Efficient evaluation of the Fourier transform over products of Slater-type orbitals on different centers

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Abstract
Using the shift-operator technique, a compact formula for the Fourier transform of a product of two Slater-type orbitals located on different atomic centers is derived. The result is valid for arbitrary quantum numbers and was found to be numerically stable for a wide range of geometrical parameters and momenta. Details of the implementation are presented together with benchmark data for representative integrals. We also discuss the assets and drawbacks of alternative algorithms available and analyze the numerical efficiency of the new scheme.

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1. Introduction

The electron–electron interaction as quantified in Coulomb or exchange integrals is at the heart of every quantum-mechanical treatment of condensed matter. Due to the simple structure of the Coulomb operator in reciprocal space, Fourier transform techniques allow for the transformation of the double integral over real space into a compact single integral in momentum space. Let us consider a typical two-electron repulsion integral as an example

$$I = \int\int \phi_\mu(\mathbf{r} - \mathbf{R}_A)\phi_\nu(\mathbf{r} - \mathbf{R}_B)\frac{1}{|\mathbf{r} - \mathbf{r}'|}\phi_\alpha(\mathbf{r}' - \mathbf{R}_C)\phi_\beta(\mathbf{r}' - \mathbf{R}_D)\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'. \tag{1}$$

If we denote the Fourier transform of the product of orbitals $\phi_\mu(\mathbf{r} - \mathbf{R}_A)$ and $\phi_\nu(\mathbf{r} - \mathbf{R}_B)$ by $\phi_{\mu\nu}(\mathbf{R}_A, \mathbf{R}_B, \mathbf{q})$, we may very schematically write (thorough definitions follow later)

$$I \propto \int \phi_{\mu\nu}(\mathbf{R}_A, \mathbf{R}_B, -\mathbf{q})\frac{1}{q^2}\phi_{\alpha\beta}(\mathbf{R}_C, \mathbf{R}_D, \mathbf{q})\,\mathrm{d}\mathbf{q}. \tag{2}$$

Methods along these lines date back at least to Bonham *et al* [1, 2] and are the de-facto standard for systems with translational symmetry. For these boundary conditions, plane

waves are the most natural type of basis functions, thanks also to their trivial behavior under Fourier transformation.

In recent years, correlated electronic structure methods such as the GW approximation of Hedin[4], which were originally developed in the context of band structure calculations, are now also applied to systems where translational symmetry is broken. Examples of this kind include super lattices, defects, surfaces and even atoms or molecules [4–8]. Obviously, atomic orbital basis sets are more appropriate in these situations and reduce the number of basis functions needed to achieve a certain accuracy considerably. Among the localized basis sets, Slater and Gaussian-type orbitals are the most prominent. The latter have the advantage that the Fourier transform of orbital products is relatively easy to obtain, while usually much less Slater than Gaussian-type orbitals are required to represent atomic or molecular electron densities. In the context of the Fourier transform methods mentioned above, the choice of Slater versus Gaussian is hence intimately connected with the ability to perform the Fourier transform of basis function products efficiently.

A direct numerical quadrature of the three-dimensional integral over reciprocal space using Fast Fourier Transform techniques is not advisable due to high memory consumption, low computational speed and very limited numerical accuracy. As an alternative, Slater functions may be fitted to a fixed linear combination of Gaussian-type orbitals like done, for example, in the popular Pople basis sets often employed in quantum chemistry [9, 10]. However, in this case the electronic structure calculation could have been performed entirely in terms of Gaussians in the first place with additional variational freedom. Several attempts to directly perform the intricate integration of Slater products analytically are documented in the literature. While the mentioned original work of Bonham [1, 2] was restricted to s-type functions, Bentley and Stewart [11] derived an expression for arbitrary angular momentum states involving an infinite series. Later, Junker [12] obtained a result in terms of finite sums and one-dimensional numerical integrations, while Straton [13, 14] was able to provide general formulae for the Fourier transform of the product of more than two orbitals.

This earlier work meets some but not all desired properties of a general solution. The latter includes the validity for arbitrary quantum numbers, the possibility for a straightforward implementation on a computer as well as high numerical efficiency and stability. Moreover, the solution should be amenable to partial wave analysis, in order to allow for an efficient evaluation of two-electron integrals in a second step. This point is maybe not so important for periodic systems, where quadrature of the remaining integral over reciprocal space in (2) may be accomplished by a summation over *special k-point* meshes [15], involving only a small number of integrand evaluations. For finite systems however, this point becomes crucial. Here it should be mentioned that the efficient evaluation of Fourier transforms is only a first step in a fast computation of multi-center integrals.

An approach which combines most of the above-mentioned merits was proposed by Trivedi and Steinborn [16]. The authors provide formulae for the Fourier transform over products of so-called B-functions. These B-functions can be transformed into Slater-type orbitals without loss of generality and accuracy. Subsequently, this technique was used by Grotendorst and Steinborn [17] to evaluate a variety of multi-center integrals required in electronic structure calculations. Alternative representations of the transforms are given in [18] and in the dissertation of Homeier [19], which also contains a deeper discussion of the B-function formalism together with numerical results and benchmark data.

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[4] In Hedin's GW approximation, the self-energy operator of quasiparticle theory is given by the product of the one-particle Green's function G and the screened Coulomb operator W, see [3].

In this work, we propose an alternative to the Trivedi–Steinborn formula, which is *directly* formulated in terms of Slater-type orbitals. The derivation is based on the shift-operator technique, which is discussed in the following section. The approach may be seen as a generalization of a recent result for overlap integrals [20] and meets all important criteria established above.

The more general aim of this contribution is to facilitate the utilization of Slater-type orbitals in the simulation of periodic and quasi-periodic systems. Currently, only a very limited number of codes employ this kind of basis set [21, 22], due to the apparent difficulties in the numerical implementation. The development of adapted algorithms is therefore of key importance in order to unveil the well-known benefits of Slater-type orbitals in atomistic calculations.

