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Expansion of atomic orbital products in terms of a complete function set*

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Summary. An alternative method for the evaluation of matrix elements required in an LCAO-SCF calculation is presented. It is based on the use of solutions of the Helmholtz equation within a spherical domain for expanding charge distributions with boundary conditions devised to make the electrostatic-potential integral particularly simple. This method allows the systematic evaluation of bielectronic integrals to be performed for any type of atomic orbitals.

Key words: Atomic orbitals – LCAO-SCF – Bielectronic integrals – Helmholtz equation

1 Introduction

The appropriate choice of basis functions to solve SCF equations within the LCAO approach must take care of the following facts: (a) the rate of convergence of molecular orbitals [1]; (b) the difficulty in computing monoelectronic and bielectronic integrals, (c) the implementation of analytical gradients, and (d) the correct molecular behaviour both near the nuclei and in the long range region. Points (b) and (c) are of the greatest importance for the prediction of molecular geometries and nuclear vibrations [2] and they are relatively well taken into account with the use of Gaussian-type orbitals (GTOs). However, in most cases it is necessary to include a large number of GTOs in order to satisfy conditions a) and d) properly. On the other hand, calculations using exponential-type orbitals (ETOs) (hydrogen-like, Slater, etc.) [3] give appropriate results with respect to points (a) and (d) [4]. Unfortunately, in this case the evaluation of the required multicenter integrals

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is so difficult that it precludes the existence of general program facilities. However, important research work has been carried out in this direction [5–20].

In the present work an algorithm to compute matrix elements of an LCAO calculation is proposed which could in principle be implemented with any type of sufficiently fast decaying atomic orbitals (ETOs, GTOs, etc., see Appendix I). This algorithm takes advantage of the fact that due to the exponential decay of AOs, the evaluation of any matrix element involved in an LCAO calculation can be reduced to an integration within a sphere of a suitably chosen radius a, neglecting the contribution from the region outside the sphere. It can be shown that the error involved in that truncation of the space decays exponentially with increasing a. To carry out the integration within the sphere, atomic orbital products $\chi_i^* \chi_j$ are expanded in terms of an appropriate basis set defined in this work, having special properties with respect to the operator $|\boldsymbol{r} - \boldsymbol{r}'|^{-1}$. In this way, Coulomb-type bielectronic integrals can be straightforwardly computed. That is, the sixfold integral is shown to be reduced to a numerical series in terms of just the expansion coefficients of the "charge distributions" $\chi_i^* \chi_j$. An upper bound to the error due to the truncation of the series can be explicitly found.

The basis set functions are built up as solutions of the Helmholtz equation, with appropriate boundary conditions so that they satisfy special integral properties with respect to the operator $|\boldsymbol{r} - \boldsymbol{r}'|^{-1}$.

Following the ideas of Shavitt et al. [6] and using well known properties of spherical harmonics and Bessel functions, the calculation of the necessary expansion coefficients is shown to lead to a finite sum of one-dimensional integrals. When GTOs are used, a further and important simplification is achieved. It is interesting to remark that there are other methods in the literature that could be implemented alternatively to evaluate these coefficients [5–20].

A method devised on these grounds would essentially scale like N^2 times n (where N is the number of basis functions) for an N-orbital molecular problem ([12] p. 120), provided the charge distributions expansions can be truncated after n terms. This number can be estimated by finding an upper bound to the truncation error considering unfavourable cases.

2 Method

2.1 Construction of the basis set

First, a set of functions $U_q(\boldsymbol{r})$ are defined within a spherical domain of radius a, having special properties with respect to the operator $|\boldsymbol{r} - \boldsymbol{r}'|^{-1}$ restricted to that sphere.

