J. Phys. B: At. Mol. Opt. Phys. **30** (1997) 2549–2567. Printed in the UK PII: S0953-4075(97)78167-7

Molecular integrals over spherical Gaussian-type orbitals: II. Modified with plane-wave phase factors

Jiyun Kuang and C D Lin
Department of Physics, Kansas State University, Manhattan, KS 66506, USA

Received 24 September 1996

Abstract. Multi-centre molecular integrals over spherical Gaussian-type orbitals modified with plane-wave phase factors, which arise in the close-coupling treatment of ion–atom collisions as well as in some molecular structure calculations, are evaluated analytically in closed form by means of the Fourier transform and the addition theorem of harmonic polynomials. The resulting integral formulae for spherical Gaussian orbitals, consisting of vector-coupling coefficients and well known functions, are more compact than those for their counterparts, Cartesian Gaussian orbitals. Practical techniques are suggested for the efficient implementation of the present formulae.

1. Introduction

In the impact parameter close-coupling treatment of ion–atom collisions, basis orbitals modified with plane-wave phase factors were first introduced by Bates and McCarroll (1958) to meet the asymptotic boundary conditions in reaction channels represented by the basis orbitals. The physical significance of the phase factors, also called electronic translational factors (ETF), is related to the Galilean invariance when a transformation is made from one frame to another. Failure to include the proper phase factors in basis orbitals leads to nonvanishing interactions in the asymptotic region and cross sections of the individual channel depending on the choice of the origin of electronic coordinates. In molecular structure calculations the s-type basis orbitals with plane-wave phase factors can simulate orbitals with larger angular momentum quantum numbers (Allison *et al* 1973). These orbitals also arise when molecular integrals are evaluated in momentum space (see our preceding paper, Kuang and Lin (1997), hereafter referred to as paper I) as well as when the relativistic interactions are included in molecular integrals.

Multi-centre molecular integrals over basis orbitals, modified with plane-wave phase factors containing $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})$, cannot be completely reduced to analytic expressions, and they are time consuming to compute if the basis orbitals are expanded in terms of Slater-type functions. The existing computational methods of the integrals over Slater-type functions have been reviewed by Bransden and McDowell (1992, appendix E). For one-electron systems, the integrals over Slater-type functions can be evaluated efficiently with the proper care being taken for one-dimensional numerical quadrature (Kuang and Lin 1996). However, for many-electron systems, the evaluation of electron repulsion integrals over Slater-type functions has proven to be a formidable task when the phase factors are present, particularly for the electron exchange term. In contrast, all the multi-centre molecular integrals with plane-wave phase factors, including the difficult electron repulsion term, can be evaluated

0953-4075/97/112549+19$19.50

analytically (Allison *et al* 1973, Errea *et al* 1979, Obara and Saika 1988) if basis orbitals are expressed in terms of Gaussian-type functions. The obvious drawback of Gaussian orbitals is that they exhibit neither cusps at the nuclei nor exponential decay at large distances. Although it is known (Dose and Semini 1974, Huzinaga 1985) that more Gaussian orbitals are required to achieve the equivalent accuracy as Slater functions, the simplicity of Gaussian integrals more than compensates for this.

Following the classic work by Boys (1950), Cartesian Gaussian-type orbitals (CGTOs) of the form $\phi_{nlm}(\alpha, \boldsymbol{r}) = N_{nlm}(\alpha)x^n y^l z^m \mathrm{e}^{-\alpha r^2}$ have been used almost by default in molecular structure calculations (for a recent review see Gill (1994)) as well as in the close-coupling treatment of ion–atom collisions (Errea *et al* 1979). This is because molecular integrals over CGTOs can be evaluated in a straightforward manner. However, the obvious disadvantage of CGTOs is that they do not possess spherical symmetry for $n + l + m \geqslant 2$ and therefore extra work is necessary in order to extract the spherical symmetry orbitals (Huzinaga 1985). As mentioned in paper I, spherical Gaussian-type orbitals (SGTOs) have a few obvious advantages: (i) spherical symmetry properties and the geometric dependence can be taken into account naturally; (ii) the well developed vector-coupling coefficients can be applied fruitfully to derive compact formulae for all molecular integrals; (iii) the resulting formulae support the efficient computation of the integrals over contracted Gaussian orbitals.

Multi-centre molecular integrals over the general Cartesian Gaussian orbitals modified with plane-wave phase factors have been considered by Errea *et al* (1979) and by Obara and Saika (1988). The closed-form formulae for nuclear attraction and electron repulsion integrals obtained by Errea *et al* contain a large number of sums which slow down the numerical computation of the formulae significantly, particularly for high angular momentum orbitals. Obara and Saika derived recurrence relations to evaluate the integrals of high angular momentum orbitals in terms of integrals, involving lower angular momentum orbitals. Since recurrence formulae require the evaluation of unwanted integrals of lower angular momentum, they need not always guarantee efficient algorithms, especially for relatively large angular momentum orbitals. In this paper we present closed-form formulae for all the multi-centre molecular integrals over spherical Gaussian orbitals with plane-wave phase factors using the same tools as in paper I. The resulting formulae are more compact than those obtained by Errea *et al* and are expected to be efficient in computation for Gaussian orbitals with arbitrary angular momentum. Based on our analysis, contracted Gaussian orbitals may be used effectively in the close-coupling calculations of ion–atom collisions.

2. Basic Gaussian functions and their properties

As in paper I, we shall only consider two types of basic (unnormalized) Gaussian functions:

$$\Phi^a_{nlm}(\alpha, \boldsymbol{r}) = \mathrm{e}^{-\alpha r^2}(\boldsymbol{r}\cdot\boldsymbol{r})^n \mathcal{Y}_{lm}(\boldsymbol{r}) \tag{1}$$

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

where $\mathcal{Y}_{lm}(\boldsymbol{r})$ is the solid harmonic (Biedenharn and Louck 1981, p 71) and $L_n^\nu(z)$ is the associated Laguerre polynomial. If these functions are used as basis orbitals, $\boldsymbol{r}$ denotes the real position vector of an electron in three-dimensional space and n is a natural number; otherwise, $\boldsymbol{r}$ is a complex vector and the index n in (1) may start from -1. Although Φ^b_{nlm} is more complicated than Φ^a_{nlm}, its Fourier transform is much simpler than that of Φ^a_{nlm}. In fact, they are reciprocal with respect to each other, see equations (8) and (9) in paper I. To simplify the reference notation, we will use (I.8) to indicate equation (8) of paper I.

Introducing harmonic polynomials

$$\mathcal{Y}^n_{lm}(\boldsymbol{r}) = (\boldsymbol{r}\cdot\boldsymbol{r})^n \mathcal{Y}_{lm}(\boldsymbol{r}) \tag{3}$$

$$\mathcal{L}^n_{lm}(\boldsymbol{r}) = L^{l+1/2}_n(\boldsymbol{r}\cdot\boldsymbol{r})\mathcal{Y}_{lm}(\boldsymbol{r}) \tag{4}$$

for $n \geqslant 0$, then Gaussian orbitals in equations (1) and (2) can be written as

$$\Phi^a_{nlm}(\alpha, \boldsymbol{r}) = \mathrm{e}^{-\alpha r^2}\mathcal{Y}^n_{lm}(\boldsymbol{r}) \tag{5}$$

$$\Phi^b_{nlm}(\alpha, \boldsymbol{r}) = \alpha^{-l/2}\mathrm{e}^{-\alpha r^2}\mathcal{L}^n_{lm}(\sqrt{\alpha}\boldsymbol{r})\,. \tag{6}$$

The harmonic polynomials defined in (3) and (4) possess unique translational properties (addition theorems) (Niukkanen and Gribov 1983, Niukkanen 1984), which were applied fruitfully to derive compact formulae for multi-centre molecular integrals over spherical Gaussian orbitals (paper I). Since the previous derivation procedure (Niukkanen and Gribov 1983, Niukkanen 1984) of the addition theorems for these polynomials does not apply to the complex arguments, a more general derivation is presented in appendix A.

It is trivial to show (Allison *et al* 1973, Dose and Semini 1974) that an s-type Gaussian orbital modified with a plane-wave phase factor is still an s-type Gaussian orbital but with a complex centre, i.e.

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\mathrm{e}^{-\alpha(\boldsymbol{r}-\boldsymbol{R})^2} = \mathcal{N}\mathrm{e}^{-\alpha(\boldsymbol{r}-\boldsymbol{R}^\dagger)^2} \tag{7}$$

where $\boldsymbol{R}^\dagger = \boldsymbol{R} + \mathrm{i}\boldsymbol{k}/2\alpha$ and $\mathcal{N} = \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R} - k^2/4\alpha)$. By means of the addition theorems of harmonic polynomials, equations (A8) and (A13) of appendix A, it follows that the above spherical Gaussian orbital modified with a plane-wave phase factor can be reduced to a linear combination of Gaussian orbitals with a complex centre $\boldsymbol{R}^\dagger$:

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\Phi^a_{nlm}(\alpha, \boldsymbol{r}-\boldsymbol{R}) = 4\pi\mathcal{N}\sum_{[\boldsymbol{n}_1,\boldsymbol{n}_2]}\mathcal{K}(\boldsymbol{n}|\boldsymbol{n}_1|\boldsymbol{n}_2)\mathcal{Y}^{n_1}_{l_1m_1}\left(\frac{\mathrm{i}\boldsymbol{k}}{2\alpha}\right)\Phi^a_{n_2l_2m_2}(\alpha, \boldsymbol{r}-\boldsymbol{R}^\dagger) \tag{8}$$

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\Phi^b_{nlm}(\alpha, \boldsymbol{r}-\boldsymbol{R}) = 4\pi\mathcal{N}'\sum_{[\boldsymbol{n}_1,\boldsymbol{n}_2]}\mathcal{B}(\boldsymbol{n}|\boldsymbol{n}_2|\boldsymbol{n}_1)\mathcal{Y}^{n_1}_{l_1m_1}\left(\frac{\mathrm{i}\boldsymbol{k}}{2\sqrt{\alpha}}\right)\Phi^b_{n_2l_2m_2}(\alpha, \boldsymbol{r}-\boldsymbol{R}^\dagger) \tag{9}$$

where $\mathcal{N}' = \alpha^{-l/2}\mathcal{N}$ and $\boldsymbol{n}$ stands for the triad of quantum numbers (n, l, m), see appendix A. It is interesting to note that one can also expand the product, $\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\Phi^b_{nlm}$, in terms of Φ^a_{nlm} by exchanging the two vectors in (A13):

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\Phi^b_{nlm}(\alpha, \boldsymbol{r}-\boldsymbol{R}) = 4\pi\mathcal{N}'\sum_{[\boldsymbol{n}_1,\boldsymbol{n}_2]}\mathcal{B}(\boldsymbol{n}|\boldsymbol{n}_1|\boldsymbol{n}_2)\alpha^{n_2+l_2/2}\mathcal{L}^{n_1}_{l_1m_1}\left(\frac{\mathrm{i}\boldsymbol{k}}{2\sqrt{\alpha}}\right)\Phi^a_{n_2l_2m_2}(\alpha, \boldsymbol{r}-\boldsymbol{R}^\dagger)\,. \tag{10}$$

If molecular integrals are evaluated in momentum space, equation (10) does not bear any advantage over equation (9) since the momentum representation of Φ^a is more complicated than that of Φ^b. As in paper I, it is of practical interest to consider the special Gaussian orbitals with $n = 0$, i.e. $\Phi_{lm}(\alpha, \boldsymbol{r}) = \mathrm{e}^{-\alpha r^2}\mathcal{Y}_{lm}(\boldsymbol{r})$. In this case, the above three equations (8)–(10) become identical and therefore can be written as a single equation

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\Phi_{lm}(\alpha, \boldsymbol{r}-\boldsymbol{R}) = 4\pi\mathcal{N}\sum_{l_1m_1}G(lm|l_1m_1)\mathcal{Y}_{l_1m_1}\left(\frac{\mathrm{i}\boldsymbol{k}}{2\alpha}\right)\Phi_{l_2m_2}(\alpha, \boldsymbol{r}-\boldsymbol{R}^\dagger) \tag{11}$$

where $l_2 = l - l_1, m_2 = m - m_1$ and G is defined in equation (I.15*b*). Clearly, the transformation for these special Gaussian orbitals, equation (11), is simpler than that for the general SGTO, equations (8)–(10), because it only contains two summations. In contrast, the similar transformation for CGTOs needs three summations (Obara and Saika 1988).