2. Definitions and the shift-operator approach

We consider real unnormalized Slater-type orbitals (STO) of the form

$$\chi_{nlm}(\mathbf{r}, \zeta) = r^{n-1}\, e^{-\zeta r} z_l^m(\mathbf{r}), \tag{3}$$

where $n = \tilde{n} - l$ in terms of the principle quantum number $\tilde{n}$. The regular harmonics z_l^m are related to the more familiar real spherical harmonics $\tilde{Y}_{lm}$:

$$
\begin{aligned}
z_l^m(\mathbf{r}) &= r^l \tilde{Y}_{lm}(\hat{\mathbf{r}}) \\
\tilde{Y}_{lm}(\hat{\mathbf{r}}) &= (-1)^m P_l^m(\cos\theta)\cos(m\phi) && m \geqslant 0 \\
\tilde{Y}_{l-m}(\hat{\mathbf{r}}) &= (-1)^m P_l^m(\cos\theta)\sin(m\phi) && m > 0,
\end{aligned} \tag{4}
$$

where $P_l^m(\cos\theta)$ denote associated Legendre polynomials as defined in [23, equation (8.812)]. In the literature on molecular integrals also complex regular harmonics $\mathcal{Y}_l^m$ are often employed. The normalized $\mathcal{Y}_l^m$ defined in [24, p 1264, equation (B.4)–(B.6)] are related to our choice of real regular harmonics in (4) as follows:

$$
\begin{aligned}
z_l^m &= \left[\frac{\pi(l+|m|)!}{(2l+1)(l-|m|)!}\right]^{\frac{1}{2}} \left((-1)^m \mathcal{Y}_l^m + \mathcal{Y}_l^{-m}\right) && m \geqslant 0 \\
z_l^{-m} &= -\mathrm{i}\left[\frac{\pi(l+|m|)!}{(2l+1)(l-|m|)!}\right]^{\frac{1}{2}} \left((-1)^m \mathcal{Y}_l^m - \mathcal{Y}_l^{-m}\right) && m > 0.
\end{aligned} \tag{5}
$$

Square normalized STO $\bar{\chi}_{nlm}$ are readily obtained as

$$\bar{\chi}_{nlm} = \sqrt{\frac{(2l+1)}{2\pi(1+\delta_{m0})}\frac{(l-|m|)!}{(l+|m|)!}\frac{(2\zeta)^{2n+2l+1}}{(2n+2l)!}}\, \chi_{nlm}. \tag{6}$$

The idea of the shift-operator approach is to evaluate the desired integral of interest, e.g., overlap or two-electron repulsion, first for the simplest STO of s-symmetry, for which a quadrature is often relatively easy. In a second step, the quantum numbers are then raised by operators that involve derivatives with respect to parameters of the integral, like decay constants and inter-center distance. The benefit of such raising and lowering operators in the solution of molecular integrals was recognized quite early and exploited by various authors [25–30].

In this approach, a STO centered at $\mathbf{R}_I$ as a function of $\mathbf{r}_I = \mathbf{r} - \mathbf{R}_I$ may be written as

$$\chi_{nlm}(\mathbf{r}_I, \zeta) = \Omega_{lm}^n(\nabla_I)\frac{e^{-\zeta r_I}}{r_I}, \tag{7}$$

with ∇_I denoting the vector $(\partial/\partial X_I, \partial/\partial Y_I, \partial/\partial Z_I)$ and

$$\Omega_{lm}^n(\nabla_I) = z_l^m(\nabla_I) \left(-\frac{\partial}{\partial\zeta}\right)^n \left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^l. \tag{8}$$

A detailed discussion of the properties of $\mathcal{Y}_l^m(\nabla_I)$, related to $z_l^m(\nabla_I)$ by means of (5), is provided in a recent review by Weniger [24].

The form in (8) is now used to construct the Fourier transform of two-center STO products which are in the focus of this work:

$$I_{n_2l_2m_2}^{n_1l_1m_1}(\mathbf{k}, \zeta_1, \zeta_2, \mathbf{R}_I, \mathbf{R}_J) = \int d\mathbf{r}\, e^{i\mathbf{kr}} \chi_{n_1l_1m_1}(\mathbf{r}_I, \zeta_1) \chi_{n_2l_2m_2}(\mathbf{r}_J, \zeta_2) \tag{9}$$

$$= \Omega_{l_1m_1}^{n_1}(\nabla_I)\Omega_{l_2m_2}^{n_2}(\nabla_J) \int d\mathbf{r}\, e^{i\mathbf{kr}} \chi_{000}(\mathbf{r}_I, \zeta_1)\chi_{000}(\mathbf{r}_J, \zeta_2). \tag{10}$$

The shift-operator approach is applicable if the basic integrals (I_{000}^{000} in our case) have a closed form which can be easily differentiated with respect to the outer parameters. The following section shows that this is indeed the case for the present Fourier transform.

3. The basic integral

As shown by Rico and co-workers [31], the product of two s-type STO can be expressed as a one-dimensional integral which is suitable for further manipulations

$$\chi_{000}(\mathbf{r}_I, \zeta_1)\chi_{000}(\mathbf{r}_J, \zeta_2) = \frac{1}{\pi}\int_0^1 du[u(1-u)]^{-\frac{3}{2}}\zeta_u^2\hat{k}_{-1}\left(\zeta_u\sqrt{R^2 + \frac{r_u^2}{u(1-u)}}\right), \tag{11}$$

with $\mathbf{R} = \mathbf{R}_J - \mathbf{R}_I, \mathbf{R}_u = u\mathbf{R}_J + (1-u)\mathbf{R}_I, \mathbf{r}_u = \mathbf{r} - \mathbf{R}_u, \zeta_u^2 = \zeta_1^2 u + \zeta_2^2(1-u)$ and $\hat{k}_\nu(x) = x^\nu K_\nu(x)$, where $K_\nu(x)$ is the modified Bessel function of the second kind [23, equation (8.407)]. Please note that for $\hat{k}_\nu$, often referred to as the reduced Bessel function, slightly differing notations and definitions exist in the literature. See, for example, the work of Shavitt [32, p 15, equation (55)] and Steinborn and Filter [33, equations (3.1)–(3.2)].

After insertion of (11) into (9) and change of the integration variable to $\mathbf{r}_u$, the angular integration is readily performed by expanding the exponential in partial waves

$$e^{i\mathbf{kr}} = \sqrt{\frac{\pi}{2kr}}\sum_{l=0}^\infty i^l(2l+1)P_l(\cos\theta)J_{l+\frac{1}{2}}(kr), \qquad \theta = \angle(\mathbf{k}, \mathbf{r}), \tag{12}$$

and using the fact that the remainder of the integrand has s-symmetry. The result reads

$$I_{000}^{000}(\mathbf{k}, \zeta_1, \zeta_2, \mathbf{R}_I, \mathbf{R}_J) = \frac{4}{k}\int_0^1 du\, e^{i\mathbf{kR}_u}[u(1-u)]^{-\frac{3}{2}}\zeta_u^2 \tag{13}$$

$$\times \int_0^\infty dr_u r_u \sin(kr_u)\hat{k}_{-1}\left(\zeta_u\sqrt{R^2 + \frac{r_u^2}{u(1-u)}}\right). \tag{14}$$

The remaining radial integral is known [23, equation (6.726.3)], which leads to the final result for the basic integral:

$$I_{000}^{000}(\mathbf{k}, \zeta_1, \zeta_2, \mathbf{R}_I, \mathbf{R}_J) = \sqrt{8\pi}R\int_0^1 du\, e^{i\mathbf{kR}_u}\hat{k}_{-\frac{1}{2}}\left(R\sqrt{\zeta_u^2 + k^2u(1-u)}\right). \tag{15}$$

For vanishing momentum transfer this formula reduces to the known result for the corresponding overlap integral as given, e.g., by Ema *et al* [20]. For this special case, the pending integral may be solved analytically and is related to confluent hypergeometric functions. In general, however, an evaluation based on the numerical integration is unavoidable at this point.