Let $U_q(\boldsymbol{r})$ be solutions of the Helmholtz equation:

$$\nabla^2 U_q(\boldsymbol{r}) = -k_q^2 U_q(\boldsymbol{r}), \tag{1}$$

where $q = (n, l, m)$ stands for a set of indices. If it is assumed that $\{U_q(\boldsymbol{r})\}$ represent sources in the Poisson equation inside a sphere of radius a [21], then:

$$\nabla^2 \left[\int_{r'<a} \mathrm{d}V' \frac{U_q(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \right] = \begin{cases} -4\pi U_q(\boldsymbol{r}) & \text{if } |\boldsymbol{r}| < a, \\ 0 & \text{if } |\boldsymbol{r}| > a. \end{cases} \tag{2}$$

For $k_q \neq 0$, it follows from Eqs. (1) and (2) that the function:

$$D_q(\boldsymbol{r}) = (1/4\pi) \int_{r'<a} \mathrm{d}V' \frac{U_q(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} - \frac{U_q(\boldsymbol{r})}{k_q^2}, \tag{3}$$

which is continuously differentiable up to second order for $|\boldsymbol{r}| \leqslant a$ (see Ref. [22] p. 596 and Ref. [23] p. A-105), satisfies the Laplace equation ([22] p. 596) in the region $|\boldsymbol{r}| < a$:

$$\nabla^2 D_q(\boldsymbol{r}) = 0 \quad (|\boldsymbol{r}| < a). \tag{4}$$

For those values of k_q which satisfy the condition:

$$D_q(\boldsymbol{r})|_{r=a} = 0 \tag{5}$$

it follows from the Laplace equation, Eq. (4), and the boundary condition, Eq. (5), that ([23] p. A-105):

$$D_q(\boldsymbol{r}) = 0 \quad \text{for } |\boldsymbol{r}| < a, \tag{6}$$

which means that the following property is satisfied by $U_q(\boldsymbol{r})$:

$$U_q(\boldsymbol{r}) = (k_q^2/4\pi) \int_{r'<a} \mathrm{d}V' \frac{U_q(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \quad \text{for } |\boldsymbol{r}| < a. \tag{7}$$

This integral property, Eq. (7), shows that integrals of the operator $|\boldsymbol{r} - \boldsymbol{r}'|^{-1}$ can be performed in a straightforward way in terms of the functions $U_q(\boldsymbol{r})$ within the sphere of radius a.

The next step is to prove that a basis of the Hilbert space of functions within the sphere can be built up with the set $\{U_q(\boldsymbol{r})\}$, and to determine explicitly their functional form.

Separation of variables in the Helmholtz equation in spherical coordinates yields:

$$U_{lmn}(\boldsymbol{r}) = B_{ln} R_{ln}(r)\, Y_{lm}(\Omega), \tag{8}$$

B_{ln} is a normalization constant, $Y_{lm}(\Omega)$ is a spherical harmonic (the phase convention of Condon and Shortley [24] is used in this work) and the functions $R_{ln}(r)$ are spherical Bessel functions ([25] p. 437):

$$R_{ln}(r) = r^{-1/2} J_{l+1/2}(k_{ln} r) = (2k_{ln}/\pi)^{1/2} j_l(k_{ln} r), \tag{9}$$

(where the requirement of regularity at $r = 0$ has been included in order to rule out the Neumann functions [22]).

Once proper boundary conditions are imposed at $r = a$, a discrete set of functions $\{R_{ln}(r), n = 1, \ldots\}$ for each value of l is obtained, whose properties in the interval $(0, a)$ must be investigated. In this case, the boundary condition at $r = a$ is the one imposed in Eq. (5) for Eq. (7) to hold, i.e.,

$$U_q(\boldsymbol{r})|_{r=a} = \frac{k_q^2}{4\pi} \int_{r'<a} \frac{U_q(\boldsymbol{r}')\,\mathrm{d}V'}{|\boldsymbol{r} - \boldsymbol{r}'|}\bigg|_{r=a}. \tag{10}$$

On making use of the expansion of the operator $|\boldsymbol{r} - \boldsymbol{r}'|^{-1}$ in terms of spherical harmonics within the region $|\boldsymbol{r}'| < |\boldsymbol{r}'| = a$,

$$|\boldsymbol{r} - \boldsymbol{r}'|^{-1}_{r=a} = (4\pi/a) \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (r'/a)^l \frac{1}{2l+1} Y^*_{lm}(\theta, \varphi)\, Y_{lm}(\theta', \varphi') \tag{11}$$

as well as Eq. (8), by orthonormality properties of spherical harmonics, the boundary condition at $r = a$ for $R_{ln}(r)$ obtained from Eq. (10) is

$$R_{ln}(a) = \frac{k_{ln}^2}{(2l+1)a^{l+1}} \int_0^a \mathrm{d}r\, r^{l+2} R_{ln}(r). \tag{12}$$

