Molecular integrals over spherical Gaussian-type orbitals: I

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Received 24 September 1996

Abstract. A novel derivation, involving the Fourier transform and the addition theorem of harmonic polynomials, is presented for multi-centre molecular integrals over spherical Gaussian-type orbitals. Compact closed-form formulae, consisting of vector-coupling coefficients and well known functions only, are obtained for all multi-centre molecular integrals. The resulting formulae manifest the angular and geometric dependence in vector-coupling coefficients and spherical harmonic functions, respectively, and require *half* as many summations as those for their counterparts, Cartesian Gaussian orbitals. An efficient computational method for molecular integrals over contracted Gaussian orbitals is suggested based on the present formulae for multi-centre molecular integrals.

1. Introduction

In *ab initio* calculations of molecular electronic structure Gaussian-type orbitals (GTOs), more specifically, Cartesian Gaussian-type orbitals (CGTOs) of the form

$$\phi_{nlm}(\alpha, \mathbf{r}) = N_{nlm}(\alpha) x^n y^l z^m \mathrm{e}^{-\alpha r^2} \tag{1}$$

have been employed due to the ease of evaluation of multi-centre molecular integrals (Boys 1950). According to the Boys' algorithm (1950), the molecular integrals over s-type (n+l+m=0) CGTOs are first evaluated and the integrals over CGTOs with higher angular momentum are then obtained by repeated differentiation of the s-type integrals. But this procedure rapidly becomes exceedingly complicated as the quantum numbers are increased. In addition, the resulting formulae are inefficient computationally, because they fail to share many common intermediates among integrals belonging to the same symmetry class. The closed-form formulae for the integrals over the general CGTOs have been worked out by Taketa et al (1966). However, these formulae are also inefficient computationally, since they contain a large number of summations and fail to take advantage of spherical symmetry properties. Since these earlier works, a lot of integral algorithms (for the most recent reviews, see Saunders (1983) and Gill (1994)) over CGTOs have appeared, which try to overcome these deficiencies. Most of these algorithms use recurrence relations (for instance, Obara and Saika (1986)) to express integrals of high angular momentum orbitals in terms of integrals, involving lower angular momentum orbitals. Since recurrence formulae require the evaluation of unwanted integrals over low angular momentum orbitals, they do not always guarantee efficient algorithms, especially for relatively large angular momentum orbitals. Moreover, Cartesian Gaussian-type orbitals of high angular momentum $(n + l + m \ge 2)$ are not eigenfunctions of angular momentum; therefore, extra work is necessary in order to extract the spherical symmetry orbitals (Huzinaga 1985).

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In molecular calculations, one can also use spherical Gaussian-type orbitals (SGTOs) of the form

$$\phi_{nlm}(\alpha, \mathbf{r}) = N_{nl}(\alpha) f_n(r^2) \mathrm{e}^{-\alpha r^2} \mathcal{Y}_{lm}(\mathbf{r}) \qquad \mathcal{Y}_{lm}(\mathbf{r}) = r^l Y_{lm}(\hat{\mathbf{r}}) \tag{2}$$

where $N_{nl}(\alpha)$ is a normalization constant, $\mathcal{Y}_{lm}(\mathbf{r})$ is the solid harmonic and $Y_{lm}(\hat{\mathbf{r}})$ is the usual spherical harmonic with the phase convention of Condon and Shortly (1935). There are two obvious advantages of SGTOs. Firstly, spherical symmetry properties as well as the geometric dependence can be taken into account naturally. Secondly, the well developed vector-coupling coefficients can be applied fruitfully to derive compact formulae for all molecular integrals.

At first glance, multi-centre molecular integrals over SGTOs are more complicated to evaluate than their counterparts, CGTOs. The Gaussian orbitals with $f_n(r^2) = r^{2n}$ have been considered by Harris (1963) and Krauss (1964). The integrals over these orbitals were evaluated by repeatedly applying rotation operations until the integrals could eventually be evaluated analytically. But the resulting formulae are so intricate that the CGTOs have been preferred in molecular calculations. Applying the Talmi transformation (Talmi 1952) and the Moshinsky-Smirnov coefficients (Moshinsky 1959, Smirnov 1961) of nuclear shell theory, Fieck (1979, 1980) and Maretis (1979) were able to evaluate all the multi-centre molecular integrals over SGTOs. Specifically, Fieck (1980) considered the SGTOs with $f_n(r^2) = r^{2n}$ (1979) and $f_n(r^2) = L_n^{l+1/2}(\alpha r^2)$, while Maretis considered $f_n(r^2) = L_n^{l+1/2}(\alpha r^2)e^{\frac{1}{2}\alpha r^2}$. Here, $L_n^{\nu}(z)$ represents the associated Laguerre polynomial. Although these SGTOs are general, a special type of Gaussian orbital with $f_n(r^2) \equiv 1$ has been most widely used instead. It can be expected that the corresponding formulae of the integrals over this special type of SGTOs would be significantly simplified, but the simplification procedure of the general formulae obtained by Fieck and Maretis is not trivial due to the presence of the sophisticated Moshinsky-Smirnov coefficients.

Recently, Dunlap (1990) has evaluated the overlap and three-centre Coulomb integrals over these special SGTOs using the differentiation operator $\mathcal{Y}_{lm}(\nabla)$ and the addition theorem of solid harmonics. The resulting formulae involve the usual vector-coupling coefficients instead of the Moshinsky–Smirnov coefficients and are therefore much simpler than the corresponding formulae obtained by Fieck and Maretis. In this paper, we present a novel derivation for multi-centre molecular integrals over SGTOs using the Fourier transform and the addition theorem of harmonic polynomials. Molecular integrals over spherical Gaussian orbitals modified with plane-wave phase factors are presented in the following paper (Kuang and Lin 1997, hereafter referred to as paper II). Our present work is largely stimulated by a series of papers from Steinborn's group (Trivedi and Steinborn 1983, Grotendorst and Steinborn 1988, Homeier and Steinborn 1992). Here, we have taken advantage of their techniques, developed for the evaluation of molecular integrals over Slater-type orbitals, to compute the integrals over spherical Gaussian orbitals.

The rest of the paper is organized as follows. In the next section we will present the Fourier transform of Gaussian orbitals as well as the basic tools used in their derivation. In section 3 the conventional molecular integrals: overlap, kinetic energy, tensor operator, overlap with plane-wave phase factor, nuclear attraction, electron repulsion, electric field, electric field gradient, spin–orbit coupling and spin–spin interaction, are evaluated over the special SGTOs. In section 4 the computation of molecular integrals over the general SGTOs is briefly discussed. Finally, in section 5 numerical strategies for the efficient implementation of the present formulae are addressed, especially for molecular integrals over contracted Gaussian orbitals.

2. Fourier transform of Gaussian orbitals

We shall first consider the Fourier transform of Gaussian orbitals (2). In this paper we will use the symmetric version of the Fourier transformation, i.e.

$$\widetilde{f}(\boldsymbol{p}) = \frac{1}{(2\pi)^{3/2}} \int d\boldsymbol{r} \, \mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}} f(\boldsymbol{r})$$

$$f(\boldsymbol{r}) = \frac{1}{(2\pi)^{3/2}} \int d\boldsymbol{p} \, \mathrm{e}^{\mathrm{i}\boldsymbol{r}\cdot\boldsymbol{p}} \widetilde{f}(\boldsymbol{p}) \,.$$
(3)

Using the well known Rayleigh (partial-wave) expansion of a plane wave and the orthonormality of the spherical harmonic (Bransden and Joachain 1983, appendix 5), we have

$$\widetilde{\phi}_{nlm}(\alpha, \mathbf{p}) = \frac{1}{(2\pi)^{3/2}} \int d\mathbf{r} \, \mathrm{e}^{-\mathrm{i}\mathbf{p}\cdot\mathbf{r}} \phi_{nlm}(\alpha, \mathbf{r}) = \frac{4\pi \, N_{nl}(\alpha)}{(2\pi)^{3/2}} (-\mathrm{i})^l Y_{lm}(\hat{\mathbf{p}}) \int_0^\infty d\mathbf{r} \, r^{l+2} j_l(pr) f_n(r^2) \mathrm{e}^{-\alpha r^2} \,.$$
(4)

Clearly, the spherical (Gaussian-type) orbitals have the same angular dependences in both coordinate and momentum space, in contrast to the Cartesian–Gaussian (or Hermite–Gaussian) Fourier transformation pairs (Živković and Maksić 1968). To obtain an analytic and simple radial expression of the Fourier transform of an SGTO, the functional form of $f_n(r^2)$ is critical. From the tables of integrals (Gradshteyn and Ryzhik 1980, pp 718, 847), we find a pair of formulae

$$\int_{0}^{\infty} dx \, x^{2n+\nu+1} e^{-\alpha x^{2}} J_{\nu}(\beta x) = \frac{2^{n} n! \beta^{\nu}}{(2\alpha)^{n+\nu+1}} L_{n}^{\nu} \Big(\frac{\beta^{2}}{4\alpha}\Big) e^{-\beta^{2}/(4\alpha)}$$
(5*a*)

$$\int_{0}^{\infty} \mathrm{d}x \, x^{\nu+1} L_{n}^{\nu}(\alpha x^{2}) \mathrm{e}^{-\alpha x^{2}} J_{\nu}(\beta x) = \frac{\beta^{2n+\nu}}{2^{n} n! (2\alpha)^{n+\nu+1}} \mathrm{e}^{-\beta^{2}/(4\alpha)}$$
(5b)

where *n* is a natural number. The above two equations suggest that convenient choices of $f_n(r^2)$ are (i) $f_n(r^2) = r^{2n}$ and (ii) $f_n(r^2) = L_n^{l+1/2}(\alpha r^2)$. In either case the Fourier transform of an SGTO has simple analytic radial expression. For convenience in notation, we shall work with unnormalized orbitals $\Phi_{nlm}(\alpha, r) = \phi_{nlm}(\alpha, r)/N_{nl}(\alpha)$, i.e.

$$\Phi^a_{nlm}(\alpha, \mathbf{r}) = \mathrm{e}^{-\alpha r^2} r^{2n} \mathcal{Y}_{lm}(\mathbf{r}) \tag{6}$$

$$\Phi^b_{nlm}(\alpha, \mathbf{r}) = \mathrm{e}^{-\alpha r^2} L_n^{l+1/2}(\alpha r^2) \mathcal{Y}_{lm}(\mathbf{r}) \,. \tag{7}$$

The Fourier transform of these unnormalized orbitals can be readily derived from equations (4), (5a) and (5b),

$$\widetilde{\Phi}^{a}_{nlm}(\alpha, p) = (-\mathrm{i})^{l} \mathcal{C}^{a}_{nl}(\alpha) \Phi^{b}_{nlm}\left(\frac{1}{4\alpha}, p\right)$$
(8)

$$\widetilde{\Phi}^{b}_{nlm}(\alpha, \boldsymbol{p}) = (-\mathbf{i})^{l} \mathcal{C}^{b}_{nl}(\alpha) \Phi^{a}_{nlm} \left(\frac{1}{4\alpha}, \boldsymbol{p}\right)$$
(9)

where $C_{nl}^a(\alpha) = 2^n n!/(2\alpha)^{n+l+3/2}$, and $C_{nl}^b(\alpha) = 1/[2^n n!(2\alpha)^{n+l+3/2}]$. As can be seen, the two forms of Gaussian orbitals are reciprocal with respect to each other.

