Theoret. Chim. Acta (Berl.) 40, 253–261 (1975)

# Approximate Charge Density Localization of Molecular Orbitals

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Received May 15, 1975/September 11, 1975

A NDO approximate procedure based on the indirect intrinsic *ab initio* localization method of von Niessen is developed. It is shown that only when the NDO approximations are introduced at the two electron level, expressions are obtained which are the charge density counterpart of those found in the approximate energy localization methods. The results of these two methods are quite similar both in the CNDO and INDO approximations. The indeterminacies observed in the CNDO localization for unsaturated systems and for molecules with two or three lone pairs on the same atom, are removed by localizing up to an INDO level. The approximate charge density localization is however computationally much easier than the approximate energy localization method and should be more appropriate in LMO studies of large organic molecules.

*Key words:* Localized MO's – Density Localization

## 1. Introduction

The canonical molecular orbitals, obtained by solving the molecular Hartree-Fock-Roothaan equations [1] are generally delocalized over the entire molecular framework and can hardly be visualized in terms of "classical chemical" concepts such as inner shells, lone pairs and two-or three center bonds. However, Fock [2] showed that a single determinantal wave function is invariant with respect to a unitary transformation among the molecular orbitals, so that the possibility exists of finding an appropriate unitary matrix converting the canonical orbitals into a new set of orbitals which are localized in well-defined regions of the molecule. This should bridge the gap between the traditional chemical concepts and the quantum mechanical formulation of the problem. Such transformations are currently known as "localization procedures".

In the Edmiston and Rüdenburg theory [3–5][1], "Energy localized MO's" (ELMO's) are obtained by maximizing the sum of the orbital self-repulsion

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[1] Hereafter abbreviated as ER.

energies. This method has since then been successfully approached up to a CNDO [6], [7] and an INDO [8] level, respectively by Trindle and Sinanoglu [9] and England and Gordon [10][2]. Recently, von Niessen [11], [12] showed that the substitution of the $r_{12}^{-1}$ separation function in the two electron integrals by the $\delta(\mathbf{r}_1-\mathbf{r}_2)$ function furnished "Density Localized MO's" (DLMO's) which are very similar to the ELMO's; the one electron "charge density overlap integrals" so obtained are however much more easily and rapidly calculated than the two-electron repulsion integrals in the ER procedure.

In this paper we propose a new indirect intrinsic approximate density localization method avoiding the tedious evaluation of two-electron integrals in the approximate ER methods.

## 2. The CNDO- and INDO-Approximations to the Density Localization Method

Von Niessen's density localization method [11] is based upon the minimalization of the sum $D'$ of the one electron interorbitalar charge density overlap integrals:

$$D'=\sum_{i<j}^{\text{occ}}\sum^{\text{occ}}[i^2j^2]=\sum_{i<j}^{\text{occ}}\sum^{\text{occ}}\int\psi_i^2(\mathbf{r})\psi_j^2(\mathbf{r})d\mathbf{r}. \tag{1}$$

The transformation of the set of CMO's $\{\psi_i\}$ into the set of LMO's $\{\psi_i'\}$ is achieved by performing successive $(2\times 2)$ rotations between the CMO's minimizing $D'$ for the two-dimensional case until invariance of (1) is obtained. The rotation angle $\theta$ is commonly chosen to be the one which, of the four angles $\alpha$, $\alpha+\pi/2$, $\alpha+\pi$, $\alpha+3\pi/2$ lies between 0 and $\pi/2$, $\alpha$ being defined as

$$\tan 4\alpha=-\frac{Bij}{Aij} \tag{2}$$

with

$$Aij=\tfrac{3}{2}[i^2j^2]-\tfrac{1}{4}[i^4]-\tfrac{1}{4}[j^4] \tag{3}$$
$$Bij=[i^3j]-[ij^3].$$

In our method, the quantities $Aij$ and $Bij$ will be approximated up to a NDO level, our localization function implying the maximalization of

$$D=\sum_i^{\text{occ}}[i^2i^2]\equiv\sum_i^{\text{occ}}[i^4] \tag{4}$$

which is equivalent to the minimization of $D'$[3]. Actually, two basic options are possible in the NDO approximations for $Aij$, $Bij$ and $D$.