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4. Transforms for higher quantum numbers

Using the shift-operator approach, Fourier transforms for higher quantum numbers may now be written as

$$I_{n_2 l_2 m_2}^{n_1 l_1 m_1}(\mathbf{k}, \zeta_1, \zeta_2, \mathbf{R}_I, \mathbf{R}_J) = z_{l_1}^{m_1}(\nabla_I) z_{l_2}^{m_2}(\nabla_J) \int_0^1 \mathrm{d}u\, \mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{R}_u} h_{n_2 l_2}^{n_1 l_1}(k, \zeta_1, \zeta_2, R, u) \tag{16}$$

with

$$h_{n_2 l_2}^{n_1 l_1}(k, \zeta_1, \zeta_2, R, u) = \sqrt{8\pi}\, R \left(-\frac{\partial}{\partial \zeta_1} \right)^{n_1} \left(-\frac{1}{\zeta_1} \frac{\partial}{\partial \zeta_1} \right)^{l_1}$$

$$\times \left(-\frac{\partial}{\partial \zeta_2} \right)^{n_2} \left(-\frac{1}{\zeta_2} \frac{\partial}{\partial \zeta_2} \right)^{l_2} \hat{k}_{-\frac{1}{2}} \left(R\sqrt{\zeta_u^2 + k^2 u(1-u)} \right), \tag{17}$$

where, as shown in appendix A, the derivatives with respect to the decay constants are relatively easy to perform. The action of the solid harmonics on the integral is more involved and requires further consideration. We proceed by introducing the equality

$$z_l^m(\nabla)(fg) = \sum_{l'=0}^{l} \sum_{m'=-(l-l')}^{l-l'} \sum_{m''=-l'}^{l'} d_{l'm'm''}^{lm} \left(z_{l-l'}^{m'}(\nabla) f \right) \left(z_{l'}^{m''}(\nabla) g \right) \tag{18}$$

for arbitrary functions $f(\mathbf{R})$, $g(\mathbf{R})$. This relation is proven in appendix B using the Leibniz rule for the differentiation of products together with the completeness and orthogonality relations of spherical harmonics. Alternative proofs were given by Dunlap [34] and Weniger [24].

Values for the coefficients $d_{l'm'm''}^{lm}$ can be obtained by straightforward differentiation for small quantum numbers. In general, the use of symbolic computation software allows the determination once and for all. Special cases include $d_{0m'm''}^{lm} = \delta_{m'm}\delta_{m''0}$ and $d_{lm'm''}^{lm} = \delta_{m'0}\delta_{m''m}$.

Applying (18) to (16), we arrive at

$$I_{n_2 l_2 m_2}^{n_1 l_1 m_1}(\mathbf{k}, \zeta_1, \zeta_2, \mathbf{R}_I, \mathbf{R}_J) = \sum_{l_1'=0}^{l_1} i^{l_1 - l_1'} \sum_{m_1'=-(l_1-l_1')}^{l_1-l_1'} \sum_{m_1''=-l_1'}^{l_1'} d_{l_1' m_1' m_1''}^{l_1 m_1}$$

$$\times \sum_{l_2'=0}^{l_2} i^{l_2 - l_2'} \sum_{m_2'=-(l_2-l_2')}^{l_2-l_2'} \sum_{m_2''=-l_2'}^{l_2'} d_{l_2' m_2' m_2''}^{l_2 m_2} \int_0^1 \mathrm{d}u$$

$$\times \left[u^{l_1-l_1'}(1-u)^{l_2-l_2'} z_{l_1-l_1'}^{m_1'}(\mathbf{k}) z_{l_2-l_2'}^{m_2'}(\mathbf{k})\, \mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{R}_u} \right]$$

$$\times \left[z_{l_1'}^{m_1''}(\nabla_I) z_{l_2'}^{m_2''}(\nabla_J) h_{n_2 l_2}^{n_1 l_1}(k, \zeta_1, \zeta_2, R, u) \right], \tag{19}$$

where we used the homogeneity of regular harmonics and the fact that plane waves are eigenfunctions of the momentum operator. The remaining derivation parallels the work of Ema *et al* [20] on overlap integrals and we will follow the nomenclature used there as close as possible to facilitate comparison. Since $h_{n_2 l_2}^{n_1 l_1}$ in the last line of (19) depends only on the norm of $\mathbf{R}$, the following theorem may be applied which goes back to Hobson [35]:

$$z_{l_1}^{m_1}(\nabla_I) z_{l_2}^{m_2}(\nabla_J) f(R) = (-1)^{l_1} \sum_{k=0}^{L_<} \frac{2^{-k}}{k!} \left[\nabla^{2k} z_{l_1}^{m_1}(\mathbf{R}) z_{l_2}^{m_2}(\mathbf{R}) \right] \left(\frac{1}{R}\frac{\partial}{\partial R} \right)^{l_1+l_2-k} f(R) \tag{20}$$

$$= (-1)^{l_1} \sum_{k=0}^{L_<} \mathcal{P}_k^{l_1 m_1 l_2 m_2}(\mathbf{R}) \left(\frac{1}{R}\frac{\partial}{\partial R} \right)^{l_1+l_2-k} f(R). \tag{21}$$

Here $L_< = \min(l_1, l_2)$ and $\mathcal{P}_k^{l_1 m_1 l_2 m_2}$ are given by

$$\mathcal{P}_k^{l_1 m_1 l_2 m_2}(\mathbf{R}) = \frac{2^k}{k!} \sum_{l=k}^{L_<} \frac{l!\Gamma(l_1+l_2-l+3/2)R^{2l-2k}}{(l-k)!\Gamma(l_1+l_2-l-k+3/2)} \sum_m c_{l_1+l_2-2lm}^{l_1 m_1 l_2 m_2} z_{l_1+l_2-2l}^m(\mathbf{R}), \qquad (22)$$

where the coefficients $c_{l_1+l_2-2lm}^{l_1 m_1 l_2 m_2}$ are directly related to real Gaunt coefficients (for a detailed derivation of (20)–(22) see appendix C).