It is of practical interest to consider the special case of n = 0, in which spherical Gaussian orbitals possess exactly the same form in both coordinate and momentum space, which can be seen by noticing that $L_0^{l+1/2}(z) \equiv 1$. These special SGTOs form an important class of Gaussian orbitals and are most widely used in quantum chemistry. We shall

first consider these special SGTOs, the representations of which in both coordinate and momentum space can be explicitly written as

$$\phi_{lm}(\alpha, \mathbf{r}) = N_l(\alpha) e^{-\alpha r^2} \mathcal{Y}_{lm}(\mathbf{r}) \qquad \widetilde{\phi}_{lm}(\alpha, \mathbf{p}) = (-i)^l \widetilde{N}_l(\alpha) e^{-p^2/(4\alpha)} \mathcal{Y}_{lm}(\mathbf{p}) \tag{10}$$

where

$$N_l(\alpha) = \left[\frac{2(2\alpha)^{l+3/2}}{\Gamma(l+3/2)}\right]^{1/2}$$

and

$$\widetilde{N}_l(\alpha) = \frac{N_l(\alpha)}{(2\alpha)^{l+3/2}} = N_l\left(\frac{1}{4\alpha}\right).$$

It is very useful to extend $\Phi_{nlm}^a(\alpha, \mathbf{r})$ for $n \ge 0$ to include n = -1, which will arise in the evaluation of nuclear attraction and electron repulsion integrals. By means of equation (4), its Fourier transform can be readily written as

$$\widetilde{\Phi}^{a}_{-1,lm}(\alpha, \boldsymbol{p}) = \frac{1}{(2\pi)^{3/2}} \int d\boldsymbol{r} \, \mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}} \Phi^{a}_{-1,lm}(\alpha, \boldsymbol{r}) = (-\mathrm{i})^{l} Y_{lm}(\hat{\boldsymbol{p}}) \frac{1}{p^{1/2}} \int_{0}^{\infty} d\boldsymbol{r} \, r^{l-1/2} \mathrm{e}^{-\alpha r^{2}} J_{l+1/2}(pr) \,.$$
(11)

Use is made of the following integral formula (Gradshteyn and Ryzhik 1980, p 717):

$$\int_0^\infty \mathrm{d}x \, x^{\nu-1} \mathrm{e}^{-\alpha x^2} J_\nu(\beta x) = \frac{2^{\nu-1}}{\beta^\nu} \gamma\left(\nu, \frac{\beta^2}{4\alpha}\right) = \left(\frac{\beta}{2\alpha}\right)^\nu \frac{1}{2z^\nu} \gamma(\nu, z) \tag{12}$$

where $z = \beta^2/4\alpha$ and $\gamma(\nu, z)$ is the incomplete gamma function (Gradshteyn and Ryzhik 1980, p 940), which, for $\nu = l + \frac{1}{2}$, is related to the well known function $F_l(z)$ (Shavitt 1963) defined by

$$F_l(z) = \int_0^1 u^{2l} e^{-zu^2} du = \frac{1}{2z^{l+1/2}} \gamma \left(l + \frac{1}{2}, z \right).$$
(13)

Combining the above three equations (11)–(13), we finally obtain

$$\widetilde{\Phi}^{a}_{-1,lm}(\alpha, \boldsymbol{p}) = (-\mathbf{i})^{l} \mathcal{C}^{a}_{-1,l}(\alpha) F_{l} \Big(\frac{p^{2}}{4\alpha}\Big) \mathcal{Y}_{lm}(\boldsymbol{p})$$
(14)

where we have defined $C_{-1,l}^{a}(\alpha) = 1/(2\alpha)^{l+1/2}$.

For subsequent reference, we shall state some basic properties regarding solid harmonics. The so-called addition theorem (Steinborn and Ruedenberg 1973) of solid harmonics reads

$$\mathcal{Y}_{lm}(\mathbf{r}_1 + \mathbf{r}_2) = 4\pi \sum_{l'=0}^{l} \sum_{m'=m'_{\min}}^{m'_{\max}} G(lm|l'm') \mathcal{Y}_{l'm'}(\mathbf{r}_1) \mathcal{Y}_{l-l',m-m'}(\mathbf{r}_2)$$
(15a)

$$G(lm|l'm') = \frac{(2l+1)!!}{(2l'+1)!![2(l-l')+1]!!} \langle lm|l'm'|l-l', m-m' \rangle$$

= $\left[\frac{2l+1}{4\pi(2l'+1)[2(l-l')+1]} \binom{l+m}{l'+m'} \binom{l-m}{l'-m'}\right]^{1/2}$ (15b)

where $m'_{\min} = \max(-l', m - l + l'), m'_{\max} = \min(l', m + l - l')$ and the second expression of G(lm|l'm') in (15b) was introduced by Homeier and Steinborn (1991). Here

 $\langle l_2 m_2 | LM | l_1 m_1 \rangle$ is the Gaunt coefficient defined as

$$\langle l_2 m_2 | LM | l_1 m_1 \rangle = \int d\hat{\mathbf{r}} Y_{l_2 m_2}^*(\hat{\mathbf{r}}) Y_{LM}(\hat{\mathbf{r}}) Y_{l_1 m_1}(\hat{\mathbf{r}})$$

$$= (-1)^{m_2} \sqrt{\frac{[l_2][L][l_1]}{4\pi}} \begin{pmatrix} l_2 & L & l_1 \\ -m_2 & M & m_1 \end{pmatrix} \begin{pmatrix} l_2 & L & l_1 \\ 0 & 0 & 0 \end{pmatrix}$$
(16)

where [l] = 2l + 1 and the quantities in large brackets are 3j symbols. The Gaunt coefficient is used to simplify the following product expansions of solid harmonics (Edmonds 1974, p 70):

$$\mathcal{Y}_{l_{1}m_{1}}^{*}(\boldsymbol{r})\mathcal{Y}_{l_{2}m_{2}}(\boldsymbol{r}) = \sum_{l} \langle l_{2}m_{2}|l_{1}m_{1}|lm\rangle r^{2n}\mathcal{Y}_{lm}(\boldsymbol{r})$$
(17*a*)

$$\mathcal{Y}_{l_1m_1}(\boldsymbol{r})\mathcal{Y}_{l_2m_2}(\boldsymbol{r}) = \sum_{l} \langle lm|l_1m_1|l_2m_2\rangle r^{2n}\mathcal{Y}_{lm}(\boldsymbol{r})$$
(17b)

where $n = (l_1 + l_2 - l)/2$ and the allowed l values are those satisfying $\Delta(l_1l_2l)$ and l_1+l_2+l = even integer due to the selection rule for the Gaunt coefficients and therefore the resulting n values are non-negative integers. It should be noted that the two equations (17*a*) and (17*b*) are equivalent except that $m = m_2 - m_1$ in (17*a*) and $m = m_2 + m_1$ in (17*b*).

3. Molecular integrals over the special SGTOs

3.1. Overlap integrals

The two-centre overlap integrals over Gaussian orbitals are defined as

$$S_{l_{a}m_{a}}^{l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B}) = \langle \phi_{l_{a}m_{a}}(\alpha,\boldsymbol{r}-\boldsymbol{A}) | \phi_{l_{b}m_{b}}(\beta,\boldsymbol{r}-\boldsymbol{B}) \rangle$$

$$= \int d\boldsymbol{q} \, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}} \widetilde{\phi}_{l_{a}m_{a}}^{*}(\alpha,\boldsymbol{q}) \widetilde{\phi}_{l_{b}m_{b}}(\beta,\boldsymbol{q})$$

$$= (-1)^{l_{b}} (2\pi)^{3/2} \widetilde{N}_{l_{a}}(\alpha) \widetilde{N}_{l_{b}}(\beta) I_{l_{a}m_{a}}^{l_{b}m_{b}}(\xi,\boldsymbol{R})$$

$$I_{l_{1}m_{1}}^{l_{2}m_{2}}(\xi,\boldsymbol{R}) = \frac{\mathrm{i}^{l_{1}+l_{2}}}{(2\pi)^{3/2}} \int d\boldsymbol{q} \, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}} \mathrm{e}^{-q^{2}/(4\xi)} \mathcal{Y}_{l_{1}m_{1}}^{*}(\boldsymbol{q}) \mathcal{Y}_{l_{2}m_{2}}(\boldsymbol{q})$$
(18)

where $\mathbf{R} = \mathbf{B} - \mathbf{A}, \xi = \alpha \beta / (\alpha + \beta)$, and we have used the Fourier transform formulae (3) and (10). The *I* integral can be readily evaluated in terms of the expansion (17*a*),

$$I_{l_{1}m_{1}}^{l_{2}m_{2}}(\xi, \mathbf{R}) = i^{l_{1}+l_{2}} \sum_{l} \langle l_{2}m_{2}|l_{1}m_{1}|lm\rangle \frac{1}{(2\pi)^{3/2}} \int d\mathbf{q} e^{-i\mathbf{q}\cdot\mathbf{R}} \Phi_{nlm}^{a} \left(\frac{1}{4\xi}, \mathbf{q}\right)$$
$$= \sum_{l} (-1)^{n} \langle l_{2}m_{2}|l_{1}m_{1}|lm\rangle \mathcal{C}_{nl}^{a} \left(\frac{1}{4\xi}\right) \Phi_{nlm}^{b}(\xi, \mathbf{R})$$
(19)

where we have used equations (4) and (8) as well as $n = (l_1 + l_2 - l)/2$. In contrast with previous work (Harris 1963, Fieck 1979, 1980), this is a remarkably compact formula for the overlap integral over SGTOs of the form (10). It only contains one sum and all the quantities in this equation can be evaluated efficiently. We could have chosen to evaluate the overlap integral in coordinate space; however, the resulting formula would not be as compact as equation (19). In the case of one-centre overlap integrals, i.e. A = B, thus R = 0, the above formula can be readily simplified as

$$I_{l_1m_1}^{l_2m_2}(\xi, \mathbf{0}) = (-1)^{l_2} \delta_{l_1l_2} \delta_{m_1m_2} \Gamma(l_2 + \frac{3}{2}) (4\xi)^{l_2 + 3/2} / [2(2\pi)^{3/2}]$$
(20)

by noting the following facts: $\mathcal{Y}_{lm}(\mathbf{0}) = \frac{1}{\sqrt{4\pi}} \delta_{l0} \delta_{m0}, \langle l_2 m_2 | l_1 m_1 | 00 \rangle = \frac{1}{\sqrt{4\pi}} \delta_{l_1 l_2} \delta_{m_1 m_2}$ and $L_n^{\nu}(\mathbf{0}) = {n+\nu \choose n} = \frac{\Gamma(n+\nu+1)}{n!\Gamma(\nu+1)}.$

3.2. Kinetic energy integrals

The two-centre kinetic energy integrals over Gaussian orbitals are defined as

$$\begin{aligned} K_{l_{a}m_{a}}^{l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B}) &= \langle \phi_{l_{a}m_{a}}(\alpha,\boldsymbol{r}-\boldsymbol{A})| - \frac{1}{2}\nabla_{\boldsymbol{r}}^{2}|\phi_{l_{b}m_{b}}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle \\ &= -\frac{1}{2}\nabla_{\boldsymbol{B}}^{2}\langle\phi_{l_{a}m_{a}}(\alpha,\boldsymbol{r}-\boldsymbol{A})|\phi_{l_{b}m_{b}}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle \\ &= -\frac{1}{2}\nabla_{\boldsymbol{B}}^{2}S_{l_{a}m_{a}}^{l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B}) \\ &= \frac{1}{2}(-1)^{l_{b}}(2\pi)^{3/2}\widetilde{N}_{l_{a}}(\alpha)\widetilde{N}_{l_{b}}(\beta)\mathcal{K}_{l_{a}m_{a}}^{l_{b}m_{b}}(\xi,\boldsymbol{R}) \end{aligned}$$
(21)

where R = B - A, $\xi = \alpha \beta / (\alpha + \beta)$, and we have used equation (18). The \mathcal{K} integral may be evaluated in the same way as I:

$$\mathcal{K}_{l_{1}m_{1}}^{l_{2}m_{2}}(\xi, \mathbf{R}) = -\nabla_{\mathbf{B}}^{2} I_{l_{1}m_{1}}^{l_{2}m_{2}}(\xi, \mathbf{R})$$

$$= \frac{i^{l_{1}+l_{2}}}{(2\pi)^{3/2}} (-\nabla_{\mathbf{B}}^{2}) \int d\mathbf{q} \, \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{R}} \mathrm{e}^{-q^{2}/(4\xi)} \mathcal{Y}_{l_{1}m_{1}}^{*}(\mathbf{q}) \mathcal{Y}_{l_{2}m_{2}}(\mathbf{q})$$

$$= \frac{i^{l_{1}+l_{2}}}{(2\pi)^{3/2}} \int d\mathbf{q} \, q^{2} \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{R}} \mathrm{e}^{-q^{2}/(4\xi)} \mathcal{Y}_{l_{1}m_{1}}^{*}(\mathbf{q}) \mathcal{Y}_{l_{2}m_{2}}(\mathbf{q})$$

$$= \sum_{l} (-1)^{n} \langle l_{2}m_{2} | l_{1}m_{1} | lm \rangle \mathcal{C}_{n+1,l}^{a} \left(\frac{1}{4\xi}\right) \Phi_{n+1,lm}^{b}(\xi, \mathbf{R})$$
(22)

where $n = (l_1 + l_2 - l)/2$ as before.