The integral $[i^2j^2]$ can be written as a two electron integral which we shall denote as $[i^2\|j^2]$ with the delta function $\delta(\mathbf{r}_1-\mathbf{r}_2)$ as operator

$$[i^2\|j^2]=[\psi_i^2\|\psi_j^2]=\iint\psi_i^2(\mathbf{r}_1)\delta(\mathbf{r}_1-\mathbf{r}_2)\psi_j^2(\mathbf{r}_2)d\mathbf{r}_1\,d\mathbf{r}_2. \tag{5}$$

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[2] Hereafter abbreviated respectively as TS and EG.

[3] $\sum_i^{\text{occ}}\sum_j^{\text{occ}}[i^2j^2]$ indeed is constant for an orthogonal transformation among the MO's.

Introducing the LCAO expansion, we obtain

$$[i^2\|j^2]=\sum_{\mu}\sum_{\nu}\sum_{\lambda}\sum_{\sigma} C_{\mu i}\, C_{\nu i}\, C_{\lambda i}\, C_{\sigma i}\, [\mu\nu\|\lambda\sigma] \tag{6}$$

where $\mu$, $\nu$, $\lambda$ and $\sigma$ stand for the atomic basisfunctions. We now clearly can start our approximations, either at the level of the two-electron integrals $[\mu\nu\|\lambda\sigma]$; i.e. before integrating out the delta function (option $A$) or at the final one-electron integral level $[\mu\nu\lambda\sigma]$ (option $B$).

In the framework of the NDO-approximations, we clearly see that, due to the higher permutational symmetry of the $[\mu\nu\lambda\sigma]$ integrals as compared to their two-electron analogues $[\mu\nu\|\lambda\sigma]$, the number of one-electron integrals retained in method $B$ will be considerably higher than the number of two-electron integrals retained in method $A$. It is obvious that only option $A$ is justified on a physical basis and will have its energy localization counterpart.

Starting from the two-electron integral expressions for $Aij$, $Bij$ and $D$ and introducing the usual CNDO-approximations [6], [7], we obtain:

$$\begin{aligned} Aij&=\sum_{A}\sum_{B}\zeta_{AB}\sum_{\lambda}^{A}\sum_{\sigma}^{B} C_{\lambda i}C_{\lambda j}C_{\sigma i}C_{\sigma j}-\tfrac{1}{4}(C_{\lambda i}^2-C_{\lambda j}^2)\,(C_{\sigma i}^2-C_{\sigma j}^2)\\ Bij&=\sum_{A}\sum_{B}\zeta_{AB}\sum_{\lambda}^{A}\sum_{\sigma}^{B}(C_{\lambda i}^2-C_{\lambda j}^2)\,C_{\sigma i}C_{\sigma j}\\ D&=\sum_{i}^{\mathrm{occ}}\sum_{A}\sum_{B}\zeta_{AB}\sum_{\lambda}^{A}\sum_{\sigma}^{B}C_{\lambda i}^2C_{\sigma i}^2 \end{aligned} \tag{7}$$

with

$$\zeta_{AB}=[s_A^2 s_B^2] \tag{8}$$

computed over valence-$s$-functions in order to satisfy orientational invariance requirements.

The theoretical evaluation of these integrals in terms of STO's will be discussed in Appendix 1.

Introductory results with the CNDO approximation indicated that, in agreement with observations made by TS [9], EG [10] and Newton *et al.* [13], some indeterminacies remained in the localization procedure for unsaturated systems and for cases where two or three lone pairs are localized on the same atom[4]. It can be proved (Section 3) that a treatment up to an INDO level removes these indeterminacies.

