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# On the Use of NDO Approximate Wavefunctions in the Evaluation of Momentum Density and Radial Momentum Density Distributions in Polyatomic Molecules

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The use of single determinantal approximate molecular wavefunctions of the LCAO MO NDO type for the calculation of the momentum density $\rho(\boldsymbol{p})$ and the radial momentum density distribution $J(p)$ is discussed. In each case, these expressions should be orientationally invariant and the momentum density should be normalized. Combining these two requirements, it is shown that only two approximations are physically significant:

(1) NDO wavefunctions are used and $\rho(\boldsymbol{p})$ and $I(p)$ are approximated respectively up to an INDO and a CNDO level;
(2) Overlap integrals are explicitly taken into account when solving the Roothaan SCF equations or deorthogonalized NDO functions are employed, together with the unapproximated expressions.

*Key words:* Momentum space properties – NDO theory – Polyatomic molecules

## 1. Introduction

Since the early 1940's, methods of obtaining momentum space wavefunctions have been the subject of numerous investigations [1].

Two essentially different ways have been explored: either Schrödinger's equation is solved directly in the momentum space, or the more easily accessible position space wavefunction is transformed to the momentum space via the Dirac transformation.

The "direct" approach has only been achieved so far for extremely simple systems such as the hydrogen atom [2], the helium atom [3] and the hydrogen molecule positive ion [4]. The extension of the method to many-electron atoms and molecules has not been realized hitherto due to the computational difficulties encountered in the treatment of the interelectronic interaction terms.

On the other hand, the current availability of position space wavefunctions in several degrees of approximation both for atoms and molecules, and the isomorphic nature of the Dirac transformation [5] makes the "transformation

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method" extremely suitable for the studies of momentum space properties of large systems.

After the pioneering article of Podolsky and Pauling [6] on the momentum space wavefunctions of hydrogenlike atoms, the Chemistry of Momentum Space [1b] started effectively in the early 1940's with a series of papers by Coulson and Duncanson [7]. This study, although carried out with rather crude position space wavefunctions, contains a lot of qualitative conclusions which still serve as a guide for the interpretation of the more recent calculations.

Investigation of molecular momentum space properties has been a rapidly expanding field in the last years. Polyatomic LCAO MO SCF *ab initio* wavefunctions have been transformed for the first time by Epstein [8]; the momentum distributions and Compton profiles for boronhydrides [9] [10] and hydrocarbons [11] were interpreted in terms of contributions from localized molecular orbitals. Bonding effects in small molecules have also been studied [12] and Kaijser *et al.* explored the effect of excitation and ionization on the momentum density maps of $N_2$ [13]. The use of Gaussian expansions of STO's for the calculation of momentum distributions in polyatomic molecules was introduced by Tanner and Epstein [14] and further investigated by Hirst and Liebmann [15]. A critical examination of the possibilities of obtaining information on atomic and molecular momentum properties from experimental Compton scattering data has been given [16, 17]. Recently, a LMO study of the momentum distribution for a series of hydrocarbons with special attention to the properties of 1s inner shell electrons has been published [18]. Detailed studies of the momentum distribution and the Compton profile of the water molecule have been achieved [19–21] and the influence of hydrogen bonding investigated [22]. Recently various detailed investigations on the momentum space properties of small molecules were undertaken by Tawil [23, 24] and Kaijser [25].

All this shows that momentum space properties undoubtedly will receive more and more attention in forthcoming years. Approximate wavefunctions of the NDO type (CNDO [26, 27], INDO [28]...) which have proved to be very valuable in comparative studies of position space properties of organic molecules, have been used in some momentum space calculations by Ahlenius and Lindner [29] while this work was submitted for publication. Our aim is to analyse here the different kinds of NDO approximations which are physically significant in the field. Using STO's as atomic basisfunctions and a simple straightforward formalism, the explicit general expressions for the total momentum density distribution $\rho(\boldsymbol{p})$ and the radial momentum density distribution $I(p)$ for a single determinantal LCAO MO wavefunction for a closed shell polyatomic molecule are written in a form suitable for the direct introduction of the NDO approximations. It is concluded that only a limited number of possibilities subsist if orientational invariance and the normalization condition are both taken into account.

## 2. General Theory and Formalism

The Dirac transformation of a $N$ particle single determinantal position space wavefunction $\Psi = \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots \boldsymbol{r}_N)$ to the corresponding momentum space wavefunction $\Phi = \Phi(\boldsymbol{p}_1, \boldsymbol{p}_2, \ldots \boldsymbol{p}_N)$ is given by [30] (atomic units are used throughout)

$$\Phi(\boldsymbol{p}_1, \boldsymbol{p}_2, \ldots \boldsymbol{p}_N) = \left(\frac{1}{2\pi}\right)^{3N/2} \int \exp\left[-i \sum_{k=1}^{N} \boldsymbol{p}_k \cdot \boldsymbol{r}_k\right] \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_N) \cdot d\boldsymbol{r}_1 d\boldsymbol{r}_2 \ldots d\boldsymbol{r}_N. \quad (1)$$