Interestingly, one can also expand Gaussian orbitals $\Phi_{lm}(\alpha, \boldsymbol{r} - \boldsymbol{R})$ directly in terms of $\Phi_{lm}(\alpha, \boldsymbol{r})$, i.e.

$$\Phi_{lm}(\alpha, \boldsymbol{r} - \boldsymbol{R}) = 4\pi \mathrm{e}^{-\alpha R^2} \sum_{l_1 m_1} G(lm|l_1 m_1) \mathcal{Y}_{l_1 m_1}(-\boldsymbol{R}) \mathrm{e}^{2\alpha \boldsymbol{R}\cdot\boldsymbol{r}} \Phi_{l_2 m_2}(\alpha, \boldsymbol{r}) \,. \tag{12}$$

Thus we obtain an alternative expansion to equation (11),

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \Phi_{lm}(\alpha, \boldsymbol{r} - \boldsymbol{R}) = 4\pi \mathrm{e}^{-\alpha R^2} \sum_{l_1 m_1} G(lm|l_1 m_1) \mathcal{Y}_{l_1 m_1}(-\boldsymbol{R}) \mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}} \Phi_{l_2 m_2}(\alpha, \boldsymbol{r}) \tag{13}$$

where $\boldsymbol{p} = \boldsymbol{k} - 2\mathrm{i}\alpha\boldsymbol{R}$. The alternative expansions to equations (8)–(10) follow in the same way. These transformation formulae, equations (8)–(13), will definitely facilitate the evaluation of multi-centre molecular integrals over SGTOs modified with plane-wave phase factors. Specifically, equation (13) may be used when the integrals are evaluated in coordinate space, while equations (8)–(11) are used when they are computed in momentum space.

Before proceeding, we need to justify that the basic integral formulae, equations (I.8), (I.9) and (I.14), still hold true for complex arguments $\boldsymbol{p}$. As in paper I, the symmetric version of the Fourier transformation is used. Consider the following Fourier transform of Gaussian orbitals (5):

$$\widetilde{\Phi}^a_{nlm}(\alpha, \boldsymbol{p}) = \frac{1}{(2\pi)^{3/2}} \int \mathrm{d}\boldsymbol{r}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}} \Phi^a_{nlm}(\alpha, \boldsymbol{r}) \tag{14}$$

where $\boldsymbol{p}$, in general, is a complex vector, while $\boldsymbol{r}$ is a real vector. Note that the well known Rayleigh (partial-wave) expansion of a plane wave cannot be used here any more. Instead, we really have to use expansion (A5) of appendix A, which is valid for complex vectors. Substituting (A5) into (14), we obtain

$$\begin{aligned}
\widetilde{\Phi}^a_{nlm}(\alpha, \boldsymbol{p}) &= \frac{1}{(2\pi)^{3/2}} \sum_{kl'm'} a_{kl'} \mathcal{Y}^k_{l',m'}(-\mathrm{i}\boldsymbol{p}) \int \mathrm{d}\boldsymbol{r}\, (-1)^{m'} \mathcal{Y}^k_{l',-m'}(\boldsymbol{r}) \mathcal{Y}^n_{lm}(\boldsymbol{r}) \mathrm{e}^{-\alpha r^2} \\
&= \frac{1}{(2\pi)^{3/2}} \sum_{k=0}^{\infty} a_{kl} \mathcal{Y}^k_{lm}(-\mathrm{i}\boldsymbol{p}) \int_0^\infty \frac{\mathrm{d}(r^2)}{2} (r^2)^{k+n+l+1/2} \mathrm{e}^{-\alpha r^2} \\
&= \frac{1}{(2\pi)^{3/2}} \mathcal{Y}_{lm}(-\mathrm{i}\boldsymbol{p}) \sum_{k=0}^{\infty} \frac{2\pi^{3/2}(-\boldsymbol{p}\cdot\boldsymbol{p})^k}{2^{2k+l} k!\, \Gamma(k + l + \frac{3}{2})} \frac{\Gamma(k + n + l + \frac{3}{2})}{2\alpha^{k+n+l+3/2}} \\
&= \frac{2^n \mathcal{Y}_{lm}(-\mathrm{i}\boldsymbol{p})}{(2\alpha)^{n+l+3/2}} \frac{\Gamma(n + l + \frac{3}{2})}{\Gamma(l + \frac{3}{2})} {}_1F_1\Big(n + l + \frac{3}{2}, l + \frac{3}{2}, -\frac{\boldsymbol{p}\cdot\boldsymbol{p}}{4\alpha}\Big)
\end{aligned}$$

where we have used the orthonormal property of spherical harmonics, and the integral formula $\int_0^\infty x^{\nu-1} \mathrm{e}^{-\mu x}\, \mathrm{d}x = \Gamma(\nu)/\mu^\nu$ for $\mathrm{Re}(\mu) > 0$ and $\mathrm{Re}(\nu) > 0$ (Gradshteyn and Ryzhik 1980, p 317). Now we need to distinguish between two different cases, i.e. $n = -1$ and $n \geqslant 0$, in which the confluent hypergeometric function ${}_1F_1(n + l + \frac{3}{2}, l + \frac{3}{2}, -z)$ will be reduced to the different known functions. For $n = -1$, using the formula $F_l(z) = (1/(2l + 1))\,{}_1F_1(l + \frac{1}{2}, l + \frac{3}{2}, -z)$, where $F_l(z)$ is the well known function (Shavitt 1963), we obtain

$$\widetilde{\Phi}^a_{-1,lm}(\alpha, \boldsymbol{p}) = (-\mathrm{i})^l \mathcal{C}^a_{-1,l}(\alpha) F_l\Big(\frac{p^2}{4\alpha}\Big) \mathcal{Y}_{lm}(\boldsymbol{p}) \tag{15}$$

where we have defined $p^2 = \boldsymbol{p}\cdot\boldsymbol{p}$ and $\mathcal{C}^a_{-1,l}(\alpha) = 1/(2\alpha)^{l+1/2}$. As can be seen, this formula has exactly the same form as $\boldsymbol{p}$ is a real vector (compare equation (I.14)). For $n \geqslant 0$, using ${}_1F_1(\alpha, \gamma, -z) = \mathrm{e}^{-z}\,{}_1F_1(\gamma - \alpha, \gamma, z)$ and $L^\nu_n(z) = \frac{\Gamma(n+\nu+1)}{n!\,\Gamma(\nu+1)}\,{}_1F_1(-n, \nu + 1, z)$, we have

$$\widetilde{\Phi}^a_{nlm}(\alpha, \boldsymbol{p}) = (-\mathrm{i})^l \mathcal{C}^a_{nl}(\alpha) \Phi^b_{nlm}\Big(\frac{1}{4\alpha}, \boldsymbol{p}\Big) \tag{16}$$

where $\mathcal{C}^{a}_{nl}(\alpha) = 2^n n!/(2\alpha)^{n+l+3/2}$, as in paper I. Similarly, we can prove

$$\widetilde{\Phi}^{b}_{nlm}(\alpha, \boldsymbol{p}) = (-\mathrm{i})^l \mathcal{C}^{b}_{nl}(\alpha)\Phi^{a}_{nlm}\left(\frac{1}{4\alpha}, \boldsymbol{p}\right) \tag{17}$$

with $\mathcal{C}^{b}_{nl}(\alpha) = 1/2^n n!(2\alpha)^{n+l+3/2}$. In the case of $n = 0$, we have $\mathcal{C}^{a}_{0l}(\alpha) = \mathcal{C}^{b}_{0l}(\alpha) \Rightarrow \mathcal{C}_l(\alpha)$.

3. Molecular integrals over spherical Gaussian orbitals—modified with plane-wave phase factors

As in paper I, we shall mainly consider the special SGTOs, which have exactly the same form in both coordinate and momentum space,

$$\phi_{lm}(\alpha, \boldsymbol{r}) = N_l(\alpha)\Phi_{lm}(\alpha, \boldsymbol{r}) \qquad \widetilde{\phi}_{lm}(\alpha, \boldsymbol{p}) = (-\mathrm{i})^l \widetilde{N}_l(\alpha)\Phi_{lm}\left(\frac{1}{4\alpha}, \boldsymbol{p}\right) \tag{18}$$

where $N_l(\alpha) = [2(2\alpha)^{l+3/2}/\Gamma(l+\frac{3}{2})]^{1/2}$ and $\widetilde{N}_l(\alpha) = N_l(\alpha)\mathcal{C}_l(\alpha)$ are the normalization constants in coordinate and momentum space, respectively. We choose to do so because these SGTOs of the form (18) have been widely used in real applications, and the resulting integral formulae for the special SGTOs are much simpler than those for the general SGTOs. However, the integral formulae for the general SGTOs can be obtained straightforwardly by making some simple modifications of the corresponding formulae for the special SGTOs (refer to paper I).

3.1. Overlap integrals with ETF

The two-centre overlap integrals with ETF arise in the close-coupling treatment of ion–atom collisions and in the evaluation of three-centre nuclear attraction and four-centre electron repulsion integrals. As can be seen from the previous section, Gaussian functions are the natural choice of the basis orbitals when ETF is presented. The overlap integrals with ETF over Gaussian orbitals have been evaluated in paper I in a different context. We shall now compute them using the technique developed in the previous section,

$$\begin{aligned}
S^{l_b m_b}_{l_a m_a}(\alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{k}) &= \langle \phi_{l_a m_a}(\alpha, \boldsymbol{r}-\boldsymbol{A})|\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}|\phi_{l_b m_b}(\beta, \boldsymbol{r}-\boldsymbol{B})\rangle \\
&= \langle \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\phi_{l_a m_a}(\alpha, \boldsymbol{r}-\boldsymbol{A})|\phi_{l_b m_b}(\beta, \boldsymbol{r}-\boldsymbol{B})\rangle \\
&= 4\pi N_{l_a}(\alpha)N_{l_b}(\beta)\mathcal{N}^{*}_{A}\sum_{l_1 m_1} G(l_a m_a|l_1 m_1)\mathcal{Y}^{*}_{l_1 m_1}\left(\frac{\mathrm{i}\boldsymbol{k}}{2\alpha}\right) \\
&\quad\times\langle \Phi_{l_2 m_2}(\alpha, \boldsymbol{r}-\boldsymbol{A}^{\dagger})|\Phi_{l_b m_b}(\beta, \boldsymbol{r}-\boldsymbol{B})\rangle \\
&= (-1)^{l_b} 4\pi(2\pi)^{3/2} N_{l_a}(\alpha)\widetilde{N}_{l_b}(\beta)\mathcal{N}^{*}_{A} \\
&\quad\times\sum_{l_1 m_1} G(l_a m_a|l_1 m_1)\mathcal{Y}^{*}_{l_1 m_1}\left(\frac{\mathrm{i}\boldsymbol{k}}{2\alpha}\right)\mathcal{C}_{l_2}(\alpha) I^{l_b m_b}_{l_2 m_2}(\xi, \boldsymbol{R}^{\dagger})
\end{aligned} \tag{19}$$

where $\boldsymbol{A}^{\dagger} = \boldsymbol{A} + \mathrm{i}\boldsymbol{k}/2\alpha, \boldsymbol{R}^{\dagger} = \boldsymbol{B} - (\boldsymbol{A}^{\dagger})^{*} = \boldsymbol{R} + \mathrm{i}\boldsymbol{k}/2\alpha, \boldsymbol{R} = \boldsymbol{B} - \boldsymbol{A}^{*}, \xi = \alpha\beta/(\alpha+\beta), \widetilde{N}_{l_b}(\beta) = N_{l_b}(\beta)\mathcal{C}_{l_b}(\beta), \mathcal{N}^{*}_{A} = \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{A}^{*} - k^2/4\alpha)$, and we have used equations (11) and (18). Here we have assumed that $\boldsymbol{A}$ and $\boldsymbol{B}$ are generally complex vectors and $\boldsymbol{A}^{*}$ denotes the complex conjugate of $\boldsymbol{A}$. In addition, we have also used formula (I.18) for the overlap integral without ETF. Integral $I^{l_2 m_2}_{l_1 m_1}(\xi, \boldsymbol{R})$ was defined in equation (I.19). As has been justified in the previous section, the evaluation procedure for this integral given in paper I is valid for the complex vector $\boldsymbol{R}^{\dagger}$, i.e.

$$I^{l_2 m_2}_{l_1 m_1}(\xi, \boldsymbol{R}^{\dagger}) = \sum_{l}(-1)^n \langle l_2 m_2|l_1 m_1|lm\rangle \mathcal{C}^{a}_{nl}\left(\frac{1}{4\xi}\right)\Phi^{b}_{nlm}(\xi, \boldsymbol{R}^{\dagger}) \tag{20}$$

where $n = (l_1 + l_2 - l)/2$. For comparison, we shall generalize the previous formula for S with real centres, equation (I.29), to the one with complex centres:

$$\begin{aligned}
S^{l_b m_b}_{l_a m_a}(\alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{k}) &= (-1)^{l_b}(4\pi)^2(2\pi)^{3/2}\widetilde{N}_{l_a}(\alpha)\widetilde{N}_{l_b}(\beta)\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{\alpha\beta}}\mathrm{e}^{-k^2/(4\zeta)} \\
&\quad\times \sum_{l'_a, m'_a} \mathrm{i}^{l'_a} G(l_a m_a | l'_a m'_a)\mathcal{Y}^*_{l'_a m'_a}\Big(-\frac{\alpha}{\zeta}\boldsymbol{k}\Big) \\
&\quad\times \sum_{l'_b, m'_b} \mathrm{i}^{l'_b} G(l_b m_b | l'_b m'_b)\mathcal{Y}_{l'_b m'_b}\Big(\frac{\beta}{\zeta}\boldsymbol{k}\Big) I^{l''_b m''_b}_{l''_a m''_a}(\xi, \boldsymbol{R})
\end{aligned} \tag{21}$$

where $l''_e = l_e - l'_e$ for $e = a$ and b, $\zeta = \alpha + \beta$, $\boldsymbol{R} = \boldsymbol{B} - \boldsymbol{A}^*$ and $\boldsymbol{R}_{\alpha\beta} = (\alpha\boldsymbol{A}^* + \beta\boldsymbol{B})/(\alpha + \beta)$. It is clear that formula (19) is apparently more compact than formula (21). However, formula (19) explicitly requires complex operations even if both $\boldsymbol{A}$ and $\boldsymbol{B}$ are real vectors. In contrast, use of formula (21) may avoid complex operations in this special case by taking proper care of the i^l terms. It is also possible to avoid complex operations with the use of (19) by expanding $\Phi^b_{nlm}(\xi, \boldsymbol{R}^\dagger)$ in terms of $\Phi^b_{nlm}(\xi, \boldsymbol{R})$ and $\mathcal{Y}^n_{lm}(\mathrm{i}\boldsymbol{k}/2\alpha)$ (refer to equation (11)). But the resulting formula is more complicated than formula (21). Since the molecular integrals with ETF are complex, complex operations are inevitable in the evaluation of other integrals, for example, nuclear attraction and electron repulsion integrals.

