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Evaluation of Fourier Transform of Two-Center Charge Distribution for Arbitrary Slater-Type Orbitals

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Fourier transform of two-center charge distributions corresponding to arbitrary Slater-type orbitals are evaluated by a Gaussian quadrature procedure without any preliminary series expansion of the integrand. Convergence and accuracy of the method are discussed and illustrated.

Key words: Two-center Slater-type orbital product, Fourier transform of ~

1. Introduction

Matrix elements of the form $\langle\chi_\alpha|\exp(i\boldsymbol{q}\cdot\boldsymbol{r})|\chi_\beta\rangle$ involving a set of given basis functions $\{\chi\}$ are important ingredients for quantum-mechanical calculations of dynamical effects of atoms and molecules.

Elastic and inelastic cross sections for collisions of fast electrons with molecular targets [1] and form factors for coherent X-ray diffraction from atoms or molecules [2–4] are only two examples where the above cited matrix elements play a role.

In addition to this clear reason of importance, which stems directly from the inspection of the analytic expressions for the relevant cross sections, we point out that the availability of the matrix $\langle\boldsymbol{\chi}|\exp(i\boldsymbol{q}\cdot\boldsymbol{r})|\boldsymbol{\chi}\rangle$ may offer a way for generalizing to high orders our knowledge of the first multipole moments associated with an arbitrary molecular charge distribution. In fact, if we take into account that any moment of the charge distribution can be generated starting from the identity

$$[\underbrace{(\nabla_q \cdots \nabla_q)}_{n\text{-times}} \exp(i\boldsymbol{q}\cdot\boldsymbol{r})]_{q=0} = (i)^n \underbrace{(\boldsymbol{r}\cdots\boldsymbol{r})}_{n\text{-times}}, \tag{1}$$

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and some efficient interpolation scheme can be devised so as to provide the explicit q-dependence of the matrix $\langle\chi|\exp(i\boldsymbol{q}\cdot\boldsymbol{r})|\chi\rangle$, then from Eq. (1) we derive the desired multipole moment.

Standard choices for the basis $\{\chi\}$ consist of Gaussian- or Slater-type orbitals, centered at the various nuclei of the molecule of interest. In both cases, approaches have been suggested for the evaluation of the matrix element $\langle\chi_\alpha|\exp(i\boldsymbol{q}\cdot\boldsymbol{r})|\chi_\beta\rangle$, usually referred to as Fourier transform of the distribution $\chi_\alpha^*\chi_\beta$ [5]. By this short paper we propose to extend the list of contributions already available for the case where $\{\chi\}$ is a set of Slater-type orbitals, surely the more complicated one. Our procedure follows very closely that put forward by Bonham *et al.* [6, 7] for the simplest two-center distribution, i.e. $1s_A1s_B$, the Fourier transform of any other distribution being then generated from the simplest one by differentiation with respect to proper parameters. Even if the emphasis of the present paper is on the computational convenience of such an approach with respect to others possible, we shall briefly dwell on the formal part (Sect. 2), devoting the last section to a presentation and discussion of typical results.

2. Mathematical Apparatus

Let us consider the general expression for Fourier transform of a product of Slater-type orbitals (STO's),

$$I_{\alpha\beta}(\boldsymbol{q}) = \int \chi_\alpha^*(\boldsymbol{r}_A)\exp(i\boldsymbol{q}\cdot\boldsymbol{r})\chi_\beta(\boldsymbol{r}_B)\,d\tau, \tag{2}$$

where $\chi_\alpha(\boldsymbol{r}_A)$ and $\chi_\beta(\boldsymbol{r}_B)$ are STO's centered at A and B respectively and the $\boldsymbol{r}$ vector appearing in $\exp(i\boldsymbol{q}\cdot\boldsymbol{r})$ is referred to an arbitrary origin 0. Since $\exp(i\boldsymbol{q}\cdot\boldsymbol{r})$ can trivially be translated from the point 0 to the center A or B, we shall limit our attention to the following integrals,

$$I_{\alpha\beta}(\boldsymbol{q}) = \int \chi_\alpha^*(\boldsymbol{r}_A)\exp(i\boldsymbol{q}\cdot\boldsymbol{r}_A)\chi_\beta(\boldsymbol{r}_B)\,d\tau. \tag{3}$$