3.3. Tensor operator integrals

The two-centre integrals of tensor operators $\mathcal{Y}_{k\mu}(\nabla)$ over Gaussian orbitals arise in the study of electronic properties of molecules and are defined as

$$T_{l_{a}m_{a}}^{l_{b}m_{b}}(k\mu,\alpha,\beta,\boldsymbol{A},\boldsymbol{B}) = \langle \phi_{l_{a}m_{a}}(\alpha,\boldsymbol{r}-\boldsymbol{A}) | \mathcal{Y}_{k\mu}(\nabla_{\boldsymbol{r}}) | \phi_{l_{b}m_{b}}(\beta,\boldsymbol{r}-\boldsymbol{B}) \rangle$$

$$= \mathcal{Y}_{k\mu}(-\nabla_{\boldsymbol{B}}) \langle \phi_{l_{a}m_{a}}(\alpha,\boldsymbol{r}-\boldsymbol{A}) | \phi_{l_{b}m_{b}}(\beta,\boldsymbol{r}-\boldsymbol{B}) \rangle$$

$$= \mathcal{Y}_{k\mu}(-\nabla_{\boldsymbol{B}}) S_{l_{a}m_{a}}^{l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B})$$

$$= (-1)^{l_{b}} (2\pi)^{3/2} \widetilde{N}_{l_{a}}(\alpha) \widetilde{N}_{l_{b}}(\beta) \mathcal{T}_{l_{a}m_{a}}^{l_{b}m_{b}}(k\mu,\xi,\boldsymbol{R})$$
(23)

where $\mathbf{R} = \mathbf{B} - \mathbf{A}$, $\xi = \alpha \beta / (\alpha + \beta)$, and we have used equation (18). The \mathcal{T} integral may be evaluated in the same way as \mathcal{K} ,

$$\begin{aligned} \mathcal{T}_{l_{1}m_{1}}^{l_{2}m_{2}}(k\mu,\xi,\boldsymbol{R}) &= \mathcal{Y}_{k\mu}(-\nabla_{\boldsymbol{B}})I_{l_{1}m_{1}}^{l_{2}m_{2}}(\xi,\boldsymbol{R}) \\ &= \frac{\mathrm{i}^{l_{1}+l_{2}}}{(2\pi)^{3/2}}\mathcal{Y}_{k\mu}(-\nabla_{\boldsymbol{B}})\int\mathrm{d}\boldsymbol{q}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}}\mathrm{e}^{-q^{2}/(4\xi)}\mathcal{Y}_{l_{1}m_{1}}^{*}(\boldsymbol{q})\mathcal{Y}_{l_{2}m_{2}}(\boldsymbol{q}) \\ &= \frac{\mathrm{i}^{l_{1}+l_{2}+k}}{(2\pi)^{3/2}}\int\mathrm{d}\boldsymbol{q}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}}\mathrm{e}^{-q^{2}/(4\xi)}\mathcal{Y}_{k\mu}(\boldsymbol{q})\mathcal{Y}_{l_{1}m_{1}}^{*}(\boldsymbol{q})\mathcal{Y}_{l_{2}m_{2}}(\boldsymbol{q}) \\ &= \mathrm{i}^{L}\sum_{l=0}^{L}\langle l_{2}m_{2},k\mu|l_{1}m_{1},lm\rangle\frac{1}{(2\pi)^{3/2}}\int\mathrm{d}\boldsymbol{q}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}}\Phi_{nlm}^{a}\left(\frac{1}{4\xi},\boldsymbol{q}\right) \\ &= \sum_{l=0}^{L}(-1)^{n}\langle l_{2}m_{2},k\mu|l_{1}m_{1},lm\rangle\mathcal{C}_{nl}^{a}\left(\frac{1}{4\xi}\right)\Phi_{nlm}^{b}(\xi,\boldsymbol{R}) \end{aligned}$$
(24)

where $L = l_1 + l_2 + k$, $n = (l_1 + l_2 + k - l)/2$ is a non-negative integer and we have applied both equations (17*a*) and (17*b*) to expand the product of the three solid harmonics. Here $\langle l_2 m_2, k \mu | l_1 m_1, lm \rangle$ stands for the following quantity:

$$\langle l_{2}m_{2}, k\mu | l_{1}m_{1}, lm \rangle = \sum_{l'} \langle l_{2}m_{2} | l_{1}m_{1} | l'm' \rangle \langle lm | k\mu | l'm' \rangle$$

=
$$\int d\hat{p} Y_{l_{2}m_{2}}^{*}(\hat{p}) Y_{k\mu}^{*}(\hat{p}) Y_{l_{1}m_{1}}(\hat{p}) Y_{lm}(\hat{p})$$
(25)

where we have used the fact that the Gaunt coefficient is real and Y_{lm} forms a complete set. It should be noted that $\langle l_2m_2, k\mu | l_1m_1, lm \rangle$ must satisfy the following conditions: $\Delta(l_2l_1l'), \Delta(kl'l), l_2+l_1+l' =$ even integer, k+l'+l = even integer and $m_2+\mu = m_1+m$ due to the selection rules of the Gaunt coefficients. Therefore, the allowed *l* values in equation (24) are those satisfying $l_1 + l_2 + k + l =$ even integer.

3.4. Overlap integrals with PWETF

The two-centre overlap integrals with plane-wave electronic translational factors (PWETF) arise in the close-coupling treatment of ion-atom collisions. Here, they also serve as the basic building blocks for three-centre nuclear attraction and four-centre electron repulsion integrals. This integral can also be viewed as the Fourier transform of a two-centre product of orbitals and is defined as

$$S_{l_{a}m_{a}}^{l_{b}m_{b}}(\alpha,\beta,A,B,p) = \langle \phi_{l_{a}m_{a}}(\alpha,r-A) | e^{-ip \cdot r} | \phi_{l_{b}m_{b}}(\beta,r-B) \rangle$$
$$= \int dr \, e^{-ip \cdot r} \phi_{l_{a}m_{a}}^{*}(\alpha,r-A) \phi_{l_{b}m_{b}}(\beta,r-B)$$
$$= e^{-ip \cdot B} \int dq \, e^{-iq \cdot R} \widetilde{\phi}_{l_{a}m_{a}}^{*}(\alpha,q) \widetilde{\phi}_{l_{b}m_{b}}(\beta,q+p)$$
(26)

where R = B - A. It is clear that we can evaluate this integral in either coordinate space or momentum space. In either case, we need to expand a product of Gaussian orbitals of the form (10) on two different centres. We shall first evaluate this integral in momentum space and refer the evaluation of this integral in coordinate space to appendix B. Using the following identity:

$$\frac{q^2}{4\alpha} + \frac{(\boldsymbol{q} + \boldsymbol{p})^2}{4\beta} = \frac{1}{4\xi} \left(\boldsymbol{q} + \frac{\alpha}{\zeta} \boldsymbol{p} \right)^2 + \frac{p^2}{4\zeta}$$
(27)

where $\xi = \alpha\beta/(\alpha + \beta)$, $\zeta = \alpha + \beta$ and letting $q + (\alpha/\zeta)p = q'$, we obtain the following expansion of a two-centre product in momentum space:

$$\widetilde{\phi}_{l_{a}m_{a}}^{*}(\alpha, q)\widetilde{\phi}_{l_{b}m_{b}}(\beta, q+p) = i^{l_{a}-l_{b}}\widetilde{N}_{l_{a}}(\alpha)\widetilde{N}_{l_{b}}(\beta)e^{-p^{2}/(4\zeta)}e^{-q^{\prime 2}/(4\zeta)}$$

$$\times \mathcal{Y}_{l_{a}m_{a}}^{*}\left(q^{\prime}-\frac{\alpha}{\zeta}p\right)\mathcal{Y}_{l_{b}m_{b}}\left(q^{\prime}+\frac{\beta}{\zeta}p\right)$$

$$= (-1)^{l_{b}}(4\pi)^{2}\widetilde{N}_{l_{a}}(\alpha)\widetilde{N}_{l_{b}}(\beta)e^{-p^{2}/(4\zeta)}$$

$$\times \sum_{l_{a}^{\prime},m_{a}^{\prime}}i^{l_{a}^{\prime}}G(l_{a}m_{a}|l_{a}^{\prime}m_{a}^{\prime})\mathcal{Y}_{l_{a}^{\prime}m_{a}^{\prime}}^{*}\left(-\frac{\alpha}{\zeta}p\right)$$

$$\times \sum_{l_{b}^{\prime},m_{b}^{\prime}}i^{l_{b}^{\prime}}G(l_{b}m_{b}|l_{b}^{\prime}m_{b}^{\prime})\mathcal{Y}_{l_{b}^{\prime}m_{b}^{\prime}}\left(\frac{\beta}{\zeta}p\right)i^{l_{a}^{\prime\prime}+l_{b}^{\prime\prime}}e^{-q^{\prime 2}/(4\xi)}\mathcal{Y}_{l_{a}^{\prime\prime}m_{a}^{\prime\prime}}^{*}(q^{\prime})\mathcal{Y}_{l_{b}^{\prime\prime}m_{b}^{\prime\prime}}(q^{\prime})$$

$$(28)$$

where $l''_e = l_e - l'_e$ for e = a, b and we have used the addition theorem of solid harmonics (15). Substituting (28) into (26), changing the variable from $q \to q'$ and making use of

equation (19), we obtain

$$S_{l_{a}m_{a}}^{l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{p}) = (-1)^{l_{b}}(4\pi)^{2}(2\pi)^{3/2}\widetilde{N}_{l_{a}}(\alpha)\widetilde{N}_{l_{b}}(\beta)e^{-i\boldsymbol{p}\cdot\boldsymbol{R}_{a\beta}}e^{-p^{2}/(4\zeta)}$$

$$\times \sum_{l_{a}',m_{a}'}i^{l_{a}'}G(l_{a}m_{a}|l_{a}'m_{a}')\mathcal{Y}_{l_{a}'m_{a}'}^{*}\left(-\frac{\alpha}{\zeta}\boldsymbol{p}\right)$$

$$\times \sum_{l_{b}',m_{b}'}i^{l_{b}'}G(l_{b}m_{b}|l_{b}'m_{b}')\mathcal{Y}_{l_{b}'m_{b}'}\left(\frac{\beta}{\zeta}\boldsymbol{p}\right)I_{l_{a}''m_{a}''}^{l_{b}''m_{b}''}(\xi,\boldsymbol{R})$$
(29)

where $\mathbf{R}_{\alpha\beta} = \mathbf{B} - (\alpha/\zeta)\mathbf{R} = (\alpha \mathbf{A} + \beta \mathbf{B})/(\alpha + \beta)$. Since the summations over *lm* in equation (29) can be readily linearized, there are, in effect, only three summations noting that there is one sum inside the integral *I*. Besides its compactness, this formula possesses another important advantage due to its clear separation of the dependence on *p* and *R*. Hence, the integral $S_{l_a m_a}^{l_b m_b}(\alpha, \beta, \mathbf{A}, \mathbf{B}, p)$ can be readily used in the evaluation of three-centre nuclear attraction and four-centre electron repulsion integrals. It is of interest to note that the integral can also be evaluated in another way by first absorbing the PWETF into the Gaussian orbital and then applying equations (18) and (19) (see paper II).

3.5. Nuclear attraction integrals

 $N_{l_a}^{l_b}$

The three-centre nuclear attraction integrals over Gaussian orbitals are defined as

$$\begin{split} {}^{m_b}_{m_a}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C}) &= \langle \phi_{l_a m_a}(\alpha,\boldsymbol{r}-\boldsymbol{A}) \left| \frac{1}{|\boldsymbol{r}-\boldsymbol{C}|} \right| \phi_{l_b m_b}(\beta,\boldsymbol{r}-\boldsymbol{B}) \rangle \\ &= \frac{1}{2\pi^2} \int \frac{d\boldsymbol{p}}{p^2} \mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{C}} \langle \phi_{l_a m_a}(\alpha,\boldsymbol{r}-\boldsymbol{A}) | \mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}} | \phi_{l_b m_b}(\beta,\boldsymbol{r}-\boldsymbol{B}) \rangle \\ &= \frac{1}{2\pi^2} \int \frac{d\boldsymbol{p}}{p^2} \mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{C}} S_{l_a m_a}^{l_b m_b}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{p}) \end{split}$$
(30)

where we have used the identity

$$\frac{1}{|r-C|} = \frac{1}{2\pi^2} \int \frac{dp}{p^2} e^{-ip \cdot (r-C)}.$$
(31)

...

Substituting equation (29) into (30), we obtain

$$N_{l_{a}m_{a}}^{l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C}) = 8(-1)^{l_{b}}(2\pi)^{3}\widetilde{N}_{l_{a}}(\alpha)\widetilde{N}_{l_{b}}(\beta)\sum_{l'_{a},m'_{a}}G(l_{a}m_{a}|l'_{a}m'_{a})\left(-\frac{\alpha}{\zeta}\right)^{l'_{a}} \times \sum_{l'_{b},m'_{b}}G(l_{b}m_{b}|l'_{b}m'_{b})\left(\frac{\beta}{\zeta}\right)^{l'_{b}}I_{l''_{a}m''_{a}}^{l''_{b}m''_{b}}(\xi,\boldsymbol{R}_{ba})J_{l'_{a}m'_{a}}^{l'_{b}m'_{b}}(\zeta,\boldsymbol{R}_{\alpha\beta c})$$
(32)

where $R_{ba} = B - A$, $R_{\alpha\beta c} = R_{\alpha\beta} - C$, and

$$J_{l_{1}m_{1}}^{l_{2}m_{2}}(\zeta, \mathbf{R}) = \frac{i^{l_{1}+l_{2}}}{(2\pi)^{3/2}} \int \frac{d\mathbf{p}}{p^{2}} e^{-i\mathbf{p}\cdot\mathbf{R}} e^{-p^{2}/(4\zeta)} \mathcal{Y}_{l_{1}m_{1}}^{*}(\mathbf{p}) \mathcal{Y}_{l_{2}m_{2}}(\mathbf{p})$$

$$= \langle l_{2}m_{2}|l_{1}m_{1}|LM\rangle \mathcal{C}_{-1,L}^{a}\left(\frac{1}{4\zeta}\right) F_{L}(\zeta R^{2}) \mathcal{Y}_{LM}(\mathbf{R})$$

$$+ \sum_{l=l_{\min}}^{L-2} (-1)^{n} \langle l_{2}m_{2}|l_{1}m_{1}|lm\rangle \mathcal{C}_{n-1,l}^{a}\left(\frac{1}{4\zeta}\right) \Phi_{n-1,lm}^{b}(\zeta, \mathbf{R})$$
(33)

where $L = l_1 + l_2$, $l_{\min} = |l_1 - l_2|$, $n = (l_1 + l_2 - l)/2$ and we have used equations (17*a*), (11), (14), (4) and (8). It is of interest to note that integrals *I* and *J* are independent of each other and therefore can be evaluated simultaneously in (33) on multi-processor machines. The evaluation of this integral in coordinate space will be presented in appendix B.