Due to the isomorphic nature of this transformation [5], the wavefunction so obtained is also a single Slater determinant built up with a set of momentum space molecular orbitals $\phi_i(\boldsymbol{p})$, related to the position space MO's $\psi_i(\boldsymbol{r})$ by the expression

$$\phi_i(\boldsymbol{p}) = \left(\frac{1}{2\pi}\right)^{3/2} \int \psi_i(\boldsymbol{r}) \exp[-i\boldsymbol{p} \cdot \boldsymbol{r}] d\boldsymbol{r}. \quad (2)$$

Expanding the position space MO's as a linear combination of atomic orbitals $\{\chi_\lambda\}$, according to

$$\Psi_i(\boldsymbol{r}) = \sum_\lambda C_{\lambda i} \chi_\lambda(\boldsymbol{r}) \quad (3)$$

and introducing the general and local atomic position space and the $(P_x, P_y, P_z)$ momentum space coordinate systems defined in Fig. 1, we can write $\phi_i(\boldsymbol{p})$ more explicitly as

$$\phi_i(\boldsymbol{p}) = \left(\frac{1}{2\pi}\right)^{3/2} \sum_{\mathrm{A}} \exp(-i\boldsymbol{p} \cdot \boldsymbol{r}_{\mathrm{A}}) \sum_{\lambda}^{\mathrm{A}} C_{\lambda i} \int \chi_\lambda(\boldsymbol{r}) \exp(-i\boldsymbol{p} \cdot \boldsymbol{r}) d\boldsymbol{r} \quad (4)$$

where the integration over $\boldsymbol{r}$ is performed in the local coordinate system on atom A, $\boldsymbol{r}_{\mathrm{A}}$ being the position vector of atom A in the general coordinate system $(X, Y, Z)$. Let us now define

$$f_\lambda(\boldsymbol{p}) = \int \chi_\lambda(\boldsymbol{r}) \exp(-i\boldsymbol{p} \cdot \boldsymbol{r}) d\boldsymbol{r} \quad (5)$$

and introduce the explicit form of a STO $\chi_\lambda$ [31] characterized by the three quantum numbers $(n_\lambda, l_\lambda, m_\lambda)$ and the orbital exponent $\zeta_\lambda$ into (5); by applying the spherical wave expansion theorem [32]

$$e^{-i\boldsymbol{p} \cdot \boldsymbol{r}} = 4\pi \sum_{l=0}^{\infty} (-i)^l \mathring{j}_l(pr) \sum_m Y_{lm}(\theta_p, \phi_p) Y_{lm}(\theta_r, \phi_r) \quad (6)$$

where the $\mathring{j}_l$ are the spherical Bessel functions, $m$ running over all the real spherical harmonics $Y_{lm}$ with the same $l$ quantum number, we obtain:

$$f_\lambda(\boldsymbol{p}) = f_{n_\lambda l_\lambda m_\lambda}(p, \theta_p, \phi_p) = (-i)^{l_\lambda} g_{n_\lambda l_\lambda}(p) Y_{l_\lambda m_\lambda}(\theta_p, \phi_p) \quad (7)$$

with

$$g_{n_\lambda l_\lambda}(p) = \frac{(2\zeta_\lambda)^{n_\lambda + \frac{1}{2}}}{\sqrt{(2n_\lambda)!}} 4\pi \int_0^\infty j_{l_\lambda}(pr) r^{n_\lambda + 1} e^{-\zeta_\lambda r} dr. \quad (8)$$

The radial parts $g_{n_\lambda l_\lambda}$ can be obtained by straightforward integration. Explicit expressions for momentum space STO's $f_\lambda(\boldsymbol{p})$ 1$s$ to 3$d$ with $Y_{lm}$ normalized to $4\pi$ have been given by Epstein [33].

The total momentum density $\rho(\boldsymbol{p})$ for a closed shell molecule, described by a single Slater determinant is defined as

$$\rho(\boldsymbol{p})=2\sum_{i}^{\mathrm{occ}}|\phi_i(\boldsymbol{p})|^2. \tag{9}$$

According to Eqs.(4), (5) and (7) we obtain

$$\rho(\boldsymbol{p})=\left(\frac{1}{2\pi}\right)^3\sum_{\mathrm{A}}\sum_{\mathrm{B}}\exp\left[-i\boldsymbol{p}\cdot(\boldsymbol{r}_{\mathrm{A}}-\boldsymbol{r}_{\mathrm{B}})\right]\sum_{\lambda}^{\mathrm{A}}\sum_{\sigma}^{\mathrm{B}}P_{\lambda\sigma}(i)^{l_\sigma-l_\lambda}\times$$
$$g_{n_\lambda l_\lambda}(p)g_{n_\sigma l_\sigma}(p)Y_{l_\lambda m_\lambda}(\theta_p,\phi_p)Y_{l_\sigma m_\sigma}(\theta_p,\phi_p) \tag{10}$$

where $P_{\lambda\sigma}$ are the elements of the $\boldsymbol{P}$ matrix and are defined as

$$P_{\lambda\sigma}=2\sum_{i}^{\mathrm{occ}}C_{\lambda i}C_{\sigma i}. \tag{11}$$

In order to have $\rho(\boldsymbol{p})$ in a form suitable for the direct introduction of the NDO approximations, we decompose expression (10) into three parts:

1) diagonal monoatomic contributions, $\rho^{(1)}(\boldsymbol{p})$ with $\lambda=\sigma$ on atom A

$$\rho^{(1)}(\boldsymbol{p})=\left(\frac{1}{2\pi}\right)^3\sum_{\mathrm{A}}\sum_{\lambda}^{\mathrm{A}}P_{\lambda\lambda}g^2_{n_\lambda l_\lambda}(p)Y^2_{l_\lambda m_\lambda}(\theta_p,\phi_p). \tag{12}$$

2) off-diagonal monoatomic contributions $\rho^{(2)}(\boldsymbol{p})$ with $\lambda\neq\sigma$ on atom A

$$\rho^{(2)}(\boldsymbol{p})=\frac{1}{4\pi^3}\sum_{\mathrm{A}}\sum^{\mathrm{A}}\sum^{\mathrm{A}}_{\lambda<\sigma}P_{\lambda\sigma}g_{n_\lambda l_\lambda}(p)g_{n_\sigma l_\sigma}(p)Y_{l_\lambda m_\lambda}(\theta_p,\phi_p)\times$$
$$Y_{l_\sigma m_\sigma}(\theta_p,\phi_p)\cos\left[\frac{\pi}{2}(l_\sigma-l_\lambda)\right]. \tag{13}$$

3) diatomic contributions $\rho^{(3)}(\boldsymbol{p})$ where $\mathrm{A}\neq\mathrm{B}$

$$\rho^{(3)}(\boldsymbol{p})=\frac{1}{4\pi^3}\sum\sum_{\mathrm{A}<\mathrm{B}}\sum_{\lambda}^{\mathrm{A}}\sum_{\sigma}^{\mathrm{B}}P_{\lambda\sigma}g_{n_\lambda l_\lambda}(p)g_{n_\sigma l_\sigma}(p)Y_{l_\lambda m_\lambda}(\theta_p,\phi_p)Y_{l_\sigma m_\sigma}(\theta_p,\phi_p)\times$$
$$\cos\left[\boldsymbol{p}\cdot(\boldsymbol{r}_{\mathrm{B}}-\boldsymbol{r}_{\mathrm{A}})+\frac{\pi}{2}(l_\sigma-l_\lambda)\right]. \tag{14}$$

Obviously, we have

$$\rho(\boldsymbol{p})=\rho^{(1)}(\boldsymbol{p})+\rho^{(2)}(\boldsymbol{p})+\rho^{(3)}(\boldsymbol{p}). \tag{15}$$

In the case of the CNDO approximation, only monoatomic diagonal contributions are taken into account

$$\rho^{\mathrm{CNDO}}(\boldsymbol{p})=\rho^{(1)}(\boldsymbol{p}). \tag{16}$$

In the case of the INDO approximation, the off-diagonal monoatomic contributions are also considered and accordingly we have

$$\rho^{\mathrm{INDO}}(\boldsymbol{p})=\rho^{\mathrm{CNDO}}(\boldsymbol{p})+\rho^{(2)}(\boldsymbol{p}). \tag{17}$$

If we now turn to the radial momentum density distribution $I(p)$ for a closed shell molecule, we have [34]

$$I(p)dp=\left(\int_0^{\pi} \sin \theta_p d\theta_p \int_0^{2\pi} d\phi_p \rho(\boldsymbol{p})\right)p^2 dp. \tag{18}$$

According to (10) this may be written as

$$I(p)=p^2\left(\frac{1}{2\pi}\right)^3 \sum_{\mathrm{A}} \sum_{\mathrm{B}} \sum_{\lambda}^{\mathrm{A}} \sum_{\sigma}^{\mathrm{B}} P_{\lambda\sigma} g_{n_\lambda l_\lambda}(p) g_{n_\sigma l_\sigma}(p)(i)^{l_\sigma - l_\lambda} \times$$
$$\int_0^{\pi} \sin \theta_p d\theta p \int_0^{2\pi} d\phi_p \exp\left[-i\boldsymbol{p}\cdot(\boldsymbol{r}_{\mathrm{A}}-\boldsymbol{r}_{\mathrm{B}})\right] Y_{l_\lambda m_\lambda}(\theta_p, \phi_p) Y_{l_\sigma m_\sigma}(\theta_p, \phi_p) \tag{19}$$

which obviously can be decomposed into a sum of mono- and diatomic contributions

$$I(p)=I(p)^{\mathrm{MONO}}_{(p)}+I^{\mathrm{DIAT}}(p). \tag{20}$$

Taking the terms where $\mathrm{A}=\mathrm{B}$ we have, due to the orthonormality of the spherical harmonics

$$I^{\mathrm{MONO}}(p)=p^2\left(\frac{1}{2\pi}\right)^3 \sum_{\mathrm{A}} \sum_{\lambda}^{\mathrm{A}} P_{\lambda\lambda} g^2_{n_\lambda l_\lambda}(p)+\frac{p^2}{4\pi^3} \sum_{\mathrm{A}} \sum_{\lambda<\sigma}^{\mathrm{A}} \sum^{\mathrm{A}} P_{\lambda\sigma} g_{n_\lambda l_\lambda}(p) \times$$
$$g_{n_\sigma l_\sigma}(p) \delta_{l_\lambda l_\sigma} \delta_{m_\lambda m_\sigma} \cos\left[\frac{\pi}{2}(l_\sigma - l_\lambda)\right]. \tag{21}$$

