Theoret. Chim. Acta (Berl.) 61, 325–333 (1982)

THEORETICA CHIMICA ACTA

The Evaluation of ω Parameters in Contracted Density Product Calculations

Franz Mascarello, Bruno Cuony, and Werner Hug

Institute of Physical Chemistry, University of Fribourg, CH-1700 Fribourg, Switzerland

General formulas for the rotational averages of two electron integrals with arbitrary combinations of spherical tensors in standard, Cartesian, and equivalent form are presented. The way in which the ω parameters of CDP type calculations can be obtained from rotational averages is discussed, and it is shown from numerical results that the interpretation of the ω parameters as space averages is compatible up to d orbitals with the CDP invariance requirements.

Key words: Space averages of two electron integrals – ω parameters – CDP-MO calculations.

1. Introduction

Electron-electron interaction terms entail the most expense in quantum chemical calculations of molecules and aggregates. In a recent paper [1] we have shown how two electron integrals over basis functions can be neglected in a systematic way without violating transformation invariance. In particular it was found that groups of integrals can be replaced by their space averages dubbed ω parameters in [1]. The use of such space averages could be of particular interest also in the calculation of intermolecular interactions in systems with a random or rapidly changing orientation of the molecules.

Formulas to evaluate the ω parameters from exact integrals have been given in [1] for basis functions up to $3p$ orbitals in Cartesian form. In this work we present first the formulas for general rotational averages of two electron integrals with arbitrary combinations of basis functions, with the only requirement that their angular part must span representations of $O^+(3)$. We then show how the

0040-5744/82/0061/0325/$01.80

space averages for CDP calculations are related to these rotational averages, and how ω parameters can be defined for real d orbitals.

The radial parts of the basis functions as well as the electron-electron interaction operator are omitted in our discussion because they are scalars and remain invariant under the operations of O(3). Thus, the angular part only of the basis functions is of concern to us. It can always be expressed by linear combinations of spherical harmonics. We therefore first derive the rotational averages of spherical harmonics in standard form [2] with the phase convention as used by Condon and Shortley [3], and use this result in turn to evaluate the rotational averages of two electron integrals over other basis functions.

2. Rotational Averages of Products of Standard Spherical Harmonics

The rotational average of a two electron integral with the standard spherical harmonics $Y^{l_X}_{n_X}$ located at the centers A, B, C, and D can be written as

$$\overline{(Y^{l_A}_{n_A}Y^{l_B}_{n_B}\,|\,Y^{l_C}_{n_C}Y^{l_D}_{n_D})}=\frac{\int_0^{2\pi}d\alpha\int_0^{\pi}d\beta\,\sin\beta\int_0^{2\pi}d\gamma\,\hat{D}(\alpha\beta\gamma)(Y^{l_A}_{n_A}Y^{l_B}_{n_B}\,|\,Y^{l_C}_{n_C}Y^{l_D}_{n_D})}{\int_0^{2\pi}d\alpha\int_0^{\pi}d\beta\,\sin\beta\int_0^{2\pi}d\gamma}. \tag{1}$$

α, β, and γ are the Eulerian angles with the integration extending over the domain of their allowed ranges, and $\hat{D}(\alpha\beta\gamma)$ is the rotation operator effecting a rotation of the coordinate system by positive angles. The effect of $\hat{D}(\alpha\beta\gamma)$ on a single function is given by

$$\hat{D}(\alpha\beta\gamma)Y^l_n=\sum_m Y^l_m\mathcal{D}^{(l)}_{mn}(\alpha\beta\gamma) \tag{2}$$

with $\mathcal{D}^{(l)}_{mn}$ representing elements of Wigner rotation matrices.

In Eq. (1) the coordinate system is simultaneously rotated for each function in the same way so that we have

$$\begin{aligned}\hat{D}(\alpha\beta\gamma)(Y^{l_A}_{n_A}Y^{l_B}_{n_B}\,|\,Y^{l_C}_{n_C}Y^{l_D}_{n_D})=&\sum_{m_A}\sum_{m_B}\sum_{m_C}\sum_{m_D}(Y^{l_A}_{m_A}Y^{l_B}_{m_B}\,|\,Y^{l_C}_{m_C}Y^{l_D}_{m_D})\\&\times\mathcal{D}^{(l_A)*}_{m_An_A}(\alpha\beta\gamma)\mathcal{D}^{(l_B)}_{m_Bn_B}(\alpha\beta\gamma)\\&\times\mathcal{D}^{(l_C)*}_{m_Cn_C}(\alpha\beta\gamma)\mathcal{D}^{(l_D)}_{m_Dn_D}(\alpha\beta\gamma).\end{aligned} \tag{3}$$