3.6. Electron repulsion integrals

The four-centre electron repulsion integrals over Gaussian orbitals are defined as

$$V_{l_{a}m_{a},l_{c}m_{c}}^{l_{b}m_{b},l_{d}m_{d}}(\alpha,\beta,\gamma,\delta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C},\boldsymbol{D}) = \langle \phi_{l_{a}m_{a}}(\alpha,r_{1}-\boldsymbol{A})\phi_{l_{c}m_{c}}(\gamma,r_{2}-\boldsymbol{C}) \left| \frac{1}{|\boldsymbol{r}_{1}-\boldsymbol{r}_{2}|} \right|$$

$$\times \phi_{l_{b}m_{b}}(\beta,\boldsymbol{r}_{1}-\boldsymbol{B})\phi_{l_{d}m_{d}}(\delta,\boldsymbol{r}_{2}-\boldsymbol{D})\rangle$$

$$= \frac{1}{2\pi^{2}} \int \frac{d\boldsymbol{p}}{p^{2}} \langle \phi_{l_{a}m_{a}}(\alpha,\boldsymbol{r}_{1}-\boldsymbol{A})$$

$$\times |\mathbf{e}^{-\mathbf{i}\boldsymbol{p}\cdot\boldsymbol{r}_{1}}|\phi_{l_{b}m_{b}}(\beta,\boldsymbol{r}_{1}-\boldsymbol{B})\rangle \langle \phi_{l_{c}m_{c}}(\gamma,\boldsymbol{r}_{2}-\boldsymbol{C})|\mathbf{e}^{\mathbf{i}\boldsymbol{p}\cdot\boldsymbol{r}_{2}}|\phi_{l_{d}m_{d}}(\delta,\boldsymbol{r}_{2}-\boldsymbol{D})\rangle$$

$$= \frac{1}{2\pi^{2}} \int \frac{d\boldsymbol{p}}{p^{2}} S_{l_{a}m_{a}}^{l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{p})$$

$$\times S_{l_{c}m_{c}}^{l_{d}m_{d}}(\gamma,\delta,\boldsymbol{C},\boldsymbol{D},-\boldsymbol{p}) \qquad (34)$$

where we have used equations (31) and (18). Substituting equation (29) into (34), we obtain $V_{l_a m_a, l_c m_c}^{l_b m_b, l_d m_d}(\alpha, \beta, \gamma, \delta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{C}, \boldsymbol{D}) = 32(-1)^{l_b+l_d}(2\pi)^{13/2} \widetilde{N}_{l_a}(\alpha) \widetilde{N}_{l_b}(\beta) \widetilde{N}_{l_c}(\gamma) \widetilde{N}_{l_d}(\delta)$

$$\times \sum_{l'_{a},m'_{a}} G(l_{a}m_{a}|l'_{a}m'_{a}) \left(-\frac{\alpha}{\zeta_{1}}\right)^{l'_{a}} \sum_{l'_{b},m'_{b}} G(l_{b}m_{b}|l'_{b}m'_{b}) \left(\frac{\beta}{\zeta_{1}}\right)^{l'_{b}} I^{l'_{b}}_{l''_{a}m''_{a}}(\xi_{1},\boldsymbol{R}_{ba}) \\ \times \sum_{l'_{c},m'_{c}} G(l_{c}m_{c}|l'_{c}m'_{c}) \left(\frac{\gamma}{\zeta_{2}}\right)^{l'_{c}} \sum_{l'_{d},m'_{d}} G(l_{d}m_{d}|l'_{d}m'_{d}) \left(-\frac{\delta}{\zeta_{2}}\right)^{l'_{d}} I^{l''_{a}m''_{d}}_{l''_{c}m''_{c}}(\xi_{2},\boldsymbol{R}_{dc}) \\ \times U^{l'_{b}m'_{b},l'_{d}m'_{d}}_{l''_{a}m'_{a}}(\zeta,\boldsymbol{R}_{\alpha\beta\gamma\delta})$$
(35)

where the parameters appearing in equation (35) are defined as follows:

$$\xi_1 = \frac{\alpha\beta}{\alpha+\beta}$$
 $\zeta_1 = \alpha+\beta$ $\xi_2 = \frac{\gamma\delta}{\gamma+\delta}$ $\zeta_2 = \gamma+\delta$ (36a)

$$\boldsymbol{R}_{ba} = \boldsymbol{B} - \boldsymbol{A} \qquad \boldsymbol{R}_{dc} = \boldsymbol{D} - \boldsymbol{C} \qquad \boldsymbol{\zeta} = \frac{\zeta_1 \zeta_2}{\zeta_1 + \zeta_2} = \frac{(\alpha + \beta)(\gamma + \delta)}{\alpha + \beta + \gamma + \delta}$$
(36b)

$$\boldsymbol{R}_{\alpha\beta} = \frac{\alpha \boldsymbol{A} + \beta \boldsymbol{B}}{\alpha + \beta} \qquad \boldsymbol{R}_{\gamma\delta} = \frac{\gamma \boldsymbol{C} + \delta \boldsymbol{D}}{\gamma + \delta} \qquad \boldsymbol{R}_{\alpha\beta\gamma\delta} = \boldsymbol{R}_{\alpha\beta} - \boldsymbol{R}_{\gamma\delta}$$
(36c)

and the integral U is defined similarly to the J integral

$$U_{l_{1}m_{1},l_{3}m_{3}}^{l_{2}m_{2},l_{4}m_{4}}(\zeta,\boldsymbol{R}) = \frac{i^{L}}{(2\pi)^{3/2}} \int \frac{d\boldsymbol{p}}{p^{2}} e^{-i\boldsymbol{p}\cdot\boldsymbol{R}} e^{-p^{2}/(4\zeta)} \mathcal{Y}_{l_{1}m_{1}}^{*}(\boldsymbol{p}) \mathcal{Y}_{l_{3}m_{3}}^{*}(\boldsymbol{p}) \mathcal{Y}_{l_{2}m_{2}}(\boldsymbol{p}) \mathcal{Y}_{l_{4}m_{4}}(\boldsymbol{p})$$

$$= \langle l_{2}m_{2}, l_{4}m_{4} | LM| l_{1}m_{1}, l_{3}m_{3} \rangle \mathcal{C}_{-1,L}^{a} \Big(\frac{1}{4\zeta}\Big) F_{L}(\zeta R^{2}) \mathcal{Y}_{LM}(\boldsymbol{R})$$

$$+ \sum_{l=l_{\min}}^{L-2} (-1)^{n} \langle l_{2}m_{2}, l_{4}m_{4} | lm| l_{1}m_{1}, l_{3}m_{3} \rangle \mathcal{C}_{n-1,l}^{a} \Big(\frac{1}{4\zeta}\Big) \Phi_{n-1,lm}^{b}(\zeta,\boldsymbol{R}) \quad (37)$$

where $L = l_1 + l_2 + l_3 + l_4$, $n = (L - l)/2 = (l_1 + l_2 + l_3 + l_4 - l)/2$ and we have applied both equations (17*a*) and (17*b*) to expand the product of the four solid harmonics. Here, $\langle l_2m_2, l_4m_4|lm|l_1m_1, l_3m_3 \rangle$ stands for the following quantity:

$$\langle l_{2}m_{2}, l_{4}m_{4}|lm|l_{1}m_{1}, l_{3}m_{3}\rangle = \sum_{l_{21}=|l_{2}-l_{1}|}^{l_{2}+l_{1}} \langle l_{2}m_{2}|l_{21}, m_{21}|l_{1}m_{1}\rangle$$
$$\times \sum_{l_{43}=|l_{4}-l_{3}|}^{l_{4}+l_{3}} \langle l_{4}m_{4}|l_{43}, m_{43}|l_{3}m_{3}\rangle \langle lm|l_{21}, m_{21}|l_{43}, m_{43}\rangle.$$
(38)

From this equation, we have three triangular relations $\Delta(l_2l_1l_{21})$, $\Delta(l_4l_3l_{43})$, $\Delta(l_{21}l_{43}l)$ and $l_2 + l_1 + l_{21}$, $l_4 + l_3 + l_{43}$, $l_{21} + l_{43} + l$ are all even integers. Therefore, the only l and m values in equation (37) are those satisfying $l_1 + l_2 + l_3 + l_4 + l$ = even integer and $m_1 + m_3 + m = m_2 + m_4$ due to the selection rule for the three Gaunt coefficients. If one can evaluate the angular parts $\langle l_2m_2, l_4m_4|lm|l_1m_1, l_3m_3\rangle$ before hand and store them for later use, equation (37) is expected to be more efficient in actual computation than the formula evaluated in coordinate space (see appendix B).

3.7. Other molecular integrals

The electric field and electric field gradient operators are obtained by differentiating the nuclear attraction operator, $\mathcal{E}_{k\mu} = \mathcal{Y}_{k\mu}(\nabla_C)/|r - C|$. For electric fields, we have k = 1, while for electric field gradients, k = 2. Using equation (30), we obtain

$$\mathcal{E}_{l_a m_a}^{l_b m_b}(k\mu, \alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{C}) = \mathcal{Y}_{k\mu}(\nabla_{\boldsymbol{C}}) N_{l_a m_a}^{l_b m_b}(\alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{C}) \,. \tag{39}$$

The resulting formula for this integral is similar to equation (32), except that we have to replace the J integral by the following E integral:

$$E_{l_{1}m_{1}}^{l_{2}m_{2}}(k\mu,\zeta,\mathbf{R}) = \mathcal{Y}_{k\mu}(\nabla_{C})J_{l_{1}m_{1}}^{l_{2}m_{2}}(\zeta,\mathbf{R})$$

$$= \frac{i^{l_{1}+l_{2}+k}}{(2\pi)^{3/2}}\int\frac{d\mathbf{p}}{p^{2}}e^{-i\mathbf{p}\cdot\mathbf{R}}e^{-p^{2}/(4\zeta)}\mathcal{Y}_{k\mu}(\mathbf{p})\mathcal{Y}_{l_{1}m_{1}}^{*}(\mathbf{p})\mathcal{Y}_{l_{2}m_{2}}(\mathbf{p})$$

$$= \langle l_{2}m_{2},k\mu|l_{1}m_{1},LM\rangle\mathcal{C}_{-1,L}^{a}\left(\frac{1}{4\zeta}\right)F_{L}(\zeta\,\mathbf{R}^{2})\mathcal{Y}_{LM}(\mathbf{R})$$

$$+ \sum_{l=l_{\min}}^{L-2}(-1)^{n}\langle l_{2}m_{2},k\mu|l_{1}m_{1},lm\rangle\mathcal{C}_{n-1,l}^{a}\left(\frac{1}{4\zeta}\right)\Phi_{n-1,lm}^{b}(\zeta,\mathbf{R})$$
(40)

where $L = l_1 + l_2 + k$, n = (L - l)/2 and $\langle l_2 m_2, k \mu | l_1 m_1, lm \rangle$ has been defined in equation (25). The space operator of the spin–orbit coupling is of the form $r_C^{-3} r_C \times \nabla_r \sim [\mathcal{Y}_{k_1\mu_1}(\nabla_C)/r_C]\mathcal{Y}_{k_2\mu_2}(\nabla_r)$ (uncoupled form), with $k_1 = k_2 = 1$. Hence, the uncoupled spin–orbit coupling integral can be evaluated as follows:

$$SO_{l_{a}m_{a}}^{l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C}) = \langle \phi_{l_{a}m_{a}}(\alpha,\boldsymbol{r}-\boldsymbol{A}) \Big| \Big[\mathcal{Y}_{k_{1}\mu_{1}}(\nabla_{\boldsymbol{C}}) \frac{1}{r_{\boldsymbol{C}}} \Big] \mathcal{Y}_{k_{2}\mu_{2}}(\nabla_{\boldsymbol{r}}) \Big| \phi_{l_{b}m_{b}}(\beta,\boldsymbol{r}-\boldsymbol{B}) \rangle$$
$$= \mathcal{Y}_{k_{1}\mu_{1}}(\nabla_{\boldsymbol{C}}) \mathcal{Y}_{k_{2}\mu_{2}}(-\nabla_{\boldsymbol{B}}) N_{l_{a}m_{a}}^{l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C})$$
$$= \mathcal{Y}_{k_{2}\mu_{2}}(-\nabla_{\boldsymbol{B}}) \mathcal{E}_{l_{a}m_{a}}^{l_{b}m_{b}}(k_{1}\mu_{1},\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C})$$
(41)

where we have used equation (39). The remaining derivative can be carried out similarly to equation (40) since $k_2 = 1$,

$$\mathcal{Y}_{1\mu_{2}}(-\nabla_{B}) \Big[I_{l_{a}'m_{a}''}^{l_{b}'m_{b}''}(\xi, \mathbf{R}_{ba}) E_{l_{a}'m_{a}'}^{l_{b}'m_{b}'}(k_{1}\mu_{1}, \zeta, \mathbf{R}_{\alpha\beta c}) \Big] = \mathcal{T}_{l_{a}'m_{a}''}^{l_{b}'m_{b}''}(k_{2}\mu_{2}, \xi, \mathbf{R}_{ba}) \\ \times E_{l_{a}'m_{a}'}^{l_{b}'m_{b}'}(k_{1}\mu_{1}, \zeta, \mathbf{R}_{\alpha\beta c}) + (-1)^{\mu_{1}}\frac{\beta}{\zeta} I_{l_{a}''m_{a}''}^{l_{b}'m_{b}''}(\xi, \mathbf{R}_{ba}) U_{l_{a}'m_{a}',k_{1},-\mu_{1}}^{l_{b}'m_{b}'}(\zeta, \mathbf{R}_{\alpha\beta c}).$$
(42)