3.2. *Kinetic energy integrals with ETF*

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

$$\begin{aligned}
K^{l_b m_b}_{l_a m_a}(\alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{k}) &= \langle \phi_{l_a m_a}(\alpha, \boldsymbol{r} - \boldsymbol{A}) | \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\{-\tfrac{1}{2}\nabla^2_{\boldsymbol{r}}\} | \phi_{l_b m_b}(\beta, \boldsymbol{r} - \boldsymbol{B})\rangle \\
&= -\tfrac{1}{2}\nabla^2_{\boldsymbol{B}}\langle \phi_{l_a m_a}(\alpha, \boldsymbol{r} - \boldsymbol{A}) | \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} | \phi_{l_b m_b}(\beta, \boldsymbol{r} - \boldsymbol{B})\rangle \\
&= -\tfrac{1}{2}\nabla^2_{\boldsymbol{B}} S^{l_b m_b}_{l_a m_a}(\alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{k}) \\
&= (-1)^{l_b}(2\pi)^{5/2} N_{l_a}(\alpha)\widetilde{N}_{l_b}(\beta)\mathcal{N}^*_A \\
&\quad\times \sum_{l_1 m_1} G(l_a m_a | l_1 m_1)\mathcal{Y}^*_{l_1 m_1}\Big(\frac{\mathrm{i}\boldsymbol{k}}{2\alpha}\Big)\mathcal{C}_{l_2}(\alpha)\mathcal{K}^{l_b m_b}_{l_2 m_2}(\xi, \boldsymbol{R}^\dagger)
\end{aligned} \tag{22}$$

where we have used equation (19), and all the parameters have the same meaning as in (19). The $\mathcal{K}$ integral is the same as before, but with the complex vector $\boldsymbol{R}^\dagger$:

$$\begin{aligned}
\mathcal{K}^{l_2 m_2}_{l_1 m_1}(\xi, \boldsymbol{R}^\dagger) &= -\nabla^2_{\boldsymbol{B}} I^{l_2 m_2}_{l_1 m_1}(\xi, \boldsymbol{R}^\dagger) \\
&= \sum_l (-1)^n \langle l_2 m_2 | l_1 m_1 | l m\rangle \mathcal{C}^a_{n+1,l}\Big(\frac{1}{4\xi}\Big)\Phi^b_{n+1,lm}(\xi, \boldsymbol{R}^\dagger)
\end{aligned} \tag{23}$$

where $n = (l_1 + l_2 - l)/2$ as before. It is of interest to note that the kinetic energy integrals can also be evaluated in terms of equation (21) since the derivative with respect to $\boldsymbol{B}$ is straightforward. Thus, we have

$$\begin{aligned}
K^{l_b m_b}_{l_a m_a}(\alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{k}) &= \tfrac{1}{2}(-1)^{l_b}(4\pi)^2(2\pi)^{3/2}\widetilde{N}_{l_a}(\alpha)\widetilde{N}_{l_b}(\beta)\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{\alpha\beta}}\mathrm{e}^{-k^2/(4\zeta)} \\
&\quad\times \sum_{l'_a, m'_a} \mathrm{i}^{l'_a} G(l_a m_a | l'_a m'_a)\mathcal{Y}^*_{l'_a m'_a}\Big(-\frac{\alpha}{\zeta}\boldsymbol{k}\Big) \\
&\quad\times \sum_{l'_b, m'_b} \mathrm{i}^{l'_b} G(l_b m_b | l'_b m'_b)\mathcal{Y}_{l'_b m'_b}\Big(\frac{\beta}{\zeta}\boldsymbol{k}\Big)\Big[\Big(\frac{\beta\boldsymbol{k}}{\zeta}\Big)^2 I^{l''_b m''_b}_{l''_a m''_a}(\xi, \boldsymbol{R}) \\
&\quad + \frac{2\mathrm{i}\beta}{\zeta}\sum_\mu (-1)^\mu k_{-\mu}\mathcal{T}^{l''_b m''_b}_{l''_a m''_a}(1\mu, \xi, \boldsymbol{R}) + \mathcal{K}^{l''_b m''_b}_{l''_a m''_a}(\xi, \boldsymbol{R})\Big]
\end{aligned} \tag{24}$$

where we have introduced the spherical tensor notation for the scalar product of two vectors, i.e. $\boldsymbol{k} \cdot \nabla_{\boldsymbol{B}} = \sum_\mu (-1)^\mu k_{-\mu} \mathcal{Y}_{1\mu}(\nabla_{\boldsymbol{B}})$. Both formulae (22) and (24) for kinetic energy integrals have the same respective merits as those, formulae (19) and (21), for overlap integrals.

3.3. Tensor operator integrals with ETF

The two-centre integrals of tensor operators $\mathcal{Y}_{k\mu}(\nabla)$ with ETF over Gaussian orbitals arise in the dynamical coupling matrix elements of the close-coupling treatment of ion–atom collisions as well as in the study of electronic properties of molecules. They are of the form

$$\begin{aligned} T^{l_b m_b}_{l_a m_a}(k\mu, \alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{k}) &= \langle \phi_{l_a m_a}(\alpha, \boldsymbol{r} - \boldsymbol{A}) | \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \mathcal{Y}_{k\mu}(\nabla_{\boldsymbol{r}}) | \phi_{l_b m_b}(\beta, \boldsymbol{r} - \boldsymbol{B}) \rangle \\ &= \mathcal{Y}_{k\mu}(-\nabla_{\boldsymbol{B}}) \langle \phi_{l_a m_a}(\alpha, \boldsymbol{r} - \boldsymbol{A}) | \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} | \phi_{l_b m_b}(\beta, \boldsymbol{r} - \boldsymbol{B}) \rangle \\ &= \mathcal{Y}_{k\mu}(-\nabla_{\boldsymbol{B}}) S^{l_b m_b}_{l_a m_a}(\alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{k}) \\ &= (-1)^{l_b} 4\pi (2\pi)^{3/2} N_{l_a}(\alpha) \widetilde{N}_{l_b}(\beta) \mathcal{N}^*_A \\ &\quad \times \sum_{l_1 m_1} G(l_a m_a | l_1 m_1) \mathcal{Y}^*_{l_1 m_1}\left(\frac{\mathrm{i}\boldsymbol{k}}{2\alpha}\right) \mathcal{C}_{l_2}(\alpha) \mathcal{T}^{l_b m_b}_{l_a m_a}(k\mu, \xi, \boldsymbol{R}^\dagger) \end{aligned} \tag{25}$$

where we have used equation (19), and the $\mathcal{T}$ integral has the same meaning as before,

$$\begin{aligned} \mathcal{T}^{l_2 m_2}_{l_1 m_1}(k\mu, \xi, \boldsymbol{R}^\dagger) &= \mathcal{Y}_{k\mu}(-\nabla_{\boldsymbol{B}}) I^{l_2 m_2}_{l_1 m_1}(\xi, \boldsymbol{R}^\dagger) \\ &= \sum_{l=0}^{l_1+l_2+k} (-1)^n \langle l_2 m_2, k\mu | l_1 m_1, lm \rangle \mathcal{C}^a_{nl}\left(\frac{1}{4\xi}\right) \Phi^b_{nlm}(\xi, \boldsymbol{R}^\dagger) \end{aligned} \tag{26}$$

where $n = (l_1 + l_2 + k - l)/2$ is a non-negative integer, and $\langle l_2 m_2, k\mu | l_1 m_1, lm \rangle$ was defined in equation (I.25). For $k = 1$, a simple alternative formula can be derived by applying equation (21) directly,

$$\begin{aligned} T^{l_b m_b}_{l_a m_a}(1\mu, \alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{k}) &= (-1)^{l_b} (4\pi)^2 (2\pi)^{3/2} \widetilde{N}_{l_a}(\alpha) \widetilde{N}_{l_b}(\beta) \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{\alpha\beta}} \mathrm{e}^{-k^2/(4\zeta)} \\ &\quad \times \sum_{l'_a, m'_a} \mathrm{i}^{l'_a} G(l_a m_a | l'_a m'_a) \mathcal{Y}^*_{l'_a m'_a}\left(-\frac{\alpha}{\zeta}\boldsymbol{k}\right) \\ &\quad \times \sum_{l'_b, m'_b} \mathrm{i}^{l'_b} G(l_b m_b | l'_b m'_b) \mathcal{Y}_{l'_b m'_b}\left(\frac{\beta}{\zeta}\boldsymbol{k}\right) \\ &\quad \times \left[\mathcal{Y}_{1\mu}\left(\mathrm{i}\frac{\beta\boldsymbol{k}}{\zeta}\right) I^{l''_b m''_b}_{l''_a m''_a}(\xi, \boldsymbol{R}) + \mathcal{T}^{l''_b m''_b}_{l''_a m''_a}(1\mu, \xi, \boldsymbol{R}) \right]. \end{aligned} \tag{27}$$

For $k > 1$, a similar formula can be derived, but the resulting formula is not as simple as equation (27). In this case, equation (25) may be preferred.

3.4. Angular momentum integrals with ETF

The three-centre angular momentum integrals with ETF over Gaussian orbitals arise in the rotational coupling matrix elements of the close-coupling treatment of ion–atom collisions, as well as in the study of magnetic properties of molecules. They are of the form

$$\boldsymbol{L}^{l_b m_b}_{l_a m_a}(\alpha, \beta, \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{C}, \boldsymbol{k}) = \langle \phi_{l_a m_a}(\alpha, \boldsymbol{r} - \boldsymbol{A}) | \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \boldsymbol{L}^C | \phi_{l_b m_b}(\beta, \boldsymbol{r} - \boldsymbol{B}) \rangle \tag{28}$$

where $\boldsymbol{L}^C = -\mathrm{i}(\boldsymbol{r}-\boldsymbol{C})\times\nabla$. Since $\boldsymbol{L}^C = \boldsymbol{L}^B - \mathrm{i}(\boldsymbol{B}-\boldsymbol{C})\times\nabla$, the above integrals can be written as

$$\begin{aligned}\boldsymbol{L}^{l_b m_b}_{l_a m_a}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C},\boldsymbol{k}) = {}& \langle\phi_{l_a m_a}(\alpha,\boldsymbol{r}-\boldsymbol{A})|\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{L}^B|\phi_{l_b m_b}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle \\ & -\mathrm{i}(\boldsymbol{B}-\boldsymbol{C})\times\langle\phi_{l_a m_a}(\alpha,\boldsymbol{r}-\boldsymbol{A})|\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\nabla|\phi_{l_b m_b}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle\,. \end{aligned}\tag{29}$$

Note that the second integral has been evaluated in equations (25) and (27). Introducing $L_\pm = L_x \pm \mathrm{i}L_y$ and using $L_\pm\mathcal{Y}_{lm}(\boldsymbol{r}) = [(l\mp m)(l\pm m+1)]^{1/2}\mathcal{Y}_{l,m\pm1}(\boldsymbol{r})$ as well as $L_z\mathcal{Y}_{lm}(\boldsymbol{r}) = m\mathcal{Y}_{lm}(\boldsymbol{r})$, we obtain the following formulae:

$$\begin{aligned} L^{B\ l_b m_b}_{\pm,l_a m_a}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{k}) &= \langle\phi_{l_a m_a}(\alpha,\boldsymbol{r}-\boldsymbol{A})|\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}L^B_\pm|\phi_{l_b m_b}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle \\ &= [(l_b\mp m_b)(l_b\pm m_b+1)]^{1/2}S^{l_b,m_b\pm1}_{l_a m_a}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{k}) \\ L^{B\,l_b m_b}_{z,l_a m_a}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{k}) &= \langle\phi_{l_a m_a}(\alpha,\boldsymbol{r}-\boldsymbol{A})|\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}L^B_z|\phi_{l_b m_b}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle \\ &= m_b S^{l_b m_b}_{l_a m_a}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{k})\,. \end{aligned}\tag{30}$$

