q, \tilde{Q}_{xy}] = [\mu_z, \tilde{Q}_{xy}] = [\tilde{Q}_{zx}, \tilde{Q}_{xy}] = 0$.

Many of the charge distributions involving d orbitals have octopole or hexadecapole moments. In fact, for a minimal spd basis, there are 44 such multipole moments with $l=3$ or $l=4$ (see Table 1). It is possible to define point charge configurations for describing these higher multipole moments. For example, eight alternating charges of magnitude $e/8$ at the corners of a cube represent three of the octopoles M_{3m} when the z axis is chosen to be either the C_3 axis connecting two opposite corners (case $m=0$), or the C_2 axis bisecting two opposite edges (case $m=1$), or the C_4 axis through the center of two opposite faces (case $m=2$), whereas six alternating charges at the corners of a regular hexagon in the xy plane represent the octopole M_{33} .

The point charge configurations that may be constructed for hexadecapoles are even more complicated. When using these point charge configurations for the higher multipoles with $l > 2$, great care must be taken to avoid certain symmetry and invariance problems, e.g. the occurrence of nonzero values for some interactions which should vanish by symmetry, particularly at $R_{AB} = 0$. Moreover, in an analytical evaluation, the interactions involving higher multipoles with $l > 2$ are usually found to be very small (see below). Therefore it would seem doubtful whether the effort of calculating such complicated higher multipole-multipole interactions is worthwhile in semiempirical calculations.

In view of this situation we have decided to neglect all interactions involving octopoles, hexadecapoles, or higher multipoles, in the evaluation of two-center two-electron integrals by the proposed point charge model. The following section presents some numerical results for these integrals to support our choice. The

ultimate justification of the proposed model will rest on a successful new MNDO parametrization with inclusion of d orbitals for the heavier elements.

3 Numerical tests

Table 3 lists the number of two-center two-electron NDDO integrals in the standard local coordinate system [10], for atoms A and B with an sp or spd basis. In the case of the spd - spd combination with a total of 491 nonzero integrals, the present model neglects 59 and retains 432 of these integrals. Due to symmetry many of these integrals in the local coordinate system are equal to each other in absolute value. Hence, in the homonuclear spd - spd case, there remain only 117 and 95 unique nonzero integrals in an analytical approach and in our model, respectively.

We have calculated the numerical values of these integrals for a wide range of internuclear distances and orbital exponents. In this section we present only few selected results for distances between 1 Å and 5 Å, and for orbital exponents $\zeta_{3s} = \zeta_{3p} = 2$ and $\zeta_{3d} = 1$ which, however, are typical and representative.

Table 4 contains analytical values for all 6 unique two-center two-electron integrals which are neglected in our point charge model for the spd - spd combination. These analytical values have been computed with the use of an STO-4G expansion [22]. They are quite small, i.e. below 0.1 eV around bonding distances,

Table 3. Number of two-center two-electron integrals in NDDO approximation^a

Basis set for atom pair A–B	sp - sp	sp - spd	spd - spd
No NDDO integrals neglected			
—Total number of integrals	100	450	2025
—Nonzero integrals	34	123	491
—Unique integrals, A \neq B	22	64	204
—Unique integrals, A = B	15	—	117
Present model (M_{lm} up to $l = 2$)			
—Nonzero integrals	34	118	432
—Unique integrals, A \neq B	22	60	163
—Unique integrals, A = B	15	—	95

^a Integrals ($\mu\nu, \lambda\sigma$) with $\mu \geq \nu$ and $\lambda \geq \sigma$, in the standard local coordinate system [10]

Table 4. Absolute analytical values (eV) of neglected two-electron integrals^{a,b}

R_{AB} (Å)	1.0	1.5	2.0	3.0	5.0
$(p_\pi p_\pi, p_\sigma d_\delta)$	0.1773	0.1008	0.0432	0.0064	0.0003
$(p_\pi d_\pi, s d_\delta)$	0.1287	0.0895	0.0466	0.0089	0.0005
$(p_\pi d_\pi, p_\sigma d_\delta)$	0.0217	0.0433	0.0295	0.0061	0.0002
$(p_\pi d_\pi, d_\sigma d_\delta)$	0.0972	0.0517	0.0163	0.0009	0.0002
$(p_\pi d_\pi, d_\pi d_\pi)$	0.0210	0.0614	0.0657	0.0281	0.0019
$(d_\delta d_\delta, d_\delta d_\delta)$	0.1249	0.0764	0.0408	0.0090	0.0003