Next we define the quantity $\tilde{\mathcal{S}}_{l_1' l_2' k}^{n_1 l_1 n_2 l_2}$ (this is a generalization of $\mathcal{S}_k^{n_1 l_1 n_2 l_2}$ in the work of Ema *et al* [20]), which is further discussed in appendix A:

$$\tilde{\mathcal{S}}_{l_1' l_2' k}^{n_1 l_1 n_2 l_2}(\mathbf{k}, \zeta_1, \zeta_2, \mathbf{R}_I, \mathbf{R}_J)$$

$$= \int_0^1 \mathrm{d}u \, \mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{R}_u} u^{l_2-l_2'}(1-u)^{l_1-l_1'} \left[\left(-\frac{1}{R}\frac{\partial}{\partial R} \right)^{l_1'+l_2'-k} h_{n_2 l_2}^{n_1 l_1}(k, \zeta_1, \zeta_2, R, u) \right]$$

$$= (-1)^{l_1'+l_2'-k} R^{1+2(l_1+l_2-l_1'-l_2')} \sum_{i=\lfloor \frac{n_1+1}{2} \rfloor}^{n_1} \sum_{j=\lfloor \frac{n_2+1}{2} \rfloor}^{n_2} c_i^{n_1}(\zeta_1) c_j^{n_2}(\zeta_2)$$

$$\times \sqrt{8\pi} \int_0^1 \mathrm{d}u \, \mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{R}_u} u^{\mu}(1-u)^{\nu} \hat{k}_{\alpha}\left(R\sqrt{\zeta_u^2 + k^2 u(1-u)} \right), \qquad (23)$$

with $\lfloor r \rfloor$ denoting the integer part of r and

$$\mu = l_1 + l_2 - l_2' + i; \qquad \nu = l_1 + l_2 - l_1' + j;$$
$$\alpha = -1/2 - l_1 - l_2 + l_1' + l_2' - i - j - k \qquad (24)$$
$$c_i^n(\zeta) = \frac{(-1)^{n+i} n! (2\zeta^2 R^2)^i}{(2\zeta)^n (2i-n)!(n-i)!}.$$

With these definitions we reach the main result of this work

$$I_{n_2 l_2 m_2}^{n_1 l_1 m_1}(\mathbf{k}, \zeta_1, \zeta_2, \mathbf{R}_I, \mathbf{R}_J) = \sum_{l_1'=0}^{l_1}(-1)^{l_1'} i^{l_1-l_1'} \sum_{m_1'=-(l_1-l_1')}^{l_1-l_1'} z_{l_1-l_1'}^{m_1'}(\mathbf{k}) \sum_{m_1''=-l_1'}^{l_1'} d_{l_1' m_1' m_1''}^{l_1 m_1}$$

$$\times \sum_{l_2'=0}^{l_2} i^{l_2-l_2'} \sum_{m_2'=-(l_2-l_2')}^{l_2-l_2'} z_{l_2-l_2'}^{m_2'}(\mathbf{k}) \sum_{m_2''=-l_2'}^{l_2'} d_{l_2' m_2' m_2''}^{l_2 m_2}$$

$$\times \sum_{k=0}^{L_<} \mathcal{P}_k^{l_1' m_1'' l_2' m_2''}(\mathbf{R}) \tilde{\mathcal{S}}_{l_1' l_2' k}^{n_1 l_1 n_2 l_2}(\mathbf{k}, \zeta_1, \zeta_2, \mathbf{R}_I, \mathbf{R}_J), \qquad (25)$$

where the product of the two regular harmonics could be rewritten as a sum over a single harmonic, if the interest lies in the partial-wave analysis of the Fourier transform. It can be easily checked that (25) reduces to the known result for the overlap of STO in the limit of vanishing momentum k.

It is now interesting to compare (25) with the related formula of Trivedi and Steinborn for the Fourier transform of B-function products [16]. At first glance the Trivedi–Steinborn result looks more compact and involves a lower number of summations. This is due to the favorable behavior of B-functions under the Fourier transform. If one is interested in STO, however, as it is often the case in quantum chemical or condensed matter problems, equation (25) provides the answer directly, while usage of the Trivedi–Steinborn form requires a summation over several individual integrals. Admittedly, for modest values of n only a small number of B-functions are necessary to represent a certain STO.

There is however another point which should be important in terms of efficiency. In a numerical quadrature a large number of function evaluations are necessary, especially if one tries to achieve high precision. In the Trivedi–Steinborn form regular spherical harmonics appear under the pending one-dimensional integral, while the integrand in (23) is simpler. Moreover, the quantity $\tilde{\mathcal{S}}^{n_1 l_1 n_2 l_2}_{l'_1 l'_2 k}$ does not depend on magnetic quantum numbers and can be precomputed for every l'_1, l'_2 and stored in an array of dimension k.

5. Implementation details

In this paragraph we provide information on the implementation of the derived expressions, discuss the issue of numerical stability and give some benchmark data.

The formulae of the last section are also valid in the special case of two STO located on the same center, due to the following property of the modified McDonald function:

$$\lim_{x \to 0} x^{2\nu} \hat{k}_{-\nu}(x) = 2^{\nu-1}(\nu - 1)! \qquad \forall \nu > 0. \tag{26}$$

Nevertheless, it is computationally much more efficient to replace the STO product by a sum over single STO using Gaunt coefficients. In this way the known analytical result for the Fourier transform of individual STO given by Belkić and Taylor [36] may be employed. Since the routine for the computation of real Gaunt coefficients is called extremely often also in the two-center case, an efficient strategy for their evaluation becomes very important. We follow the recent work of Pinchon and Hoggan [37], who devised a new index function to retrieve precomputed Gaunts for complex spherical harmonics. Only those coefficients that do not vanish due to selection rules are actually stored initially. Real Gaunt coefficients may then be obtained as outlined by Homeier and Steinborn [38].

The remaining computational bottleneck is given by the numerical integration. As already mentioned in the previous section, the term $\tilde{\mathcal{S}}^{n_1 l_1 n_2 l_2}_{l'_1 l'_2 k}$ is constructed right after looping over l'_1, l'_2 as a one-dimensional temporary array. The integrals over given values of μ, ν and α in (24) are computed only once and then stored, since they appear repeatedly for different combinations of the summation variables. For the numerical quadrature itself, we use adaptive integration as implemented in the *qag* routine of the QUADPACK library with a (7,15) Gauss–Kronrod rule [39]. With this approach an accuracy of typically 14 significant figures is achieved for the basic integrals as well as the overall Fourier transform.