Considering, for the moment, s-type STO's only, and making use of the integral representation [6]

$$r_B^{n'-1}\exp(-\zeta' r_B) = (1/2\pi^2)(-\partial/\partial\zeta')^{n'}\int d\boldsymbol{k}\exp(i\boldsymbol{k}\cdot\boldsymbol{r}_B)/(k^2+\zeta'^2). \tag{4}$$

Equation (3) can be cast into the form

$$\begin{aligned} I_{ns_A,n's_B}(\boldsymbol{q}) = {} & [(2\zeta)^{2n+1}(2\zeta')^{2n'+1}/(2n)!\,(2n')!]^{1/2}(1/4\pi)(1/2\pi^2) \\ & \cdot(-\partial/\partial\zeta')^{n'}\int r_A^{n-1}\exp(-\zeta r_A + i\boldsymbol{q}\cdot\boldsymbol{r}_A)\,d\boldsymbol{r}_A \\ & \times\int d\boldsymbol{k}\exp(i\boldsymbol{k}\cdot\boldsymbol{r}_B)/(k^2+\zeta'^2). \end{aligned} \tag{5}$$

After translation of the factor $\exp(i\boldsymbol{k}\cdot\boldsymbol{r}_B)$ from the center B to A, the integral in Eq. (5) can be rewritten as

$$\int d\boldsymbol{k} \exp(-i\boldsymbol{k}\cdot\boldsymbol{R})/(k^2 + \zeta'^2) \int d\boldsymbol{r}_A r_A^{n-1} \exp[-\zeta r_A + i(\boldsymbol{q} + \boldsymbol{k})\cdot\boldsymbol{r}_A] \qquad (\boldsymbol{R} = \boldsymbol{r}_A - \boldsymbol{r}_B).$$

The integration in $\boldsymbol{r}_A$ can readily be carried out:

$$\int d\boldsymbol{r}_A r_A^{n-1} \exp[-\zeta r_A + i(\boldsymbol{q} + \boldsymbol{k})\cdot\boldsymbol{r}_A] = 4\pi(-\partial/\partial\zeta)^n[1/(\zeta^2 + |\boldsymbol{q} + \boldsymbol{k}|^2)];$$

moreover, from the Feynman identity $(ab)^{-1} = \int_0^1 d\alpha[a + (b - a)\alpha]^{-2}$ and the substitution $\boldsymbol{k} = \boldsymbol{p} - \alpha\boldsymbol{q}$, we may transform the expression in Eq. (5) as follows:

$$I_{ns_A,n's_B}(\boldsymbol{q}) = [(2\zeta)^{2n+1}(2\zeta')^{2n'+1}/(2n)!\,(2n')!]^{1/2}(1/2\pi^2)(-1)^{n+n'} \cdot(\partial^{n+n'}/\partial\zeta^n\partial\zeta'^{n'}) \int_0^1 d\alpha \exp(i\alpha\boldsymbol{q}\cdot\boldsymbol{R}) \int d\boldsymbol{p} \exp(-i\boldsymbol{p}\cdot\boldsymbol{r})/[p^2 + M(\alpha)]^2 \tag{6}$$

where $M(\alpha) = \zeta'^2 + (\zeta^2 - \zeta'^2)\alpha + q^2\alpha(1 - \alpha)$.

