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Calculation of coulomb integrals in molecules over an *spd* basis of STO

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A spherical tensor expansion of $1/r_{12}$ (where r_{12} is the separation considered) is used to represent Coulomb integrals in a molecular context for an MNDO method over an *spd* basis of STO. This is rendered invariant of the space fixed axes chosen using Wigner rotation matrices which transform the integrals from the molecular frame (as distinct from Dewar [1]). This procedure is found to be rigorous only in the long range limit but is satisfactory at separations of the order of most single bond lengths (as Dewar [1]). The pole at $R_{ab}=0$ is avoided by adding a constant to the separation, which takes the value that reproduces the Slater-Condon monocentric integrals there. Extension over the whole range is carried out using a unique multiplicative polynomial from the Legendre function expansion of $1/(R_{ab}^2+A^2)$ for small R_{ab} and an exponential decay in R_{ab} is dictated by symmetry in the overlap region expression, which retains rotational invariance.

This calculation results in an easy evaluation of these functions and their first derivatives leading to a very rapid molecular geometry optimisation taking the d-orbitals into account in an MNDO hypothesis.

Key words: MNDO — *spd* basis — Spherical tensors — Bi-electronic integrals

1. Introduction

Quantum chemical calculations rely on evaluating several kinds of integral computed over the basis of atomic orbitals x_i. Coulomb integrals, which are of

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the general form:

$$(ij|kl) = \langle x_i(1)x_j(1)|1/r12|x_k(2)x_l(2)\rangle$$

in which r_{12} is the interelectronic separation, are the most difficult to evaluate. In semi-empirical methods they are determined by means of various approximate formulae.

In the MNDO metohd (in which only bicentric terms are considered) Dewar [1] used a point charge model over an *sp* basis. This model is not well adapted to the case of a basis containing *d*-orbitals, (or fully generalised bases).

In this work, we re-examine the evaluation of these integrals, using a notation due to Steinborn [7] for the integrals considered by Roothaan [2], the decomposition of the integrals into fundamental multipolar terms, tabulated by Dyatkina [3] and the multipolar expansion of $1/r_{12}$ in terms of spherical tensors [4]. This procedure assures the rotational invariance and generality of basis.

At short interatomic distances R_{ab}, this multipole expansion ceases to be a good approximation. It is generalised in [5] and the integral should converge to an atomic Slater–Condon term when this distance tends to zero. This difficulty is overcome by using an additive constant A bringing into play the expansion of $1/(R_{ab}^2+A^2)$. The value of A must give the correct monocentric term and the expansion of the total gives an associated Legendre polynomial, which is multiplicative and provides the interpolation of the integral at any separation (see [6]).

Therefore, the method which we propose appears to be more general than Dewar's . In addition, it permits an easy analytical derivation of the integral with respect to interatomic distance and the direction cosines of the bond under consideration. This property makes our method very efficient for useful geometry optimisations.

2. Theoretical analysis

2.1. *The long range limit*

in the case of large separations we have from [4]:

$$\frac{1}{r_{12}} = \sum_{l_1}^{l<} \sum_{l_2} \sum_{m=-l<} \frac{f(l_1, l_2, m)}{R_{ab}^{l_1+l_2+1}} S_{l_1}^{m}(\mathcal{O}\boldsymbol{R}_a) S_{l_2}^{m*}(\mathcal{O}\boldsymbol{R}_b),$$

where $l<$ is the minimum of l_1 and l_2 and

$$f(l_1, l_2, m) = \frac{(-1)^{l_2+|m|}(l_1+l_2)!}{[(l_1-m)!(l_1+m)!(l_2-m)!(l_2+m)!]^{1/2}}. \tag{1.1}$$

The $S_l^m(\mathcal{O}\boldsymbol{R})$ represent spherical tensors [7] with appropriate arguments in the vectorial rotation matrix $\mathcal{O}$ acting on $\boldsymbol{R}$. An arbitrary rotation of axes can thus be considered.