3.5. Nuclear attraction integrals with ETF

The three-centre nuclear attraction integrals with ETF are defined as

$$\begin{aligned} N^{l_b m_b}_{l_a m_a}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C},\boldsymbol{k}) &= \langle\phi_{l_a m_a}(\alpha,\boldsymbol{r}-\boldsymbol{A})\left|\frac{\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}}{|\boldsymbol{r}-\boldsymbol{C}|}\right|\phi_{l_b m_b}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle \\ &= \langle\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\phi_{l_a m_a}(\alpha,\boldsymbol{r}-\boldsymbol{A})\left|\frac{1}{|\boldsymbol{r}-\boldsymbol{C}|}\right|\phi_{l_b m_b}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle \\ &= 4\pi N_{l_a}(\alpha)N_{l_b}(\beta)\mathcal{N}^*_A\sum_{l_1 m_1}G(l_a m_a|l_1 m_1)\mathcal{Y}^*_{l_1 m_1}\left(\frac{\mathrm{i}\boldsymbol{k}}{2\alpha}\right) \\ &\quad\times\langle\Phi_{l_2 m_2}(\alpha,\boldsymbol{r}-\boldsymbol{A}^\dagger)\left|\frac{1}{|\boldsymbol{r}-\boldsymbol{C}|}\right|\Phi_{l_b m_b}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle \\ &= (-1)^{l_b}(4\pi)^4 N_{l_a}(\alpha)\widetilde{N}_{l_b}(\beta)\mathcal{N}^*_A \\ &\quad\times\sum_{l_1 m_1}G(l_a m_a|l_1 m_1)\mathcal{Y}^*_{l_1 m_1}\left(\frac{\mathrm{i}\boldsymbol{k}}{2\alpha}\right)\mathcal{C}_{l_2}(\alpha)\sum_{l'_2,m'_2}G(l_2 m_2|l'_2 m'_2)\left(-\frac{\alpha}{\zeta}\right)^{l'_2} \\ &\quad\times\sum_{l'_b,m'_b}G(l_b m_b|l'_b m'_b)\left(\frac{\beta}{\zeta}\right)^{l'_b}I^{l''_b m''_b}_{l''_2 m''_2}(\xi,\boldsymbol{R}^\dagger_{ba})J^{l'_b m'_b}_{l'_2 m'_2}(\zeta,\boldsymbol{R}^\dagger_{\alpha\beta c}) \end{aligned}\tag{31}$$

where $\boldsymbol{R}^\dagger_{ba} = \boldsymbol{B}-(\boldsymbol{A}^\dagger)^*$, $\boldsymbol{R}^\dagger_{\alpha\beta c} = \boldsymbol{R}^\dagger_{\alpha\beta}-\boldsymbol{C}$, $\boldsymbol{R}^\dagger_{\alpha\beta} = (\alpha(\boldsymbol{A}^\dagger)^*+\beta\boldsymbol{B})/(\alpha+\beta)$, and we have used equations (11) and (21) as well as equations (I.30)–(I.32). The integral $J^{l_2 m_2}_{l_1 m_1}(\zeta,\boldsymbol{R})$ in equation (31) was defined in equation (I.33) for real $\boldsymbol{R}$. It also holds true for complex $\boldsymbol{R}$, i.e.

$$\begin{aligned} J^{l_2 m_2}_{l_1 m_1}(\zeta,\boldsymbol{R}^\dagger) = {}& \langle l_2 m_2|l_1 m_1|LM\rangle\mathcal{C}^a_{-1,L}\left(\frac{1}{4\zeta}\right)F_L\big(\zeta(\boldsymbol{R}^\dagger)^2\big)\mathcal{Y}_{LM}(\boldsymbol{R}^\dagger) \\ & +\sum_{l=l_{\min}}^{L-2}(-1)^n\langle l_2 m_2|l_1 m_1|lm\rangle\mathcal{C}^a_{n-1,l}\left(\frac{1}{4\zeta}\right)\Phi^b_{n-1,lm}(\zeta,\boldsymbol{R}^\dagger) \end{aligned}\tag{32}$$

where $(\boldsymbol{R}^\dagger)^2 = \boldsymbol{R}^\dagger\cdot\boldsymbol{R}^\dagger$, $L = l_1+l_2$, $l_{\min} = |l_1-l_2|$, $n = (l_1+l_2-l)/2$. As before, we can derive the alternative formulae for nuclear attraction integrals without using the trick of the complex centre, equation (11). Using the identity $1/|\boldsymbol{r}-\boldsymbol{C}| = (1/2\pi^2)\int(\mathrm{d}\boldsymbol{p}/p^2)\mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot(\boldsymbol{r}-\boldsymbol{C})}$, we obtain

$$\begin{aligned}
N_{l_am_a}^{l_bm_b}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C},\boldsymbol{k}) &= \langle\phi_{l_am_a}(\alpha,\boldsymbol{r}-\boldsymbol{A})\bigg|\frac{\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}}{|\boldsymbol{r}-\boldsymbol{C}|}\bigg|\phi_{l_bm_b}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle \\
&= \frac{1}{2\pi^2}\int\frac{\mathrm{d}\boldsymbol{p}}{p^2}\mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{C}}\langle\phi_{l_am_a}(\alpha,\boldsymbol{r}-\boldsymbol{A})|\mathrm{e}^{-\mathrm{i}(\boldsymbol{p}+\boldsymbol{k})\cdot\boldsymbol{r}}|\phi_{l_bm_b}(\beta,\boldsymbol{r}-\boldsymbol{B})\rangle \\
&= \frac{1}{2\pi^2}\int\frac{\mathrm{d}\boldsymbol{p}}{p^2}\mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{C}}S_{l_am_a}^{l_bm_b}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{p}+\boldsymbol{k}) \qquad (33)
\end{aligned}$$

where $\boldsymbol{A}$ and $\boldsymbol{B}$ are both real vectors. Substituting equation (I.29) into (33), we have

$$\begin{aligned}
N_{l_am_a}^{l_bm_b}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C},\boldsymbol{k}) &= (-1)^{l_b}(4\pi)^3\widetilde{N}_{l_a}(\alpha)\widetilde{N}_{l_b}(\beta)\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{\alpha\beta}}\mathrm{e}^{-k^2/(4\zeta)} \\
&\quad\times\sum_{l_a',m_a'}G(l_am_a|l_a'm_a')\Big(-\frac{\alpha}{\zeta}\Big)^{l_a'}\sum_{l_b',m_b'}G(l_bm_b|l_b'm_b')\Big(\frac{\beta}{\zeta}\Big)^{l_b'} \\
&\quad\times I_{l_a''m_a''}^{l_b''m_b''}(\xi,\boldsymbol{R}_{ba})\mathcal{A}_{l_a'm_a'}^{l_b'm_b'}(\zeta,\boldsymbol{R}_{\alpha\beta c},\boldsymbol{k}) \qquad (34)
\end{aligned}$$

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

$$\begin{aligned}
\mathcal{A}_{l_1m_1}^{l_2m_2}(\zeta,\boldsymbol{R},\boldsymbol{k}) &= \frac{\mathrm{i}^{l_1+l_2}}{(2\pi)^{3/2}}\int\frac{\mathrm{d}\boldsymbol{p}}{p^2}\mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{R}^\dagger}\mathrm{e}^{-p^2/(4\zeta)}\mathcal{Y}_{l_1m_1}^*(\boldsymbol{p}+\boldsymbol{k})\mathcal{Y}_{l_2m_2}(\boldsymbol{p}+\boldsymbol{k}) \\
&= (4\pi)^2\sum_{l_1',m_1'}\mathrm{i}^{l_1'}G(l_1m_1|l_1'm_1')\mathcal{Y}_{l_1'm_1'}^*(\boldsymbol{k}) \\
&\quad\times\sum_{l_2',m_2'}\mathrm{i}^{l_2'}G(l_2m_2|l_2'm_2')\mathcal{Y}_{l_2'm_2'}(\boldsymbol{k})J_{l_1''m_1''}^{l_2''m_2''}(\zeta,\boldsymbol{R}^\dagger) \qquad (35)
\end{aligned}$$

where $l_j'' = l_j - l_j'$ for $j = 1$ and 2, $\boldsymbol{R}^\dagger = \boldsymbol{R}-\mathrm{i}\boldsymbol{k}/2\zeta$, and we have used the addition theorem of solid harmonics, equation (I.15a). The J integral in (35) has been given in equation (32). As can be seen, most of quantities in formulae (34) and (35) are real and therefore can be computed relatively faster. However, these formulae require one more summation than equation (31). Since function $F_L(z)$ depends on the complex argument $z = \zeta\boldsymbol{R}^\dagger\cdot\boldsymbol{R}^\dagger$, it is impossible to avoid complex operations completely in either case. Which one of the two sets of formulae is more efficient in computation really depends on the implementation.

3.6. Electron repulsion integrals with ETF

The four-centre electron repulsion integrals with ETF are defined as

$$\begin{aligned}
&V_{l_am_a,l_cm_c}^{l_bm_b,l_dm_d}(\alpha,\beta,\gamma,\delta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C},\boldsymbol{D},\boldsymbol{k}_1,\boldsymbol{k}_2) \\
&\qquad= \langle\phi_{l_am_a}(\alpha,\boldsymbol{r}_1-\boldsymbol{A})\phi_{l_cm_c}(\gamma,\boldsymbol{r}_2-\boldsymbol{C})\bigg|\frac{\mathrm{e}^{-\mathrm{i}(\boldsymbol{k}_1\cdot\boldsymbol{r}_1+\boldsymbol{k}_2\cdot\boldsymbol{r}_2)}}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\bigg| \\
&\qquad\quad\times\phi_{l_bm_b}(\beta,\boldsymbol{r}_1-\boldsymbol{B})\phi_{l_dm_d}(\delta,\boldsymbol{r}_2-\boldsymbol{D})\rangle \\
&\qquad= \langle\mathrm{e}^{\mathrm{i}\boldsymbol{k}_1\cdot\boldsymbol{r}_1}\phi_{l_am_a}(\alpha,\boldsymbol{r}_1-\boldsymbol{A})\mathrm{e}^{\mathrm{i}\boldsymbol{k}_2\cdot\boldsymbol{r}_2}\phi_{l_cm_c}(\gamma,\boldsymbol{r}_2-\boldsymbol{C})\bigg|\frac{1}{r_{12}}\bigg| \\
&\qquad\quad\times\phi_{l_bm_b}(\beta,\boldsymbol{r}_1-\boldsymbol{B})\phi_{l_dm_d}(\delta,\boldsymbol{r}_2-\boldsymbol{D})\rangle \\
&\qquad= (4\pi)^2N_{l_a}(\alpha)N_{l_b}(\beta)N_{l_c}(\gamma)N_{l_d}(\delta)\mathcal{N}_A^*\mathcal{N}_C^* \\
&\qquad\quad\times\sum_{l_1m_1}G(l_am_a|l_1m_1)\mathcal{Y}_{l_1m_1}^*\Big(\frac{\mathrm{i}\boldsymbol{k}_1}{2\alpha}\Big)\sum_{l_3m_3}G(l_cm_c|l_3m_3)\mathcal{Y}_{l_3m_3}^*\Big(\frac{\mathrm{i}\boldsymbol{k}_2}{2\gamma}\Big)
\end{aligned}$$

$$
\begin{aligned}
&\times\langle\Phi_{l_2m_2}(\alpha,\boldsymbol{r}_1-\boldsymbol{A}^\dagger)\Phi_{l_4m_4}(\gamma,\boldsymbol{r}_2-\boldsymbol{C}^\dagger)\left|\frac{1}{r_{12}}\right| \\
&\times\Phi_{l_bm_b}(\beta,\boldsymbol{r}_1-\boldsymbol{B})\Phi_{l_dm_d}(\delta,\boldsymbol{r}_2-\boldsymbol{D})\rangle \\
={}& 32(-1)^{l_b+l_d}(4\pi)^2(2\pi)^{13/2}N_{l_a}(\alpha)\widetilde{N}_{l_b}(\beta)N_{l_c}(\gamma)\widetilde{N}_{l_d}(\delta)\mathcal{N}_A^*\mathcal{N}_C^* \\
&\times\sum_{l_1m_1}G(l_am_a|l_1m_1)\mathcal{C}_{l_2}(\alpha)\mathcal{Y}^*_{l_1m_1}\left(\frac{\mathrm{i}\boldsymbol{k}_1}{2\alpha}\right)\sum_{l_3m_3}G(l_cm_c|l_3m_3)\mathcal{C}_{l_4}(\gamma)\mathcal{Y}^*_{l_3m_3}\left(\frac{\mathrm{i}\boldsymbol{k}_2}{2\gamma}\right) \\
&\times\sum_{l'_2,m'_2}G(l_2m_2|l'_2m'_2)\left(-\frac{\alpha}{\zeta_1}\right)^{l'_2}\sum_{l'_b,m'_b}G(l_bm_b|l'_bm'_b)\left(\frac{\beta}{\zeta_1}\right)^{l'_b}I^{l''_bm''_b}_{l''_2m''_2}(\xi_1,\boldsymbol{R}^\dagger_{ba}) \\
&\times\sum_{l'_4,m'_4}G(l_4m_4|l'_4m'_4)\left(\frac{\gamma}{\zeta_2}\right)^{l'_4}\sum_{l'_d,m'_d}G(l_dm_d|l'_dm'_d)\left(-\frac{\delta}{\zeta_2}\right)^{l'_d}I^{l''_dm''_d}_{l''_4m''_4}(\xi_2,\boldsymbol{R}^\dagger_{dc}) \\
&\times U^{l'_bm'_b,l'_dm'_d}_{l'_2m'_2,l'_4m'_4}(\zeta,\boldsymbol{R}^\dagger_{\alpha\beta\gamma\delta})
\end{aligned}
\tag{36}
$$