The appropriate INDO approximations to the $[\mu\nu\|\lambda\sigma]$ integrals are basically the same as in the CNDO method, except that one-center integrals $[\mu\nu\|\mu\nu]$ with $\mu\neq\nu$ are also retained. The resulting expressions for $Aij$, $Bij$ and $D$ are:

$$\begin{aligned} Aij=\sum_{A}\Bigg\{\sum_{\lambda}^{A}[\lambda^4]\,(\tfrac{3}{2}C_{\lambda i}^2C_{\lambda j}^2-\tfrac{1}{4}C_{\lambda i}^4-\tfrac{1}{4}C_{\lambda j}^4)+\sum_{\lambda\neq\sigma}^{A}\sum^{A}[\lambda^2\sigma^2]\,(3C_{\lambda i}C_{\lambda j}C_{\sigma i}C_{\sigma j}\\ +\tfrac{3}{2}C_{\lambda i}^2C_{\sigma j}^2-\tfrac{3}{4}C_{\lambda i}^2C_{\sigma i}^2-\tfrac{3}{4}C_{\lambda j}^2C_{\sigma j}^2)\Bigg\} \end{aligned}$$

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[4] In agreement with the CNDO energy localization method, lone pair and double and triple bond LMO's resulting from CNDO-density localization invariably are of the $\sigma$, $\pi$ type.

$$+\sum_{A\neq B}\sum \zeta_{AB}\sum_{\lambda}^{A}\sum_{\sigma}^{B}\left(C_{\lambda i}C_{\lambda j}C_{\sigma i}C_{\sigma j}-\tfrac{1}{4}C_{\lambda i}^{2}C_{\sigma i}^{2}-\tfrac{1}{4}C_{\lambda j}^{2}C_{\sigma j}^{2}+\tfrac{1}{2}C_{\lambda i}^{2}C_{\sigma j}^{2}\right)$$

$$Bij=\sum_{A}\left\{\sum_{\lambda}^{A}[\lambda^{4}]\ C_{\lambda i}C_{\lambda j}\left(C_{\lambda i}^{2}-C_{\lambda j}^{2}\right)+3\sum_{\lambda\neq\sigma}\sum[\lambda^{2}\sigma^{2}]\ C_{\sigma i}C_{\sigma j}\left(C_{\lambda i}^{2}-C_{\lambda j}^{2}\right)\right\}$$

$$+\sum_{A\neq B}\sum \zeta_{AB}\sum_{\lambda}^{A}\sum_{\sigma}^{B}\left(C_{\lambda i}^{2}-C_{\lambda j}^{2}\right)C_{\sigma i}C_{\sigma j}$$

$$D=\sum_{i}^{\mathrm{occ}}\left\{\sum_{A}\sum_{\lambda}^{A}[\lambda^{4}]\ C_{\lambda i}^{4}+3\sum_{\lambda\neq\sigma}\sum[\lambda^{2}\sigma^{2}]\ C_{\lambda i}^{2}C_{\sigma i}^{2})+\sum_{A\neq B}\sum \zeta_{AB}\sum_{\lambda}^{A}\sum_{\sigma}^{B}C_{\lambda i}^{2}C_{\sigma i}^{2}\right\}.$$

## 3. Indeterminacies in NDO Localizations

Let us first consider a molecule with $n_A$ lone pairs $\psi_i$ located on the same atom $A$. The partial localization function $D_A$, defined as

$$D_A=\sum_{i=1}^{n_A}\iint \psi_i^2(\mathbf{r}_1)f(r_{12})\psi_i^2(\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2 \tag{10}$$

where $f(r_{12})$ denotes a general separation function, becomes in the CNDO approximation (assuming perfectly localized LMO's)

$$D_A=\xi_{AA}\sum_{i=1}^{n_A}\sum_{k}^{A}\sum_{m}^{A}C_{ki}^2C_{mi}^2=n_A\,\xi_{AA} \tag{11}$$

where $\xi_{AA}$ stands for the spherically averaged one center integral over valence-$s$-functions.

$$\xi_{AA}=\iint \chi_{s_A}^2(\mathbf{r}_1)f(r_{12})\chi_{s_A}^2(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2 \tag{12}$$