The evaluation of the diatomic term is readily achieved by using the spherical wave expansion for $\exp[-i\boldsymbol{p}\cdot(\boldsymbol{r}_{\mathrm{A}}-\boldsymbol{r}_{\mathrm{B}})]$; this yields

$$I^{\mathrm{DIAT}}(p)=p^2\left(\frac{1}{2\pi}\right)^3 \sum\sum_{\mathrm{A}\neq\mathrm{B}} \sum_{\lambda}^{\mathrm{A}} \sum_{\sigma}^{\mathrm{B}} P_{\lambda\sigma} g_{n_\lambda l_\lambda}(p) g_{n_\sigma l_\sigma}(p)(i)^{l_\sigma - l_\lambda} 4\pi \times$$
$$\sum_{l=0}^{\infty} \sum_{m} (-i)^l j_l(pr_{\mathrm{AB}}) Y_{lm}(\theta_{r_{\mathrm{A}}-r_{\mathrm{B}}}, \phi_{r_{\mathrm{A}}-r_{\mathrm{B}}}) \times$$
$$\int\int \sin \theta_p d\theta_p d\phi_p Y_{lm}(\theta_p, \phi_p) Y_{l_\lambda m_\lambda}(\theta_p, \phi_p) Y_{l_\sigma m_\sigma}(\theta_p, \phi_p). \tag{22}$$

A product of real spherical harmonics on one center can however be expanded as a finite linear combination of real spherical harmonics

$$Y_{lm}(\theta_p, \phi_p) Y_{l'm'}(\theta_p, \phi_p)=\sum_{M} \sum_{L=|l-l'|}^{l+l'} C_{Lll'}^{Mmm'} Y_{LM}(\theta_p, \phi_p) \tag{23}$$

where the $C_{Lll'}^{Mmm'}$ are properly chosen coefficients. Combining Eqs.(22) and (23) we obtain

$$I^{\mathrm{DIAT}}(p)=p^2\left(\frac{1}{2\pi}\right)^3 4\pi \sum\sum_{\mathrm{A}\neq\mathrm{B}} \sum_{\lambda}^{\mathrm{A}} \sum_{\sigma}^{\mathrm{B}} P_{\lambda\sigma} g_{n_\lambda l_\lambda}(p) g_{n_\sigma l_\sigma}(p) \times$$
$$(i)^{l_\sigma - l_\lambda} \sum_{l=0}^{\infty} \sum_{m} (-i)^l j_l(pr_{\mathrm{AB}}) Y_{lm}(\theta_{r_{\mathrm{A}}-r_{\mathrm{B}}}, \phi_{r_{\mathrm{A}}-r_{\mathrm{B}}}) \times$$
$$\sum_{M} \sum_{L} C_{Ll_\lambda l_\sigma}^{Mm_\lambda m_\sigma} \int\int Y_{lm}(\theta_p, \phi_p) Y_{LM}(\theta_p, \phi_p) \sin \theta_p d\theta_p d\phi_p. \tag{24}$$

Taking again account of the orthonormality of real spherical harmonics and observing that according to the parity of these functions [35]

$$Y_{LM}(\theta_{r_{\mathrm{A}}-r_{\mathrm{B}}}, \phi_{r_{\mathrm{A}}-r_{\mathrm{B}}})=(-1)^{L}Y_{LM}(\theta_{r_{\mathrm{B}}-r_{\mathrm{A}}}, \phi_{r_{\mathrm{B}}-r_{\mathrm{A}}}) \tag{25}$$

expression (24) reduces to

$$I^{\mathrm{DIAT}}(p)=p^{2}\,\frac{1}{\pi^{2}}\,\sum_{\mathrm{A}<\mathrm{B}}\sum\sum_{\lambda}^{\mathrm{A}}\sum_{\sigma}^{\mathrm{B}} P_{\lambda\sigma}g_{n_{\lambda}l_{\lambda}}(p)g_{n_{\sigma}l_{\sigma}}(p)\times$$

$$\sum_{M}\sum_{L} C_{Ll_{\lambda}l_{\sigma}}^{Mm_{\lambda}m_{\sigma}}\, j_{L}(pr_{\mathrm{AB}})Y_{LM}(\theta_{r_{\mathrm{A}}-r_{\mathrm{B}}}, \phi_{r_{\mathrm{A}}-r_{\mathrm{B}}})\cos\left[\frac{\pi}{2}(L+l_{\lambda}-l_{\sigma})\right]. \tag{26}$$

If we now apply the CNDO or INDO approximations to $I(p)$ we clearly have

$$I^{\mathrm{CNDO}}(p)=I^{\mathrm{INDO}}(p)=p^{2}\left(\frac{1}{2\pi}\right)^{3}\sum_{\mathrm{A}}\sum_{\lambda} p_{\lambda\lambda}g_{n_{\lambda}l_{\lambda}}^{2}(p). \tag{27}$$

Indeed, due to the presence of the Kronecker deltas in the second term of Eq.(21), off-diagonal monoatomic contributions are equal to zero if an atomic valence basis set is used. The expressions for $\rho(\boldsymbol{p})$ and $I(p)$ derived above in their unapproximated and NDO approximated forms, are very suitable for computer programmation.