By using the relations [4]

$$\begin{aligned}&\mathcal{D}^{(l_A)}_{-m_A-n_A}(\alpha\beta\gamma)\mathcal{D}^{(l_B)}_{m_Bn_B}(\alpha\beta\gamma)\\&\quad=\sum_{l_{AB}}(2l_{AB}+1)\begin{pmatrix}l_A & l_B & l_{AB}\\ -m_A & m_B & m_{AB}\end{pmatrix}\begin{pmatrix}l_A & l_B & l_{AB}\\ -n_A & n_B & n_{AB}\end{pmatrix}\mathcal{D}^{(l_{AB})*}_{m_{AB}n_{AB}}(\alpha\beta\gamma)\end{aligned} \tag{4}$$

and

$$\mathscr{D}^{(l)*}_{mn}(\alpha\beta\gamma)=(-1)^{m-n}\mathscr{D}^{(l)}_{-m-n}(\alpha\beta\gamma) \tag{5}$$

the fourfold product in Eq. (3) can be simplified to

$$\begin{aligned}
&\mathscr{D}^{(l_A)*}_{m_An_A}(\alpha\beta\gamma)\mathscr{D}^{(l_B)}_{m_Bn_B}(\alpha\beta\gamma)\mathscr{D}^{(l_C)*}_{m_Cn_C}(\alpha\beta\gamma)\mathscr{D}^{(l_D)}_{m_Dn_D}(\alpha\beta\gamma)\\
&\quad=\sum_{l_{AB}}\sum_{l_{CD}}(2l_{AB}+1)(2l_{CD}+1)\begin{pmatrix} l_A & l_B & l_{AB}\\ -m_A & m_B & m_{AB}\end{pmatrix}\\
&\quad\quad\times\begin{pmatrix} l_C & l_D & l_{CD}\\ -m_C & m_D & m_{CD}\end{pmatrix}\begin{pmatrix} l_A & l_B & l_{AB}\\ -n_A & n_B & n_{AB}\end{pmatrix}\begin{pmatrix} l_C & l_D & l_{CD}\\ -n_C & n_D & n_{CD}\end{pmatrix}\\
&\quad\quad\times(-1)^{m_A-n_A}(-1)^{m_C-n_C}(-1)^{m_{CD}-n_{CD}}\mathscr{D}^{(l_{AB})*}_{m_{AB}n_{AB}}(\alpha\beta\gamma)\mathscr{D}^{(l_{CD})}_{-m_{CD}-n_{CD}}(\alpha\beta\gamma).
\end{aligned} \tag{6}$$

In the Wigner 3-j symbols in Eqs. (4) and (6) one has $n_{AB}=n_A-n_B$, and similarly for m_{AB}, n_{CD}, and m_{CD}. The range of values for l_{AB} and l_{CD} is restricted by the "triangular condition" $l_A+l_B\geq l_{AB}\geq|l_A-l_B|$ and $l_C+l_D\geq l_{CD}\geq|l_C-l_D|$. If Eq. (6) is introduced in Eq. (3) and Eq. (3) in Eq. (1) one obtains

$$\begin{aligned}
&\overline{(Y^{l_A}_{n_A}Y^{l_B}_{n_B}\mid Y^{l_C}_{n_C}Y^{l_D}_{n_D})}\\
&\quad=\sum_{m_A}\sum_{m_B}\sum_{m_C}\sum_{m_D}(Y^{l_A}_{m_A}Y^{l_B}_{m_B}\mid Y^{l_C}_{m_C}Y^{l_D}_{m_D})\\
&\quad\quad\times\sum_{l_{AB}}\sum_{l_{CD}}(2l_{AB}+1)(2l_{CD}+1)(-1)^{m_A-n_A}(-1)^{m_C-n_C}(-1)^{m_{CD}-n_{CD}}\\
&\quad\quad\times\begin{pmatrix} l_A & l_B & l_{AB}\\ -m_A & m_B & m_{AB}\end{pmatrix}\begin{pmatrix} l_C & l_D & l_{CD}\\ -m_C & m_D & m_{CD}\end{pmatrix}\\
&\quad\quad\times\begin{pmatrix} l_A & l_B & l_{AB}\\ -n_A & n_B & n_{AB}\end{pmatrix}\begin{pmatrix} l_C & l_D & l_{CD}\\ -n_C & n_D & n_{CD}\end{pmatrix}\\
&\quad\quad\times\frac{\displaystyle\int_0^{2\pi}d\alpha\int_0^{\pi}d\beta\sin\beta\int_0^{2\pi}d\gamma\,\mathscr{D}^{(l_{AB})*}_{m_{AB}n_{AB}}(\alpha\beta\gamma)\mathscr{D}^{(l_{CD})}_{-m_{CD}-n_{CD}}(\alpha\beta\gamma)}{\displaystyle\int_0^{2\pi}d\alpha\int_0^{\pi}d\beta\sin\beta\int_0^{2\pi}d\gamma}.
\end{aligned} \tag{7}$$