After an orthogonal transformation among the $n_A$ lone pairs, new LMO's $\psi_i'$ and new orbital coefficients $C_{ki}'$ are obtained

$$\psi_i'=\sum_{k=1}^{n_A}T_{ik}\psi_k \tag{13}$$

$$C_{ki}'=\sum_{r=1}^{n_A}T_{ir}C_{kr}.$$

The transformation matrix **T** being an orthogonal matrix, the new partial localization function

$$D_A'=\xi_{AA}\sum_{i=1}^{n_A}\sum_{k}\sum_{m}C_{ki}'^2C_{mi}'^2 \tag{14}$$

reduces to

$$D_A'=n_A\,\xi_{AA}=D_A. \tag{15}$$

Thus, within the assumption of perfect localization the lone pair CNDO-LMO's are not univocally determined; as a particular case $\sigma$, $\pi$ type and equivalent lone pairs lead to the same partial localization value.

However, if we perform our localization up to an INDO level it is easily proved that the contribution of equivalent lone pairs to the localization function is greater than that of their $\sigma$, $\pi$ type counterparts.

In the case of the HF molecule, for example, locating the hydrogen atom at the origin of the coordinate system and the fluorine atom on the positive $x$-axis, the $\sigma$, $\pi$ lone pairs are given by

$$\begin{aligned}&\psi_\sigma = \omega s + \sqrt{1-\omega^2}\, P_x \text{ with } 0 < \omega < 1 \\ &\psi_\pi = p_y \\ &\psi'_\pi = p_z\end{aligned} \tag{16}$$

their transformation to three equivalent lone pairs $\psi_\tau$, $\psi_{\tau'}$, $\psi_{\tau''}$ is achieved by the following matrix relation

$$\begin{bmatrix}\psi_\tau \\ \\ \psi_{\tau'} \\ \\ \psi_{\tau''}\end{bmatrix} = \begin{bmatrix}\frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}}\end{bmatrix} \begin{bmatrix}\psi_\sigma \\ \\ \psi_\pi \\ \\ \psi_{\pi'}\end{bmatrix} \tag{17}$$

If we now perform our localization up to an INDO level, starting from the explicit expressions for the partial localization functions in both cases

$$D_A^{\text{eq.lp}} = 3[\psi_\tau^2 \| \psi_\tau^2] \tag{18}$$

$$D_A^{\sigma,\pi} = [\psi_\sigma^2 \| \psi_\sigma^2] + 2[\psi_\pi^2 \| \psi_\pi^2] \tag{19}$$

we obtain, in the case of density localization

$$\Delta D_A = D_A^{\text{eq.lp}} - D_A^{\sigma,\pi} = 8\omega^4 \frac{\mathscr{R}}{15\pi} \tag{20}$$

where $\mathscr{R}$ denotes the radial part of the charge density integral and has always a positive value.

In the case of the energy localization method, we obtain

$$\Delta D_A = 8\omega^4\left(\tfrac{1}{9}G^1 - \tfrac{1}{75}F^2\right) \tag{21}$$

where $G^1$ and $F^2$ are the Slater-Condon parameters [8]; due to their relative magnitude, $\Delta D_A$ will here also always be positive (0.2865 $\omega^4$ a.u. in the case of a fluorine atom). INDO localization thus not only removes the CNDO indeterminacies but also favours the equivalent lone pairs picture in agreement with *ab initio* results [12].