## 3. Orientational Invariance and Normalization Conditions in the Momentum Space

Let us calculate the total momentum density $\rho(\boldsymbol{p})$ at a given point $\boldsymbol{p}$ in the momentum space coordinate system ($P_x$, $P_y$, $P_z$) for a given orientation of the molecule in the position space general coordinate system ($X$, $Y$, $Z$) of Fig. 1. If we subject the molecule and the impulse vector $\boldsymbol{p}$ to the same rotation $\mathscr{R}$, respectively

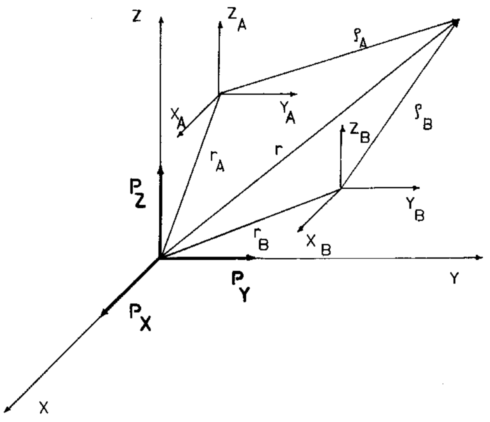

Fig. 1. General ($X$, $Y$, $Z$) and local atomic ($X_m$, $Y_m$, $Z_m$) position space coordinate systems and momentum space coordinate system ($P_x$, $P_y$, $P_z$)

in the $(X, Y, Z)$ and the $(P_x, P_y, P_z)$ coordinate systems and recalculate the momentum density $\rho'$ at the point $\boldsymbol{p}'$ given by

$$\boldsymbol{p}' = \mathscr{R}\boldsymbol{p} \tag{28}$$

then we clearly must have

$$\rho'(\boldsymbol{p}') = \rho(p). \tag{29}$$

This demand is the momentum-space counterpart of the orientational invariance requirement of the electron density in the position space [36].

Decomposing $\rho'(\boldsymbol{p}')$ into monoatomic and diatomic terms we have, according to Eq.(17)

$$\rho'^{\mathrm{MONO}}(\boldsymbol{p}') = \rho'^{\mathrm{INDO}}(\boldsymbol{p}') = \rho'^{\mathrm{CNDO}}(\boldsymbol{p}') + \rho'^{(2)}(\boldsymbol{p}') \tag{30}$$

which, reintroducing the LCAO expansion coefficients, can be written (considering Eqs.(12), (13)) as

$$\begin{aligned} \rho'^{\mathrm{MONO}}(\boldsymbol{p}') = \left(\frac{1}{2\pi}\right)^3 \sum_{\mathrm{A}} \sum_{n_{\mathrm{A}}} \sum_{l_{\mathrm{A}}} \sum_{m_{\mathrm{A}}} \sum_{n'_{\mathrm{A}}} \sum_{l'_{\mathrm{A}}} \sum_{m'_{\mathrm{A}}} 2 \sum_{i}^{\mathrm{occ}} C'_{n_{\mathrm{A}} l_{\mathrm{A}} m_{\mathrm{A}}, i} \times \\ C'_{n'_{\mathrm{A}} l'_{\mathrm{A}} m'_{\mathrm{A}}, i} g_{n_{\mathrm{A}} l_{\mathrm{A}}}(p) g_{n'_{\mathrm{A}} l'_{\mathrm{A}}}(p) Y_{l_{\mathrm{A}} m_{\mathrm{A}}}(\theta_{p'}, \phi_{p'}) Y_{l'_{\mathrm{A}} m'_{\mathrm{A}}}(\theta_{p'}, \phi_{p'}) (i)^{l'_{\mathrm{A}} - l_{\mathrm{A}}}. \end{aligned} \tag{31}$$

The diatomic term then can be written (according to Eq.(14)) as

$$\begin{aligned} \rho'^{\mathrm{DIAT}}(\boldsymbol{p}') = \rho'^{(3)}(\boldsymbol{p}') = \frac{1}{4\pi^3} \sum_{\mathrm{A<B}} \sum_{n_{\mathrm{A}}} \sum_{l_{\mathrm{A}}} \sum_{m_{\mathrm{A}}} \sum_{n_{\mathrm{B}}} \sum_{l_{\mathrm{B}}} \sum_{m_{\mathrm{B}}} 2 \sum_{i}^{\mathrm{occ}} C'_{n_{\mathrm{A}} l_{\mathrm{A}} m_{\mathrm{A}}, i} \times \\ C'_{n_{\mathrm{B}} l_{\mathrm{B}} m_{\mathrm{B}}, i} g_{n_{\mathrm{A}} l_{\mathrm{A}}}(p) g_{n_{\mathrm{B}} l_{\mathrm{B}}}(p) Y_{l_{\mathrm{A}} m_{\mathrm{A}}}(\theta_{p'}, \phi_{p'}) Y_{l_{\mathrm{B}} m_{\mathrm{B}}}(\theta_{p'}, \phi_{p'}) \times \\ \cos\left[\boldsymbol{p}' \cdot (\boldsymbol{r}'_{\mathrm{B}} - \boldsymbol{r}'_{\mathrm{A}}) - \frac{\pi}{2}(l_{\mathrm{B}} - l_{\mathrm{A}})\right]. \end{aligned} \tag{32}$$