^a Homonuclear case, orbital exponents $\zeta_{3s} = \zeta_{3p} = 2$ and $\zeta_{3d} = 1$

^b 53 other integrals are equal in absolute value to the 6 unique integrals listed

and they quickly approach zero with increasing distance. Compared with two-center Coulomb integrals which are of the order of 5–15 eV and with other two-electron integrals in an *sp* basis (see Fig. 4 of Ref. [10]) it seems justified to neglect the integrals in Table 4, especially when considering that the effects of such a neglect may partly be absorbed by the parametrization procedure.

By construction the semiempirical two-electron integrals obtained from the point charge model show the correct analytical behaviour for large internuclear distances ($R_{AB} \rightarrow \infty$), and they reproduce semiempirical one-center two-electron integrals for $R_{AB} = 0$. The latter are usually determined either from experimental atomic spectra or from a semiempirical parametrization. In both cases they are found to be significantly smaller than the analytical one-center two-electron integrals since the effects of electron correlation are included in the semiempirical one-center two-electron integrals, in an average sense [5, 23–25]. The point charge model provides an interpolation between the limits $R_{AB} = 0$ (correlation included) and $R_{AB} = \infty$ (no correlation) so that some allowance for electron correlation is also made at small internuclear distances. Therefore it seems reasonable to expect [10] that the differences between the analytical and semiempirical two-electron integrals should decrease with increasing internuclear distance and that both types of integrals should show qualitatively the same distance dependence, e.g. with regard to the occurrence of extrema and zero points. These expectations are generally confirmed by our present numerical results for two-electron integrals involving *d* orbitals, in analogy to previous results for an *sp* basis [10].

In order to compare the distance dependence of the analytical and semiempirical two-electron integrals in a more quantitative manner, we have carried out some test calculations where analytical one-center integrals were used in Eqs. (19)–(26) to determine the additive terms $q_i^{\mu\nu}$. With this choice the semiempirical and analytical integrals are equal both for $R_{AB} = 0$ and $R_{AB} \rightarrow \infty$. Deviations at intermediate distances can then be taken as a measure of the difference in the distance dependence of the analytical and semiempirical integrals (I_i^A and I_i^S , respectively). For N integrals considered we define a root-mean-square (*rms*) deviation Δ_{rms} and an average relative deviation Δ_{rel} :

$$\Delta_{rms} = \left[N^{-1} \sum_{i=1}^N (I_i^A - I_i^S)^2 \right]^{1/2} \quad (27)$$

$$\Delta_{rel} = N^{-1} \sum_{i=1}^N |I_i^A - I_i^S| / I_i^A \quad (28)$$

Table 5 lists these deviations for our standard test case, i.e. a homonuclear pair of atoms with an *spd* basis ($\zeta_{3s} = \zeta_{3p} = 2$, $\zeta_{3d} = 1$) and distances between 1 Å and 5 Å. Considering all 491 nonzero integrals (see Table 3) the proposed point charge model leads to *rms* deviations (labeled MNDO) of about 0.3 eV around bonding distances, and less at larger distances. These *rms* deviations turn out to be higher for the subset of 81 Coulomb integrals, and appreciably smaller for the other 410 integrals. However, in the case of the Coulomb integrals, the average relative deviations remain around 10% or less which seems tolerable.

For the sake of comparison, Table 5 also includes data for semiempirical integrals from the Hoggan–Rinaldi [9] scheme (labeled HR). Generally the deviations for HR are of similar magnitude as those for MNDO, the latter ones being often slightly smaller. Judging from Table 5 the simple MNDO point charge model thus performs at least as well as the more elaborate HR scheme [9].