Just as for the electric field and field gradient, integrals over the space part of the electron spin–spin interaction, $S_{k\mu} = \mathcal{Y}_{k\mu}(\nabla_{r_1})/r_{12}$, can be easily evaluated using the following substitution:

$$S_{k\mu} = \mathcal{Y}_{k\mu}(\nabla_{r_1}) \frac{1}{r_{12}} = \frac{1}{2\pi^2} \int \frac{\mathrm{d}p}{p^2} \mathrm{e}^{-\mathrm{i}p \cdot (r_1 - r_2)} \mathcal{Y}_{k\mu}(-\mathrm{i}p) \,. \tag{43}$$

The space part of the two-electron spin–orbit coupling operator has the form $r_{12}^{-3} r_{12} \times \nabla_{r_1} \sim [\mathcal{Y}_{k_1\mu_1}(\nabla_{r_1})/r_{12}]\mathcal{Y}_{k_2\mu_2}(\nabla_{r_1})$, with $k_1 = k_2 = 1$. The resulting integral can be expressed as

 $\mathcal{Y}_{k_2\mu_2}(-\nabla_B)\mathcal{S}_{l_am_a,l_cm_c}^{l_bm_b,l_dm_d}(k_1\mu_1,\alpha,\beta,\gamma,\delta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C},\boldsymbol{D})$, as in equation (40). Here \mathcal{S} is the space integral of the electron spin–spin interaction.

4. Molecular integrals over the general SGTOs

Having evaluated all the molecular integrals over the special type of SGTOs of the form (10), we shall now consider these integrals for the more general SGTOs. Although the SGTOs used by Fieck (1979, 1980) and Maretis (1979) are general, the resulting formulae for molecular integrals contain the sophisticated Moshinsky–Smirnov coefficients from nuclear shell theory. As pointed out by Niukkanen (1980), these coefficients consist of very complicated sevenfold sums with two continuous parameters. In this section, we will show that molecular integrals over the general SGTOs can be evaluated in the same way as over the special SGTOs with the least modification and the resulting formulae are almost as simple as in the case of the special SGTOs. Our formulae for the general SGTOs do not contain the Moshinsky–Smirnov coefficients and therefore are simpler than those obtained by Fieck and Maretis.

To facilitate the evaluation of molecular integrals in momentum space, we shall first consider the Gaussian-type orbitals of the form (7), the momentum representation of which is of the form (9). We will consider Gaussian-type orbitals of the form (6) in appendix B. Since the two kinds of general SGTOs (6) and (7) are reciprocal with respect to each other, it is expected that the resulting formulae for the molecular integrals will also be reciprocal. Before proceeding, we need to generalize the two indispensable tools: the addition theorem of solid harmonics (15) and the product expansion formulae (17). The general harmonic polynomial is introduced as

$$\mathcal{Y}_{lm}^n(\mathbf{r}) = (\mathbf{r} \cdot \mathbf{r})^n \mathcal{Y}_{lm}(\mathbf{r}) = r^{2n+l} Y_{lm}(\hat{\mathbf{r}}) \tag{44}$$

where $\mathcal{Y}_{lm}(\mathbf{r})$ is simply the solid harmonic as before and $Y_{lm}(\hat{\mathbf{r}})$ is the usual spherical harmonic. Now the general SGTOs, equation (9), can be written as

$$\widetilde{\phi}_{nlm}(\alpha, \mathbf{p}) = (-\mathbf{i})^l \widetilde{N}_{nl}(\alpha) \mathrm{e}^{-p^2/(4\alpha)} \mathcal{Y}_{lm}^n(\mathbf{p})$$
(45)

where $\widetilde{N}_{nl}(\alpha) = N^b_{nl}(\alpha) C^b_{nl}(\alpha)$, with

$$N_{nl}^{b}(\alpha) = 2^{n} n! \left[\frac{2(2\alpha)^{l+3/2}}{\Gamma(2n+l+3/2)} \right]^{1/2}$$

Note that we have dropped the index b of equation (9). It is worth noting that the above representation of the general SGTOs has exactly the same form as the special SGTOs of form (10) except that the solid harmonic in equation (10) has been replaced by the general harmonic polynomial. The translational property (addition theorem) of the general harmonic polynomial (Niukkanen 1980, Niukkanen and Gribov 1983) can be written as

$$\mathcal{Y}_{lm}^{n}(\boldsymbol{r}_{1}+\boldsymbol{r}_{2}) = 4\pi \sum_{[\boldsymbol{n}_{1},\boldsymbol{n}_{2}]} \mathcal{K}(\boldsymbol{n}|\boldsymbol{n}_{1}|\boldsymbol{n}_{2}) \mathcal{Y}_{l_{1}m_{1}}^{n_{1}}(\boldsymbol{r}_{1}) \mathcal{Y}_{l_{2}m_{2}}^{n_{2}}(\boldsymbol{r}_{2})$$
(46a)

$$\mathcal{K}(\boldsymbol{n}|\boldsymbol{n}_1|\boldsymbol{n}_2) = \frac{(2n)!!}{(2n_1)!!(2n_2)!!} \frac{[2(n+l)+1]!!\langle lm|l_1m_1|l_2m_2\rangle}{[2(n_1+l_1)+1]!![2(n_2+l_2)+1]!!}$$
(46b)

where *n* stands for the triad of quantum numbers (n, l, m), and $n_i = (n_i, l_i, m_i)$ for i = 1, 2. It immediately follows from (46*b*) that $\mathcal{K}(n|n_2|n_1) = \mathcal{K}(n|n_1|n_2)$. The square brackets over the summation indices n_1 and n_2 in (46*a*) mean that the summation is constrained by the selection rules of the Gaunt coefficient and by the relation $n = n_1 + n_2 + \Delta$. Specifically, these constraints are as follows:

$$\begin{array}{ll}
0 \leqslant l_{1} \leqslant l + 2n & |l - l_{1}| \leqslant l_{2} \leqslant \min(l_{1} + l, l + 2n - l_{1}) \\
0 \leqslant n_{1} \leqslant n - \Delta & \Delta = (l_{1} + l_{2} - l)/2 \\
\max(-l_{1}, m - l_{2}) \leqslant m_{1} \leqslant \min(l_{1}, m + l_{2}) \\
n_{2} = n - n_{1} - \Delta & m_{2} = m - m_{1} \\
l_{1} + l_{2} + l = \text{even number}.
\end{array}$$
(46c)

It is clear that only four indices out of six (n_1, n_2) are independent and they can be either (n_1, l_1, m_1, l_2) , or (n_2, l_2, m_2, l_1) . Note that we have simplified the coefficients in equation (46*a*) given by Niukkanen and Gribov (1983). A more general derivation of the above addition theorem will be presented in the appendix of paper II. It immediately follows that the above formulae (46*a*)–(46*c*) reduce to the addition theorem of the solid harmonic when n = 0. In this case, we have $n_1 = n_2 = 0$ and $l_1 + l_2 = l$, thus the 4-tuple summation will be reduced to a 2-tuple summation and the coefficient \mathcal{K} becomes *G* in equation (15). Compared with the addition theorem of the solid harmonic, equation (15), the additional 2-tuple summation in equation (46*a*) is the price we have to pay for the generalization. The product expansion formulae can be easily derived from equations (17*a*) and (17*b*),

$$\left[\mathcal{Y}_{l_{1}m_{1}}^{n_{1}}(\boldsymbol{r})\right]^{*}\mathcal{Y}_{l_{2}m_{2}}^{n_{2}}(\boldsymbol{r}) = \sum_{l} \langle l_{2}m_{2}|l_{1}m_{1}|lm\rangle \mathcal{Y}_{lm}^{n}(\boldsymbol{r})$$
(47*a*)

$$\mathcal{Y}_{l_1m_1}^{n_1}(\boldsymbol{r})\mathcal{Y}_{l_2m_2}^{n_2}(\boldsymbol{r}) = \sum_{l} \langle lm|l_1m_1|l_2m_2\rangle \mathcal{Y}_{lm}^{n}(\boldsymbol{r})$$
(47b)

where $n = n_1 + n_2 + \Delta$ with $\Delta = (l_1 + l_2 - l)/2$ and the allowed *l* values as well as other constraints are the same as before.

Since the generalized formulae for the harmonic polynomial have exactly the same forms as those for the solid harmonic, it is a simple matter to generalize the preceding formulae of molecular integrals to the general SGTOs (equation (45)). We will illustrate in detail how the overlap integral over the general SGTOs is evaluated, while the remaining integrals are summarized in appendix A:

$$S_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\alpha, \beta, \boldsymbol{A}, \boldsymbol{B}) = \langle \phi_{n_{a}l_{a}m_{a}}(\alpha, \boldsymbol{r} - \boldsymbol{A}) | \phi_{n_{b}l_{b}m_{b}}(\beta, \boldsymbol{r} - \boldsymbol{B}) \rangle$$

$$= \int d\boldsymbol{q} \, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}} \widetilde{\phi}_{n_{a}l_{a}m_{a}}^{*}(\alpha, \boldsymbol{q}) \widetilde{\phi}_{n_{b}l_{b}m_{b}}(\beta, \boldsymbol{q})$$

$$= (-1)^{l_{b}} (2\pi)^{3/2} \widetilde{N}_{n_{a}l_{a}}(\alpha) \widetilde{N}_{n_{b}l_{b}}(\beta) I_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\xi, \boldsymbol{R})$$

$$I_{n_{1}l_{1}m_{1}}^{n_{2}l_{2}m_{2}}(\xi, \boldsymbol{R}) = \frac{\mathrm{i}^{l_{1}+l_{2}}}{(2\pi)^{3/2}} \int d\boldsymbol{q} \, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}} \mathrm{e}^{-q^{2}/(4\xi)} \big[\mathcal{Y}_{l_{1}m_{1}}^{n_{1}}(\boldsymbol{q}) \big]^{*} \mathcal{Y}_{l_{2}m_{2}}^{n_{2}}(\boldsymbol{q})$$

$$(48)$$

where $\mathbf{R} = \mathbf{B} - \mathbf{A}$ and $\xi = \alpha \beta / (\alpha + \beta)$ as before. The integral *I* can be evaluated in the same way as equation (19) by means of the expansion (47*a*),

$$I_{n_{1}l_{1}m_{1}}^{n_{2}l_{2}m_{2}}(\xi, \mathbf{R}) = i^{l_{1}+l_{2}} \sum_{l} \langle l_{2}m_{2}|l_{1}m_{1}|lm\rangle \frac{1}{(2\pi)^{3/2}} \int d\mathbf{q} e^{-i\mathbf{q}\cdot\mathbf{R}} \Phi_{nlm}^{a} \left(\frac{1}{4\xi}, \mathbf{q}\right)$$
$$= \sum_{l} (-1)^{\Delta} \langle l_{2}m_{2}|l_{1}m_{1}|lm\rangle \mathcal{C}_{nl}^{a} \left(\frac{1}{4\xi}\right) \Phi_{nlm}^{b}(\xi, \mathbf{R})$$
(49)

where $\Delta = (l_1 + l_2 - l)/2$, $n = n_1 + n_2 + \Delta$ and we have used equations (4) and (8). As can be seen, equation (49) is almost as simple as (19). In other words, introducing the general SGTOs does not increase the complexity of the overlap integral. This also

holds true for the integrals of kinetic energy and of the tensor operator, see appendix B. However, the formulae for overlap integrals with PWETF as well as nuclear attraction and electron repulsion integrals over the general SGTOs will inevitably introduce more sums because of the two extra summations in the addition theorem of the harmonic polynomial (46a).