The summation on $m_{\mathrm{A}}$ runs over the $2l_{\mathrm{A}}+1$ real spherical harmonics with the same $l_{\mathrm{A}}$ quantum number. If the molecule is subjected to a rotation $\mathscr{R}$ to which a $[3 \times 3]$ Cartesian coordinate transformation matrix is associated, noted as $(\boldsymbol{O}^{l=1})$, then the molecular orbital coefficients $C_{\lambda i}$ where $\lambda$ refers to the atomic orbitals with the same $l$ quantum number of atom A, transform according to $[(2l_{\mathrm{A}}+1) \times (2l_{\mathrm{A}}+1)]$ matrices noted as $(\boldsymbol{O}^{l=l_{\mathrm{A}}})^{-1}$

$$C'_{n_{\mathrm{A}} l_{\mathrm{A}} m_{\mathrm{A}}, i} = \sum_{q} (\boldsymbol{O}^{l_{\mathrm{A}}})^{-1}_{m_{\mathrm{A}} q} C_{n_{\mathrm{A}} l_{\mathrm{A}} q, i} \tag{33}$$

Furthermore, defining $F_{n_{\mathrm{A}} l_{\mathrm{A}} m_{\mathrm{A}}}(\boldsymbol{p}')$ as

$$F_{n_{\mathrm{A}} l_{\mathrm{A}} m_{\mathrm{A}}}(\boldsymbol{p}') = g_{n_{\mathrm{A}} l_{\mathrm{A}}}(p') Y_{l_{\mathrm{A}} m_{\mathrm{A}}}(\theta_{p'}, \phi_{p'}) \tag{34}$$

we can write, according to Wigner [37]

$$F_{n_{\mathrm{A}} l_{\mathrm{A}} m_{\mathrm{A}}}(\boldsymbol{p}') = F_{n_{\mathrm{A}} l_{\mathrm{A}} m_{\mathrm{A}}}(\mathscr{R}\boldsymbol{p}) = \mathscr{R}^{-1} F_{n_{\mathrm{A}} l_{\mathrm{A}} m_{\mathrm{A}}}(\boldsymbol{p}) = \sum_{q} (O^{l_{\mathrm{A}}})^{-1}_{m_{\mathrm{A}} q} F_{n_{\mathrm{A}} l_{\mathrm{A}} q}(\boldsymbol{p}). \tag{35}$$

Having in mind that $\boldsymbol{p}'\cdot(\boldsymbol{r}'_{\mathrm{B}}-\boldsymbol{r}'_{\mathrm{A}})=\boldsymbol{p}\cdot(\boldsymbol{r}_{\mathrm{B}}-\boldsymbol{r}_{\mathrm{A}})$ we obtain for $\rho'^{\mathrm{INDO}}(\boldsymbol{p}')$ and $\rho'^{\mathrm{DIAT}}(\boldsymbol{p}')$

$$\rho'^{\mathrm{INDO}}(\boldsymbol{p}')=\left(\frac{1}{2\pi}\right)^3\sum_{\mathrm{A}}\sum_{n_{\mathrm{A}}}\sum_{n'_{\mathrm{A}}}\sum_{l_{\mathrm{A}}}\sum_{l'_{\mathrm{A}}}\sum_{m_{\mathrm{A}}}\sum_{m'_{\mathrm{A}}}2\sum_{i}^{\mathrm{occ}}\sum_{q}(O^{l_{\mathrm{A}}})^{-1}_{m_{\mathrm{A}}q}C_{n_{\mathrm{A}}l_{\mathrm{A}}q,i}\times$$
$$\sum_{r}(O^{l'_{\mathrm{A}}})^{-1}_{m'_{\mathrm{A}}r}C_{n_{\mathrm{A}}l_{\mathrm{A}}r,i}g_{n_{\mathrm{A}}l_{\mathrm{A}}}(p)g_{n'_{\mathrm{A}}l'_{\mathrm{A}}}(p)\sum_{s}(O^{l_{\mathrm{A}}})^{-1}_{m_{\mathrm{A}}s}Y_{l_{\mathrm{A}}s}(\theta_p,\phi_p)\times$$
$$\sum_{t}(O^{l'_{\mathrm{A}}})^{-1}_{m'_{\mathrm{A}}t}Y_{l'_{\mathrm{A}}t}(\theta_p,\phi_p)(i)^{l'_{\mathrm{A}}-l_{\mathrm{A}}}. \tag{36}$$