The integral in the denominator yields $8\pi^2$, and for the numerator one has the relation [4]

$$\begin{aligned}
&\int_0^{2\pi}d\alpha\int_0^{\pi}d\beta\sin\beta\int_0^{2\pi}d\gamma\,\mathscr{D}^{(l_{AB})*}_{m_{AB}n_{AB}}(\alpha\beta\gamma)\mathscr{D}^{(l_{CD})}_{-m_{CD}-n_{CD}}(\alpha\beta\gamma)\\
&\quad=\frac{8\pi^2}{2l_{AB}+1}\delta_{m_{AB},-m_{CD}}\delta_{n_{AB},-n_{CD}}\delta_{l_{AB},l_{CD}}.
\end{aligned} \tag{8}$$

The rotational average (1) for standard spherical harmonics therefore yields

$$\overline{(Y^{l_A}_{n_A}Y^{l_B}_{n_B}\,|\,Y^{l_C}_{n_C}Y^{l_D}_{n_D})}=\sum_{m_A}\sum_{m_B}\sum_{m_C}\sum_{m_D}(Y^{l_A}_{m_A}Y^{l_B}_{m_B}\,|\,Y^{l_C}_{m_C}Y^{l_D}_{m_D})\Omega^{l_Al_Bl_Cl_D}_{m_Am_Bm_Cm_Dn_An_Bn_Cn_D}\tag{9}$$

where we have set

$$\begin{aligned}\Omega^{l_Al_Bl_Cl_D}_{m_Am_Bm_Cm_Dn_An_Bn_Cn_D}=&\sum_l(2l+1)(-1)^{m_A-n_A}(-1)^{m_C-n_C}(-1)^{m_{CD}-n_{CD}}\\&\times\begin{pmatrix}l_A & l_B & l\\ -m_A & m_B & m_{AB}\end{pmatrix}\begin{pmatrix}l_C & l_D & l\\ -m_C & m_D & m_{CD}\end{pmatrix}\\&\times\begin{pmatrix}l_A & l_B & l\\ -n_A & n_B & n_{AB}\end{pmatrix}\begin{pmatrix}l_C & l_D & l\\ -n_C & n_D & n_{CD}\end{pmatrix}\\&\times\delta_{m_{AB},-m_{CD}}\delta_{n_{AB},-n_{CD}},\end{aligned}\tag{10}$$

and where the summation over l is restricted by the condition

$$\mathrm{Min}\,(l_A+l_B,\,l_C+l_D)\geq l\geq\mathrm{Max}\,(|l_A-l_B|,\,|l_C-l_D|).$$

3. Rotational Averages of Real Orthogonal Basis Sets

Standard spherical harmonics are rarely used in numerical quantum chemical computations because of their complex nature. In general sets of irreducible or reducible real tensors are employed. Irreducible real tensors X^l_r are related to the spherical harmonics by a unitary transformation

$$X^l_r=\sum_n U_{rn}Y^l_n\tag{11a}$$

$$Y^l_m=\sum_t U^+_{mt}X^l_t=\sum_t U^*_{tm}X^l_t.\tag{11b}$$

The rotational average for the functions X^l_r can be expressed with (11)

$$\begin{aligned}\overline{(X^{l_A}_{r_A}X^{l_B}_{r_B}\,|X^{l_C}_{r_C}X^{l_D}_{r_D})}&=\sum_{n_A}\sum_{n_B}\sum_{n_C}\sum_{n_D}U^*_{r_An_A}U_{r_Bn_B}U^*_{r_Cn_C}U_{r_Dn_D}\overline{(Y^{l_A}_{n_A}Y^{l_B}_{n_B}\,|\,Y^{l_C}_{n_C}Y^{l_D}_{n_D})}\\&=\sum_{t_A}\sum_{t_B}\sum_{t_C}\sum_{t_D}(X^{l_A}_{t_A}X^{l_B}_{t_B}\,|X^{l_C}_{t_C}X^{l_D}_{t_D})\Omega'^{l_Al_Bl_Cl_D}_{t_At_Bt_Ct_Dr_Ar_Br_Cr_D}\end{aligned}\tag{12}$$