Let us now discuss the case of unsaturated systems, e.g. ethylene. Considering this molecule with the CC bond along the $x$-axis, the $(XY)$ plane being the molecular plane. The CC double bond can be described in terms of $\sigma$, $\pi$ or bent ($\tau$) bonds (noted respectively as $\psi_\sigma$ and $\psi_\pi$ or $\psi_\tau$ and $\psi_{\tau'}$); these are related through the following matrix relation

$$\begin{bmatrix} \psi_\tau \\ \\ \psi_{\tau'} \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} \psi_\sigma \\ \\ \psi_\pi \end{bmatrix} \tag{22}$$

Completely analogously to the lone-pairs case it is easily shown that in the CNDO approximation the localization function for the CC double bond becomes

$$D^{\sigma,\pi} = D^{\tau,\tau'} = \xi_{\mathrm{CC}} + \xi_{\mathrm{C_1C_2}} \tag{23}$$

where $\xi_{\mathrm{C_1C_2}}$ denotes the spherically averaged two center integral. In the case of a triple bond, e.g. for acetylene, we have

$$D^{\sigma,\pi,\pi'} = D^{\tau,\tau',\tau''} = \tfrac{3}{2}(\xi_{\mathrm{CC}} + \xi_{\mathrm{C_1C_2}}). \tag{24}$$

Thus, the CNDO localization clearly does not distinguish between the two descriptions.

If the localization is performed up to an INDO level, we obtain in the case of charge density localization

$$\begin{aligned} &-\text{for ethylene} \quad \Delta D = D^{\tau,\tau'} - D^{\sigma,\pi} = \frac{4}{5}\frac{\omega^4}{\pi}\mathscr{R} \\ &-\text{for acetylene} \quad \Delta D = D^{\tau,\tau',\tau''} - D^{\sigma,\pi',\pi'} = \frac{16}{15}\frac{\omega^4}{\pi}\mathscr{R}. \end{aligned} \tag{25}$$

$\mathscr{R}$ is the positive radial part of the charge density overlap integral and $\omega$ is the $s$ contribution of $C_1$ and $C_2$ in the $\sigma$ orbital

$$\psi_\sigma = \omega(s_1 + s_2) + \frac{1}{\sqrt{2}}\sqrt{1 - 2\omega^2}\,(P_{x_1} - P_{x_2}). \tag{26}$$

In the case of the energy localization method, we obtain:

$$\text{for ethylene} \quad \Delta D = 4\omega^4(\tfrac{1}{3}G^1 - \tfrac{1}{25}F^2) = 0.3292\omega^4 \tag{27}$$

$$\text{for acetylene} \quad \Delta D = 16\omega^4(\tfrac{1}{9}G^1 - \tfrac{1}{75}F^2) = 0.4375\omega^4 \tag{28}$$

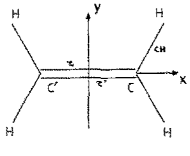
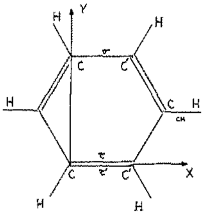
Here again, INDO localization not only removes the CNDO degeneracies but yields bent bonds in agreement with *ab initio* results [12], [14], [15].

## 4. Results – Comparison with Other Methods

A comparison of the CNDO-charge density LMO's for several molecules with the CNDO-energy localization results of e.g. Trindle and Sinanoglu [9] reveals that all LMO coefficients are identical up to $1 \cdot 10^{-4}$. Also the LMO's for ethylene and benzene (Table 1) obtained by our INDO density localization theory and the INDO energy localization procedure of England and Gordon [10] are quite similar. For ethylene and other simple unsaturated molecules $\tau$ bonds are obtained instead of a $\sigma$, $\pi$ system and for benzene a Kékule structure, consisting of three C–C $\sigma$ bonds and three pairs of equivalent banana bonds is found.

These results are in close agreement with *ab initio* conclusions [16].

Table 1. Comparison between INDO-energy [A] and INDO-charge density [B] localized CH and CC bond orbitals in ethylene and benzene[b]