Normalised spherical tensors are rotated from body-fixed axes to space fixed axes using the Wigner rotation marices (matrices of the rotation group). The argument thus appearing in the above formula hence refers to rotation of the vectors $\boldsymbol{R}_a$, $\boldsymbol{R}_b$ to the space fixed axes. This can be directly expressed in terms of the spherical tensor with the unrotated vectors as arguments due to the spherical symmetry of the functions (see [6]).

$$S_{l_1}^{m}(\mathscr{O}\boldsymbol{R}_a)=\sum_{m'=-l_1}^{l_1} D_{mm'}^{l_1}(\Omega_a)S_{l_1}^{m'}(\boldsymbol{R}_a).$$

Here the real D are used with the usual convention for negative m; and the spherical tensors with position vector $\boldsymbol{R}_a$ as argument. This takes a simple form in terms of normalised spherical harmonics with Condon-Shortly phases.

$$S_{l_1}^{m}(\mathscr{O}\boldsymbol{R}_a)=\left(\frac{4\pi}{2l_1+1}\right)^{1/2}\boldsymbol{R}_a^{l_1}\sum_{m'=-l_1}^{l_1} D_{mm'}^{l_1}(\Omega_a)S_{l_1m'}(\Theta_1,\Phi_1). \tag{1.2}$$

The Coulomb integrals occuring in the MNDO approximation [1] of Roothaan's equations are represented by $(i_aj_a|k_bl_b)$ where $i_x(j_xk_xl_x)$ stands for a Slater type orbital centred on atom x, with quantum numbers $N_\mathrm{x}L_\mathrm{x}M_\mathrm{x}$. According to Roothaan [2] the total Coulomb integral is then obtained using the coefficients of [3]:

$$(i_aj_a|k_bl_b)=W_aW_b\sum_{L_aM_a}\sum_{L_bM_b} a_{L_aM_a}\,a_{L_bM_b}[N_aL_aM_a|N_bL_bM_b]\delta_{M_a,M_b}. \tag{1.3}$$

The W represent atomic multipole moments defined in accordance with [3].

$$W=\frac{\left(\dfrac{2\zeta(i)}{K}\right)^{n_i+1/2}\left(\dfrac{2\zeta(j)}{K}\right)^{n_j+1/2}}{[(2n_i)!(2n_j)]^{1/2}}\text{ and } N=n_i+n_j-1.$$

the coefficients $a_{L_aM_a}$ give the contributions of individual integrals and $[N_aL_aM_a|N_bL_bM_b]$ is an individual integral expressed in terms of STO and $1/r_{12}$:

$$\text{from}\qquad [N_aL_aM_a|=\left(\frac{2L_a+1}{4\pi}\right)^{1/2}2^{L_a}K_a^{N_a+2}R_a^{N_a-1}\exp(-K_aR_a)S_{L_aM_a}(\Theta,\Phi). \tag{1.4}$$

The standard expression for an STO with $K_a=\zeta(i_a)+\zeta(j_a)$ in the long range limit $x(N_a+L_a+1)!$ Using (1.1) and (1.2) $[N_aL_aM_a|N_bL_bM_b]$ is approximated by:

$$\Gamma_{L_a,M_a,L_b,M_b}=\sum_{l_1}\sum_{l_2}\sum_{m=-l<}^{1<}\frac{f(l_1,l_2,m)}{R_{ab}^{l_1+l_2+1}}I_aI_b. \tag{1.5}$$

The individual integrals can be carried out where I_a and I_b have similar expressions leading to:

$$\Gamma_{L_a,M_a,L_b,M_b}=\sum_{m=-L<}^{L<}\frac{f(L_a,L_b,m)2^{L_a+L_b}}{R_{ab}^{L_a+L_b+1}K_a^{L_a}K_b^{L_b}}D_{mM_a}^{L_a}(\Omega_a)D_{mM_b}^{L_b}(\Omega b). \tag{1.6}$$

2.2. Treatment of the pole at $R_{ab}=0$ and polynomial of interpolation

The expression (1.6) is not universally applicable outside the long range zone and must be generalised.

The values of monocentric electronic integrals are well known and are given by the Slater-Condon integrals [8]. In order to assure a correct behaviour of Coulomb integrals these values must be reproduced in the short range limit. A method of additive constants was first introduced by Dewar [1] in which these constants are calculated either analytically or numerically from the monocentric terms. Our procedure gives the monocentric integrals directly at $R_{ab} \doteq 0$.