where we have set

$$\begin{aligned}\Omega'^{l_Al_Bl_Cl_D}_{t_At_Bt_Ct_Dr_Ar_Br_Cr_D}=&\sum_{m_A}\sum_{m_B}\sum_{m_C}\sum_{m_D}\sum_{n_A}\sum_{n_B}\sum_{n_C}\sum_{n_D}U^*_{r_An_A}U_{r_Bn_B}U^*_{r_Cn_C}U_{r_Dn_D}\\&\times U_{t_Am_A}U^*_{t_Bm_B}U_{t_Cm_C}U^*_{t_Dm_D}\Omega^{l_Al_Bl_Cl_D}_{m_Am_Bm_Cm_Dn_An_Bn_Cn_D}.\end{aligned}\tag{13}$$

In CDP calculations with irreducible tensors there are two real basis sets which are of practical interest, namely the irreducible Cartesian tensors H^l_r [5] and the sets of equivalent orbitals $V_{j/g}$ [6], where g is the dimension of the set and j takes the values $0, 1, \ldots g-1$. For the *Cartesian tensors* the elements U_m of the unitary transformation matrix, consistent with our choice of phases in (10), follow from the equations

$$\begin{aligned} H^l_\sigma &= Y^l_0 \\ H^l_{\lambda c} &= \frac{1}{\sqrt{2}}(-1)^\lambda Y^l_\lambda + \frac{1}{\sqrt{2}} Y^l_{-\lambda} \\ H^l_{\lambda s} &= \frac{1}{i\sqrt{2}}(-1)^\lambda Y^l_\lambda - \frac{1}{i\sqrt{2}} Y^l_{-\lambda} \\ \lambda &= |m|. \end{aligned} \tag{14}$$

The most widely employed *ab initio* programs use reducible Cartesian tensors, however, for basis functions other than s and p orbitals. The integrals $(H^{l_A}_{t_A} H^{l_B}_{t_B} \,|\, H^{l_C}_{t_C} H^{l_D}_{t_D})$ must then be expressed as linear combinations of integrals over such basis functions. For standard real d orbitals e.g. one has the functional form

$$\begin{aligned} H^2_\sigma &= \tfrac{1}{2}(2z^2 - x^2 - y^2) \\ H^2_{1s} &= \sqrt{3}zy \\ H^2_{1c} &= \sqrt{3}zx \\ H^2_{2s} &= \sqrt{3}xy \\ H^2_{2c} &= \tfrac{1}{2}\sqrt{3}(x^2 - y^2). \end{aligned} \tag{15}$$

In terms of *ab initio* integrals calculated with a reducible set a typical CDP integral with the functions H^2_{1c} and H^2_{2c} would thus be given by

$$\begin{aligned} (H^2_{1c}H^2_{1c} \,|\, H^2_{2c}H^2_{2c}) = {} & \tfrac{9}{4}(zx\,zx \,|\, x^2x^2) - \tfrac{9}{4}(zx\,zx \,|\, x^2y^2) \\ & - \tfrac{9}{4}(zx\,zx \,|\, y^2x^2) + \tfrac{9}{4}(zx\,zx \,|\, y^2y^2), \end{aligned} \tag{16}$$

and similarly for integrals with other combinations of basis functions.

Equivalent orbitals are orbitals directed along the slant edges of a trigonal, pentagonal, heptagonal, etc. pyramid for *p*, *d*, *f*, etc. functions, respectively [6] [7]. Except for the *p* case, where the equivalent orbitals simply correspond to the ordinary Cartesian *p* functions in a rotated coordinate frame, there is always more than one set of equivalent orbitals. The functions of different sets have a different shape and the pyramids along the edges of which they are directed are more or less steep. For *d* orbitals two sets exist. They are obtained from the standard spherical harmonics, with the phase convention as used in this work, by the transformation matrix given in Table 1.