5. Numerical strategies and concluding remarks

Since the relative merits of spherical Gaussian-type orbitals over Cartesian Gaussian-type orbitals have been addressed by a number of authors (Fieck 1980, Huzinaga 1985, Dunlap 1990), we will not reiterate them. Instead, we shall concentrate on how to efficiently implement the preceding formulae, especially for four-centre electron repulsion integrals. Before proceeding, we shall summarize the typical features of the present formulae. Firstly, all the angular parts are treated analytically by means of vector-coupling coefficients (Gaunt coefficients), which can be efficiently evaluated to any desired accuracy for arbitrary high angular momentum. Secondly, the important geometric dependence with respect to multicentres comes into play through the solid harmonic functions $\mathcal{Y}_{lm}(\mathbf{R})$. Here, we have to distinguish between the two different cases according to whether R depends on the exponents of Gaussian orbitals. Thirdly, only the term $\mathcal{Y}_{lm}(\mathbf{R})$ in the present formulae involves complex number operations. The solid harmonics appear in the forms of $\mathcal{Y}(\mathbf{R})$ (equations (19), (22) and (24)), $\mathcal{Y}(\mathbf{R}_1)\mathcal{Y}(\mathbf{R}_2)$ (equation (32)) and $\mathcal{Y}(\mathbf{R}_1)\mathcal{Y}(\mathbf{R}_2)\mathcal{Y}(\mathbf{R}_3)$ (equation (35)). When real Gaussian orbitals are used, these formulae can be readily adapted so that only real number operations are needed. Finally, for the special SGTO, only two indices *lm* are needed to specify an orbital while for the corresponding CGTO, three indices are needed. The present formula for each integral only needs half as many summations as its Cartesian Gaussian orbitals counterpart (Taketa et al 1966). This is still true even after we have improved the original treatment (Taketa et al 1966) of nuclear attraction and electron repulsion integrals over CGTOs, see appendix B of paper II.

As can be seen, Gaunt coefficients appear throughout the present formulation. A reliable scheme for the evaluation of these coefficients is available (Weniger and Steinborn 1982). It is advisable that the Gaunt coefficients be pre-evaluated and stored in memory. The storage requirement is of the order of l_{\max}^5 , which should not be prohibitive on any reasonable system. Meanwhile, the G(lm|l'm') coefficients in equation (15) should also be evaluated first and the corresponding storage is only of the order of l_{max}^4 . It would be desirable that $\langle l_2m_2, l_4m_4|lm|l_1m_1, l_3m_3\rangle$ be evaluated and stored first if the memory is available, since about l_{max}^9 values are required. All the integrals require the evaluation of solid harmonics $\mathcal{Y}_{lm}(\mathbf{R})$, and the associated Laguerre polynomials of the form $L_n^{l+1/2-2n}(z)$ with $n \leq \lfloor l/2 \rfloor$. An efficient recursive scheme for computing $\mathcal{Y}_{lm}(\mathbf{R})$ is presented in paper II. For low angular momentum the explicit form of the associated Laguerre polynomials may be used, while for high angular momentum the recurrence evaluation may be preferable. In the cases of nuclear attraction and electron repulsion integrals, a sequence of the functions $F_m(z)$ needs to be evaluated. The efficient computation of this function has been discussed by a number of authors (Shavitt 1963, Grotendorst and Steinborn 1986 and references therein) and it is generally agreed that a carefully constructed interpolation scheme, such as that described by Gill et al (1991), is the most effective approach.

It is computationally more effective to introduce contracted Gaussian-type orbitals,

which are defined as

$$\phi_{lm}^{c}(\alpha, \mathbf{r}) = \left\{ \sum_{k=1}^{K} C_{k} \mathrm{e}^{-\alpha_{k} r^{2}} \right\} \mathcal{Y}_{lm}(\mathbf{r})$$
(50)

where *K* is the degree of contraction and C_k are contraction coefficients. The original uncontracted Gaussian-type orbitals are called the primitive functions. It should be noted that all the primitive functions in a contracted orbital share the same centre and angular momentum. The contracted orbitals, in some sense, eliminate our need for the general spherical Gaussian-type orbitals of the form (45). However, this leads to the so-called contraction problem. Assuming that all the orbitals are *K*-fold contracted, the molecular integrals over these contracted orbitals (AB|CD) may be expressed in a straightforward way as a sum of their component primitive integrals [AB|CD] which, in turn, are computed individually, i.e.

$$(AB|CD) = \sum_{i=1}^{K} \sum_{j=1}^{K} \sum_{k=1}^{K} \sum_{l=1}^{K} C_i^a C_j^b C_k^c C_l^d [A_i B_j | C_k D_l].$$
(51)

It immediately follows that the computational effort to generate the desired class of (AB|CD) integrals will rise with the fourth power of K, which is termed the contraction problem (for a recent review, see Gill (1994)). To reduce the computational cost of generating the integral class, it is crucial to make use of the fact that the primitive functions in a contracted basis orbital all share the same centre and the same angular parts. Our formulation of the integrals has fully separated the geometric and angular dependence from the exponent dependence. For instance, in the case of the four-centre electron repulsion integral (35), we can pull the geometric and angular dependence out of the summation over the primitive parts by substituting equation (35) into (51) and replacing the *I* integral with equation (19),

$$(\boldsymbol{AB}|\boldsymbol{CD}) = 32(-1)^{l_b+l_d} (2\pi)^{13/2} \sum_{l'_a, m'_a} G(l_a m_a | l'_a m'_a) \sum_{l'_b, m'_b} G(l_b m_b | l'_b m'_b) \\ \times \sum_{l_1} (-1)^{n_1} n_1! \langle l''_b m''_b | l''_a m''_a | l_1 m_1 \rangle \mathcal{Y}_{l_1 m_1} (\boldsymbol{R}_{ba}) \sum_{l'_c, m'_c} G(l_c m_c | l'_c m'_c) \\ \times \sum_{l'_d, m'_d} G(l_d m_d | l'_d m'_d) \sum_{l_2} (-1)^{n_2} n_2! \langle l''_d m''_d | l''_c m''_c | l_2 m_2 \rangle \mathcal{Y}_{l_2 m_2} (\boldsymbol{R}_{dc}) \\ \times \sum_{i=1}^{K} \sum_{j=1}^{K} \sum_{k=1}^{K} \sum_{l=1}^{K} C_i^a C_j^b C_k^c C_l^d F_{n_1, l_1}^{l'_a, l'_b} (\alpha_i, \beta_j, R_{ba}) \\ \times F_{n_2, l_2}^{l'_d, l'_c} (\delta_l, \gamma_k, R_{dc}) U_{l'_d m'_b, l'_d m'_d}^{l'_b m'_b, l'_d m'_d} (\zeta, \boldsymbol{R}_{\alpha\beta\gamma\delta}^{ijkl})$$
(52)

where ζ and $\mathbf{R}_{\alpha\beta\gamma\delta}^{ijkl}$ depend on the primitive exponents $\alpha_i, \beta_j, \gamma_k$ and δ_l as defined in equations (36*a*)–(36*c*). Here *F* stands for

$$F_{n,l}^{l_1,l_2}(\alpha,\beta,R) = \left(-\frac{\alpha}{\alpha+\beta}\right)^{l_1} \left(\frac{\beta}{\alpha+\beta}\right)^{l_2} \mathcal{C}_{nl}^a\left(\frac{1}{4\xi}\right) e^{-\xi R^2} L_n^{l+1/2}(\xi R^2)$$
(53)

with $\xi = \alpha \beta / (\alpha + \beta)$. It is clear from (52) that the evaluation of the integral class over contracted orbitals is nearly optimal under all circumstances, since there is not too much additional cost in the evaluation of the integral class for contracted orbitals compared with that for primitive functions.

In summary, we have derived all the multi-centre molecular integrals over spherical Gaussian-type orbitals by using the Fourier transform and the addition theorem of harmonic

polynomials. The resulting formulae, involving only the Gaunt coefficients and well known functions, are simpler than those obtained previously by Fieck (1980). The special spherical Gaussian orbitals of the form (10) are preferable in the actual molecular computation since they have simpler integral formulae than the general Gaussian orbitals (45). The loss of flexibility with the special SGTOs may be readily compensated for by using contracted Gaussian orbitals. Most importantly, the present formulation supports the efficient evaluation of molecular integrals over contracted Gaussian orbitals.

Acknowledgments

This work was supported in part by the US Department of Energy, Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences. We would like to thank Dr E Sidky for proofreading the manuscript.

Appendix A. Molecular integrals over the general SGTOs in momentum space

The molecular integrals of kinetic energy and tensor operators for general spherical Gaussian-type orbitals can be easily worked out as for the special SGTOs. We shall just provide the corresponding formulae below.

Kinetic energy integral

$$K_{n_{a}l_{a}m_{a}}^{h_{b}l_{b}m_{b}}(\boldsymbol{\alpha},\boldsymbol{\beta},\boldsymbol{A},\boldsymbol{B}) = \langle \phi_{n_{a}l_{a}m_{a}}(\boldsymbol{\alpha},\boldsymbol{r}-\boldsymbol{A})| - \frac{1}{2}\nabla_{\boldsymbol{r}}^{2}|\phi_{n_{b}l_{b}m_{b}}(\boldsymbol{\beta},\boldsymbol{r}-\boldsymbol{B})\rangle$$
$$= \frac{1}{2}(-1)^{l_{b}}(2\pi)^{3/2}\widetilde{N}_{n_{a}l_{a}}(\boldsymbol{\alpha})\widetilde{N}_{n_{b}l_{b}}(\boldsymbol{\beta})\mathcal{K}_{n_{a}l_{a}m_{a}}^{h_{b}l_{b}m_{b}}(\boldsymbol{\xi},\boldsymbol{R})$$
(A1)

$$\mathcal{K}_{n_{1}l_{1}m_{1}}^{n_{2}l_{2}m_{2}}(\xi,\boldsymbol{R}) = \sum_{l} (-1)^{\Delta} \langle l_{2}m_{2}|l_{1}m_{1}|lm\rangle \mathcal{C}_{n+1,l}^{a} \left(\frac{1}{4\xi}\right) \Phi_{n+1,lm}^{b}(\xi,\boldsymbol{R})$$
(A2)

where $\xi = \alpha \beta (\alpha + \beta)$ as before, $\Delta = (l_1 + l_2 - l)/2$ and $n = n_1 + n_2 + \Delta$.

Integral of a tensor operator $\mathcal{Y}_{lm}(\nabla)$

$$T_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B}) = \langle \phi_{n_{a}l_{a}m_{a}}(\alpha,\boldsymbol{r}-\boldsymbol{A}) | \mathcal{Y}_{lm}(\nabla_{\boldsymbol{r}}) | \phi_{n_{b}l_{b}m_{b}}(\beta,\boldsymbol{r}-\boldsymbol{B}) \rangle$$
$$= (-1)^{l_{b}} (2\pi)^{3/2} \widetilde{N}_{n_{a}l_{a}}(\alpha) \widetilde{N}_{n_{b}l_{b}}(\beta) \mathcal{T}_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\xi,\boldsymbol{R})$$
(A3)

$$\mathcal{T}_{n_{1}l_{1}m_{1}}^{n_{2}l_{2}m_{2}}(\xi,\boldsymbol{R}) = \sum_{l=0}^{l_{1}+l_{2}+k} (-1)^{\Delta} \langle l_{2}m_{2}, k\mu | l_{1}m_{1}, lm \rangle \mathcal{C}_{nl}^{a} \Big(\frac{1}{4\xi}\Big) \Phi_{nlm}^{b}(\xi,\boldsymbol{R})$$
(A4)

where $\xi = \alpha \beta (\alpha + \beta)$ as before, $\Delta = (l_1 + l_2 + k - l)/2$ and $n = n_1 + n_2 + \Delta$. The allowed *l* values are the same as before.

As we mentioned in section 4, overlap integrals with PWETF as well as nuclear attraction and electron repulsion integrals may be evaluated by means of the addition theorem of harmonic polynomials, at the expense of introducing more sums. However, the derivation is straightforward.