Table 5. Deviations^a between semiempirical and analytical integrals^b

Integrals considered	N	Deviation ^{a,c}	R_{AB} (Å)					
			1.0	1.5	2.0	3.0	4.0	5.0
All nonzero	491	<i>rms</i> , MNDO	0.426	0.349	0.297	0.196	0.112	0.063
		<i>rms</i> , HR	0.373	0.371	0.338	0.215	0.118	0.065
Coulomb	81	<i>rms</i> , MNDO	0.937	0.781	0.685	0.465	0.268	0.152
		<i>rms</i> , HR	0.790	0.823	0.762	0.500	0.281	0.157
		<i>rel</i> , MNDO	0.063	0.092	0.105	0.093	0.068	0.048
		<i>rel</i> , HR	0.075	0.085	0.100	0.091	0.068	0.048
Other nonzero	410	<i>rms</i> , MNDO	0.210	0.158	0.114	0.059	0.028	0.012
		<i>rms</i> , HR	0.208	0.184	0.148	0.076	0.034	0.015

^a *Rms* deviations Δ_{rms} in eV, Eq. (27), and dimensionless relative deviations Δ_{rel} , Eq. (28)

^b Homonuclear case, orbital exponents $\zeta_{3s} = \zeta_{3p} = 2$ and $\zeta_{3d} = 1$

^c MNDO integrals from point charge model (this work), HR integrals from Hoggan–Rinaldi scheme (Ref. [9])

4 Preliminary results for chlorine

A preliminary MNDO parametrization with *d* orbitals has been carried out for chlorine to demonstrate the validity of the proposed point charge model for the two-center two-electron integrals. The remaining terms in the MNDO formalism [1] have been extended to *d* orbitals in the following manner.

For a minimal *spd* basis there are 265 nonzero one-center two-electron integrals ($\mu^A \nu^A, \lambda^A \sigma^A$) with $\mu \geq \nu$ and $\lambda \geq \sigma$ (81 Coulomb, 36 exchange, and 148 hybrid integrals). All these integrals are retained to ensure rotational invariance [26]. Due to symmetry many of these integrals are equal in absolute value so that there are only 45 unique one-center two-electron integrals (14 Coulomb, 11 exchange, and 21 hybrid integrals, where one unique exchange and hybrid integral are equal to each other). The analytical evaluation of these integrals using Slater–Zener orbitals requires the calculation of 14 Slater–Condon parameters ($F_{ss}^0, F_{pp}^0, F_{dd}^0, F_{sp}^0, F_{sd}^0, F_{pd}^0, F_{pp}^2, F_{dd}^2, F_{pd}^2, F_{dd}^4, G_{sp}^1, G_{pd}^1, G_{sd}^2, G_{pd}^3$) and 3 additional radial integrals ($R_{sppd}^1, R_{sdpp}^2, R_{sddd}^2$). In the original MNDO formalism for an *sp* basis [1, 18] the 5 unique one-center two-electron integrals are determined from experimental atomic data. This procedure is generally not feasible for an *spd* basis since some of the 17 independent one-center two-electron parameters (see above) cannot be determined from atomic spectra, in principle, and also since suitable experimental data are sometimes lacking for the heavier elements. In this situation one may either adopt a combination of experimentally and theoretically derived one-center two-electron parameters, as e.g. in the SINDO1 method [27] or optimize these parameters independently, as e.g. in the PM3 method [3] where all 5 unique one-center two-electron integrals for an *sp* basis are determined by the parametrization. The latter approach obviously becomes impractical for an *spd* basis due to the much larger number of unique integrals (see above). We have therefore chosen the following procedure: The one-center Coulomb integrals g_{ss} , g_{pp} , and g_{dd} are optimized in the semiempirical parametrization, and used to derive corresponding orbital exponents ($\tilde{\zeta}_s, \tilde{\zeta}_p, \tilde{\zeta}_d$) which analytically reproduce these semiempirical integrals. Using these orbital exponents all other one-center two-electron integrals are