We first define the atomic multipoles as tthey are used in the algorithm:

$$M_a^{L_a} = W_a \left(\frac{2}{K_a} \right)^{L_a} \tag{2.1}$$

Now

$$\begin{aligned} &(i_a j_a | k_b l_b) \\ &\quad = \sum_{L_a M_a} \sum_{L_b M_b} \sum_{m=-1<}^{1<} \frac{f(L_a, L_b, m) M_a^{L_a} M_b^{L_b}}{(R_{ab}^2 + A_{ab}^2)(L_a + L_b + 1)/2} \\ &\qquad \times a_{L_a M_a} a_{L_a M_a} D_{m M_a}^{L_a}(\Omega_a) D_{m M_b}^{L_b}(\Omega_b). \end{aligned} \tag{2.2}$$

A_{ab} is determined from the individual integrals of [3] at $R_{ab} = 0$ where the atoms are no longer distinct (we adopt the label L_a).

To complete the interpolation, a multiplicative polynomial is necessary for full generalisation, where we are guided by the analytical integrals as an upper bound and rotation invariance of the result. These conditions are obviously satisfied by the expansion using associated Legendre functions about $R = 0$ of $1/(R^2 + A^2)$ at small values of A and R. These are standard methods from resolution by spherical functions of differential equations [6]. The polynomials which assure the coincidence between the individual integrals calculated here and those of Dewar calculated in a point charge scheme in the limit of zero charge separation for the *sp* basis appear to be of the form

$$E_l^m(R, A) = \frac{2^m m!(l-2m)!}{l!} \left(\frac{U}{A} \right)^m P_{l-m}^m \left(\frac{R}{U} \right). \tag{2.3}$$

In this expression $l = L_a + L_b$, m is the minimum value of l corresponding to the individual integral concerned, the variable R is short for R_{ab}, A being the equivalent for A_{ab}, $U = (R^2 + A^2)^{1/2}$, $P_{l-m}^m(X)$ is an associated Legendre function of X.

We have omitted subscripts to simplify the expression which is dependent on the pair of atoms and the quantum numbers labeling the individual integral under consideration.

The polynomials (2.3) are generated by

$$E_l^m(R, A) = \frac{(-1)^{l-2m}(2m)!}{l!} U^{l+1} \frac{d^{l-2m}}{dR^{l-2m}} \left(\frac{1}{U^{1+2m}} \right). \tag{2.4}$$

The numerators are themselves polynomials in R, (the denominator being U^{l-2m}) satisfying the simple recurrence relation:

$$\frac{dE_{l+1}^{m}(R, A)}{dR}=(l+1)E_l^m(R, A). \tag{2.5}$$

In the $R=0$ limit these polynomials must reduce to a constant term giving the appropriate Slater–Condon parameter. This condition is satisfied as follows:

Comparison of (2.2), (2.3), and (1.6), in this limit leads to:

$$[N_aL_aM_a|N_bL_bM_b]=\frac{f(L_a, L_a, M_a)(M_a^{L_a})^2E_l^m(Q, A)}{(2L_a+1)}. \tag{2.6}$$

Here we identify the left-hand side of (2.6) with a single Slater–Condon parameter $FG(ij)$.

A_{ab} is expressed on decomposing as follows:

$$A_{ab}=\rho(L_a, i_aj_a)+\rho(L_b, i_bj_b) \tag{2.7}$$

with the ρ being the portions of monocentric integrals ascribed to each atom which take the following form:

$$\rho(L_a, i_aj_a)=\frac{1}{2}\left[\frac{(M_a^{L_a})^2f(L_a, L_a, M_a)E_{2L_a}^{M_a}(0, A)}{2L_aFG(i_aj_a)}\right]^{(1/(2L_a+1))} \tag{2.8}$$

The simple form of the ρ results from the formulation of the M. The FG represent the basic integrals composing the monocentric terms, where the index ij serves to select the value corresponding to a basic coulomb (F) or exchange (G) integral. We thus have, for the differnt values of L_a the following scheme:

(1) $L_a=0$ corresponds to $F^0(ij)$:

We have $F^0(ss)$, $F^0(sp)$, $F^0(pp)$, $F^0(sd)$, $F^0(pd)$ and $F^0(dd)$. These terms are known exactly and follow the symmetry of the $M_a^{L_a}$. According to (2.7) and (2.8):

$$F^0(sp)=\frac{F^0(ss)+F^0(pp)}{2}; \qquad F^0(sd)=\frac{F^0(ss)+F^0(dd)}{2};$$

and

$$F^0(pd)=\frac{F^0(pp)+F^0(dd)}{2}.$$

(2) $L_a=1$ corresponds to $G^1(ij)$:

We use $G^1(sp)$ and $G^1(pd)$ directly, no other integrals being non-zero in this case.

(3) $L_a=2$ corresponds to $F^2(ij)$ or $G^2(ij)$ with $F^2(pp)$, $F^2(pd)$ and $F^2(dd)$.

$F^2(pd)=\frac{F^2(pp)+F^2(dd)}{2}\cdot$ $G^2(ij)$ is uniquely $G^2(sd)$.

(4) $L_a = 3$ leads to $G^3(pd)$

(5) $L_a = 4$ leads to $F^4(dd)$

Another condition must be satisfied at $R_{ab} = 0$, namely the symmetry requirement for individual integrals which is a necessary condition to assure that the latter transform correctly under rotations:

$$[N_a L_a M_a | N_b L_b M_a]_{(R_{ab}=0)} = (-1)^{M_a} \delta_{L_a, L_b} \delta_{M_a, M_b} [N_a L_a M_a | N_b L_a M_a] \tag{2.9}$$

(see Roothaan [2]). Condition (22.9) imposes a term $\varepsilon(R_{ab})$, dictated by the $\delta_{L_a L_b}$. Its form being in accord with the bipolar expansion in the close or overlap region (5) and agreeing, when expanded with the leading terms of Roothaan's analytical integrals [2]. We get:

$$\left.\begin{array}{l} [N_a L_a M_a | N_b L_b M_b] = \Gamma_{L_a, M_a, L_b, M_b} \varepsilon(R_{ab}) \\ \text{where, for } L_a = L_b,\ \varepsilon(R_{ab}) = 1 \\ \text{and } \varepsilon(R_{ab}) = (1 - \exp(-(K_a + K_b) R_{ab})) \text{ otherwise.} \end{array}\right\} \tag{2.10}$$

The equality of magnitude of individual integrals sharing the same L value at $R_{ab} = 0$ is also a necessary condition for correct rotational transformation. This condition is now fulfilled by the appropriate definition of the polynomials used to interpolate the value of the integrals between the exact limits.

We are now in a position to write the expression for the complete integral, valid over the whole range of R_{ab}:

From (2.2) and using (2.10) and (2.4), we obtain:

$$\begin{aligned} (i_a j_a | k_b l_b) = \sum_{L_a M_a} \sum_{L_b M_b} \sum_{m} \frac{f(L_a, L_b, m)}{U_{ab}^{L_a + L_b + 1}} M_a^{L_a} M_b^{L_b} a_{L_a M_a} a_{L_b M_b} \\ \times D_{m M_a}^{L_a}(\Omega_a) D_{m M_b}^{L_b}(\Omega_b) E_{L_a + L_b}^{m}(R_{ab}, A_{ab}) \varepsilon(R_{ab}) \end{aligned} \tag{2.11}$$

This form of the integrals possesses all the required transformation properties, is continuous and well-behaved and is relatively simple. We may thus suppose that the first derivatives with respect to R_{ab} and the corresponding direction cosines exist at all values of the function and they will be evaluated in Sect. 2.3.