Considering Eq. (9), the variables changes $x = k_{ln}r$, $y = k_{ln}a$ and setting $v = l + 1/2$, Eq. (12) transforms into:

$$J_v(y) = \frac{1}{2v\,y^v} \int_0^y \mathrm{d}x\, x^{v+1} J_v(x). \tag{13}$$

The following two properties of Bessel functions can be used to simplify Eq. (13) ([25] p. 361):

$$x^{v+1} J_v(x) = \frac{\mathrm{d}}{\mathrm{d}x}[x^{v+1} J_{v+1}(x)] \quad \forall v \tag{14}$$

$$xJ_v'(x) + vJ_v(x) = xJ_{v-1}(x) \quad \forall v \tag{15}$$

yielding the explicit form for the boundary condition at $r = a$:

$$k_{ln}a \cdot J_{l-1/2}(k_{ln}a) = 0. \tag{16}$$

The solutions of this equation yield a discrete set of values of $\{k_{ln}\}$, from which the orthogonal ([27] p. 264) set $\{j_l(k_{ln}r), n = 1, \ldots\}$ can be constructed for each l. The $k_{ln} = 0$ value (which is a solution of Eq. (16)) is excluded because the corresponding "eigenfunction" $r^{l+1/2}$ is not orthogonal to $J_{l+1/2}(k_{ln}r)$ for any $k_{ln} \neq 0$ (see Eqs. (13) and (16)) ([23] p. 762). Using Eq. (15), Eq. (16) can be rewritten as

$$(k_{ln}a)J_v'(k_{ln}a) + vJ_v(k_{ln}a) = 0. \tag{17}$$

This boundary condition has the form required in Ref. [26] p. 580 to define a Dini expansion. Convergence properties of the Dini expansion of any continuous function $f(r)$ in $[0, a]$ are well known from the literature ([26] p. 602). The expansion uniformly converges in $[\delta, a - \delta]$ with δ arbitrarily small.

Following Smirnov ([28] p. 127), it is possible to demonstrate that the basis $\{U_q(\boldsymbol{r})\}$ is complete. As a consequence of the finiteness of ([22] p. 271):

$$F(\boldsymbol{r}) = \int_{r'<a} \frac{\mathrm{d}V'}{|\boldsymbol{r} - \boldsymbol{r}'|^2} \quad \forall r < a, \tag{18}$$

it follows immediately ([28] p. 130) that the integral linear self-conjugate operator I defined as

$$I(\varphi) = \frac{1}{4\pi} \int_{r'<a} \frac{\mathrm{d}V'\varphi(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \quad r < a \tag{19}$$

is "completely continuous" ([28] p. 121). It is also bounded ([28] p. 115), as can be seen from

$$\begin{aligned} \|I(\varphi)\|^2 &= \frac{1}{(4\pi)^2} \int_{r<a} \mathrm{d}V \left[\int_{r'<a} \frac{\mathrm{d}V'\varphi(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \right]^2 \\ &\leqslant \frac{1}{(4\pi)^2} \int_{r<a} \mathrm{d}V \left[\int_{r'<a} \frac{\mathrm{d}V'}{|\boldsymbol{r} - \boldsymbol{r}'|^2} \int_{r'<a} \varphi^2(\boldsymbol{r}')\,\mathrm{d}V' \right] \\ &= \frac{1}{(4\pi)^2} \left[\int_{r<a} \mathrm{d}V \int_{r'<a} \frac{\mathrm{d}V'}{|\boldsymbol{r} - \boldsymbol{r}'|^2} \right] \cdot \|\varphi\|^2 = N \cdot \|\varphi\|^2, \end{aligned} \tag{20}$$

where use has been made of the Cauchy–Schwarz inequality and N is a constant independent of φ.