calculated analytically. It is evident that this approach satisfies rotational invariance and allows the parametrization to adjust the magnitude of the one-center two-electron interactions independently for *s*, *p*, and *d* electrons. Based on previous experience [1–3, 23–25] the semiempirical one-center two-electron integrals should be smaller than the integrals calculated analytically from the orbital exponents ($\zeta_s, \zeta_p, \zeta_d$) used elsewhere in the MNDO formalism [1]. Hence we expect $\tilde{\zeta}_s < \zeta_s$, $\tilde{\zeta}_p < \zeta_p$, and $\tilde{\zeta}_d < \zeta_d$ since the analytical formulas for $(\mu^A \nu^A, \lambda^A \sigma^A)$ are linear in the orbital exponent if all orbitals belong to the same shell.

In the original MNDO method [1] the core-electron attractions and the core-core repulsions are expressed in terms of two-center two-electron integrals:

$$V_{\mu\nu,B} = -Z_B(\mu^A \nu^A, s^B s^B) \quad (29)$$

$$E_{AB}^{core} = Z_A Z_B (s^A s^A, s^B s^B) (1 + e^{-\alpha_A R_{AB}} + e^{-\alpha_B R_{AB}}) \quad (30)$$

where Z_A and Z_B denote the core charges while α_A and α_B are adjustable parameters. In Eqs. (29) and (30) the effect of the atomic core is simulated by the valence-shell charge distribution ss which, like the core, has no multipole moments higher than the monopole. This choice leads to a realistic balance of the electrostatic interactions [1] in the case of first-row atoms where the *s* and *p* orbitals are generally of comparable size. This may no longer be true for an *spd* basis, e.g. in the case of transition metals where the *s*, *p*, and *d* orbital exponents may be quite different. We have therefore decided to represent the core by a monopole [q_{core}] which is associated with an own additive term q_{core} . For elements with an *sp* basis we use $q_{core} = q_0^{ss}$, see Eq. (19), as in the original MNDO formalism [1]. For elements with an *spd* basis, however, q_{core} is treated as an independent adjustable parameter so that the balance between attractive and repulsive Coulomb interactions is determined by the semiempirical parametrization. Hence we have in general:

$$V_{\mu\nu,B} = -Z_B(\mu^A \nu^A, q_{core}^B) \quad (31)$$

$$E_{AB}^{core} = Z_A Z_B (q_{core}^A, q_{core}^B) (1 + e^{-\alpha_A R_{AB}} + e^{-\alpha_B R_{AB}}) \quad (32)$$

where the relevant interactions are evaluated according to the point charge model (see Sect. 2), e.g.:

$$(q_{core}^A, q_{core}^B) = e^2 [R_{AB}^2 + (q_{core}^A + q_{core}^B)^2]^{-1/2} \quad (33)$$

This completes the description of the proposed extensions to the MNDO formalism [1] since all other definitions in MNDO remain unchanged when including *d* orbitals. For an element with an *spd* basis there are thus 14 parameters to be optimized, i.e. U_{ss} , U_{pp} , U_{dd} (one-center one-electron energies); g_{ss} , g_{pp} , g_{dd} (one-center two-electron Coulomb integrals); α , q_{core} (to evaluate core-electron attractions and core-core repulsions); and β_s , β_p , β_d , ζ_s , ζ_p , ζ_d (to calculate resonance integrals). It should be noted for comparison that MNDO and PM3 normally employ 7 and 18 adjustable parameters, respectively, for atoms with an *sp* basis.

Table 6 lists preliminary values for the optimized parameters of chlorine which generally appear to be of reasonable magnitude. Table 7 compares the MNDO results obtained with *d* orbitals to those from standard MNDO [1, 28], AM1 [2, 29], and PM3 [3]. The statistical evaluation in Table 7 is based on a set of 82 test molecules (70 with monovalent Cl, 12 with hypervalent Cl) which consists of the 47 test molecules (46 with monovalent Cl and ClF₃) used in AM1