where the parameters which appeared in equation (36) are defined as follows:

$$
\begin{aligned}
&\mathcal{N}_A^*=\exp\left(-\mathrm{i}\boldsymbol{k}_1\cdot\boldsymbol{A}-\frac{k_1^2}{4\alpha}\right)\qquad \mathcal{N}_C^*=\exp\left(-\mathrm{i}\boldsymbol{k}_2\cdot\boldsymbol{C}-\frac{k_2^2}{4\gamma}\right) \\
&\xi_1=\frac{\alpha\beta}{\alpha+\beta}\qquad \zeta_1=\alpha+\beta\qquad \xi_2=\frac{\gamma\delta}{\gamma+\delta}\qquad \zeta_2=\gamma+\delta \\
&\boldsymbol{R}^\dagger_{ba}=\boldsymbol{B}-(\boldsymbol{A}^\dagger)^*\qquad \boldsymbol{R}^\dagger_{dc}=\boldsymbol{D}-(\boldsymbol{C}^\dagger)^*\qquad \zeta=\frac{\zeta_1\zeta_2}{\zeta_1+\zeta_2}=\frac{(\alpha+\beta)(\gamma+\delta)}{\alpha+\beta+\gamma+\delta} \\
&\boldsymbol{R}^\dagger_{\alpha\beta}=\frac{\alpha(\boldsymbol{A}^\dagger)^*+\beta\boldsymbol{B}}{\alpha+\beta}\qquad \boldsymbol{R}_{\gamma\delta}=\frac{\gamma(\boldsymbol{C}^\dagger)^*+\delta\boldsymbol{D}}{\gamma+\delta}\qquad \boldsymbol{R}^\dagger_{\alpha\beta\gamma\delta}=\boldsymbol{R}^\dagger_{\alpha\beta}-\boldsymbol{R}^\dagger_{\gamma\delta}\,.
\end{aligned}
\tag{37}
$$

The U integral with the complex vector $\boldsymbol{R}^\dagger$ is defined in the same way as with the real vector, equation (I.37),

$$
\begin{aligned}
U^{l_2m_2,l_4m_4}_{l_1m_1,l_3m_3}(\zeta,\boldsymbol{R}^\dagger)={}&\langle l_2m_2,l_4m_4|LM|l_1m_1,l_3m_3\rangle\mathcal{C}^a_{-1,L}\left(\frac{1}{4\zeta}\right)F_L\big(\zeta(\boldsymbol{R}^\dagger)^2\big)\mathcal{Y}_{LM}(\boldsymbol{R}^\dagger) \\
&+\sum_{l=l_{\min}}^{L-2}(-1)^n\langle l_2m_2,l_4m_4|lm|l_1m_1,l_3m_3\rangle\mathcal{C}^a_{n-1,l}\left(\frac{1}{4\zeta}\right)\Phi^b_{n-1,lm}(\zeta,\boldsymbol{R}^\dagger)
\end{aligned}
\tag{38}
$$

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 $\langle l_2m_2,l_4m_4|lm|l_1m_1,l_3m_3\rangle$ are as defined in (I.38). We shall now evaluate the electron repulsion integral in the 'real' form. Using the identity $1/|\boldsymbol{r}_1-\boldsymbol{r}_2|=(1/2\pi^2)\int(\mathrm{d}\boldsymbol{p}/p^2)\mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)}$, we obtain

$$
\begin{aligned}
&V^{l_bm_b,l_dm_d}_{l_am_a,l_cm_c}(\alpha,\beta,\gamma,\delta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{C},\boldsymbol{D},\boldsymbol{k}_1,\boldsymbol{k}_2) \\
&\quad=\frac{1}{2\pi^2}\int\frac{\mathrm{d}\boldsymbol{p}}{p^2}S^{l_bm_b}_{l_am_a}(\alpha,\beta,\boldsymbol{A},\boldsymbol{B},\boldsymbol{k}_1+\boldsymbol{p})S^{l_dm_d}_{l_cm_c}(\gamma,\delta,\boldsymbol{C},\boldsymbol{D},\boldsymbol{k}_2-\boldsymbol{p}) \\
&\quad=32(-1)^{l_b+l_d}(2\pi)^{13/2}\widetilde{N}_{l_a}(\alpha)\widetilde{N}_{l_b}(\beta)\widetilde{N}_{l_c}(\gamma)\widetilde{N}_{l_d}(\delta)\mathrm{e}^{-\mathrm{i}(\boldsymbol{k}_1\cdot\boldsymbol{R}_{\alpha\beta}+\boldsymbol{k}_2\cdot\boldsymbol{R}_{\gamma\delta})} \\
&\qquad\times\sum_{l'_a,m'_a}G(l_am_a|l'_am'_a)\left(-\frac{\alpha}{\zeta_1}\right)^{l'_a}\sum_{l'_b,m'_b}G(l_bm_b|l'_bm'_b)\left(\frac{\beta}{\zeta_1}\right)^{l'_b}I^{l''_bm''_b}_{l''_am''_a}(\xi_1,\boldsymbol{R}_{ba}) \\
&\qquad\times\sum_{l'_c,m'_c}G(l_cm_c|l'_cm'_c)\left(\frac{\gamma}{\zeta_2}\right)^{l'_c}\sum_{l'_d,m'_d}G(l_dm_d|l'_dm'_d)\left(-\frac{\delta}{\zeta_2}\right)^{l'_d}I^{l''_dm''_d}_{l''_cm''_c}(\xi_2,\boldsymbol{R}_{dc}) \\
&\qquad\times\mathrm{e}^{-[k_1^2/(4\zeta_1)+k_2^2/(4\zeta_2)]}E^{l'_bm'_b,l'_dm'_d}_{l'_am'_a,l'_cm'_c}(\zeta,\boldsymbol{R}_{\alpha\beta\gamma\delta},\boldsymbol{k}_1,\boldsymbol{k}_2)
\end{aligned}
\tag{39}
$$

where all the parameters in (39) are the same as those in equation (I.36*a*–*c*), and integral E is defined as follows:

$$\begin{aligned}
E^{l_2m_2,l_4m_4}_{l_1m_1,l_3m_3}(\zeta,\boldsymbol{R},\boldsymbol{k}_1,\boldsymbol{k}_2) &= \frac{\mathrm{i}^L}{(2\pi)^{3/2}}\int\frac{\mathrm{d}\boldsymbol{p}}{p^2}\mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{R}^\dagger}\mathrm{e}^{-p^2/(4\zeta)} \\
&\quad\times\mathcal{Y}^*_{l_1,m_1}(\boldsymbol{p}+\boldsymbol{k}_1)\mathcal{Y}_{l_2,m_2}(\boldsymbol{p}+\boldsymbol{k}_1)\mathcal{Y}^*_{l_3,m_3}(\boldsymbol{p}-\boldsymbol{k}_2)\mathcal{Y}_{l_4,m_4}(\boldsymbol{p}-\boldsymbol{k}_2) \\
&= (4\pi)^4\sum_{l_1',m_1'}\mathrm{i}^{l_1'}G(l_1m_1|l_1'm_1')\mathcal{Y}^*_{l_1'm_1'}(\boldsymbol{k}_1)\sum_{l_2',m_2'}\mathrm{i}^{l_2'}G(l_2m_2|l_2'm_2')\mathcal{Y}_{l_2'm_2'}(\boldsymbol{k}_1) \\
&\quad\times\sum_{l_3',m_3'}\mathrm{i}^{l_3'}G(l_3m_3|l_3'm_3')\mathcal{Y}^*_{l_3'm_3'}(-\boldsymbol{k}_2) \\
&\quad\times\sum_{l_4',m_4'}\mathrm{i}^{l_4'}G(l_4m_4|l_4'm_4')\mathcal{Y}_{l_4'm_4'}(-\boldsymbol{k}_2)U^{l_2''m_2'',l_4''m_4''}_{l_1''m_1'',l_3''m_3''}(\zeta,\boldsymbol{R}^\dagger)
\end{aligned}\tag{40}$$

where $L = l_1 + l_2 + l_3 + l_4$, $\boldsymbol{R}^\dagger = \boldsymbol{R} - \mathrm{i}(\boldsymbol{k}_1/2\zeta_1 - \boldsymbol{k}_2/2\zeta_2)$, and we have used the addition theorem of solid harmonics, equation (I.15*a*). The U integral in (40) has been given in equation (38). Compared with formula (36), formulae (39) and (40) introduce two more summations. However, most of the terms in the latter are real.

4. Computational consideration and concluding remarks

In section 3 we have derived two sets of formulae for all the molecular integrals over spherical Gaussian orbitals, modified with plane-wave phase factors. If complex operations can be executed efficiently in a computer, the first set of formulae with complex centres may be used. Otherwise, the second set of formulae should be used. Since the formulae have exactly the same form as those in paper I without the phase factors, the general numerical strategies discussed there should still be applicable here for the efficient computation of these integrals. However, due to the presence of the phase factors, both sets of formulae for three-centre nuclear attraction and four-centre electron repulsion integrals contain complex vectors. Therefore, the complex operations can no longer be avoided. As in paper I, there are three basic functions, i.e. solid harmonics $\mathcal{Y}_{lm}(\boldsymbol{R})$, Laguerre polynomials $L_n^{l+1/2}(z)$ and auxiliary functions $F_m(z)$, which have to be evaluated over a range of indices. Note that the arguments $\boldsymbol{R}$ and z are complex vectors and numbers, respectively. We shall now consider how to evaluate them.

First of all, we notice that $\mathcal{Y}_{lm}(\boldsymbol{R})$, for a complex vector $\boldsymbol{R} \in \boldsymbol{C}^3$, has only the polynomial definition (Biedenharn and Louck 1981, pp 71, 302). In other words, one cannot write $\mathcal{Y}_{lm}(\boldsymbol{R}) = R^l Y_{lm}(\widehat{\boldsymbol{R}})$ since $\widehat{\boldsymbol{R}}$ is meaningless here. Secondly, the complex conjugate of $\mathcal{Y}_{lm}(\boldsymbol{R})$ has the form $\mathcal{Y}^*_{lm}(\boldsymbol{R}) = (-1)^m\mathcal{Y}_{l,-m}(\boldsymbol{R}^*)$, which can be readily proved from the definition polynomial of solid harmonics. The most efficient and reliable way to generate a sequence of solid harmonics is to use the following recurrence formula:

$$c(l+1,m)\mathcal{Y}_{l+1,m}(\boldsymbol{R}) = Z\mathcal{Y}_{lm}(\boldsymbol{R}) - c(l,m)(\boldsymbol{R}\cdot\boldsymbol{R})\mathcal{Y}_{l-1,m}(\boldsymbol{R}) \tag{41}$$

where $c(l,m) = [\{(l-m)(l+m)\}/\{(2l-1)(2l+1)\}]^{1/2}$ and Z is the third component of $\boldsymbol{R} = (X, Y, Z)$. Note that equation (41) holds true not only for the real vector but also for the complex vector, which can be readily justified by the definition of solid harmonics. The choice of this recurrence relation is based on the argument by Press *et al* (1992) about the stable computation of the associated Legendre functions. The recurrence evaluation of solid harmonics starts from the following two values:

$$\mathcal{Y}_{l-1,l}(\boldsymbol{R}) = 0 \qquad \mathcal{Y}_{ll}(\boldsymbol{R}) = s(l)(X+\mathrm{i}Y)^l \tag{42}$$

where $s(l) = [(-1)^l/2^l l!][(2l+1)!/4\pi]^{1/2}$. To achieve the maximum performance, we suggest that the constants $c(l,m)$ and $s(l)$ be pre-computed. For $m < 0$, we can first calculate the $\mathcal{Y}_{l,-m}(\boldsymbol{R}^*)$, and then take its complex conjugate multiplied by $(-1)^m$.