As for Cartesian tensors the integrals over equivalent orbitals entering Eq. (12) will have to be expressed in terms of *ab initio* integrals, similarly to Eq. (16). Alternatively, they might be directly calculated from equivalent orbitals represented by individual Gaussian functions. For *d* orbitals an optimized set has been suggested [8] with each orbital represented by three Gaussians. The use of such

Table 1. Transformation matrix

$$U=\sqrt{\tfrac{1}{5}}\begin{pmatrix} 1 & 1 & \pm 1 & -1 & 1 \\ (-\cos\delta+i\sin\delta) & (\cos 2\delta+i\sin 2\delta) & \pm 1 & (-\cos 2\delta+i\sin 2\delta) & (-\cos\delta-i\sin\delta) \\ (\cos 2\delta-i\sin 2\delta) & (-\cos\delta+i\sin\delta) & \pm 1 & (\cos\delta+i\sin\delta) & (\cos 2\delta+i\sin 2\delta) \\ (\cos 2\delta+i\sin 2\delta) & (-\cos\delta-i\sin\delta) & \pm 1 & (\cos\delta-i\sin\delta) & (\cos 2\delta-i\sin 2\delta) \\ (-\cos\delta-i\sin\delta) & (\cos 2\delta-i\sin 2\delta) & \pm 1 & (-\cos 2\delta-i\sin 2\delta) & (-\cos\delta+i\sin\delta) \end{pmatrix}$$

Where there are two signs the $+$ sign holds for the steep and the $-$ sign for the shallow set. δ is equal to $\pi/5$. The row index n, Eq. (11a), is $-l$ for the top row and $+l$ for the bottom row functions in CDP calculations obviously leads to considerable computational savings.

4. Space Averages and ω Parameters

The contracted density product equations (18) in Ref. [1] are invariant against orthogonal transformations. In order to be meaningful the ω parameters entering the CDP calculations must be invariant against rotations of the coordinate system, i.e. the operations of $O^+(3)$. The rotational averages as discussed in Sects. 2 and 3 fulfill this requirement. In addition it is desirable that the ω parameters be independent of the handedness of the coordinate system in which the calculations are performed. This requires invariance against the operations of O(3). We have defined the space averages in CDP calculations in such a way, as follows from Sect. II.D. and III.A., Ref. [1]. They are therefore obtained as the arithmetic mean of the rotational averages calculated in a left-handed and a right-handed coordinate system.

For d and higher orbitals the ω parameters are not yet uniquely defined by considering them to represent such space averages, even for a given functional form of the basis functions. This is apparent at once if one considers e.g. the space average $\overline{(\mu\mu|\nu\nu)}$ for d orbitals in Cartesian form. Four nonequivalent combinations of basis functions exist in this case and they all lead to different numerical values. This is illustrated by an example in Table 2. The CDP calculations can be carried out correctly by using four values for ω^1, ω^2, and ω^3 each because the condition $\omega^2 = (\omega^0 - \omega^1)/2$ [1] is fulfilled for each of the four sets of space averages. The computations become complicated, however, by the need to distinguish the different products of MO coefficients according to the particular values of ω^1, ω^2, and ω^3 by which they are to be multiplied.

If the calculations are done with equivalent d orbitals the number of nonequivalent combinations of basis functions in CDP type integrals is reduced to two. The two combinations correspond to the situation where two different d

Table 2. Numerical values (10^{-6} a.u.) of the space averages occurring in the ω parameters of a four centre integral for $3d$ orbitals in Cartesian form

		$\overline{(\mu\mu\|\mu\mu)}$	$\overline{(\mu\mu\|\nu\nu)}$	$\frac{1}{2}[\overline{(\mu\nu\|\mu\nu)} + (\mu\nu\|\nu\mu)]$	$\frac{1}{2}[\overline{(\mu\nu\|\mu\nu)} - (\mu\nu\|\nu\mu)]$
$\mu = H^2_{\sigma}$,	$\nu = \{H^2_{1c}, H^2_{1s}\}$	86.37	324.78	−119.21	0.32
$\mu = H^2_{\sigma}$,	$\nu = \{H^2_{2c}, H^2_{2s}\}$	86.37	251.75	−82.69	69.24
$\mu = H^2_{1c}$,	$\nu = H^2_{1s}$	86.37	276.10	−94.87	46.27
$\mu = \{H^2_{1c}, H^2_{1s}\}$	$\nu = \{H^2_{2c}, H^2_{2s}\}$	86.37	276.10	−94.87	46.27
$\mu = H^2_{2c}$,	$\nu = H^2_{2s}$	86.37	349.12	−131.38	−22.66

The four atoms were arbitrarily chosen to be Fe, Ti, V and Cr located at (a.u.) (0, 0, 0), (2, −2, 1), (2, 3, 1.5) and (−1, 1.2, 3) respectively. The exponents and contraction coefficients of the Gaussian basis set were taken from Wachters, A. J. H.: J. Chem. Phys. **52**, 1033 (1970)