Overlap integral with PWETF

$$S_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\alpha,\beta,A,B,p) = \langle \phi_{n_{a}l_{a}m_{a}}(\alpha,r-A) | e^{-ip \cdot r} | \phi_{n_{b}l_{b}m_{b}}(\beta,r-B) \rangle$$

$$= i^{l_{a}-l_{b}} \widetilde{N}_{n_{a}l_{a}}(\alpha) \widetilde{N}_{n_{b}l_{b}}(\beta) e^{-ip \cdot R_{\alpha\beta}} e^{-p^{2}/(4\zeta)}$$

$$\times \int dq \, e^{-iq \cdot R} e^{-q^{2}/(4\xi)} \Big[\mathcal{Y}_{l_{a}m_{a}}^{n_{a}} \Big(q - \frac{\alpha}{\zeta} p \Big) \Big]^{*} \mathcal{Y}_{l_{b}m_{b}}^{n_{b}} \Big(q + \frac{\beta}{\zeta} p \Big)$$
(A5)

where all the parameters appearing in the above equation have the same definitions as before. Now the integral (A5) can be evaluated by means of the addition theorem of harmonic polynomials (46a),

$$S_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\alpha,\beta,A,B,p) = (-1)^{l_{b}}(4\pi)^{2}(2\pi)^{3/2}\widetilde{N}_{n_{a}l_{a}}(\alpha)\widetilde{N}_{n_{b}l_{b}}(\beta)e^{-ip\cdot\boldsymbol{R}_{a\beta}}e^{-p^{2}/(4\zeta)}$$

$$\times \sum_{[\boldsymbol{n}_{a}',\boldsymbol{n}_{a}'']} i^{l_{a}-l_{a}''}\mathcal{K}(\boldsymbol{n}_{a}|\boldsymbol{n}_{a}'|\boldsymbol{n}_{a}'') \Big[\mathcal{Y}_{l_{a}'m_{a}'}^{n_{a}'}\Big(-\frac{\alpha}{\zeta}\boldsymbol{p}\Big)\Big]^{*}$$

$$\times \sum_{[\boldsymbol{n}_{b}',\boldsymbol{n}_{b}'']} i^{l_{b}-l_{b}''}\mathcal{K}(\boldsymbol{n}_{b}|\boldsymbol{n}_{b}'|\mathcal{Y}_{l_{b}'m_{b}'}^{n_{b}'}\Big(\frac{\beta}{\zeta}\boldsymbol{p}\Big)I_{n_{a}''l_{a}''m_{a}''}^{n_{b}''}(\xi,R)$$
(A6)

where n_a stands for the triad of quantum numbers $(n_a, l_a, m_a), n'_a = (n'_a, l'_a, m'_a)$, and $n''_a = (n''_a, l''_a, m''_a)$.

Nuclear attraction integral

$$N_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\alpha,\beta,A,B,C) = \langle \phi_{n_{a}l_{a}m_{a}}(\alpha,r-A) \bigg| \frac{1}{|r-C|} \bigg| \phi_{n_{b}l_{b}m_{b}}(\beta,r-B) \rangle$$

$$= 8(-1)^{l_{b}}(2\pi)^{3} \widetilde{N}_{n_{a}l_{a}}(\alpha) \widetilde{N}_{n_{b}l_{b}}(\beta) \sum_{[\mathbf{n}'_{a},\mathbf{n}''_{a}]} (-1)^{\Delta_{a}} \mathcal{K}(\mathbf{n}_{a}|\mathbf{n}'_{a}|\mathbf{n}''_{a}) \Big(-\frac{\alpha}{\zeta}\Big)^{2n'_{a}+l'_{a}}$$

$$\times \sum_{[\mathbf{n}'_{b},\mathbf{n}''_{b}]} (-1)^{\Delta_{b}} \mathcal{K}(\mathbf{n}_{b}|\mathbf{n}'_{b}) \Big(\frac{\beta}{\zeta}\Big)^{2n'_{b}+l'_{b}} I_{\mathbf{n}''_{a}l''_{a}m''_{a}}^{n''_{b}l'_{b}m'_{b}}(\xi,R_{ba}) J_{\mathbf{n}'_{a}l'_{a}m'_{a}}^{n'_{b}l'_{b}m'_{b}}(\zeta,R_{\alpha\betac}) \quad (A7)$$

where $\Delta_a = (l'_a + l''_a - l_a)/2$, $\Delta_b = (l'_b + l''_b - l_b)/2$, and all the rest of parameters are the same as before. The integral J is defined similarly

$$J_{n_{1}l_{1}m_{1}}^{n_{2}l_{2}m_{2}}(\xi, \mathbf{R}) = \langle l_{2}m_{2}|l_{1}m_{1}|LM\rangle \mathcal{C}_{-1,L}^{a}\left(\frac{1}{4\zeta}\right) F_{L}(\zeta R^{2}) \mathcal{Y}_{LM}(\mathbf{R}) + \sum_{l=l_{\min}}^{L-2} (-1)^{\Delta} \langle l_{2}m_{2}|l_{1}m_{1}|lm\rangle \mathcal{C}_{n-1,l}^{a}\left(\frac{1}{4\zeta}\right) \Phi_{n-1,lm}^{b}(\zeta, \mathbf{R})$$
(A8)
where $L = l_{1} + l_{2}, \Delta = (l_{1} + l_{2} - l)/2$ and $n = n_{1} + n_{2} + \Delta$.

Electron repulsion integral

$$\begin{split} V_{n_{a}l_{a}m_{a},n_{c}l_{c}m_{c}}^{n_{b}l_{b}m_{b},n_{d}l_{d}m_{d}}(\alpha,\beta,\gamma,\delta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C},\boldsymbol{D}) &= \frac{1}{2\pi^{2}} \int \frac{\mathrm{d}\boldsymbol{p}}{\boldsymbol{p}^{2}} S_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{p}) \\ &\times S_{n_{c}l_{c}m_{c}}^{n_{d}l_{d}m_{d}}(\gamma,\delta,\boldsymbol{C},\boldsymbol{D},-\boldsymbol{p}) \\ &= 32(-1)^{l_{b}+l_{d}}(2\pi)^{13/2} \widetilde{N}_{n_{a}l_{a}}(\alpha) \widetilde{N}_{n_{b}l_{b}}(\beta) \widetilde{N}_{n_{c}l_{c}}(\gamma) \widetilde{N}_{n_{d}l_{d}}(\delta) \\ &\times \sum_{[\boldsymbol{n}_{a}',\boldsymbol{n}_{a}'']} (-1)^{\Delta_{a}} \mathcal{K}(\boldsymbol{n}_{a}|\boldsymbol{n}_{a}'|\boldsymbol{n}_{a}'') \Big(-\frac{\alpha}{\zeta_{1}}\Big)^{2n_{a}'+l_{a}'} \end{split}$$

Molecular integrals over Gaussian orbitals: I

$$\times \sum_{[\mathbf{n}_{b}^{\prime},\mathbf{n}_{b}^{\prime}]} (-1)^{\Delta_{b}} \mathcal{K}(\mathbf{n}_{b} | \mathbf{n}_{b}^{\prime} | \mathbf{n}_{b}^{\prime\prime}) \left(\frac{\beta}{\zeta_{1}}\right)^{2n_{b}^{\prime} + l_{b}^{\prime}} I_{n_{a}^{\prime\prime} l_{a}^{\prime\prime} m_{a}^{\prime\prime}}^{n_{b}^{\prime\prime} l_{b}^{\prime\prime} m_{b}^{\prime\prime}} (\xi_{1}, \mathbf{R}_{ba})$$

$$\times \sum_{[\mathbf{n}_{c}^{\prime},\mathbf{n}_{c}^{\prime\prime}]} (-1)^{\Delta_{c}} \mathcal{K}(\mathbf{n}_{c} | \mathbf{n}_{c}^{\prime} | \mathbf{n}_{c}^{\prime\prime}) \left(\frac{\gamma}{\zeta_{2}}\right)^{2n_{c}^{\prime} + l_{c}^{\prime}}$$

$$\times \sum_{[\mathbf{n}_{c}^{\prime},\mathbf{n}_{c}^{\prime\prime}]} (-1)^{\Delta_{d}} \mathcal{K}(\mathbf{n}_{d} | \mathbf{n}_{d}^{\prime} | \mathbf{n}_{d}^{\prime\prime}) \left(-\frac{\delta}{\zeta_{2}}\right)^{2n_{d}^{\prime} + l_{d}^{\prime}} I_{n_{c}^{\prime\prime} l_{c}^{\prime\prime} m_{c}^{\prime\prime}}^{n_{d}^{\prime\prime} l_{d}^{\prime\prime} m_{d}^{\prime\prime}} (\xi_{2}, \mathbf{R}_{dc})$$

$$\times U_{n_{b}^{\prime} l_{d}^{\prime\prime} m_{d}^{\prime\prime} n_{c}^{\prime\prime} l_{c}^{\prime\prime} m_{c}^{\prime}} (\zeta, \mathbf{R}_{\alpha\beta\gamma\delta})$$

$$(A9)$$

where $\Delta_e = (l'_e + l''_e - l_e)/2$ for e = a, b, c, d, and all the rest of parameters have the same definitions as before. The integral U may be evaluated accordingly,

$$U_{n_{1}l_{1}m_{1},n_{3}l_{3}m_{3}}^{n_{2}l_{2}m_{2},n_{4}l_{4}m_{4}}|LM|l_{1}m_{1},l_{3}m_{3}\rangle\mathcal{C}_{-1,L}^{a}\left(\frac{1}{4\zeta}\right)F_{L}(\zeta R^{2})\mathcal{Y}_{LM}(R) + \sum_{l=l_{\min}}^{L-2}(-1)^{\Delta}\langle l_{2}m_{2},l_{4}m_{4}|lm|l_{1}m_{1},l_{3}m_{3}\rangle\mathcal{C}_{n-1,l}^{a}\left(\frac{1}{4\zeta}\right)\Phi_{n-1,lm}^{b}(\zeta,R)$$
(A10)

where $L = l_1 + l_2 + l_3 + l_4$, $\Delta = (L - l)/2$ and $n = n_1 + n_2 + n_3 + n_4 + \Delta$. The allowed *l* values are those satisfying $l_1 + l_2 + l_3 + l_4 + l =$ even integer.

Appendix B. Molecular integrals over the general SGTOs in coordinate space

As we mentioned in the text, overlap integrals with PWETF as well as nuclear attraction and electron repulsion integrals can also be evaluated in coordinate space without introducing too much complexity. To evaluate overlap integrals with PWETF, we need to expand a product of Gaussian orbitals of the form (6) on two different centres. Using the following identity:

$$\alpha (\boldsymbol{r} - \boldsymbol{A})^2 + \beta (\boldsymbol{r} - \boldsymbol{B})^2 = \zeta (\boldsymbol{r} - \boldsymbol{R}_{\alpha\beta})^2 + \xi R^2$$
(B1)

with $\xi = \alpha\beta/(\alpha + \beta)$, $\zeta = \alpha + \beta$, $R_{\alpha\beta} = (\alpha A + \beta B)/(\alpha + \beta)$ and letting $r - R_{\alpha\beta} = r'$, we obtain the following expansion:

$$\Phi_{n_{a}l_{a}m_{a}}^{*}(\alpha, r - A) \Phi_{n_{b}l_{b}m_{b}}(\beta, r - B)$$

$$= e^{-[\alpha(r - A)^{2} + \beta(r - B)^{2}]} [\mathcal{Y}_{l_{a}m_{a}}^{n_{a}}(r - A)]^{*} \mathcal{Y}_{l_{b}m_{b}}^{n_{b}}(r - B)$$

$$= e^{-\xi R^{2}} e^{-\zeta r'^{2}} \left[\mathcal{Y}_{l_{a}m_{a}}^{n_{a}}\left(r' + \frac{\beta}{\zeta}R\right) \right]^{*} \mathcal{Y}_{l_{b}m_{b}}^{n_{b}}\left(r' - \frac{\alpha}{\zeta}R\right)$$

$$= (4\pi)^{2} e^{-\xi R^{2}} \sum_{[n'_{a},n''_{a}]} \mathcal{K}(n_{a}|n'_{a}|n''_{a}) \left[\mathcal{Y}_{l'_{a}m'_{a}}^{n'_{a}}\left(\frac{\beta}{\zeta}R\right) \right]^{*}$$

$$\times \sum_{[n'_{b},n''_{b}]} \mathcal{K}(n_{b}|n'_{b}|n''_{b}) \mathcal{Y}_{l'_{b}m'_{b}}^{n'_{b}}\left(-\frac{\alpha}{\zeta}R\right)$$

$$\times \sum_{l_{2}} \langle l''_{b}m''_{b}| l''_{a}m''_{a}| l_{2}m_{2}\rangle \Phi_{n_{2}l_{2}m_{2}}^{a}(\zeta,r') \quad \text{with } R = B - A \quad (B2)$$

where $n_2 = n_a'' + n_b'' + \Delta_2$ with $\Delta_2 = (l_a'' + l_b'' - l_2)/2$ and we have used equations (46*a*) and (47*a*). Combining the two solid harmonics \mathcal{Y} with (47*a*), we could obtain a more

symmetric formula,

$$\Phi_{n_{a}l_{a}m_{a}}^{*}(\alpha, \boldsymbol{r} - \boldsymbol{A})\Phi_{n_{b}l_{b}m_{b}}(\beta, \boldsymbol{r} - \boldsymbol{B})$$

$$= (4\pi)^{2} \sum_{[n'_{a}, n''_{a}]} \mathcal{K}(n_{a}|n'_{a}|n''_{a}) \left(\frac{\beta}{\zeta}\right)^{2n'_{a}+l'_{a}} \sum_{[n'_{b}, n''_{b}]} \mathcal{K}(n_{b}|n'_{b}|n''_{b}) \left(-\frac{\alpha}{\zeta}\right)^{2n'_{b}+l'_{b}}$$

$$\times \sum_{l_{1}} \langle l'_{b}m'_{b}|l'_{a}m'_{a}|l_{1}m_{1}\rangle \sum_{l_{2}} \langle l''_{b}m''_{b}|l''_{a}m''_{a}|l_{2}m_{2}\rangle \Phi_{n_{1}l_{1}m_{1}}^{a}(\xi, \boldsymbol{R})\Phi_{n_{2}l_{2}m_{2}}^{a}(\zeta, \boldsymbol{r}')$$
(B3)

where $n_1 = n'_a + n'_b + \Delta_1$ with $\Delta_1 = (l'_a + l'_b - l_1)/2$. If all the coefficients in equation (B3) are collectively written as a single coefficient, the above formula (B3) would look like that obtained by Fieck (1979) using the Talmi transformation. However, it should be noted that formula (B3), though more symmetric, does not bear any computational advantage over formula (B2) and is actually more complicated because of one more summation involved. In the following derivation, formula (B2) will be used exclusively.