As in paper I, most integrals here require the computation of a sequence of associated Laguerre polynomials of the form $L_n^{l+1/2-2n}(z)$ with $n \leqslant [l/2]$. Regardless of whether z is complex or not, the associated Laguerre polynomials can be computed straightforwardly by means of its explicit form

$$L_n^{l+1/2-2n}(z) = a_0(nl) + z\{a_1(nl) + z[a_2(nl) + \cdots + za_n(nl)]\} \tag{43}$$

where $a_k(nl) = [(-1)^k/k!]\binom{l+1/2-n}{n-k}$ are the coefficients of the associated Laguerre polynomials. Again, we suggest that these coefficients be pre-computed and stored in memory. The storage requirement for $a_k(nl)$ is of the order l_{max}^3. In the cases of nuclear attraction and electron repulsion integrals, we need to evaluate a sequence of auxiliary functions $F_m(z)$ with a complex argument. This is the most difficult part with the phase factors in Gaussian orbitals. Since there are two free parameters (real part and imaginary part) for $F_m(z)$, the interpolation scheme may not be very effective any more. The procedure for calculating $F_m(z)$ for a limited range of m and z has been discussed by Errea *et al* (1979). As a supplement, we think that the nonlinear convergence accelerators (Grotendorst and Steinborn 1986) may be employed for the efficient evaluation of $F_m(z)$, even though z is a complex number.

In the actual close-coupling calculations of ion–atom collisions, equations (36)–(39) for the general four-centre electron repulsion integrals can be immediately simplified, since there are only two centres. In this case, the most difficult integral is the so-called two-centre exchange one, i.e. $\boldsymbol{A} = \boldsymbol{C}$ and $\boldsymbol{B} = \boldsymbol{D}$; then we have $\boldsymbol{R}_{ba} = \boldsymbol{R}_{dc}$, which implies that we only have to calculate one set of solid harmonics $\mathcal{Y}_{lm}(\boldsymbol{R}_{ba})$. On the other hand, $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ are either parallel or anti-parallel to the incident direction; therefore, we only have to compute one set of solid harmonics $\mathcal{Y}_{lm}(\boldsymbol{k}_1)$ in equation (40). Further reduction is possible by choosing the proper quantization axis (i.e. the z-axis of a coordinate frame). In fact, in the actual calculations we choose either the internuclear direction (the so-called body frame) or the incident direction (laboratory frame) as the quantization axis. In the body frame we have $\boldsymbol{R}_{ba} = \boldsymbol{R}_{dc} = R\hat{\boldsymbol{z}}$, while in the laboratory frame we have $\boldsymbol{k}_1 = \pm\boldsymbol{k}_2 = k\hat{\boldsymbol{z}}$. By noticing that $\mathcal{Y}_{lm}(\boldsymbol{r} = r\hat{\boldsymbol{z}}) = ((2l+1)/4\pi)^{1/2}\delta_{m,0}r^l$, we can immediately get rid of quite a few summations over magnetic quantum numbers and meanwhile the corresponding solid harmonics need not be computed. By inspection of equations (39) and (40), the laboratory frame is preferred if these two formulae are chosen to evaluate the exchange integral.

In summary, we have evaluated multi-centre molecular integrals over spherical Gaussian orbitals in closed form. The resulting formulae are more compact than those obtained by Errea *et al* (1979), even after we have significantly improved the kernel part of their treatment, see appendix B. Considering that Cartesian Gaussian orbitals of high angular momentum ($n + l + m \geqslant 2$) are not the eigenfunctions of angular momentum, therefore additional sums have to be included in order to extract the spherical orbitals. This is also true for the recursive evaluation of the integrals (Obara and Saika 1988). Furthermore, we can rearrange the formulae for the electron repulsion integral in a way similar to equation (I.52) so that the integral over contracted Gaussian orbitals can be efficiently computed. We expect that the present work will encourage researchers to explore the spherical Gaussian orbitals with plane-wave phase factors in the study of ion–atom collisions as well as in molecular structure calculations.

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 Y Zhou for useful discussions and Dr E Sidky for proofreading the manuscript.

Appendix A. Addition theorem for harmonic polynomials

Since the derivation procedure of the addition theorem of harmonic polynomials given by Niukkanen and Gribov (1983) does not apply to the complex arguments, we shall present a general derivation with the help of rotational invariants of two complex vectors under (complex) rotations (Biedenharn and Louck 1981, p 302),

$$I_l(\boldsymbol{p},\boldsymbol{r}) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l}(-1)^m \mathcal{Y}_{l,-m}(\boldsymbol{p})\mathcal{Y}_{lm}(\boldsymbol{r})\,. \tag{A1}$$

Clearly, $I_l(\boldsymbol{p},\boldsymbol{r})$ is a polynomial that is homogeneous of degree l in $\boldsymbol{p}$ and $\boldsymbol{r}$ separately, and is symmetric under the interchange of $\boldsymbol{p}$ and $\boldsymbol{r}$; therefore, it should be possible to expand the rotational invariant $(\boldsymbol{p}\cdot\boldsymbol{r})^n$ in terms of $I_l(\boldsymbol{p},\boldsymbol{r})$ and the other two basic invariants $\boldsymbol{p}\cdot\boldsymbol{p}$ and $\boldsymbol{r}\cdot\boldsymbol{r}$, i.e.

$$\left(\boldsymbol{p}\cdot\boldsymbol{r}\right)^n = \sum_{k=0}^{[n/2]} c_{nk}(\boldsymbol{p}\cdot\boldsymbol{p})^k(\boldsymbol{r}\cdot\boldsymbol{r})^k I_{n-2k}(\boldsymbol{p},\boldsymbol{r}) \tag{A2}$$

where the coefficients c_{nk} can be determined as follows. Choosing $\boldsymbol{p}$ and $\boldsymbol{r}$ to be real unit vectors $\boldsymbol{p}=\hat{\boldsymbol{p}}$ and $\boldsymbol{r}=\hat{\boldsymbol{r}}$, then equations (A1) and (A2) yield

$$(\cos\theta)^n = \sum_{k=0}^{[n/2]} c_{nk}P_{n-2k}(\cos\theta) \tag{A3}$$

where $\cos\theta = \hat{\boldsymbol{p}}\cdot\hat{\boldsymbol{r}}$ and P_l is the Legendre polynomial. Here we have used the addition theorem of the spherical harmonic and thus $I_l(\hat{\boldsymbol{p}},\hat{\boldsymbol{r}}) = P_l(\cos\theta)$. Comparing equation (A3) with the known expansion of $(\cos\theta)^n$ (Gradshteyn and Ryzhik 1980, p 1027), we obtain the coefficients $c_{nk} = \frac{n![2(n-2k)+1]}{(2k)!!(2n-2k+1)!!}$. Using equation (A2), we can readily expand

$$\mathrm{e}^{\boldsymbol{p}\cdot\boldsymbol{r}} = \sum_{n=0}^{\infty}\frac{\left(\boldsymbol{p}\cdot\boldsymbol{r}\right)^n}{n!} = \sum_{n=0}^{\infty}\sum_{k=0}^{[n/2]}\frac{c_{nk}}{n!}(\boldsymbol{p}\cdot\boldsymbol{p})^k(\boldsymbol{r}\cdot\boldsymbol{r})^k I_{n-2k}(\boldsymbol{p},\boldsymbol{r})\,. \tag{A4}$$

Inserting equation (A1) into (A4) and rearranging the summation indices, we finally obtain

$$\mathrm{e}^{\boldsymbol{p}\cdot\boldsymbol{r}} = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-1)^m a_{kl}\mathcal{Y}^k_{l,-m}(\boldsymbol{p})\mathcal{Y}^k_{lm}(\boldsymbol{r}) \tag{A5}$$

where $a_{kl} = \frac{4\pi}{(2k)!!(2k+2l+1)!!}$ and $\mathcal{Y}^k_{lm}(\boldsymbol{r}) = (\boldsymbol{r}\cdot\boldsymbol{r})^k\mathcal{Y}_{lm}(\boldsymbol{r})$. For $\boldsymbol{p} = \mathrm{i}\boldsymbol{q}$ and real vectors $\boldsymbol{q}$ and $\boldsymbol{r}$, the summation over k can be readily identified as a spherical Bessel function of order k (Gradshteyn and Ryzhik 1980, p 959), and therefore equation (A5) becomes the well known Rayleigh expansion of a plane wave. In fact, Niukkanen and Gribov (1983) derived equation (A5) for the real arguments using the modified expansion of a plane wave. It should be noted that expansion (A5) applies to the complex case based on the present derivation.

The addition theorem for $\mathcal{Y}^n_{lm}$ follows directly from the obvious identity $\mathrm{e}^{\boldsymbol{p}\cdot(\boldsymbol{r}_1+\boldsymbol{r}_2)} = \mathrm{e}^{\boldsymbol{p}\cdot\boldsymbol{r}_1}\mathrm{e}^{\boldsymbol{p}\cdot\boldsymbol{r}_2}$. Applying equation (A5) for all three terms, we obtain

$$\begin{aligned}\sum_{nlm} a_{nl}(-1)^m \mathcal{Y}^n_{l,-m}(\boldsymbol{p})\mathcal{Y}^n_{lm}(\boldsymbol{r}_1+\boldsymbol{r}_2) \\ = \sum_{n_1l_1m_1}\sum_{n_2l_2m_2} a_{n_1l_1}a_{n_2l_2}(-1)^{m_1+m_2}\mathcal{Y}^{n_1}_{l_1,-m_1}(\boldsymbol{p})\mathcal{Y}^{n_2}_{l_2,-m_2}(\boldsymbol{p})\mathcal{Y}^{n_1}_{l_1m_1}(\boldsymbol{r}_1)\mathcal{Y}^{n_2}_{l_2m_2}(\boldsymbol{r}_2)\,. \qquad \text{(A6)}\end{aligned}$$

Using the product expansion of two solid harmonics (Edmonds 1974, p 70), one obtains

$$\mathcal{Y}^{n_1}_{l_1m_1}(\boldsymbol{p})\mathcal{Y}^{n_2}_{l_2m_2}(\boldsymbol{p}) = \sum_{l=|l_1-l_2|}^{l_1+l_2}\langle lm|l_1m_1|l_2m_2\rangle\mathcal{Y}^n_{lm}(\boldsymbol{p}) \qquad \text{(A7)}$$

where $m = m_1+m_2$ and the only l values are those satisfying $l+l_1+l_2 =$ even integer and $\Delta(l_1l_2l)$ due to the selection rules of the Gaunt coefficient. Here the variable n is defined as $n = n_1+n_2+\Delta$ with $\Delta = (l_1+l_2-l)/2$. It can be readily justified that equation (A7) also applies to complex vectors based on the rotational property of solid harmonics under (complex) rotations. Substituting (A7) into the right-hand side of (A6) and rearranging the summation indices, we find that the right-hand side of equation (A6) can be written in the same form as the left-hand side with respect to $\mathcal{Y}^n_{l,-m}(\boldsymbol{p})$. Since the functions $\mathcal{Y}^n_{lm}$ are linearly independent, the corresponding coefficients can be equated with each other. Thus, we obtain

$$\mathcal{Y}^n_{lm}(\boldsymbol{r}_1+\boldsymbol{r}_2) = 4\pi\sum_{[\boldsymbol{n}_1,\boldsymbol{n}_2]}\mathcal{K}(\boldsymbol{n}|\boldsymbol{n}_1|\boldsymbol{n}_2)\mathcal{Y}^{n_1}_{l_1m_1}(\boldsymbol{r}_1)\mathcal{Y}^{n_2}_{l_2m_2}(\boldsymbol{r}_2) \qquad \text{(A8)}$$

$$\mathcal{K}(\boldsymbol{n}|\boldsymbol{n}_1|\boldsymbol{n}_2) = \mathcal{K}(nlm|n_1l_1m_1|n_2l_2m_2) = \frac{a_{n_1l_1}a_{n_2l_2}}{4\pi a_{nl}}\langle lm|l_1m_1|l_2m_2\rangle \qquad \text{(A9)}$$

where $\boldsymbol{n}$ stands for the triad of quantum numbers (n, l, m), and $\boldsymbol{n}_i = (n_i, l_i, m_i)$ for $i = 1, 2$. It follows immediately from (A9) that $\mathcal{K}(\boldsymbol{n}|\boldsymbol{n}_2|\boldsymbol{n}_1) = \mathcal{K}(\boldsymbol{n}|\boldsymbol{n}_1|\boldsymbol{n}_2)$. The square brackets over the summation indices $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ in (A8) mean that the summation is constrained by the selection rules of the Gaunt coefficient and by the relation $n = n_1+n_2+\Delta$. The detailed constraints on the summation indices were given in paper I.