In Eq. (6) the $\boldsymbol{p}$-integration can be performed which leads to the final result

$$I_{ns_A,n's_B}(\boldsymbol{p}) = (1/2)[(2\zeta)^{2n+1}(2\zeta')^{2n'+1}/(2n)!\,(2n')!]^{1/2}(-1)^{n+n'}\cdot(\partial^{n+n'}/\partial\zeta^n\partial\zeta'^{n'}) \times \int_0^1 d\alpha \exp(i\alpha\boldsymbol{q}\cdot\boldsymbol{R} - R[M(\alpha)]^{1/2})/[M(\alpha)]^{1/2}. \tag{7}$$

All integrals involving s-type STO's can therefore be obtained by carrying out in Eq. (7) the appropriate number of differentiations with respect to ζ or ζ'. Explicit formulae are easily obtainable for each case, even though at the expense of somewhat long and tedious work.

Passing to the case of orbitals associated with higher spherical harmonics, the relevant formulae can be derived from Eq. (7) by differentiation with respect to appropriate parameters, as we shall see in a moment.

If a local coordinate framework is assumed, whose z-axis lies along the $\boldsymbol{R}$ vector, all integrals involving STO's with $l = 1, 2, \ldots$ are obtained in a fairly simple way. For instance, an integral containing a np_x orbital centered at A becomes

$$\begin{aligned} I_{np_{xA}ns'_B}(\boldsymbol{q}) &= [3(2\zeta)^{2n+1}(2\zeta')^{2n'+1}/(2n)!\,(2n')!]^{1/2}(1/4\pi) \\ &\quad\cdot\int r_A^{n-2} r_B^{n'-1} x_A \exp(-\zeta r_A + i\boldsymbol{q}\cdot\boldsymbol{r}_A - \zeta' r_B)\, d\tau \\ &= [3(2\zeta)^{2n+1}(2\zeta')^{2n'+1}/(2n)!\,(2n')!]^{1/2}(1/4\pi)(1/i) \\ &\quad\cdot(\partial/\partial q_x)\int r_A^{n-2} r_B^{n'-1} \exp(-\zeta r_A + i\boldsymbol{q}\cdot\boldsymbol{r}_A - \zeta' r_B)\, d\tau \\ &= -2\zeta i[3/2n(2n-1)]^{1/2}(\partial/\partial q_x)\int \chi_{(n-1)s}(r_A) \exp(i\boldsymbol{q}\cdot\boldsymbol{r}_A)\chi_{n's}(r_B)\, d\tau, \end{aligned}$$

which involves a simple differentiation with respect to the component q_x. If the orbital with $l = 1, 2, \ldots$ is centered at B, it is sufficient to consider that, in the chosen local reference system, $x_B = x_A$, $y_B = y_A$, $z_B = z_A - R$ for obtaining formulae for any type of integrals. It should not be surprising that the expressions for integrals involving STO's associated with higher principal and azimuthal quantum numbers become rapidly complicated; for instance, the matrix element $\langle 2p_{z_A}|\exp(i\boldsymbol{q}\cdot\boldsymbol{r}_A)|3d_{z_{B2}}\rangle$ involves eight contributions:

$$\begin{aligned}\langle 2p_{z_A}|\exp(i\boldsymbol{q}\cdot\boldsymbol{r}_A)|3d_{z_{B2}}\rangle = & -(4i/3\sqrt{2})(\zeta_A^7\zeta_B^9)^{1/2} \\ & \times\Big\{-2q_z\int_0^1 d\alpha(1-\alpha)^3\alpha^3F_3(\alpha) \\ & +(iR/2)(q_x^2+q_y^2-2q_z^2)\int_0^1 d\alpha(1-\alpha)^3\alpha^4F_3(\alpha) \\ & -(q_z/2)(q_x^2+q_y^2-2q_z^2)\int_0^1 d\alpha(1-\alpha)^4\alpha^4F_4(\alpha) \\ & +iR^3\int_0^1 d\alpha(1-\alpha)^3\alpha^2F_1(\alpha)-R^2q_z \\ & \times\int_0^1 d\alpha(1-\alpha)^4\alpha^2F_2(\alpha)-2iR \\ & \times\int_0^1 d\alpha(1-\alpha)^3\alpha^2F_2(\alpha)+2R^2q_z \\ & \times\int_0^1 d\alpha(1-\alpha)^3\alpha^3F_2(\alpha)+2iRq_z^2 \\ & \times\int_0^1 d\alpha(1-\alpha)^4\alpha^3F_3(\alpha)\Big\}\end{aligned}$$