The algorithm presented here is numerically stable for a wide range of quantum numbers, inter-center distances and momenta **k**. In situations where the ratio of decay constants ζ_1/ζ_2 is large, we however do find a significant digital erosion. For example, we still found 13 figures accuracy for a certain integral with a decay constant ratio of 50, which reduced to 11 figures at a ratio of 100 and finally three figures at a ratio of 150. This drawback was also observed in related earlier studies [17, 40] and possible remedies were suggested by Homeier and Steinborn [41] and recently by Safouhi and Berlu [42]. In most real world applications the atomic numbers of elements constituting the structure in question usually do not differ grossly. If the interest is however in properties like electronic excited states or polarizabilities, additional diffuse basis functions with small decay constants are required. In these cases a careful and more sophisticated evaluation of the basic integrals is necessary as outlined for example by Homeier and Steinborn [41]. In tables 1 and 2 we provide some benchmark results for selected parameter values. The numerical error is estimated by a comparison with a direct three-dimensional integration (equation (9)) performed with the computer algebra package *maple* that features arbitrary precision arithmetic. The CPU timings of the algorithm were performed on an Intel Pentium IV at 3.40 GHz. The evaluation of a Fourier transform

Table 1. Fourier transforms over products of *normalized* STO which share the following parameters: $\mathbf{R}_I = (0.3, -0.6, 0.9)$, $\mathbf{R}_J = (1.8, 0.9, 0.1)$, $\mathbf{k} = (0.4, -0.7, 0.1)$, $\tilde{n}_1 = 5$, $\tilde{n}_2 = 4$ (principal quantum number), $\zeta_1 = 3.0$, $\zeta_2 = 9.0$.

l_1	m_1	l_2	m_2	$\int d\mathbf{r}\, e^{i\mathbf{kr}}\, \bar{\chi}_{n_1 l_1 m_1}(\mathbf{r}_I, \zeta_1)\, \bar{\chi}_{n_2 l_2 m_2}(\mathbf{r}_J, \zeta_2)$								
0	0	0	0	1.3252	7422	8497	$\times 10^{-1}$	i	1.8979	8247	0877	$\times 10^{-2}$
1	1	0	0	1.4512	7601	7773	$\times 10^{-1}$	i	3.0116	4031	2294	$\times 10^{-2}$
1	-1	1	-1	-1.6452	5684	6177	$\times 10^{-1}$	-i	3.6525	2296	6886	$\times 10^{-2}$
1	-1	1	0	3.0597	8029	2345	$\times 10^{-2}$	i	7.9667	4828	0853	$\times 10^{-3}$
1	-1	1	1	-6.0005	5763	7932	$\times 10^{-2}$	i	1.6370	3748	7660	$\times 10^{-2}$
2	-2	2	2	5.3441	5583	8640	$\times 10^{-3}$	-i	1.4183	8452	6288	$\times 10^{-2}$
2	-1	2	2	-1.5707	4135	8199	$\times 10^{-2}$	i	1.0656	8041	5381	$\times 10^{-2}$
2	0	2	2	-2.3656	8841	5942	$\times 10^{-3}$	i	4.7624	2474	0227	$\times 10^{-3}$
2	1	2	2	8.0619	0229	2047	$\times 10^{-3}$	i	1.6691	6554	4101	$\times 10^{-2}$
2	2	2	2	-3.2683	5274	0242	$\times 10^{-2}$	-i	9.6119	2920	0390	$\times 10^{-3}$

Table 2. Comparison of accuracy and numerical efficiency of the algorithm presented in this work with that of Trivedi and Steinborn in the implementation of Homeier and Steinborn [41]. Parameters for the various integrals are the same as in table 1. The provided number of significant digits (Digits) is the minimum of the digits for real and imaginary part, respectively. CPU times in ms (Time) correspond to the computation of $(2l_1 + 1) \times (2l_2 + 1)$ integrals and present an average over 1000 evaluations.

				This work		Trivedi–Steinborn	
l_1	m_1	l_2	m_2	Digits	Time	Digits	Time
0	0	0	0	15	0.80	14	0.25
1	1	0	0	15	1.05	14	0.88
1	-1	1	-1	14	1.62	14	2.40
1	-1	1	0	14		13	
1	-1	1	1	14		14	
2	-2	2	2	14	2.75	13	10.69
2	-1	2	2	13		0	
2	0	2	2	13		13	
2	1	2	2	13		13	
2	2	2	2	13		14	

takes roughly some hundreds of μs which can be compared to the computational cost of a simple overlap integral on a similar machine, which was reported to be about three orders of magnitude lower [20]. This had to be expected, since in the latter case no numerical quadrature is required. In addition, equation (25) shows a much higher complexity than the expression for the overlap. An important point for calculations in extended basis sets is also apparent from table 1. The general computational cost increases with increasing angular momentum, but the integrals for different combinations of the magnetic quantum number come at little additional cost. In fact, the CPU time per integral is *decreasing* with increasing l. This is a consequence of the fact that the major bottleneck of this scheme is the construction of the quantity $\bar{\mathcal{S}}^{n_1 l_1 n_2 l_2}_{l'_1 l'_2 k}$ (23) which is independent of m.

In order to further explore the numerical efficiency of our approach, we performed test calculations with the FT2B code of Homeier, which implements the Trivedi–Steinborn formula and is described in detail in [41]. Using Möbius-transformation-based quadrature rules, these authors were able to handle the highly oscillatory integrand of the remaining one-dimensional

quadrature very efficiently. Utilizing the known formulae for the conversion of B-functions to STO (see, e.g., [19]), we were able to reproduce the results of table 1, with one exception[5]. The comparative timings given in table 2 were performed on the same machine and with comparable code optimization. Since the FT2B implementation is based on complex spherical harmonics, evaluations for different combinations of magnetic quantum numbers were necessary to obtain Fourier transforms of real STO. This additional effort was not included in the timings, since the Trivedi–Steinborn formula might be equally well formulated in real spherical harmonics.

We find, for the special choice of quantum numbers given in table 2, that the FT2B implementation is superior to our approach for individual integrals by roughly a factor of four. In general, one STO product may be represented by $(\lfloor(\tilde{n} - l)/2\rfloor + 1)^2$ B-function products, so that this result is strongly parameter dependent. In applications one is usually interested in the full set of integrals for different combinations of m-values and here our approach is numerically more efficient as table 2 shows. These computational savings will moreover increase with increasing angular momentum.

Code improvements are possible for both the B-function approach and for our scheme. Homeier mentions in his dissertation [19], that storage of some intermediate quantities might improve the performance for higher angular momentum. Our implementation might benefit from the Möbius quadrature put forward in [41]. While the integrand is evaluated at 36 points in the FT2B implementation, our adaptive integration requires 135 points for the same precision. A speed-up of a factor of four seems therefore achievable.

6. Summary

In this work a compact general purpose formula for the Fourier transform of STO products with arbitrary quantum numbers and geometrical parameters was derived. We highlighted the relation to earlier work based on B-functions and found differences that are relevant for the numerical efficiency. It should be stressed that the derivation presented here is completely independent. Moreover, the final formula cannot be reduced to the Trivedi–Steinborn result by a mere transformation from B-functions to STO. Regarding numerical stability which is often an issue in STO related studies [43], we achieved in general a completely satisfying accuracy apart from the known problems with very unsymmetric orbital products. We expect that the typical computational cost of several μs per integral allows for a very efficient evaluation of the notoriously complicated four-center electron repulsion integrals. The Fourier transform technique hence provides a viable alternative to existing direct methods in the field.