2.3. Evaluation of the derivatives used in the optimisation

Evidently, from (2.11), the only terms of $(i_a j_a | k_b l_b)$ depending on R_{ab} are U, E and $\varepsilon(R_{ab})$ thus the first derivative with respect to R_{ab} is the partial derivative concerned, regarding the rest of the expression as constant.

$$\frac{dU_{ab}^{-(L_a + L_b + 1)}}{dR_{ab}} = -(L_a + L_b + 1) R_{ab} U_{ab}^{-(L_a + L_b + 3)} \tag{3.1}$$

$$\frac{dE'^{m}_{L_a + L_b}(R_{ab}, A_{ab})}{dR_{ab}} = \frac{\left(\dfrac{U_{ab}}{A_{ab}}\right) \left[m R_{ab} P^m_{L_a + L_b - m}\left(\dfrac{R_{ab}}{U_{ab}}\right) + \dfrac{A_{ab}^2}{U_{ab}} dP^m_{L_a + L_b - m}\left(\dfrac{R_{ab}}{U_{ab}}\right) \right]}{U_{ab}^2},$$

where:

$$E^{m}_{L_a+L_b}(R_{ab}, A_{ab}) = \frac{2^m m!(L_a+L_b-m)!}{(L_a+L_b)!} E'^{m}_{L_a+L_b}(R_{ab}, A_{ab}) \tag{3.2}$$

from (2.4).
When $L_a = L_b$, the derivative of $\varepsilon(R_{ab})$ is 0, otherwise we have:

$$\frac{d\varepsilon(R_{ab})}{dR_{ab}} = -(K_a+K_b)\exp(-(K_a+K_b)R_{ab}) \tag{3.3}$$

for completeness.

Thus the complete R_{ab} derivative takes the form:

$$\frac{d(i_a j_a|k_b l_b)}{dR_{ab}} = \sum_{L_a M_a} \sum_{L_b M_b} \sum_{m} V_{ab}\left(\frac{dE}{dR_{ab}}\varepsilon + E\frac{d\varepsilon}{dR_{ab}} - \frac{(L_a+L_b+1)R_{ab}}{U_{ab}U_{ab}} E\varepsilon\right), \tag{3.4}$$

where

$$V_{ab} = f(L_a, L_b, m) M_a^{L_a} M_b^{L_b} a_{L_a M_a} a_{L_b M_b} D^{L_a}_{mM_a}(\Omega_a) D^{L_b}_{mM_b}(\Omega_b)$$

the term independent of R_{ab}.

We next observe that only the Wigner rotation matrices depend on the direction cosines facilitating this part of the calculation because we already have an algorithm which calculates the relevant derivatives [10].

The gradient is then readily calculated by adding the derivatives with respect to the direction cosine to that with respect to R_{ab}. This gradient is summed over all atom pairs in the molecule and treated according to the method given by [8].

3. Results

Figure 1 compares certain integrals calculated by the MNDO type method (presented here) with the corresponding analytical curves from the expressions given in [2] and the values obtained in [1], for the C_2 pair over the range $R = 0$ to $R = 5$ Å. The ratio of cpu times for the calculation of these integrals in the present method and in [1] is 0.48.

For a Cl_2 pair the 2025 integrals in an *spd* basis are consistent with analytical values (2) and are calculated in an arbitrary frame of reference with a cpu ratio of 1.41 compared with the 100 integrals of an *sp* basis in MNDO.

The molecules F_2, CH_4, CF_4, NH_3, H_2O, Cl_2 and CCl_4 were optimised with regard to molecular geometry in the present hypothesis and in the MNDO hypothesis (11) with respect to cartesian coordinates in both cases using, for the former, an original optimisation algorithm [12] and, for the latter, the method described here. MNDO parameters [13] were used in both cases for molecules treated over an *sp* basis but it was found necessary to adopt the NDDO parameters and Burns exponents for molecules treated over an *spd* basis. The parameters will serve as the starting point for a least squares fitting procedure for a new MNDO parametrisation.