where we have put

$$\begin{aligned}F_n(\alpha) = & (2/\pi)\exp(i\alpha\boldsymbol{q}\cdot\boldsymbol{R})R^{2n+3}/[R\sqrt{M(\alpha)}]^{n+1} \\ & \times\{[(\pi/2)/(R\sqrt{M(\alpha)})]^{1/2}\cdot K_{(n+1)+1/2}[R\sqrt{M(\alpha)}]\},\end{aligned}$$

$[(\pi/2)/(R\sqrt{M(\alpha)})]^{1/2}K_{(n+1)+1/2}[R\sqrt{M(\alpha)}]$ being a modified spherical Bessel function of the third kind [8].

Integrals with increasing values of n and l involve higher and higher numbers of contributions: for instance, integrals of the form $\langle 5d_{z^2}|\exp(i\boldsymbol{q}\cdot\boldsymbol{r})|5d_{z^2}\rangle$ require 56 contributions. In any case, the integrals to be evaluated by numerical quadrature are of the following general form:

$$\mathscr{T}_k^{mn} = \int_0^1 d\alpha(1-\alpha)^m\alpha^nF_k(\alpha). \tag{8}$$

3. Results

The problem we are faced with is the evaluation of the integral appearing in Eq. (8). Unfortunately we are unable to calculate it in a closed analytic form even for the simplest case $I_{1s_A1s_B}$, and recourse to numerical quadrature is needed (eventually

preceded by suitable manipulations of the integrand [5] in order to make it as smooth as possible). As far as we are concerned, we have found convenient a straightforward quadrature based on the form of Eq. (8), by simply choosing a proper subdivision of the integration range in sub-intervals along with an optimal integration point grid. Thus, if within the sub-interval (a_j, b_j) we put $\alpha_j(t) = (a_j + b_j)/2 + (b_j - a_j)t/2$, then Eq. (8) becomes

$$\mathscr{T}_k^{mn} = \sum_j (b_j - a_j)/2 \int_{-1}^{1} dt(1 - \alpha_j(t))^m \alpha_j^n(t) F_k(\alpha_j(t))$$

$$= \tfrac{1}{2} \sum_j \Delta_j \sum_s (1 - \alpha_j(t_s))^m \alpha_j(t_s)^n F_k(\alpha_j(t_s)) H_s, \tag{9}$$

where $\Delta_j = b_j - a_j$ and $\{H_s\}$ is the required set of Gauss quadrature weights [9].

A preliminary manipulation of the integrand along the lines suggested in Ref. [5] so as to get rid of troubles arising from its oscillatory nature in our experience did not prove to be practically convenient for STO's of arbitrary principal quantum numbers. In fact, an annoying feature of our attempts founded on the Lommel series expansion of the integrand [5] was that a considerably increasing number of terms had to be introduced in order to obtain a satisfying convergence.

On the other hand, the procedure based on the direct numerical quadrature, Eq. (9), requires that both the number of sub-intervals and integration grid are prefixed so as to come in any case to a reasonable compromise between accuracy and economy, a goal attained only on empirical grounds.

Table 1. Matrix elements of the type $\langle 1s_A | \exp(i\boldsymbol{q}\cdot\boldsymbol{r}_A) | 1s'_B \rangle$ evaluated either by direct quadrature or by Monkhorst *et al.* procedure: a comparison ($\theta = \cos^{-1}[\boldsymbol{q}\cdot\boldsymbol{R}/|\boldsymbol{q}|R]$)

$\zeta_A = 1.2$, $\zeta_B = 5.7$, $R = 2.0$ a.u.