| Molecule | Atomic Orbital | CH Bond[a] A | CH Bond[a] B | CC′ $\tau$ Bonds[a] A | CC′ $\tau$ Bonds[a] B | CC′ $\sigma$ Bond[a] A | CC′ $\sigma$ Bond[a] B |
|---|---|---|---|---|---|---|---|
| | $H_s$ | 0.7050 | 0.7052 | | | | |
|  | $C_s$ | 0.3996 | 0.3943 | 0.3296 | 0.3347 | | |
| | $C_{px}$ | 0.3283 | 0.3338 | −0.3760 | −0.3712 | | |
| | $C_{py}$ | 0.4760 | 0.4759 | 0 | 0 | | |
| | $C_{pz}$ | 0 | 0 | ±0.5000 | ±0.5000 | | |
| | $C'_s$ | | | 0.3296 | 0.3347 | | |
| | $C'_{px}$ | | | 0.3760 | 0.3714 | | |
| | $C'_{py}$ | | | 0 | 0 | | |
| Ethylene | $C'_{pz}$ | | | ±0.5000 | ±0.5000 | | |
|  | $H_s$ | 0.7108 | 0.7112 | | | | |
| | $C_s$ | 0.3834 | 0.3791 | 0.3106 | 0.3170 | 0.4200 | 0.4135 |
| | $C_{px}$ | 0.5818 | 0.5838 | 0.3880 | 0.3835 | 0.5627 | 0.5665 |
| | $C_{py}$ | −0.0059 | −0.0101 | −0.0212 | −0.0199 | 0.0416 | 0.0494 |
| | $C_{pz}$ | 0 | 0 | ±0.4553 | ±0.4547 | 0 | 0 |
| | $C'_s$ | | | 0.3106 | 0.3170 | 0.4200 | 0.4135 |
| | $C'_{px}$ | | | −0.3880 | −0.3835 | −0.5627 | −0.5667 |
| | $C'_{py}$ | | | −0.0212 | −0.0199 | 0.0416 | 0.0494 |
| Benzene | $C'_{pz}$ | | | ±0.4553 | ±0.4547 | 0 | 0 |

[a] Tailing contributions from atoms not involved in the CH and CC bonds are not given.

[b] Experimental geometries for ethylene [19] and benzene [20], [21] are used in the calculation.

In the case of molecules where two or more lone pairs are localized on the same atom the resulting INDO-DLMO's were in every case equivalent lone pairs and not their $\sigma$, $\pi$ type counterparts, in agreement with the arguments developed in Section 3.

## 5. Conclusions

A new NDO-density localization procedure which gives results very similar to the CNDO and INDO energy localization methods is developed. Indeterminacies in the CNDO-LMO's are suppressed when working at an INDO level. The method is computationally easy and rapid and is a suitable tool for the study of LMO's in large organic molecules. The intrinsic [17] character of the method is an extremely important property as compared to the external procedures, which although computationally still easier, require preconceptions of the final LMO's. Our method has recently been successfully applied in a LMO-study of directly bonded $^{13}$C–H nuclear spin-spin coupling constants and C–H bond distances [18].

## Appendix. Evaluation of Charge Density Overlap Integrals in a STO-Basis Set

One- and two center charge density overlap integrals in a STO-basis set represent a new type of integral whose evaluation is given here:

### *1. One Center Integrals*

Considering first and second row elements, these integrals can be classified into four types $[s^2s^2]$, $[s^2p^2]$, $[p^2p^2]$ and $[p^2p'^2]$. Starting from the definition of a STO [22]

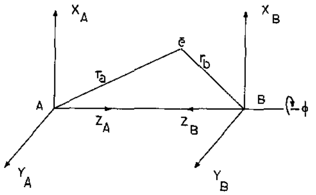


Fig. 1. Two center coordinate system

$$\chi_{nlm}(r, \Theta, \Phi) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1} e^{-\zeta r} Y_{lm}(\Theta, \Phi) \tag{29}$$

where the $Y_{lm}$ are the spherical harmonics in real form, it is easily seen that these integrals can be factorised in a radial and an angular part. If equal orbital exponents are taken for $s$ and $p$ orbitals, the radial part $\mathscr{R}$ of the integrals reduces to

$$\mathscr{R} = \frac{\zeta^3}{2^{4n-4}} \frac{(4n-2)!}{[(2n)!]^2} \tag{30}$$

whereas the angular integrals are given by

$$\begin{aligned} [Y_{00}^2 Y_{00}^2] &= [Y_{00}^2 Y_{lm}^2] = \frac{1}{4\pi} \\ [Y_{lm}^2 Y_{lm}^2] &= \frac{9}{20\pi} \\ [Y_{lm}^2 Y_{lm'}^2] &= \frac{3}{20\pi} \end{aligned} \tag{31}$$

where $Y_{lm}$ and $Y_{lm'}$ denote the $px$, $py$ and $pz$ functions ($m \neq m'$).