$$\rho'^{\mathrm{DIAT}}(\boldsymbol{p}')=\frac{1}{4\pi^3}\sum_{\mathrm{A}<\mathrm{B}}\sum_{n_{\mathrm{A}}}\sum_{l_{\mathrm{A}}}\sum_{m_{\mathrm{A}}}\sum_{n_{\mathrm{B}}}\sum_{l_{\mathrm{B}}}\sum_{m_{\mathrm{B}}}2\sum_{i}^{\mathrm{occ}}\sum_{q}(O^{l_{\mathrm{A}}})^{-1}_{m_{\mathrm{A}}q}C_{n_{\mathrm{A}}l_{\mathrm{A}}q,i}\times$$
$$\sum_{r}(O^{l_{\mathrm{B}}})^{-1}_{m_{\mathrm{B}}r}C_{n_{\mathrm{B}}l_{\mathrm{B}}r,i}g_{n_{\mathrm{A}}l_{\mathrm{A}}}(p)g_{n_{\mathrm{B}}l_{\mathrm{B}}}(p)\sum_{s}(O^{l_{\mathrm{A}}})^{-1}_{m_{\mathrm{A}}s}\times$$
$$Y_{l_{\mathrm{A}}s}(\theta_p,\phi_p)\sum_{t}(O^{l_{\mathrm{B}}})^{-1}_{m_{\mathrm{B}}t}Y_{l_{\mathrm{B}}t}(\theta_p,\phi_p)\cos\left[\boldsymbol{p}\cdot(\boldsymbol{r}_{\mathrm{B}}-\boldsymbol{r}_{\mathrm{A}})+\frac{\pi}{2}(l_{\mathrm{B}}-l_{\mathrm{A}})\right]. \tag{37}$$

Due to the orthogonality of the $\boldsymbol{O}^{l_{\mathrm{A}}}$, $\boldsymbol{O}^{l'_{\mathrm{A}}}$ and $\boldsymbol{O}^{l_{\mathrm{B}}}$ matrices these expressions reduce to

$$\rho'^{\mathrm{INDO}}(\boldsymbol{p}')=\left(\frac{1}{2\pi}\right)^3\sum_{\mathrm{A}}\sum_{n_{\mathrm{A}}}\sum_{l_{\mathrm{A}}}\sum_{n'_{\mathrm{A}}}\sum_{l'_{\mathrm{A}}}\sum_{q}\sum_{r}2\sum_{i}^{\mathrm{occ}}C_{n_{\mathrm{A}}l_{\mathrm{A}}q,i}C_{n'_{\mathrm{A}}l'_{\mathrm{A}}r,i}\times$$
$$g_{n_{\mathrm{A}}l_{\mathrm{A}}}(p)g_{n'_{\mathrm{A}}l'_{\mathrm{A}}}(p)Y_{l_{\mathrm{A}}q}(\theta_p,\phi_p)Y_{l'_{\mathrm{A}}r}(\theta_p,\phi_p)(i)^{l'_{\mathrm{A}}-l_{\mathrm{A}}} \tag{38}$$

$$\rho'^{\mathrm{DIAT}}(\boldsymbol{p}')=\frac{1}{4\pi^3}\sum_{\mathrm{A}<\mathrm{B}}\sum_{n_{\mathrm{A}}}\sum_{l_{\mathrm{A}}}\sum_{n_{\mathrm{B}}}\sum_{l_{\mathrm{B}}}\sum_{q}\sum_{r}2\sum_{i}^{\mathrm{occ}}C_{n_{\mathrm{A}}l_{\mathrm{A}}q,i}C_{n_{\mathrm{B}}l_{\mathrm{B}}r,i}\times$$
$$g_{n_{\mathrm{A}}l_{\mathrm{A}}}(p)g_{n_{\mathrm{B}}l_{\mathrm{B}}}(p)\cos\left[\boldsymbol{p}\cdot(\boldsymbol{r}_{\mathrm{B}}-\boldsymbol{r}_{\mathrm{A}})+\frac{\pi}{2}(l_{\mathrm{B}}-l_{\mathrm{A}})\right]. \tag{39}$$

so that

$$\begin{aligned}\rho'^{\mathrm{INDO}}(\boldsymbol{p}')&=\rho^{\mathrm{INDO}}(\boldsymbol{p})\\ \rho'^{\mathrm{DIAT}}(\boldsymbol{p}')&=\rho^{\mathrm{DIAT}}(\boldsymbol{p}).\end{aligned} \tag{40}$$

Hence, it appears that the INDO approximation to $\rho(\boldsymbol{p})$ is orientation invariant. However, if momentum densities are approximated up to the CNDO level, then we have, after rotation

$$\rho'^{\mathrm{CNDO}}(\boldsymbol{p}')=\left(\frac{1}{2\pi}\right)^3\sum_{\mathrm{A}}\sum_{n_{\mathrm{A}}}\sum_{l_{\mathrm{A}}}\sum_{m_{\mathrm{A}}}2\sum_{i}^{\mathrm{occ}}\sum_{p}(O^{l_{\mathrm{A}}})^{-1}_{m_{\mathrm{A}}p}C_{n_{\mathrm{A}}l_{\mathrm{A}}p,i}\times$$
$$\sum_{q}(O^{l_{\mathrm{A}}})^{-1}_{m_{\mathrm{A}}q}C_{n_{\mathrm{A}}l_{\mathrm{A}}q,i}g_{n_{\mathrm{A}}l_{\mathrm{A}}}(p)\,g_{n_{\mathrm{A}}l_{\mathrm{A}}}(p)\times$$
$$\sum_{s}(O^{l_{\mathrm{A}}})^{-1}_{m_{\mathrm{A}}s}Y_{l_{\mathrm{A}}s}(\theta_p,\phi_p)\sum_{t}(O^{l_{\mathrm{A}}})^{-1}_{m_{\mathrm{A}}t}Y_{l_{\mathrm{A}}t}(\theta_p,\phi_p). \tag{41}$$

which obviously cannot be further simplified. Overlap densities of the form

$$g_{n_{\mathrm{A}}l_{\mathrm{A}}}Y_{l_{\mathrm{A}}s}g_{n_{\mathrm{A}}l_{\mathrm{A}}}Y_{l_{\mathrm{A}}t}\quad\text{with } t\neq s$$

which do not occur in the expression for $\rho^{\mathrm{CNDO}}(\boldsymbol{p})$ appear and will be neglected in the CNDO theory; accordingly different numerical results will be obtained.