		Our procedure		Ref. [5]	
		Re (I)	Im (I)	Re (I)	Im (I)
$\lvert q\rvert = 4.0$	$\theta = 0.0$	0.285215(−1)	−0.114950(−1)	0.28521(−1)	−0.11495(−1)
$\lvert q\rvert = 5.0$	$\theta = \pi/4$	0.200005(−1)	0.106220(−1)	0.20001(−1)	0.10622(−1)
$\lvert q\rvert = 6.0$	$\theta = \pi/4$	−0.513332(−2)	0.150802(−1)	−0.51335(−2)	0.15080(−1)
$\lvert q\rvert = 7.0$	$\theta = \pi/4$	−0.110622(−1)	−0.197652(−2)	−0.11062(−1)	−0.19764(−2)
$\lvert q\rvert = 8.0$	$\theta = \pi/4$	0.244479(−3)	−0.800233(−2)	0.24453(−3)	−0.80026(−2)
$\lvert q\rvert = 9.0$	$\theta = \pi/4$	0.574536(−2)	−0.653660(−3)	0.57454(−2)	−0.65364(−3)
$\lvert q\rvert = 10.0$	$\theta = \pi/4$	0.107503(−2)	0.410165(−2)	0.10750(−2)	0.41016(−2)

$R = 1.5$ a.u., $\theta = 0.0$, $|q| = 4.0$ a.u.

		Our procedure		Ref. [5]	
		Re (I)	Im (I)	Re (I)	Im (I)
$\zeta_A = 1.2$	$\zeta_B = 1.2$	0.627941(−2)	−0.895108(−3)	0.627861(−2)	−0.894995(−3)
$\zeta_A = 1.2$	$\zeta_B = 0.5$	0.543222(−2)	−0.341204(−2)	0.542674(−2)	−0.347684(−2)
$\zeta_A = 1.2$	$\zeta_B = 2.0$	0.124710(−1)	0.124633(−1)	0.124689(−1)	0.124620(−1)
$\zeta_A = 0.5$	$\zeta_B = 0.5$	0.137431(−2)	−0.195903(−3)	0.137279(−2)	−0.195687(−3)
$\zeta_A = 0.5$	$\zeta_B = 2.0$	0.142290(−1)	−0.104122(−1)	0.142124(−1)	−0.103950(−1)
$\zeta_A = 2.0$	$\zeta_B = 2.0$	0.721025(−4)	0.102780(−4)	0.720884(−4)	0.102760(−4)

Table 2. Convergence tests for several integrals $\langle n_A l_A m_A; \zeta_A | \exp(i\boldsymbol{q}\cdot\boldsymbol{r}_A) | n_B l_B m_B; \zeta_B \rangle$ as either integration point number N or subinterval width Δ (or both) change (see text) ($R = 1.4$ a.u.)