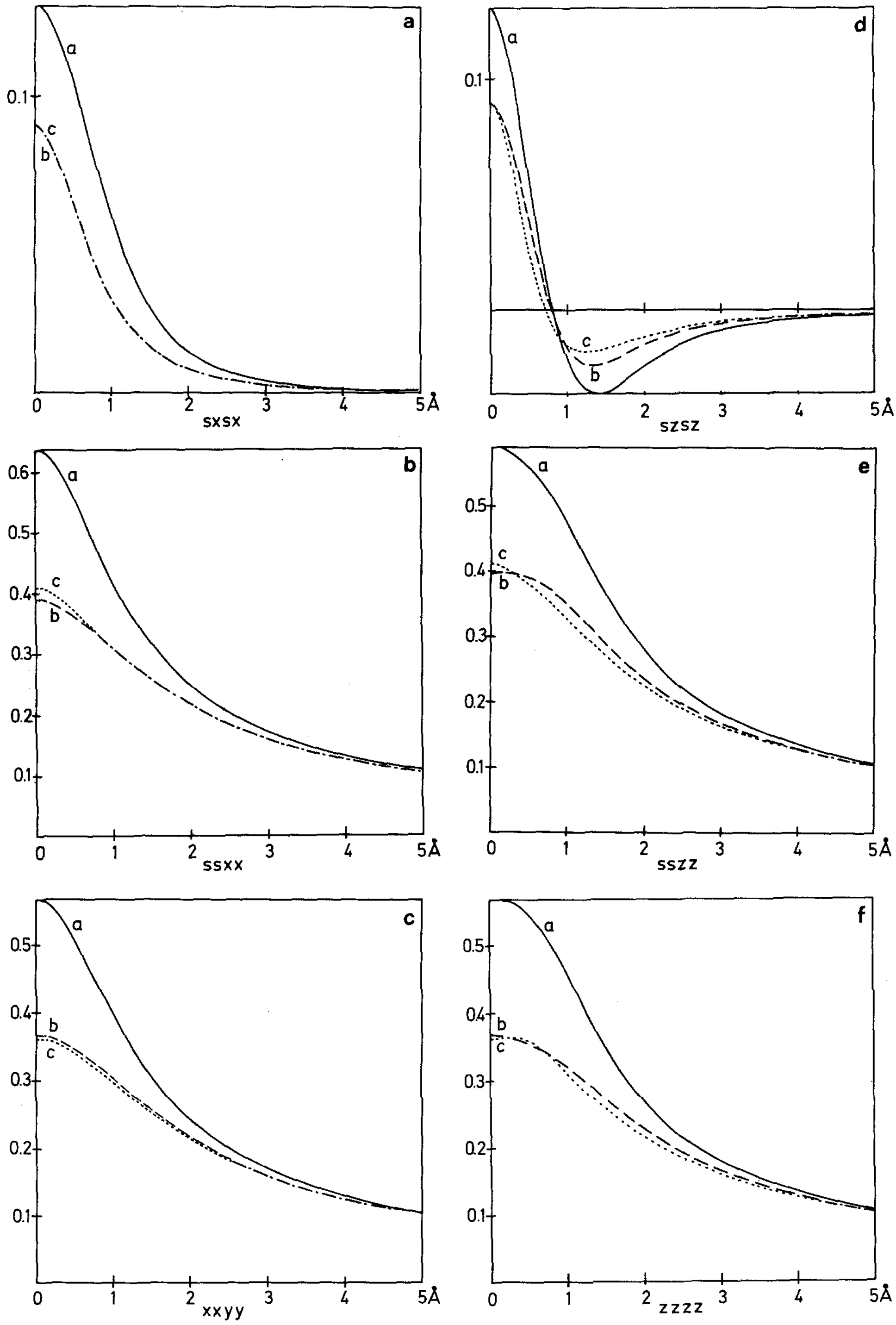

Fig. 1a–f. Coulomb integrals for a *c-c* atom pair. Comparison of values calculated from [1] (*a*), [4] (*b*) and the present work (*c*). Energy vs separation plots in Angstroms and *u.a.*, respectively.

4. Conclusion

We have presented a rotationally invariant method which permits us to compute bicentric coulomb integrals over a basis which is not restricted to *s* and *p* orbitals, as was previously the case. It therefore extends the field of application of MNDO type calculations to the second period of the periodic table and beyond. Derivatives of the integrals with respect to R_{ab} and to the direction cosines of the vector linking the pair of atoms under consideration are readily evaluated. This permits the incorporation of the algorithm into the optimisation of molecular geometry due to Rinaldi [8]. The result is that optimisation can now be carried out very rapidly in an MNDO approximation icluding *d*-orbitals. Molecules including heavy atoms are therefore included in the series of possibilities.

The present optimisation will be available as an option of GEOMOS Q.C.P.E (to be published).

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