According to the definition of the radial momentum density distribution (Eq.(18)) and bearing in mind that $\rho^{\mathrm{INDO}}(\boldsymbol{p})$ is orientation invariant, it appears clearly that $\mathrm{I}(p)$ as given by Eq.(27) will satisfy the same requirement if approximated up to a CNDO level.

The nature or extent of the NDO approximations should also lead to expressions for $\rho(\boldsymbol{p})$ which obey the normalization condition, i.e.

$$\int \rho(\boldsymbol{p})d\boldsymbol{p} = N \tag{42}$$

where $N$ is the total number of (valence) electrons present in the molecule. Let us first show that the value of the overlap integral between two atomic basis functions remains unchanged when going over from the position into the momentum space. These integrals will be noted respectively as $S^{\boldsymbol{R}}_{\mu\nu}$ and $S^{\boldsymbol{P}}_{\mu\nu}$. If $\eta_\mu(\boldsymbol{p})$ and $\eta_\nu(\boldsymbol{p})$ are the momentum space transforms of $\chi_\mu(\boldsymbol{r})$ and $\chi_\nu(\boldsymbol{r})$, then we have, according to Eq.(1)

$$\begin{aligned} S^{\boldsymbol{P}}_{\mu\nu} = \int \eta^*_\mu(\boldsymbol{p})\eta_\nu(\boldsymbol{p})d\boldsymbol{p} &= \left(\frac{1}{2\pi}\right)^3 \int\int\int e^{i\boldsymbol{p}\cdot\boldsymbol{r}}\chi^*_\mu(\boldsymbol{r})e^{-i\boldsymbol{p}\cdot\boldsymbol{r}'}\chi_\nu(\boldsymbol{r}')d\boldsymbol{r}d\boldsymbol{r}'d\boldsymbol{p} \\ &= \int\int d\boldsymbol{r}d\boldsymbol{r}'\chi^*_\mu(\boldsymbol{r})\chi_\nu(\boldsymbol{r}')\left(\frac{1}{2\pi}\right)^3 \int e^{i\boldsymbol{p}\cdot(\boldsymbol{r}-\boldsymbol{r}')}d\boldsymbol{p} \end{aligned} \tag{43}$$

or introducing the Dirac $\delta$-function [38], we obtain

$$S^{\boldsymbol{P}}_{\mu\nu} = \int\int d\boldsymbol{r}d\boldsymbol{r}'\chi^*_\mu(\boldsymbol{r})\chi_\nu(\boldsymbol{r}')\delta(\boldsymbol{r}-\boldsymbol{r}') = \int d\boldsymbol{r}\chi^*_\mu(\boldsymbol{r})\chi_\nu(\boldsymbol{r}) = S^{\boldsymbol{R}}_{\mu\nu}. \tag{44}$$

Now, according to Eq.(9) we have that

$$\begin{aligned} \int \rho(\boldsymbol{p})d\boldsymbol{p} &= 2\sum_i^{\mathrm{occ}} \int |\phi_i(\boldsymbol{p})|^2 d\boldsymbol{p} = 2\sum_i^{\mathrm{occ}} \sum_\mu \sum_\nu C_{\mu i}C_{\nu i} \int \eta^*_\mu(\boldsymbol{p})\eta_\nu(\boldsymbol{p})d\boldsymbol{p} \\ &= \sum_\mu \sum_\nu P_{\mu\nu}S^{\boldsymbol{P}}_{\mu\nu} = \sum_\mu \sum_\nu P_{\mu\nu}S^{\boldsymbol{R}}_{\mu\nu} = tr(\boldsymbol{P}\boldsymbol{S}^{\boldsymbol{R}}). \end{aligned} \tag{45}$$

which is equal to the total number of electrons $N$ only if overlap integrals are explicitly taken into account when solving the Roothaan equations, or if deorthogonalized NDO type wavefunctions [39] are used. In the case of simple NDO theory, the overlap matrix $\boldsymbol{S}$ reduces to a unit matrix and accordingly, diatomic terms in (45) should be neglected.

Combining the orientational and normalization requirements we can conclude that only two physically significant possibilities subsist: either one uses the NDO wavefunctions and approximates $\rho(\boldsymbol{p})$ and $I(p)$ respectively up to an INDO and a CNDO level, or the NDO wavefunctions are deorthogonalized and $\rho(\boldsymbol{p})$ and $I(p)$ are evaluated without any approximation. These combinations, at least for $\rho(\boldsymbol{p})$ are the exact counterparts of the position space possibilities [36].

This theory, which has already been programmed on the CDC 6500 Computer of the Free University of Brussels, will be used to perform a systematic study of the trends in the momentum space properties of large organic molecules. The results of these investigations will be the subject of subsequent publications.

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