Acknowledgments

Appendix A. Some derivatives and further definitions

The derivative of the modified McDonald function $\hat{k}_\nu(x)$ has the following simple form:

$$\frac{d\hat{k}_\nu(x)}{dx} = -x\hat{k}_{\nu-1}(x). \tag{A.1}$$

---

[5] The case of $l_1 = 2, m_1 = -1, l_2 = 2, m_2 = 2$.

In order to evaluate the quantity $h_{n_2 l_2}^{n_1 l_1}$ in (17) an expression for the repeated action of the operator $-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}$ on $\hat{k}$ is required. Straightforward differentiation leads to

$$\left(-\frac{1}{\zeta_1}\frac{\partial}{\partial\zeta_1}\right)^l \hat{k}_\nu\left(R\sqrt{\zeta_u^2 + k^2 u(1-u)}\right) = R^{2l} u^l \hat{k}_{\nu-l}\left(R\sqrt{\zeta_u^2 + k^2 u(1-u)}\right),$$

$$\left(-\frac{1}{\zeta_2}\frac{\partial}{\partial\zeta_2}\right)^l \hat{k}_\nu\left(R\sqrt{\zeta_u^2 + k^2 u(1-u)}\right) = R^{2l}(1-u)^l \hat{k}_{\nu-l}\left(R\sqrt{\zeta_u^2 + k^2 u(1-u)}\right).$$

(A.2)

The action of the operator $-\frac{\partial}{\partial\zeta}$ is more involved but can be reduced to (A.2)

$$\left(-\frac{\partial}{\partial\zeta}\right)^n = \frac{n!(-1)^n}{(2\zeta)^n}\sum_{i=\lfloor\frac{n+1}{2}\rfloor}^{n}\frac{(-2\zeta^2)^i}{(2i-n)!(n-i)!}\left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^i,$$

(A.3)

which gives rise to the definitions of the coefficients $c_i^n(\zeta)$ in (24).

We now prove (A.3) by using induction. The induction basis for $n = 1$ is trivial. We further have ($\delta_{i,k}$ denoting the Kronecker delta)

$$\left(-\frac{\partial}{\partial\zeta}\right)\left(-\frac{\partial}{\partial\zeta}\right)^n = \sum_{i=\lfloor\frac{n+1}{2}\rfloor}^{n}\frac{n!(-1)^{n+1+i}2^{i-n}}{(2i-n-1)!(n-i)!}\zeta^{2i-n-1}(1-\delta_{i,n/2})\left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^i$$

$$+ \sum_{i'=\lfloor\frac{n+1}{2}\rfloor+1}^{n+1}\frac{n!(-1)^{n+1+i'}2^{i'-n-1}}{(2i'-n-2)!(n+1-i')!}\zeta^{2i'-n-1}\left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^{i'},$$

(A.4)

where we used the induction hypothesis and changed the summation index to $i' = i + 1$ in the second sum. Separating the term for the lower limit $i = \lfloor\frac{n+1}{2}\rfloor$ in the first sum and the upper limit $i' = n + 1$ in the second sum, we arrive at

$$\left(-\frac{\partial}{\partial\zeta}\right)^{n+1} = \frac{n!(-1)^{n+\lfloor\frac{n+1}{2}\rfloor+1}2^{\lfloor\frac{n+1}{2}\rfloor-n}}{(2\lfloor\frac{n+1}{2}\rfloor-n-1)!(n-\lfloor\frac{n+1}{2}\rfloor)!}\zeta^{2\lfloor\frac{n+1}{2}\rfloor-n-1}\left(1-\delta_{\lfloor\frac{n+1}{2}\rfloor,n/2}\right)\left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^{\lfloor\frac{n+1}{2}\rfloor}$$

$$+ \sum_{i=\lfloor\frac{n+1}{2}\rfloor+1}^{n}\frac{(n+1)!(-1)^{n+1+i}2^{i-n-1}}{(2i-n-1)!(n+1-i)!}\zeta^{2i-n-1}\left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^i + \zeta^{n+1}\left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^{n+1}.$$

(A.5)

For even n, we have $\lfloor\frac{n+1}{2}\rfloor = n/2$, and the first term in (A.5) vanishes. Since in this case $\lfloor\frac{n+1}{2}\rfloor + 1 = \lfloor\frac{n+2}{2}\rfloor$, it follows:

$$\left(-\frac{\partial}{\partial\zeta}\right)^{n+1} = \sum_{i=\lfloor\frac{n+2}{2}\rfloor}^{n+1}\frac{(n+1)!(-1)^{n+1+i}2^{i-n-1}}{(2i-n-1)!(n+1-i)!}\zeta^{2i-n-1}\left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^i.$$

(A.6)

For odd n, we have $\lfloor\frac{n+1}{2}\rfloor = (n+1)/2$, as well as $\lfloor\frac{n+1}{2}\rfloor + 1 = \lfloor\frac{n+2}{2}\rfloor + 1$. If we now extend the second sum in (A.5) to the lower limit $i = \lfloor\frac{n+2}{2}\rfloor$ the compensating term cancels exactly the first term in (A.5). Also in this case we therefore arrive at (A.6), that is the hypothesis for $n + 1$, which was to be demonstrated.

Derivatives with respect to the inter-center distance R are likewise readily obtained as

$$\left(\frac{1}{R}\frac{\partial}{\partial R}\right)^l R^{-2\nu}\hat{k}_\nu\left(R\sqrt{\zeta_u^2 + k^2 u(1-u)}\right) = (-1)^l R^{-2(\nu+l)}\hat{k}_{\nu+l}\left(R\sqrt{\zeta_u^2 + k^2 u(1-u)}\right),$$

(A.7)

where we have used the following recursion:

$$\hat{k}_{\nu+1}(x) = 2\nu\hat{k}_\nu(x) + x^2\hat{k}_{\nu-1}(x).$$

(A.8)

A combination of (A.2)–(A.7) leads to the second line in (23).