n_A	l_A	m_A	ζ_A	n_B	l_B	m_B	ζ_B	N	Δ_1	N'	Δ_1'	Re (I)	Im (I)	Re (I)	Im (I)
												$\lvert\boldsymbol{q}\rvert = 2$ a.u. $\theta = 0.0$		$\lvert\boldsymbol{q}\rvert = 6$ a.u. $\theta = 0.0$	
1	0	0	10.0	1	0	0	10.0	96	0.1			0.862789(−5)	0.500235(−4)	0.105056(−5)	0.186767(−5)
								128	0.05			0.862789(−5)	0.500235(−4)	0.105056(−5)	0.186767(−5)
1	0	0	10.0	5	1	0	0.2	140	0.0005			−0.225727(−5)	0.443823(−6)	−0.116627(−5)	0.569964(−6)
								260	0.0005			−0.225727(−5)	0.443823(−6)	−0.116627(−5)	0.569964(−6)
1	0	0	10.0	5	2	0	0.3	96	0.1	140	0.0005	0.224239(−4)	−0.143093(−5)	0.108162(−4)	0.239309(−5)
								128	0.05	140	0.0005	0.224120(−4)	−0.483253(−5)	0.119405(−4)	−0.564738(−5)
								224	0.05	320	0.0005	0.224120(−4)	−0.483253(−5)	0.119405(−4)	−0.564738(−5)
1	0	0	10.0	2	1	0	2.0	96	0.1			−0.108457(0)	−0.962138(−2)	−0.629720(−1)	−0.136319(−1)
								128	0.05			−0.108457(0)	−0.962138(−2)	−0.629720(−1)	−0.136319(−1)
4	0	0	0.5	4	1	0	0.4	96	0.1	140	0.0005	−0.960591(−4)	0.149829(−4)	−0.672764(−8)	0.301122(−7)
								128	0.05	140	0.0005	−0.960591(−4)	0.149829(−4)	−0.672251(−8)	0.299413(−7)
								224	0.05	320	0.0005			−0.672251(−8)	0.299413(−7)
2	1	0	2.0	2	1	0	2.0	96	0.1			−0.860047(−1)	−0.498645(0)	−0.222334(−2)	−0.395261(−2)
								128	0.05			−0.860047(−1)	−0.498645(0)	−0.222334(−2)	−0.395261(−2)
2	1	0	2.0	5	1	0	0.2	96	0.1	140	0.0005	0.548604(−4)	−0.193280(−4)	−0.476932(−6)	0.111200(−6)
								128	0.05	140	0.0005	0.548624(−4)	−0.193317(−4)	−0.476551(−6)	0.112739(−6)
								224	0.05	320	0.0005	0.548624(−4)	−0.193317(−4)	−0.476551(−6)	0.112739(−6)
2	1	0	2.0	5	2	0	0.3	96	0.1	140	0.0005	0.443512(−3)	−0.103903(−3)	0.482719(−5)	−0.496244(−6)
								128	0.05	140	0.0005	0.443292(−3)	−0.104010(−3)	0.447270(−5)	−0.116109(−5)
								224	0.05	224	0.0005	0.443292(−3)	−0.104010(−3)	0.447270(−5)	−0.116109(−5)
3	2	0	1.5	5	2	0	0.3	96	0.1	140	0.0005	0.634404(−3)	0.736062(−3)	0.106234(−5)	0.130092(−5)
								128	0.05	140	0.0005	0.634349(−3)	0.736136(−3)	0.104219(−5)	0.138943(−5)
								224	0.05	320	0.0005	0.634349(−3)	0.736136(−3)	0.104219(−5)	0.138943(−5)

Table 3. Reliability tests for the matrix elements $\langle n_A l_A m_A;\ \zeta_A | \exp(i\boldsymbol{q}\cdot\boldsymbol{r}_A) | n_B l_B m_B;\ \zeta_B \rangle$

n_A	l_A	m_A	ζ_A	n_B	l_B	m_B	ζ_B	Re (I)	Im (I)	Re (I)	Im (I)
								$\lvert q\rvert = 2.0,\ \theta = 0,\ R = 0.005$ a.u.		$\lvert q\rvert = 2.0,\ \theta = 0,\ R = 0.0$	
1	0	0	10.0	1	0	0	10.0	0.979870(0)	0.489939(−2)	0.980296(0)	0.0
2	0	0	3.0	2	0	0	3.0	0.583184(0)	0.291592(−2)	0.583200(0)	0.0
1	0	0	10.0	2	1	0	2.0	−0.333710(−2)	0.423724(−1)	0.0	0.423790(−1)
3	0	0	1.5	4	1	0	0.4	0.121954(−4)	−0.171097(−2)	0.0	−0.171100(−2)
2	1	0	2.0	2	1	0	2.0	−0.102416(0)	−0.512085(−3)	−0.102400(0)	0.0
1	0	0	10.0	3	2	0	1.5	−0.157299(−2)	−0.157962(−3)	−0.157916(−2)	0.0
2	1	0	2.0	5	2	0	0.3	0.106113(−5)	−0.226982(−3)	0.0	−0.226983(−3)
3	2	0	1.5	5	2	0	0.3	0.685938(−3)	0.189090(−5)	0.685938(−3)	0.0
								$\lvert q\rvert = 0.0001,\ \theta = 0,\ R = 1.4$ a.u.		$\lvert q\rvert = 0.0,\ \theta = 0,\ R = 1.4$ a.u.	
1	0	0	10.0	1	0	0	10.0	0.667995(−4)	0.467596(−8)	0.667995(−4)	0.0
5	0	0	0.1	5	0	0	0.1	0.999632(0)	0.699742(−4)	0.999637(0)	0.0
1	0	0	10.0	2	1	0	2.0	−0.117414(0)	−0.534511(−6)	−0.117414(0)	0.0
4	0	0	0.5	4	1	0	0.4	−0.123035(0)	0.530858(−3)	−0.123035(0)	0.0
2	1	0	2.0	2	1	0	2.0	−0.100740(0)	−0.705183(−5)	−0.100740(0)	0.0
2	1	0	2.0	5	2	0	0.3	−0.233230(−2)	0.479325(−6)	−0.233230(−2)	0.0
3	2	0	1.5	5	2	0	0.3	0.122836(−1)	−0.248674(−5)	0.122836(−1)	0.0