Table 6. MNDO with *d* orbitals: Preliminary optimized parameters for chlorine

U_{ss} (eV)	-60.163796	β_s (eV)	-14.215175
U_{pp} (eV)	-54.822875	β_p (eV)	-16.400251
U_{dd} (eV)	-22.213087	β_d (eV)	-0.597872
g_{ss} (eV)	10.379211	ζ_s (au)	3.442061
g_{pp} (eV)	7.948007	ζ_p (au)	2.321293
g_{dd} (eV)	6.197289	ζ_d (au)	1.315332
α (\AA^{-1})	2.213706	q_{core}	1.232854

[29] and 35 additional molecules for which reliable experimental data are available (mostly from the PM3 tabulations [3]). For each semiempirical method all 82 test molecules have been calculated using the same computer program, the same geometry input, and the same experimental reference data in the statistical evaluation to avoid any technical errors. The statistical results certainly depend on the choice of the test molecules, but we do believe that their number and diversity are large enough to provide a fair qualitative assessment.

Table 7. Mean absolute errors for chlorine compounds

Property ^a	Molecules ^b	N ^c	MNDO ^d <i>spd</i>	MNDO ^e <i>sp</i>	AM1	PM3
ΔH_f (kcal/mol)	All	82	4.44	28.93	21.61	9.42
	Monovalent	70	4.35	4.57	4.74	6.42
	Hypervalent	12	5.00	167.61	119.99	26.93
	Ref. [29]	47	4.19	6.05	5.43	5.04
R_{Cl-X} (\AA)	All	46	0.030	0.063	0.063	0.036
	Monovalent	34	0.029	0.037	0.037	0.037
	Hypervalent	12	0.034	0.138	0.137	0.036
	X = C	25	0.017	0.033	0.028	0.034
θ_{ClXY} (deg)	All	35	3.27	3.91	4.45	4.47
	Monovalent	27	2.43	1.84	2.21	2.52
	Hypervalent	8	6.12	10.91	11.99	11.06
	X = C	22	1.76	1.57	1.98	2.24
IP (eV)	All	45	0.47	0.87	0.36	0.62
	Monovalent	43	0.43	0.87	0.36	0.60
	Ref. [29]	36	0.47	0.92	0.37	0.54
μ (D)	All	31	0.27	0.32	0.28	0.45
	Monovalent	29	0.27	0.31	0.27	0.45
	Ref. [29]	22	0.24	0.31	0.28	0.43

^a Heat of formation ΔH_f , bond length R_{Cl-X} involving chlorine, bond angle θ_{ClXY} involving chlorine, first ionization potential IP according to Koopmans' theorem, and dipole moment μ

^b See text

^c Number of comparisons

^d Preliminary MNDO parametrization with *d* orbitals, this work

^e Standard MNDO with an *sp* basis [1, 28]

It is obvious from Table 7 that MNDO(*spd*), MNDO(*sp*), AM1, and PM3 give results of comparable quality for monovalent chlorine compounds, with a slight overall advantage for MNDO(*spd*). However, the inclusion of *d* orbitals in MNDO(*spd*) leads to considerable improvements for hypervalent chlorine compounds, particularly with regard to heats of formation. While MNDO(*sp*) and AM1 were not designed to cover hypervalent chlorine compounds [28, 29] the PM3 parametrization was aimed at reproducing the properties of both normalvalent and hypervalent compounds [3]. However, the mean absolute error for the heats of formation of hypervalent chlorine compounds is much higher in PM3 (26.93 kcal/mol) than in MNDO(*spd*) with *d* orbitals (5.00 kcal/mol) indicating that the elaborate PM3 parametrization with 18 adjustable parameters could not overcome the lack of *d* orbitals in this case. In our opinion, this underscores the need for including *d* orbitals in semiempirical calculations of hypervalent molecules. Judging from the data in Table 7, MNDO(*spd*) succeeds in providing a balanced description of normalvalent and hypervalent chlorine compounds.

As stated before the MNDO(*spd*) results in Table 7 are preliminary. They are quoted here to demonstrate that the proposed point charge model for the two-center two-electron integrals and the other extensions of the MNDO formalism to *d* orbitals have been implemented and that these developments lead to significant improvements in the expected areas. Further parametrization work is in progress and will be reported in due course.

Acknowledgements. This study was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Alfred-Krupp-Förderpreis.

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