Finally, we define the coefficients $c_{l_3m_3}^{l_1m_1l_2m_2}$ that appear in (22). A product of two regular harmonics with same argument can be linearized as follows:

$$z_{l_1}^{m_1}(\mathbf{R})z_{l_2}^{m_2}(\mathbf{R}) = \sum_{l_3}\sum_{m_3} c_{l_3m_3}^{l_1m_1l_2m_2} z_{l_3}^{m_3}(\mathbf{R}) R^{l_1+l_2-l_3}. \qquad (A.9)$$

In terms of the Gaunt-like coefficients for the real *unnormalized* spherical harmonics of (4)

$$[l_1m_1|l_2m_2|l_3m_3] = \int \tilde{Y}_{l_1m_1}(\Omega)\tilde{Y}_{l_2m_2}(\Omega)\tilde{Y}_{l_3m_3}(\Omega)\,d\Omega, \qquad (A.10)$$

these coefficients read

$$c_{l_3m_3}^{l_1m_1l_2m_2} = \left(\frac{(2l_3+1)}{2\pi(1+\delta_{m_30})}\frac{(l_3-|m_3|)!}{(l_3+|m_3|)!}\right)[l_1m_1|l_2m_2|l_3m_3]. \qquad (A.11)$$

Please note that notation (A.10) differs from that usually employed for Gaunt coefficients [44]. The linearization formula (A.9) may be considerably simplified by taking advantage of the selection rules for the Gaunt-like coefficients (A.10), which were discussed by Homeier and Steinborn [38]:

$$z_{l_1}^{m_1}(\mathbf{R})z_{l_2}^{m_2}(\mathbf{R}) = \sum_{l=0}^{L_<}\sum_m c_{l_1+l_2-2lm}^{l_1m_1l_2m_2} z_{l_1+l_2-2l}^m(\mathbf{R}) R^{2l}$$

$$m \in \{m_1+m_2, m_1-m_2, -m_1+m_2, -m_1-m_2\} \qquad (A.12)$$

Appendix B. Leibniz theorem for regular harmonics

Here we prove equation (18) of section 4

$$z_l^m(\nabla)(fg) = \sum_{l'=0}^{l}\sum_{m'=-(l-l')}^{l-l'}\sum_{m''=-l'}^{l'} d_{l'm'm''}^{lm}\left(z_{l-l'}^{m'}(\nabla)f\right)\left(z_{l'}^{m''}(\nabla)g\right). \qquad (B.1)$$

The regular harmonic $z_l^m(\nabla)$ is given in cartesian form as

$$z_l^m(\nabla) = \sum_{i=0}^{l}\sum_{j=0}^{l-i} C_{ij}^{lm}\left(\frac{\partial}{\partial x}\right)^{(i)}\left(\frac{\partial}{\partial y}\right)^{(j)}\left(\frac{\partial}{\partial z}\right)^{(l-i-j)}, \qquad (B.2)$$

where $(\partial/\partial x)^{(n)}$ denotes the *n*th partial derivative with respect to *x* and the coefficients C_{ij}^{lm} are known constants (see, e.g., [30], equations (3) and (4)). Applying the Leibniz theorem for the differentiation of products we have

$$z_l^m(\nabla)(fg) = \sum_{i=0}^{l}\sum_{j=0}^{l-i} C_{ij}^{lm}\sum_{i'=0}^{i}\sum_{j'=0}^{j}\sum_{k'=0}^{l-i-j}\binom{i}{i'}\binom{j}{j'}\binom{l-i-j}{k'}$$

$$\times\left[\left(\frac{\partial}{\partial x}\right)^{(i-i')}\left(\frac{\partial}{\partial y}\right)^{(j-j')}\left(\frac{\partial}{\partial z}\right)^{(l-i-j-k')}f\right]$$

$$\times\left[\left(\frac{\partial}{\partial x}\right)^{(i')}\left(\frac{\partial}{\partial y}\right)^{(j')}\left(\frac{\partial}{\partial z}\right)^{(k')}g\right]. \qquad (B.3)$$

Using now the completeness of the regular harmonics we may expand the product $x^i y^j z^k$ into harmonics of angular momentum $l = i + j + k$:

$$x^i y^j z^k = \sum_{m=-l}^{l} B_m^l z_l^m(\mathbf{r}); \qquad l = i + j + k$$

$$B_m^l = \int x^i y^j z^k r^{-2l} z_l^m(\mathbf{r}) \, d\Omega. \qquad (B.4)$$

Inserting this expansion into (B.3) we find

$$z_l^m(\nabla)(fg) = \sum_{i=0}^{l} \sum_{j=0}^{l-i} C_{ij}^{lm} \sum_{i'=0}^{i} \sum_{j'=0}^{j} \sum_{k'=0}^{l-i-j} \binom{i}{i'}\binom{j}{j'}\binom{l-i-j}{k'}$$

$$\times \left[\sum_{m'=-(l-i'-j'-k')}^{l-i'-j'-k'} B_{m'}^{l-i'-j'-k'} z_{l-i'-j'-k'}^{m'}(\nabla)f \right]$$

$$\times \left[\sum_{m''=-(i'+j'+k')}^{i'+j'+k'} B_{m''}^{i'+j'+k'} z_{i'+j'+k'}^{m''}(\nabla)g \right], \qquad (B.5)$$

which can be simplified after changing the summation order according to

$$\sum_{a=0}^{a'} \sum_{b=0}^{b'} \sum_{c=0}^{c'} F(a,b,c) = \sum_{a=0}^{a'+b'+c'} \sum_{b=0}^{\min(a,b')} \sum_{c=\max(0,a-b-a')}^{\min(a-b,c')} F(a-b-c, b, c), \qquad (B.6)$$

for arbitrary F. With the help of the coefficients $A_{lm}^{l'}$

$$A_{lm}^{l'} = \sum_{i=0}^{l} \sum_{j=0}^{l-i} C_{ij}^{lm} \sum_{j'=0}^{\min(l',j)} \sum_{k'=\max(0,l'-j'-i')}^{\min(l'-j',l-i-j)} \binom{i}{l'-j'-k'}\binom{j}{j'}\binom{l-i-j}{k'}, \qquad (B.7)$$

with $l' = i' + j' + k'$, we finally arrive at

$$z_l^m(\nabla)(fg) = \sum_{l'=0}^{l} A_{lm}^{l'} \sum_{m'=-(l-l')}^{l-l'} \sum_{m''=-l'}^{l'} \left[B_{m'}^{l-l'} z_{l-l'}^{m'}(\nabla)f \right]\left[B_{m''}^{l'} z_{l'}^{m''}(\nabla)g \right], \qquad (B.8)$$

which is equivalent to (18) if we set $d_{l'm'm''}^{lm} = A_{lm}^{l'} B_{m''}^{l'} B_{m'}^{l-l'}$.