Table 3. Numerical values (10^{-6} a.u.) of the space averages occurring in the ω parameters for $3d$ orbitals in equivalent form

		$\overline{(\mu\mu\|\mu\mu)}$	$\overline{(\mu\mu\|\nu\nu)}$	$\frac{1}{2}[\overline{(\mu\nu\|\mu\nu)}+\overline{(\mu\nu\|\nu\mu)}]$	$\frac{1}{2}[\overline{(\mu\nu\|\mu\nu)}-\overline{(\mu\nu\|\nu\mu)}]$
$^{a}\mu = V_{0/5}$,	$\nu = V_{1/5}$	86.37	312.87	−113.25	11.57
$\mu = V_{0/5}$,	$\nu = V_{2/5}$	86.37	263.67	−88.65	58.00
$^{b}\mu = V_{0/5}$,	$\nu = V_{1/5}$	86.37	270.20	−91.92	51.84
$\mu = V_{0/5}$,	$\nu = V_{2/5}$	86.37	306.33	−109.98	17.73

[a] For the steep set

[b] For the shallow set

The atoms, geometry, and the exponents and contraction coefficients of the Gaussian basis set in Cartesian form are the same as in Table 2

orbitals are directed along neighbouring and non-neighbouring edges of a pentagonal bipyramide, respectively. This is illustrated by the numerical results collected in Table 3 for the two sets of equivalent orbitals. Again, as for the Cartesian set, one finds for the most general situation of a four centre integral, to which the figures of Tables 2 and 3 correspond, that the condition $\omega^2 = (\omega^0 - \omega^1)/2$ holds in all cases, and that moreover ω^0 assumes the same value for all three basis sets.

The distinction between different combinations of functions of the same set of irreducible tensors can be altogether eliminated by taking the *arithmetic mean* of the space averages for all combinations of orbitals occurring in CDP type integrals. One then has

$$\omega^0 = \frac{1}{g} \sum_{\mu=1}^{g} \overline{(\mu\mu|\mu\mu)} \tag{18a}$$

$$\omega^1 = \frac{1}{g(g-1)} \sum_{\mu\neq\nu}^{g} \overline{(\mu\mu|\nu\nu)} \tag{18b}$$

$$\omega^2 = \frac{1}{2g(g-1)} \sum_{\mu\neq\nu}^{g} \left[\overline{(\mu\nu|\mu\nu)} + \overline{(\mu\nu|\nu\mu)}\right] \tag{18c}$$

$$\omega^3 = \frac{1}{2g(g-1)} \sum_{\mu\neq\nu}^{g} \left[\overline{(\mu\nu|\mu\nu)} - \overline{(\mu\nu|\nu\mu)}\right]. \tag{18d}$$

With this definition the ω parameters assume identical values for Cartesian and equivalent d orbitals as follows from Tables 2 and 3. This property is general for d orbitals in real form [9].

5. Conclusions

The rotational averages of products of spherical tensors can be expressed as sums of products of Wigner 3-j symbols. This allows the calculation of the space averages of arbitrary two electron integrals in molecular orbital calculations, and thus of the ω parameters of the fully or partly contracted schemes which are possible within the frame of the contracted density product idea. Explicit numerical results for the most general case of a four center two electron integral show that the condition $\omega^2 = (\omega^0 - \omega^1)/2$, crucial for the validity of the CDP equations, is fulfilled for d orbitals in real Cartesian form, or in the form of equivalent orbitals, if the ω's are considered to represent space averages. The conception of space averages leads to difficulties for CDP calculations with f and higher orbitals, or with basis functions in complex form, as will be shown in a subsequent publication [9]. In such cases a reinterpretation of the ω's in terms of invariants is required. The use of equivalent orbitals, rarely considered up to now in quantum chemical calculations, reduces the number of possible combinations of different basis functions in CDP type integrals.

If two electron integrals are evaluated directly for such basis functions, as has been suggested [8], the computational work for forming the space averages is considerably reduced. Conceptually more important, though, is the fact that equivalent orbitals can be considered to be the "natural" basis functions in CDP type calculations where the majority of the differences between local electron-electron interaction terms is systematically swamped out.

Acknowledgment. The authors express their gratitude to Mr. F. Benett for his help in adapting an IBMOL VI program to the calculation of the *ab initio* integrals required for their ω parameters.

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Received January 25, 1982