With the help of expansion (A5), we can also derive the addition theorem for the harmonic Laguerre polynomials $\mathcal{L}^n_{lm}(\boldsymbol{r}) = L^{l+1/2}_n(\boldsymbol{r}\cdot\boldsymbol{r})\mathcal{Y}_{lm}(\boldsymbol{r})$ (Niukkanen 1984). To do that we need to expand the generating function $\mathrm{e}^{-\boldsymbol{p}\cdot\boldsymbol{p}+2\boldsymbol{p}\cdot\boldsymbol{r}}$. Using formula (A5), we obtain

$$\mathrm{e}^{-\boldsymbol{p}\cdot\boldsymbol{p}+2\boldsymbol{p}\cdot\boldsymbol{r}} = \sum_{lm}(-1)^m\left\{\mathrm{e}^{-\boldsymbol{p}\cdot\boldsymbol{p}}\sum_{k=0}^{\infty}a_{kl}2^{2k+l}(\boldsymbol{p}\cdot\boldsymbol{p})^k(\boldsymbol{r}\cdot\boldsymbol{r})^k\right\}\mathcal{Y}_{l,-m}(\boldsymbol{p})\mathcal{Y}_{lm}(\boldsymbol{r}) \qquad \text{(A10)}$$

where we have used the homogeneous property of $\mathcal{Y}^n_{lm}$, i.e. $\mathcal{Y}^n_{lm}(\lambda\boldsymbol{r}) = \lambda^{2k+l}\mathcal{Y}^n_{lm}(\boldsymbol{r})$. With $\Gamma(n+\frac{3}{2}) = (\sqrt{\pi}/2^{n+1})(2n+1)!!$ and $(2k)!! = 2^kk!$, we have $a_{kl}2^{2k+l} = 2\pi^{3/2}/[k!\Gamma(k+l+\frac{3}{2})]$. Using the Taylor expansion for e^{-x}, one can perform the multiplication of power series (Gradshteyn and Ryzhik 1980, p 15) explicitly as follows:

$$\mathrm{e}^{-x}\sum_{k=0}^{\infty}\frac{(xy)^k}{k!\Gamma(k+\nu+1)} = \sum_{k=0}^{\infty}\frac{(-x)^k}{k!}\sum_{k=0}^{\infty}\frac{(-y)^k(-x)^k}{k!\Gamma(k+\nu+1)} = \sum_{n=0}^{\infty}c_n(-x)^n \qquad \text{(A11)}$$

where $x = \boldsymbol{p}\cdot\boldsymbol{p}$, $y = \boldsymbol{r}\cdot\boldsymbol{r}$, $\nu = l+\frac{1}{2}$ and

$$c_n = \sum_{k=0}^{n}\frac{1}{(n-k)!}\frac{(-y)^k}{k!\Gamma(k+\nu+1)} = \frac{L^\nu_n(y)}{\Gamma(n+\nu+1)}$$

where we have used the explicit form for the associated Laguerre polynomial $L_n^{\nu}(z)$ (Gradshteyn and Ryzhik 1980, p 1037). Substituting equation (A11) into (A10), we obtain the following expansion formula:

$$\mathrm{e}^{-\boldsymbol{p}\cdot\boldsymbol{p}+2\boldsymbol{p}\cdot\boldsymbol{r}} = \sum_{n=0}^{\infty}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-1)^m b_{nl}\mathcal{Y}^n_{l,-m}(\boldsymbol{p})\mathcal{L}^n_{lm}(\boldsymbol{r}) \tag{A12}$$

with $b_{nl} = 2\pi^{3/2}(-1)^n/\,\Gamma(n+l+\frac{3}{2})$. The expansion formula (A12) is the same as that obtained by Kumar (1966) as well as by Niukkanen (1984) via different procedures for the real arguments. However, our derivation also applies to the complex case. The addition theorem for $\mathcal{L}^n_{lm}$ follows from the identity $\mathrm{e}^{-\boldsymbol{p}\cdot\boldsymbol{p}+2\boldsymbol{p}\cdot(\boldsymbol{r}_1+\boldsymbol{r}_2)} = \mathrm{e}^{-\boldsymbol{p}\cdot\boldsymbol{p}+2\boldsymbol{p}\cdot\boldsymbol{r}_1}\mathrm{e}^{2\boldsymbol{p}\cdot\boldsymbol{r}_2}$. By applying equations (A12) and (A5), and through the same procedure as for deriving (A8), we obtain

$$\mathcal{L}^n_{lm}(\boldsymbol{r}_1+\boldsymbol{r}_2) = 4\pi\sum_{[\boldsymbol{n}_1,\boldsymbol{n}_2]}\mathcal{B}(\boldsymbol{n}|\boldsymbol{n}_1|\boldsymbol{n}_2)\mathcal{L}^{n_1}_{l_1m_1}(\boldsymbol{r}_1)\mathcal{Y}^{n_2}_{l_2m_2}(\boldsymbol{r}_2) \tag{A13}$$

$$\begin{aligned}\mathcal{B}(\boldsymbol{n}|\boldsymbol{n}_1|\boldsymbol{n}_2) &= \frac{b_{n_1l_1}a_{n_2l_2}2^{2n_2+l_2}}{4\pi b_{nl}}\langle lm|l_1m_1|l_2m_2\rangle \\ &= (-1)^{n-n_1}\frac{n_1!}{n!}\mathcal{K}(\boldsymbol{n}|\boldsymbol{n}_1|\boldsymbol{n}_2)\end{aligned} \tag{A14}$$

where the summation constraints over the indices are the same as those for formula (A8). Note that $\mathcal{B}(\boldsymbol{n}|\boldsymbol{n}_2|\boldsymbol{n}_1) \neq \mathcal{B}(\boldsymbol{n}|\boldsymbol{n}_1|\boldsymbol{n}_2)$, in contrast with $\mathcal{K}$. The addition theorem (A13) was first derived by Niukkanen (1984) for the real vectors. Based on the present derivation, it clearly holds true for the complex vectors. It is interesting to note that both formulae (A8) and (A13) include the addition theorem of solid harmonics as the special case of $n = 0$.

Appendix B. Improved treatment for molecular integrals over CGTOs

We have noticed that the original closed form formulae (Taketa *et al* 1966) for three-centre nuclear attraction and four-centre electron repulsion integrals can be simplified with the following transformation. Consider an isotropic three-dimensional harmonic oscillator, the eigenfunctions of which can be expressed in both spherical polar coordinates and in Cartesian coordinates,

$$\psi_{nlm}(\alpha,\boldsymbol{r}) = N_{nl}(\alpha)\mathrm{e}^{-\alpha r^2/2}L_n^{l+1/2}(\alpha r^2)\mathcal{Y}_{lm}(\sqrt{\alpha}\boldsymbol{r}) \tag{B1}$$

$$\psi_{n_xn_yn_z}(\alpha,\boldsymbol{r}) = N_{\boldsymbol{n}}(\alpha)\mathrm{e}^{-\alpha r^2/2}H_{n_x}(\sqrt{\alpha}x)H_{n_y}(\sqrt{\alpha}y)H_{n_z}(\sqrt{\alpha}z) \tag{B2}$$

where $N_{nl}(\alpha) = \left[\frac{2\alpha^{3/2}n!}{\Gamma(n+l+3/2)}\right]^{1/2}$ and $N_{\boldsymbol{n}}(\alpha) = \left[\frac{(\alpha/\pi)^{3/2}}{(2n_x)!!(2n_y)!!(2n_z)!!}\right]^{1/2}$ are the normalization constants, respectively. Here $H_n(z)$ denotes the Hermite polynomial of degree n. The eigenvalues corresponding to the eigenfunctions, in units of $\hbar\omega$ ($\alpha = m\omega/\hbar$), are $E_N = 2n + l + \frac{3}{2} = n_x + n_y + n_z + \frac{3}{2} = N + \frac{3}{2}$. These energy levels are degenerate of degree $(N+1)(N+2)/2$. The two sets of eigenfunctions are related to each other through a unitary transformation,

$$\psi_{n_xn_yn_z}(\alpha,\boldsymbol{r}) = \sum_{lm}\langle nlm|n_xn_yn_z\rangle\psi_{nlm}(\alpha,\boldsymbol{r}) \tag{B3}$$

where $\langle nlm|n_xn_yn_z\rangle$ as well as the summation over l is constrained by $2n + l = N = n_x + n_y + n_z$. The transformation matrix elements read

$$\begin{aligned}\langle nlm|n_xn_yn_z\rangle &= N_{nl}(\alpha)N_{\boldsymbol{n}}(\alpha)\int \mathrm{d}\boldsymbol{r}\;\psi^*_{nlm}(\alpha,\boldsymbol{r})\psi_{n_xn_yn_z}(\alpha,\boldsymbol{r}) \\ &= \frac{N_{nl}(\alpha)N_{\boldsymbol{n}}(\alpha)}{\alpha^{3/2}}\int \mathrm{d}\boldsymbol{r}\;\mathrm{e}^{-r^2}L_n^{l+1/2}(r^2)\mathcal{Y}^*_{lm}(\boldsymbol{r})H_{n_x}(x)H_{n_y}(y)H_{n_z}(z)\end{aligned} \tag{B4}$$

where we have changed the integral variable from $\sqrt{\alpha}\boldsymbol{r} \rightarrow \boldsymbol{r}$. It is obvious that the transformation matrix elements are independent of α. By eliminating the exponential factor on both sides of equation (B3), we obtain the transformation equations of the polynomials,

$$H_{n_x}(x)H_{n_y}(y)H_{n_z}(z) = \sum_{lm}(nlm|n_x n_y n_z)\mathcal{L}^n_{lm}(\boldsymbol{r}) \tag{B5}$$

$$\mathcal{L}^n_{lm}(\boldsymbol{r}) = \sum_{[\boldsymbol{n}]}(n_x n_y n_z|nlm)H_{n_x}(x)H_{n_y}(y)H_{n_z}(z) \tag{B6}$$

where the symbol $[\boldsymbol{n}]$ indicates that the summation over (n_x, n_y, n_z) is subject to $2n + l = n_x + n_y + n_z$, and we have defined $(nlm|n_x n_y n_z) = [N_{nl}(\alpha)/N_{\boldsymbol{n}}(\alpha)]\langle nlm|n_x n_y n_z\rangle$ and $(n_x n_y n_z|nlm) = [N_{\boldsymbol{n}}(\alpha)/N_{nl}(\alpha)]\langle nlm|n_x n_y n_z\rangle^*$. Notice that both transformation matrix elements $(nlm|n_x n_y n_z)$ and $(n_x n_y n_z|nlm)$ are independent of α. These matrix elements can be readily evaluated from equation (B4) using symbolic manipulation languages, for instance, *Mathematica*. It is of interest to note that equations (B5) and (B6) also provide the transformation between solid harmonics $\mathcal{Y}_{lm}(\boldsymbol{r})$ and $H_{n_x}(x)H_{n_y}(y)H_{n_z}(z)$ by imposing the restriction $l = n_x + n_y + n_z$. By multiplying $\exp(-\alpha r^2)$ on both sides of (B5) and changing variables from $\boldsymbol{r} \rightarrow \sqrt{\alpha}\boldsymbol{r}$, we can transform Cartesian Hermite–Gaussian orbitals (Živković and Maksić 1968) to spherical Gaussian orbitals (Fieck 1980) and vice versa.

Following the derivation procedure by Taketa *et al* (1966), the nuclear attraction integral requires the evaluation of the following I integral (Taketa *et al* 1966, p 2317):

$$\begin{aligned}
I &= 2\pi^2 \int \mathrm{d}\boldsymbol{r}_P \, \frac{1}{r_C} x_P^i y_P^j z_P^k \exp(-\gamma r_P^2) \\
&= \left(\frac{\pi}{\gamma}\right)^{3/2}\left(\frac{1}{4\gamma}\right)^{(i+j+k)/2} \int \frac{\mathrm{d}\boldsymbol{k}}{k^2} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \mathrm{i}^{i+j+k} H_i\left(\frac{k_x}{\sqrt{4\gamma}}\right) H_j\left(\frac{k_y}{\sqrt{4\gamma}}\right) H_k\left(\frac{k_z}{\sqrt{4\gamma}}\right) \mathrm{e}^{-k^2/(4\gamma)} \\
&= \left(\frac{\pi}{\gamma}\right)^{3/2}\left(\frac{1}{4\gamma}\right)^{(i+j+k)/2} \sum_{lm}(-1)^n (nlm|ijk)\left(\frac{1}{4\gamma}\right)^{l/2} \mathrm{i}^l \int \frac{\mathrm{d}\boldsymbol{k}}{k^2} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \Phi^b_{nlm}\left(\frac{1}{4\gamma}, \boldsymbol{k}\right) \\
&= (2\pi)^{3/2}\left(\frac{\pi}{\gamma}\right)^{3/2} \sum_{lm}(-1)^n (nlm|ijk)\left(\frac{1}{4\gamma}\right)^{n+l} \mathcal{N}_{nlm}(\gamma, -\boldsymbol{R})
\end{aligned} \tag{B7}$$

where we have used equations (B5) and (6), and the fact that $i + j + k = 2n + l$. $\mathcal{N}_{nlm}$ in (B7) has been defined in equation (I.B6). The above formula (containing three sums, where one sum is inside $\mathcal{N}_{nlm}$) is clearly more compact than the original one (containing six sums) obtained by Taketa *et al*, who evaluated the integral I in a more elaborate way. Since the transformation matrix $(nlm|ijk)$ can be computed and stored in memory beforehand (storage of the order of l^5_{max}), we expect that formula (B7) is more efficient in computation than the original one. Similarly, for the electron repulsion integral, we can improve the evaluation procedure of integral I' (Taketa *et al* 1966, p 2318) as follows:

$$\begin{aligned}
I' = \iint \mathrm{d}\boldsymbol{r}_{P_1}\, \mathrm{d}\boldsymbol{r}_{Q_2}\, & x_{P_1}^{i_1} y_{P_1}^{j_1} z_{P_1}^{k_1} \exp(-\gamma_1 r_{P_1}^2) \frac{1}{r_{12}} x_{Q_2}^{i_2} y_{Q_2}^{j_2} z_{Q_2}^{k_2} \exp(-\gamma_2 r_{Q_2}^2) \\
&= \frac{\pi(2\pi)^{3/2}}{2(\gamma_1\gamma_2)^{3/2}} \sum_{l_1 m_1}(-1)^{n_1+l_1}(n_1 l_1 m_1|i_1 j_1 k_1)\left(\frac{1}{4\gamma_1}\right)^{n_1+l_1} \\
&\quad \times \sum_{l_2 m_2}(-1)^{n_2}(n_2 l_2 m_2|i_2 j_2 k_2)\left(\frac{1}{4\gamma_2}\right)^{n_2+l_2} \mathcal{V}^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\gamma_1, \gamma_2, -\boldsymbol{R})
\end{aligned} \tag{B8}$$

where $\boldsymbol{R} = \boldsymbol{Q} - \boldsymbol{P}$ according to Taketa *et al* (1966) and $\mathcal{V}^{n_2 l_2 m_2}_{n_1 l_1 m_1}$ has been defined in equation (I.B8). Again, by pre-computing all necessary constants, it is expected that equation (B8) is more efficient in computation than the original one.