## 2. Two Center Integrals

The evaluation of these integrals over valence-$s$-functions is performed analogously to the computation of overlap integrals by Mulliken *et al.* [23].

If $R$ denotes the distance between the atomic centers $A$ and $B$, we have (cf. Fig. 1)

$$\zeta_{AB} = \frac{1}{4\pi} \frac{(2\zeta_1)^{2n_1+1}}{(2n_1)!} \frac{(2\zeta_2)^{2n_2+1}}{(2n_2)!} \int r_a^{2n_1-2} r_b^{2n_2-2} e^{-2(\zeta_1 r_a + \zeta_2 r_b)} d\mathrm{r} \tag{32}$$

or, introducing the prolate spheroidal coordinates ($\mu$, $\nu$, $\Phi$) defined as

$$\begin{aligned} \mu &= \frac{r_a + r_b}{R} \\ \nu &= \frac{r_a - r_b}{R} \\ \Phi a &= \Phi b = \Phi \end{aligned} \tag{33}$$

$$\begin{aligned} \zeta_{AB} = \frac{1}{\pi} \frac{1}{(2n_1)!\,(2n_2)!} \zeta_1^{2n_1+1} \zeta_2^{2n_2+1} R^{2(n_1+n_2)-1} \\ \int_{\mu=1}^{\infty} \int_{\nu=-1}^{+1} (\mu+\nu)^{2n_1-1} (\mu-\nu)^{2n_2-1} e^{-(\alpha+\beta)\mu} e^{-(\alpha-\beta)\nu} d\mu d\nu \end{aligned} \tag{34}$$

where $\alpha$ and $\beta$ are given by

$$\begin{aligned} \alpha &= \zeta_1 R \\ \beta &= \zeta_2 R. \end{aligned} \tag{35}$$

Defining further

$$\begin{aligned} N_A &= 2n_1 - 1 \\ N_B &= 2n_2 - 1 \end{aligned} \tag{36}$$

we have according to the binomial expansion

$$\zeta_{AB} = \frac{1}{\pi} \frac{\zeta_1^{2n_1+1} \zeta_2^{2n_2+1}}{(2n_1)!\,(2n_2)!} R^{2(n_1+n_2)-1} \sum_{p=0}^{N_A} \sum_{q=0}^{N_B} C_{N_A}^p C_{N_B}^q (-)^{N_B-q} \int_{\mu=1}^{\infty} \mu^{p+q} e^{-(\alpha+\beta)\mu}\, d\mu \int_{\nu=-1}^{+1} \nu^{N_A+N_B-p-q} e^{-(\alpha-\beta)\nu}\, d\nu. \tag{37}$$

These integrals are precisely the $A$ and $B$ integrals of Mulliken *et al.* [23] so that we finally obtain

$$\zeta_{AB} = \frac{1}{\pi} \frac{\zeta_1^{2n_1+1} \zeta_2^{2n_2+1}}{(2n_1)!\,(2n_2)!} R^{2(n_1+n_2)-1} \sum_{p=0}^{N_A} \sum_{q=0}^{N_B} C_{N_A}^p C_{N_B}^q (-)^{N_B-q} A_{p+q}^{(\alpha+\beta)} B_{N_A+N_B-p-q}^{(\alpha-\beta)}. \tag{38}$$

*Acknowledgements.* The authors wish to thank the Université Libre de Bruxelles (ULB) for a generous computer grant in support of this work. Predoctoral fellowships from the NFWO to P.G. and C.V.A. and from the IWONL to P.R. are gratefully acknowledged.

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