In Table 1 we report some typical values for integrals of the type $\int d\boldsymbol{r} 1s_A(r_A) \exp(i\boldsymbol{q}\cdot\boldsymbol{r}_A) 1s'_B(r_B)$, corresponding to a given pair of orbital exponents ζ and different $\boldsymbol{q}$'s (first part of the table) or a fixed $\boldsymbol{q}$ and different pairs of ζ values. The real part Re (I) and the imaginary part Im (I) of the various integrals evaluated by our procedure are compared with those obtained by the Monkhorst *et al.* procedure [5]: in particular, the entries listed under the heading "Ref. [5]" in the first part of the table are easily deduced starting from Table 1 of Ref. [5]. The remarkable agreement between the two approaches needs no comment; as an element of critical assessment, however, we emphasize that in our experience the computational time is definitely favourable to the direct numerical quadrature procedure, with respect to the Monkhorst *et al.* procedure, as proved by the average computational time per integral which passes from $\simeq 0.22$ sec to $\simeq 0.11$ sec (on IBM 370/158).

As pointed out in Ref. [5], in many cases (depending on the values of the orbital exponents ζ_A, ζ_B, internuclear separation R and $\boldsymbol{q}$ vector), the value of the integrals $\mathscr{T}_k^{mn}$, Eq. (9), is severely controlled by the contributions arising from the first and/or the last sub-interval. The convergence of the integration procedure has therefore been probed by varying in a suitable way either the width Δ of such sub-intervals or the number N of integration points there used. Since most matrix elements consist of several integrals $\mathscr{T}_k^{mn}$, and these converge for different values of N and/or Δ, it is convenient to use proper N and Δ values for each $\mathscr{T}_k^{mn}$ in order to minimize the computational time.

The matrix elements reported in Table 2 display some peculiar features arising from the chosen quantum numbers n, l, orbital exponent ζ and $|\boldsymbol{q}|$. (N, Δ_1) denotes respectively the overall integration point number and the width adopted for the first or last sub-interval, as long as a single choice is sufficient; (N', Δ'_1) has an entirely analogous meaning when more slowly convergent integrals $\mathscr{T}_k^{mn}$ occur. The inspection of Table 2 shows how a satisfying convergence is assured in most cases by a relatively acceptable point number.

In Table 3 we present matrix elements $I_{n_A l_A m_A; n_B l_B m_B}(\boldsymbol{q})$ corresponding to limit values of R and $|\boldsymbol{q}|$, so as they reduce to known or easily evaluated quantities. As $R \to 0$, the above matrix elements approach the corresponding one-center ones, which are easily expressed in simple analytical form. On the other hand, as $|\boldsymbol{q}| \to 0$, $\lim_{|\boldsymbol{q}|\to 0} \times I_{n_A l_A m_A; n_B l_B m_B}(\boldsymbol{q}) \to S_{n_A l_A m_A; n_B l_B m_B}$, the overlap integral between the same pair of STO's. The clearly conformal behaviour of the reported quantities is a further element of confidence in the numerical procedure suggested in this paper.

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