The McMurchie–Davidson (MD) algorithm (McMurchie and Davidson 1978) is certainly among the most important algorithms in quantum chemistry. The basic integral in the MD algorithm is defined as

$$[NLM|r_C^{-1}] = (\partial/\partial P_x)^N(\partial/\partial P_y)^L(\partial/\partial P_z)^M[000|r_C^{-1}] \tag{B9}$$

where $[000|r_C^{-1}] = \int \mathrm{d}\boldsymbol{r}(1/r_C)\mathrm{e}^{-\alpha r_P^2}$. By means of equation (B5), we can derive a compact closed form formula for this integral as follows:

$$\begin{aligned}[NLM|r_C^{-1}] &= \int \mathrm{d}\boldsymbol{r}\frac{1}{r_C}\Lambda_N(x_P;\alpha)\Lambda_L(y_P;\alpha)\Lambda_M(z_P;\alpha)\mathrm{e}^{-\alpha r_P^2}\\ &= \alpha^{(N+L+M)/2}\int \mathrm{d}\boldsymbol{r}\frac{1}{r_C}H_N(\alpha^{1/2}x_P)H_L(\alpha^{1/2}y_P)H_M(\alpha^{1/2}z_P)\mathrm{e}^{-\alpha r_P^2}\\ &= \sum_{lm}(nlm|NLM)\alpha^{n+l}\int \mathrm{d}\boldsymbol{r}\frac{1}{r_C}\Phi^b_{nlm}(\alpha,\boldsymbol{r}_P)\\ &= \frac{1}{2\pi^2}\sum_{lm}(nlm|NLM)\alpha^{n+l}\int\frac{\mathrm{d}\boldsymbol{k}}{k^2}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\int \mathrm{d}\boldsymbol{r}_P\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_P}\Phi^b_{nlm}(\alpha,\boldsymbol{r}_P)\\ &= \frac{(2\pi)^{3/2}}{2\pi^2}\sum_{lm}(nlm|NLM)\alpha^{n+l}(-\mathrm{i})^l\mathcal{C}^b_{nl}(\alpha)\int \mathrm{d}\boldsymbol{k}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\Phi^a_{n-1,lm}\left(\frac{1}{4\alpha},\boldsymbol{k}\right)\\ &= \frac{2\pi}{\alpha}R_{NLM}\end{aligned} \tag{B10}$$

where we have used the identity $(1/|\boldsymbol{r}-\boldsymbol{C}|) = (1/2\pi^2)\int(\mathrm{d}\boldsymbol{k}/k^2)\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{C})}$, and equations (1)–(6) as well as (14)–(17). It should be noted that the summation over l in (B10) is subject to $2n+l = N+L+M = \ell$. Here $\boldsymbol{R} = \boldsymbol{C}-\boldsymbol{P}$ and R_{NLM} represents the rest of the integral

$$\begin{aligned}R_{NLM} &= \sum_m(0\ell m|NLM)\alpha^\ell F_\ell(\alpha R^2)\mathcal{Y}_{\ell m}(\boldsymbol{R}) + \sum_{lm}^{\ell-2}(nlm|NLM)\frac{\alpha^{n+l}}{2n}\Phi^b_{n-1,lm}(\alpha,\boldsymbol{R})\\ &= \alpha^\ell F_\ell(\alpha R^2)\Theta^\ell_{NLM}(\boldsymbol{R}) + \mathrm{e}^{-\alpha R^2}\sum_l^{\ell-2}\frac{\alpha^{n+l}}{2n}L^{l+1/2}_{n-1}(\alpha R^2)\Theta^l_{NLM}(\boldsymbol{R})\end{aligned} \tag{B11}$$

where $\Theta^l_{NLM}(\boldsymbol{R})$ stands for the angular part, $\Theta^l_{NLM}(\boldsymbol{R}) = \sum_m(nlm|NLM)\mathcal{Y}_{lm}(\boldsymbol{R})$. The remarkable feature of equation (B11) for the auxiliary function R_{NLM} is that it contains only one $F_\ell(T)$ function and the remainder consists of just Laguerre polynomials. In contrast, both the closed form formula and recurrence relation for R_{NLM} derived by McMurchie and Davidson (1978) depend on a sequence of $F_m(T)$ functions. Careful coding of the present formula should speed up the evaluation of R_{NLM}, which is of critical importance in the MD algorithm.

For molecular integrals over CGTOs modified with plane-wave phase factors, Errea *et al* (1979) derived the closed-form formulae for all the integrals using exactly the same technique as Taketa *et al* (1966). Therefore, there is room for improvement, as can be seen from our preceding sections, see equations (B7) and (B8). As an illustration, we shall evaluate the I_{ijk} integral (Errea *et al* 1979, p 73), resulting from the three-centre nuclear attraction integral,

$$I_{ijk} = \int\frac{\mathrm{d}\boldsymbol{K}}{K^2}\mathrm{e}^{\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}}H_i\left(\frac{K_x-u_x}{\sqrt{4\gamma}}\right)H_j\left(\frac{K_y-u_x}{\sqrt{4\gamma}}\right)H_k\left(\frac{K_z-u_x}{\sqrt{4\gamma}}\right)\mathrm{e}^{-(\boldsymbol{K}-\boldsymbol{u})^2/(4\gamma)} \tag{B12}$$

where $\boldsymbol{R} = \boldsymbol{P}-\boldsymbol{C}$, following their notation. To reduce the integral into the standard form, equation (B7), we have to use the addition theorem for Hermite polynomials (Gradshteyn and Ryzhik 1980, p 1035): $2^{n/2}H_n(x+y) = \sum_{k=0}^{n}\binom{n}{k}H_k(x\sqrt{2})H_{n-k}(y\sqrt{2})$. Then we obtain

$$\begin{aligned} I_{ijk} &= 2^{-(i+j+k)/2}\mathrm{e}^{-u^2/(4\gamma)}\sum_{i'j'k'}H_{i''}\left(\frac{-u_x}{\sqrt{2\gamma}}\right)H_{j''}\left(\frac{-u_x}{\sqrt{2\gamma}}\right)H_{k''}\left(\frac{-u_x}{\sqrt{2\gamma}}\right)I'_{ijk} \\ I'_{ijk} &= \int\frac{\mathrm{d}\boldsymbol{K}}{K^2}\mathrm{e}^{\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}^\dagger}H_{i'}\left(\frac{K_x}{\sqrt{2\gamma}}\right)H_{j'}\left(\frac{K_y}{\sqrt{2\gamma}}\right)H_{k'}\left(\frac{K_z}{\sqrt{2\gamma}}\right)\mathrm{e}^{-K^2/(4\gamma)} \end{aligned} \tag{B13}$$

where $\boldsymbol{R}^\dagger = \boldsymbol{R} - \mathrm{i}\boldsymbol{u}/2\gamma$ and $n' + n'' = n$ for $n = i, j, k$. Notice the difference between equations (B7) and I'_{ijk}, i.e. the scaling factor for Hermite polynomials. Using equation (B5), we obtain

$$\begin{aligned} I'_{ijk} &= (2\pi)^{3/2}\sum_{lm}\left(\frac{\mathrm{i}}{\sqrt{2\gamma}}\right)^l (nlm|i'j'k')\mathcal{N}'_{nlm}(\gamma, \boldsymbol{R}^\dagger) \\ \mathcal{N}'_{nlm}(\gamma, \boldsymbol{R}^\dagger) &= \frac{(-\mathrm{i}\sqrt{2\gamma})^l}{(2\pi)^{3/2}}\int\frac{\mathrm{d}\boldsymbol{K}}{K^2}\mathrm{e}^{\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}^\dagger}\mathcal{L}^n_{lm}\left(\frac{\boldsymbol{K}}{\sqrt{2\gamma}}\right)\mathrm{e}^{-K^2/(4\gamma)} \\ &= \binom{n+l+\frac{1}{2}}{n}\mathcal{C}^a_{-1,l}\left(\frac{1}{4\gamma}\right)F_l(\gamma\boldsymbol{R}^\dagger\cdot\boldsymbol{R}^\dagger)\mathcal{Y}_{lm}(\boldsymbol{R}^\dagger) \\ &\quad +\sum_{k=1}^{n}\frac{(-1)^k}{k!(2\gamma)^k}\binom{n+l+\frac{1}{2}}{n-k}\mathcal{C}^a_{k-1,l}\left(\frac{1}{4\gamma}\right)\Phi^b_{k-1,lm}(\gamma, \boldsymbol{R}^\dagger)\,. \end{aligned} \tag{B14}$$

Compared with the corresponding formula for I_{ijk}, equation (25) (Errea *et al* 1979, p 74), the present formulae, equations (B13) and (B14), contain only six sums in total and are therefore much more concise (their equations contain 12 sums). Although the present formulae need to evaluate Hermite and Laguerre polynomials, their computational advantage is obvious since the required polynomials can be computed efficiently with the known recurrence relations. Similarly, we can apply the above technique to derive compact expressions for four-centre electron repulsion integrals. Alternatively, one can also use the complex centre (Obara and Saika 1988) to find more concise closed-form formulae for molecular integrals over CGTOs modified with plane-wave phase factors. In particular, we can develop the MD algorithm for the molecular integrals over Cartesian Gaussian orbitals with complex centres.

References

Allison D J, Handy N C and Boys S F 1973 *Mol. Phys.* **26** 715

Bates D R and McCarroll R 1958 *Proc. R. Soc.* A **245** 175

Biedenharn L C and Louck J D 1981 *Angular Momentum in Quantum Physics: Theory and Application* (Reading, MA: Addison-Wesley)

Boys S F 1950 *Proc. R. Soc.* A **200** 542

Bransden B H and McDowell M R C 1992 *Charge Exchange and the Theory of Ion–Atom Collisions* (Oxford: Clarendon)

Dose V and Semini C 1974 *Helv. Phys. Acta* **47** 609

Edmonds A R 1974 *Angular Momentum in Quantum Mechanics* (Princeton, NJ: Princeton University Press)

Errea L F, Méndez L and Riera A 1979 *J. Phys. B: At. Mol. Opt. Phys.* **12** 69

Fieck G 1980 *Theor. Chim. Acta* **54** 323

Gradshteyn I S and Ryzhik I M 1980 *Tables of Integrals, Series and Products* (New York: Academic)

Gill P M W 1994 *Adv. Quantum Chem.* **25** 141

Grotendorst J and Steinborn E O 1986 *J. Chem. Phys.* **84** 5617

Huzinaga S 1985 *Comput. Phys. Rep.* **2** 279

Kuang J and Lin C D 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** L889

——1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 2529–48

Kumar K 1966 *J. Math. Phys.* **7** 671

McMurchie L E and Davidson E R 1978 *J. Comput. Phys.* **26** 218

Niukkanen A W 1984 *J. Math. Phys.* **25** 698
Niukkanen A W and Gribov L A 1983 *Theor. Chim. Acta* **62** 443
Obara S and Saika A 1988 *J. Chem. Phys.* **89** 1540
Press W H, Teukolsky S A, Vetterling W T and Flannery B P 1992 *Numerical Recipes in FORTRAN* 2nd edn (Cambridge: Cambridge University Press)
Shavitt I 1963 *Methods in Computational Physics* vol 2, ed B Adler, S Fernbach and M Rotenberg (New York: Academic) p 15
Taketa H, Huzinaga S and O-ohata K 1966 *J. Phys. Soc. Japan* **21** 2313
Živković and Maksić 1968 *J. Chem. Phys.* **49** 3083