Appendix C. Proof of equation (20)

An old theorem given by Hobson [35] (see also [28]) states that if $R = (X^2 + Y^2 + Z^2)^{\frac{1}{2}}$ and $H(X, Y, Z)$ is a homogeneous polynomial of degree l in the X, Y, Z variables, then

$$H\left(\frac{\partial}{\partial X}, \frac{\partial}{\partial Y}, \frac{\partial}{\partial Z}\right) f(R) = \sum_{k=0}^{l} \frac{2^{l-2k}}{k!} [\nabla^{2k} H(X, Y, Z)]\left(\frac{\partial}{\partial R^2}\right)^{l-k} f(R). \qquad (C.1)$$

Taking into account that $\frac{\partial}{\partial X} = -\frac{\partial}{\partial X_I} = \frac{\partial}{\partial X_J}$ from $\mathbf{R} = \mathbf{R}_J - \mathbf{R}_I$, we may apply (C.1) to the product of the regular harmonics $z_{l_1}^{m_1}(\nabla)$ and $z_{l_2}^{m_2}(\nabla)$, which is a homogeneous polynomial of degree $l_1 + l_2$. Hence,

$$z_{l_1}^{m_1}(\nabla_I) z_{l_2}^{m_2}(\nabla_J) f(R) = (-1)^{l_1} \sum_{k=0}^{l_1+l_2} \frac{2^{l_1+l_2-2k}}{k!} \left[\nabla^{2k} z_{l_1}^{m_1}(\mathbf{R}) z_{l_2}^{m_2}(\mathbf{R}) \right] \left(\frac{\partial}{\partial R^2}\right)^{l_1+l_2-k} f(R)$$

$$= (-1)^{l_1} \sum_{k=0}^{l_1+l_2} \frac{2^{-k}}{k!} \left[\nabla^{2k} z_{l_1}^{m_1}(\mathbf{R}) z_{l_2}^{m_2}(\mathbf{R}) \right] \left(\frac{1}{R}\frac{\partial}{\partial R}\right)^{l_1+l_2-k} f(R), \qquad (C.2)$$

which is the same as (20) apart from the upper limit in the sum over *k*. In [20] it was shown that

$$
\nabla^{2k} z_p^m(\mathbf{R}) R^{2l} = \begin{cases} \dfrac{2^{2k} l! \, \Gamma(p+l+3/2)}{(l-k)! \, \Gamma(p+l-k+3/2)} z_p^m(\mathbf{R}) R^{2l-2k} & : \quad k \leqslant l \\ 0 & : \quad k > l \end{cases} \tag{C.3}
$$

Combining (C.2) with (A.12) and (C.3) we arrive at (20), (21) and (22) of the main paper.

References

[1] Bonham R A, Peacher J L and Cox H L 1964 *J. Chem. Phys.* **40** 3083
[2] Bonham R A 1965 *J. Phys. Soc. Japan* **20** 2260
[3] Hedin L 1965 *Phys. Rev.* A **139** 796
[4] Rohlfing M and Louie S G 1998 *Phys. Rev. Lett.* **80** 3320
[5] Rohlfing M 2000 *Int. J. Quantum Chem.* **80** 807
[6] Ohta Y, Maki J, Yoshimoto T, Shigeta Y, Nagao H and Nishikawa K 2001 *Int. J. Quantum Chem.* **84** 348
[7] Niehaus T A, Rohlfing M, Sala F Della, Carlo A Di and Frauenheim T 2005 *Phys. Rev.* A **71** 022508
[8] Neaton J B, Hybertsen M S and Louie S G 2006 *Phys. Rev. Lett.* **97** 216405
[9] Pople J A and Beveridge J L 1970 *Approximate Molecular Orbital Theory* (New York: McGraw-Hill)
[10] Pisani C and Dovesi R 1980 *Int. J. Quantum Chem.* **17** 501
[11] Bentley J and Stewart R F 1973 *J. Comput. Phys.* **11** 127
[12] Junker B R 1980 *J. Phys. B: At. Mol. Phys.* **13** 1049
[13] Straton J C 1987 *Phys. Rev.* A **35** 2729
[14] Straton J C 1988 *Phys. Rev.* A **37** 4531
[15] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[16] Trivedi H P and Steinborn E O 1983 *Phys. Rev.* A **27** 670
[17] Grotendorst J and Steinborn E O 1988 *Phys. Rev.* A **38** 3857
[18] Grotendorst J and Steinborn E O 1985 *J. Comput. Phys.* **61** 195
[19] Homeier H H H 1990 *Integraltransformationsmethoden und Quadraturverfahren für Molekülintegrale mit B-Funktionen* (S. Roderer: Regensburg)
[20] Ema I, López R, Fernández J J, Ramírez G and Rico J F 2008 *Int. J. Quantum Chem.* **108** 25
[21] Velde G te, Bickelhaupt F M, Baerends E J, Guerra C Fonseca, van Gisbergen S J A, Snijders J G and Ziegler T 2001 *J. Comput. Chem.* **22** 931
[22] Fernando G W, Davenport J W, Watson R E and Weinert M 1989 *Phys. Rev.* B **40** 2757
[23] Gradshteyn I S and Ryzhik I M 1980 *Table of Integrals, Series and Products* (London: Academic)
[24] Weniger E J 2005 *Collect. Czech. Chem. Commun.* **70** 1225
[25] Barnett M P and Coulson C A 1951 *Phil. Trans. R. Soc.* A **243** 221
[26] Guidotti G, Arrighini G P and Marinelli F 1979 *Theor. Chim. Acta* **53** 165
[27] Fieck G 1980 *Theor. Chim. Acta* **54** 323
[28] Weniger E J and Steinborn E O 1983 *J. Chem. Phys.* **78** 6121
[29] Rico J F, Fernández J J, López R and Ramírez G 2000 *Int. J. Quantum Chem.* **78** 83
[30] Rico J F, López R and Ramírez G 2001 *J. Mol. Struct. Theochem* **537** 27
[31] Rico J F, Ema I, López R, Ramírez G and Ishida K 2008 *Recent Advances in Computational Chemistry, Molecular Integrals over Slater Orbitals* ed T Ozdogan and B Ruiz (Kerala, India: Transworld Research Network) (chapter 5)
[32] Shavitt I 1963 *Methods in Computational Physics* vol 2 *Quantum Mechanics* ed B Alder, S Fernbach and M Rotenberg (New York: Academic) pp 1–45
[33] Steinborn E O and Filter E 1975 *Theor. Chim. Acta* **38** 273
[34] Dunlap B I 1990 *Phys. Rev.* A **42** 1127
[35] Hobson E W 1965 *The Theory of Spherical and Ellipsoidal Harmonics* (New York: Chelsea) p 127 (equation (7))
[36] Belkić D and Taylor H S 1989 *Phys. Scr.* **39** 226
[37] Pinchon D and Hoggan P E 2007 *Int. J. Quantum Chem.* **107** 2186
[38] Homeier H H H and Steinborn E O 1996 *J. Mol. Struct. Theochem* **368** 31

[39] Piessens R, de Doncker-Kapenga E and Überhuber C W 1983 *QUADPACK: A Subroutine Package for Automatic Integration* (Berlin: Springer)
[40] Monkhorst H J and Harris F E 1972 *Int. J. Quantum Chem.* **6** 601
[41] Homeier H H H and Steinborn E O 1992 *Int. J. Quantum Chem.* **41** 399
[42] Safouhi H and Berlu L 2006 *J. Comput. Phys.* **216** 19
[43] Barnett M B 2002 *Theor. Chem. Acc.* **107** 241
[44] Gaunt J A 1929 *Phil. Trans. R. Soc.* A **228** 151