Overlap integral with PWETF

$$S_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\alpha,\beta,A,B,p) = \langle \phi_{n_{a}l_{a}m_{a}}(\alpha,r-A)|e^{-i\mathbf{p}\cdot\mathbf{r}}|\phi_{n_{b}l_{b}m_{b}}(\beta,r-B)\rangle$$

$$= \int d\mathbf{r} e^{-i\mathbf{p}\cdot\mathbf{r}} \phi_{n_{a}l_{a}m_{a}}^{*}(\alpha,r-A)\phi_{n_{b}l_{b}m_{b}}(\beta,r-B)$$

$$= (4\pi)^{2}(2\pi)^{3/2}N_{n_{a}l_{a}}(\alpha)N_{n_{b}l_{b}}(\beta)e^{-\xi R^{2}}e^{-i\mathbf{p}\cdot\mathbf{R}_{\alpha\beta}}$$

$$\times \sum_{[\mathbf{n}'_{a},\mathbf{n}''_{a}]} \mathcal{K}(\mathbf{n}_{a}|\mathbf{n}'_{a}|\mathbf{n}''_{a}) \Big[\mathcal{Y}_{l'_{a}m'_{a}}^{n'_{a}}\left(\frac{\beta}{\zeta}R\right)\Big]^{*}$$

$$\times \sum_{[\mathbf{n}'_{b},\mathbf{n}''_{b}]} \mathcal{K}(\mathbf{n}_{b}|\mathbf{n}'_{b}|\mathbf{n}''_{b})\mathcal{Y}_{l'_{b}m'_{b}}^{n'_{b}}\left(-\frac{\alpha}{\zeta}R\right)$$

$$\times \sum_{l} (-i)^{l} \langle l''_{b}m''_{b}|l''_{a}m''_{a}|lm\rangle \mathcal{C}_{nl}^{a}(\zeta)\Phi_{nlm}^{b}\left(\frac{1}{4\zeta},p\right)$$
(B4)

where $N_{nl}(\alpha) = \left[\frac{2(2\alpha)^{2n+l+3/2}}{\Gamma(2n+l+3/2)}\right]^{1/2}$ is the normalization constant, and we have used equations (B2), (4) and (8).

Nuclear attraction integral

$$N_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C}) = \langle \phi_{n_{a}l_{a}m_{a}}(\alpha,\boldsymbol{r}-\boldsymbol{A}) \left| \frac{1}{|\boldsymbol{r}-\boldsymbol{C}|} \left| \phi_{n_{b}l_{b}m_{b}}(\beta,\boldsymbol{r}-\boldsymbol{B}) \right\rangle \\ = \frac{1}{2\pi^{2}} \int \frac{d\boldsymbol{p}}{p^{2}} e^{i\boldsymbol{p}\cdot\boldsymbol{C}} S_{n_{a}l_{a}m_{a}}^{n_{b}l_{b}m_{b}}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{p}) \\ = 8(2\pi)^{3} N_{n_{a}l_{a}}(\alpha) N_{n_{b}l_{b}}(\beta) e^{-\xi R^{2}} \\ \times \sum_{[\boldsymbol{n}'_{a},\boldsymbol{n}''_{a}]} \mathcal{K}(\boldsymbol{n}_{a}|\boldsymbol{n}'_{a}|\boldsymbol{n}''_{a}) \left[\mathcal{Y}_{l'_{a}m'_{a}}^{n'_{a}} \left(\frac{\beta}{\zeta} \boldsymbol{R}_{ba} \right) \right]^{*} \\ \times \sum_{[\boldsymbol{n}'_{b},\boldsymbol{n}''_{b}]} \mathcal{K}(\boldsymbol{n}_{b}|\boldsymbol{n}'_{b}|\boldsymbol{n}''_{b}) \mathcal{Y}_{l'_{b}m'_{b}}^{n'_{b}} \left(-\frac{\alpha}{\zeta} \boldsymbol{R}_{ba} \right) \\ \times \sum_{l} (-1)^{l} \langle l''_{b}m''_{b}|l''_{a}m''_{a}|lm\rangle \mathcal{C}_{nl}^{a}(\zeta) \mathcal{N}_{nlm}(\zeta,\boldsymbol{R}_{\alpha\beta c})$$
(B5)

where $R_{ba} = B - A$, $R_{\alpha\beta c} = R_{\alpha\beta} - C$, and

$$\mathcal{N}_{nlm}(\zeta, \mathbf{R}) = \frac{i^{l}}{(2\pi)^{3/2}} \int \frac{d\mathbf{p}}{p^{2}} e^{-i\mathbf{p}\cdot\mathbf{R}} \Phi^{b}_{nlm}\left(\frac{1}{4\zeta}, \mathbf{p}\right)$$
$$= \binom{n+l+\frac{1}{2}}{n} \mathcal{C}^{a}_{-1,l}\left(\frac{1}{4\zeta}\right) F_{l}(\zeta R^{2}) \mathcal{Y}_{lm}(\mathbf{R})$$
$$+ \sum_{k=1}^{n} \frac{(-1)^{k}}{k!(4\zeta)^{k}} \binom{n+l+1/2}{n-k} \mathcal{C}^{a}_{k-1,l}\left(\frac{1}{4\zeta}\right) \Phi^{b}_{k-1,lm}(\zeta, \mathbf{R})$$
(B6)

where we have used equations (11), (14), (4) and (8) as well as the explicit form of the associated Laguerre polynomial $L_n^{\nu}(z)$ (Gradshteyn and Ryzhik 1980, p 1037)

$$L_n^{\nu}(z) = \sum_{k=0}^n (-1)^k \binom{n+\nu}{n-k} \frac{z^k}{k!}.$$
 (B7)

Electron repulsion integral

 $V_{n_{a}l_{a}m_{a},n_{c}l_{c}m_{c}}^{n_{b}l_{b}m_{b},n_{d}l_{d}m_{d}}(\alpha,\beta,\gamma,\delta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C},\boldsymbol{D})$

$$= 32(2\pi)^{13/2} N_{n_{a}l_{a}}(\alpha) N_{n_{b}l_{b}}(\beta) N_{n_{c}l_{c}}(\gamma) N_{n_{d}l_{d}}(\delta) e^{-(\xi_{1}R_{ba}^{2}+\xi_{2}R_{dc}^{2})} \\ \times \sum_{[n'_{a},n''_{a}]} \mathcal{K}(n_{a}|n'_{a}|n''_{a}) \left[\mathcal{Y}_{l'_{a}m'_{a}}^{n'_{a}} \left(\frac{\beta}{\xi_{1}} R_{ba} \right) \right]^{*} \\ \times \sum_{[n'_{b},n''_{b}]} \mathcal{K}(n_{b}|n'_{b}|n''_{b}) \mathcal{Y}_{l'_{b}m'_{b}}^{n'_{b}} \left(-\frac{\alpha}{\xi_{1}} R_{ba} \right) \\ \times \sum_{[n'_{c},n''_{c}]} \mathcal{K}(n_{c}|n'_{c}|n''_{c}) \left[\mathcal{Y}_{l'_{c}m'_{c}}^{n'_{c}} \left(\frac{\delta}{\xi_{2}} R_{dc} \right) \right]^{*} \\ \times \sum_{[n'_{d},n''_{d}]} \mathcal{K}(n_{d}|n'_{d}|n''_{d}) \mathcal{Y}_{l'_{d}m'_{d}}^{n'_{d}} \left(-\frac{\gamma}{\xi_{2}} R_{dc} \right) \\ \times \sum_{[n'_{d},n''_{d}]} \mathcal{K}(n_{d}|n''_{d}|n''_{d}) \mathcal{Y}_{l'_{d}m'_{d}}^{n'_{d}} \left(-\frac{\gamma}{\xi_{2}} R_{dc} \right) \\ \times \sum_{l_{1}} (-1)^{l_{1}} \langle l''_{b}m''_{b}|l''_{a}m''_{a}|l_{1}m_{1}\rangle \mathcal{C}_{n_{1}l_{1}}^{a}(\xi_{1}) \\ \times \sum_{l_{2}} \langle l''_{d}m''_{d}|l''_{c}m''_{c}|l_{2}m_{2}\rangle \mathcal{C}_{n_{2}l_{2}}^{a}(\xi_{2}) \mathcal{V}_{n_{1}l_{1}m_{1}}^{n_{2}l_{2}m_{2}}(\xi_{1},\xi_{2},R_{\alpha\beta\gamma\delta})$$
(B8)

where all the parameters have been defined in (36a)-(36c), and

$$\mathcal{V}_{n_{1}l_{1}m_{1}}^{n_{2}l_{2}m_{2}}(\zeta_{1},\zeta_{2},\boldsymbol{R}) = \frac{\mathbf{i}^{l_{1}-l_{2}}}{(2\pi)^{3/2}} \int \frac{\mathrm{d}\boldsymbol{p}}{\boldsymbol{p}^{2}} e^{-\mathbf{i}\boldsymbol{p}\cdot\boldsymbol{R}} \Phi_{n_{1}l_{1}m_{1}}^{b} \left(\frac{1}{4\zeta_{1}},\boldsymbol{p}\right) \Phi_{n_{2}l_{2}m_{2}}^{b} \left(\frac{1}{4\zeta_{2}},-\boldsymbol{p}\right) \\
= \langle LM|l_{1}m_{1}|l_{2}m_{2}\rangle \mathcal{D}_{n_{1}n_{2},0}^{l_{1}l_{2}} \left(\frac{1}{4\zeta_{1}},\frac{1}{4\zeta_{2}}\right) \mathcal{C}_{-1,L}^{a} \left(\frac{1}{4\zeta}\right) F_{L}(\zeta R^{2}) \mathcal{Y}_{LM}(\boldsymbol{R}) \\
+ \sum_{l} \langle lm|l_{1}m_{1}|l_{2}m_{2}\rangle \\
\times \sum_{k(n\neq 0)}^{n_{1}+n_{2}} (-1)^{n} \mathcal{D}_{n_{1}n_{2},k}^{l_{1}l_{2}} \left(\frac{1}{4\zeta_{1}},\frac{1}{4\zeta_{2}}\right) \mathcal{C}_{n-1,l}^{a} \left(\frac{1}{4\zeta}\right) \Phi_{n-1,lm}^{b}(\zeta,\boldsymbol{R}) \tag{B9}$$

where $L = l_1 + l_2$, $n = (l_1 + l_2 - l)/2 + k$ and \mathcal{D} is determined through the product expansion of the two associated Laguerre polynomials, i.e.

$$L_{n_1}^{\nu_1}(a_1z)L_{n_2}^{\nu_2}(a_2z) = \sum_{k=0}^{n_1+n_2} \mathcal{D}_{n_1n_2,k}^{l_1l_2}(a_1,a_2)(-z)^k$$
(B10)

with $v_i = l_i + \frac{1}{2}$. By means of (B7), we can find

$$\mathcal{D}_{n_1 n_2, k}^{l_1 l_2}(a_1, a_2) = \sum_{j=\max(0, k-n_2)}^{\min(n_1, k)} \frac{a_1^j a_2^{k-j}}{j!(k-j)!} \binom{n_1 + \nu_1}{n_1 - j} \binom{n_2 + \nu_2}{n_2 - k + j}.$$
 (B11)

As can be seen, the formula for \mathcal{V} , equation (B10), is much more complicated than the one for U, equation (37). Therefore, formula (35) is expected to more effective for computation than (B9), especially, when one can evaluate the angular parts $\langle l_2m_2, l_4m_4|lm|l_1m_1, l_3m_3\rangle$ before hand and store them for later use. The formulae for \mathcal{N} and \mathcal{V} are similar to those obtained by Krauss (1964). Nevertheless, they are not recommended for the evaluation of nuclear attraction and electron repulsion integrals.

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