These two properties of the operator I (i.e. complete continuity and boundedness) are sufficient to ensure that the corresponding eigenfunctions (i.e. the functions $\{U_q(\boldsymbol{r})\}$ of Eq. (7)) form a complete orthogonal basis of $L^2(r < a)$ ([28] p. 127 and p. 135), i.e.,

$$\int_{r'<a} U_q^*(\boldsymbol{r}) \cdot U_{q'}(\boldsymbol{r})\, \mathrm{d}V = \delta_{qq'} \tag{21}$$

and any function $\phi(\boldsymbol{r}) \in L^2(r < a)$ can be expanded as

$$\phi(\boldsymbol{r}) = \sum_{lmn} C_{lmn}\, U_{lmn}(\boldsymbol{r}), \tag{22}$$

with coefficients:

$$C_{lmn} = \int_{r<a} \phi(\boldsymbol{r})\, U_{lmn}^*(\boldsymbol{r})\, \mathrm{d}V, \tag{23}$$

where the convergence is in the mean.

By construction, every $U_q(\boldsymbol{r})$ satisfies Eq. (7). Its importance lies in the following fact. If $U_q^*(\boldsymbol{r})$ and $U_{q'}(\boldsymbol{r}')$ are thought of as charge distributions, the Coulomb interaction between them can be evaluated as

$$\int_{r<a} \int_{r'<a} \frac{U_q^*(\boldsymbol{r})\, U_{q'}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\, \mathrm{d}V\, \mathrm{d}V' = \frac{4\pi}{k_q^2}\, \delta_{qq'} \tag{24}$$

Therefore, the Coulomb interaction between any two charge distributions $\rho_1(\boldsymbol{r})$ and $\rho_2(\boldsymbol{r})$ within the sphere can be straightforwardly expressed in terms of their Fourier-type coefficients.

The usefulness of these properties to evaluate matrix elements of an LCAO-SCF calculation is discussed in the following section.

2.2 *Evaluation of matrix elements*

To evaluate matrix elements of an LCAO-SCF calculation, consider a basis set of AOs $\{\chi_i(\boldsymbol{r})\}$ centered on arbitrary positions. The functions $\chi_i(\boldsymbol{r})$ can be real or complex, exponential-type orbitals (ETOs) or Gaussian-type orbitals (GTOs). The calculation of each matrix element requires an integration extended to the whole space of charge distribution products $\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})$ involving at most two centers. These charge distribution products can be expanded in terms of the functions defined in the previous section, provided a convenient choice of the a parameter (i.e. the radius of the sphere) can be made in order to ensure that the sphere encloses the region of the space where $\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})$ is significant. This is always possible due to the exponential decay of AOs. On the other hand, the error involved can be made arbitrarily small by choosing a sufficiently large value of a. Details of this statement are given in Appendix I. Thus,

$$\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r}) = \sum_q C_q^{ij}\, U_q(\boldsymbol{r}) = \sum_{n=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C_{lmn}^{ij}\, U_{lmn}(\boldsymbol{r}), \tag{25}$$

where

$$C_q^{ij} = \int_{r<a} \mathrm{d}V\, \chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})\, U_q^*(\boldsymbol{r}). \tag{26}$$

Since $U^*_{lmn} = (-1)^m U_{l-mn}$([33] p. 185), the following relation holds:

$$C^{ij}_{lmn} = (-1)^m C^{ji*}_{l-mn}. \tag{27}$$

Once all coefficients C^{ij}_q are determined for all products $\chi_i^*(r)\chi_j(r)$, the evaluation of matrix elements is straightforward. Thus, bielectronic integrals can be approximately calculated as follows:

$$\begin{aligned}(ij|rs) &= \int dV\, dV' \frac{\chi_i^*(r)\chi_j(r)\chi_r^*(r')\chi_s(r')}{|r-r'|} \\ &\cong \int_{r,r'<a} dV\, dV' \frac{\chi_i^*(r)\chi_j(r)\chi_r^*(r')\chi_s(r')}{|r-r'|} \\ &= 4\pi \sum_{n=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{C^{ji*}_{lmn} C^{rs}_{lmn}}{k^2_{ln}}\end{aligned} \tag{28}$$

by virtue of Eq. (24). In practical applications, however, the series must be truncated at given values $l = L$ and $n = N$. An upper bound to the error involved in this truncation is given explicitly in Appendix IIa. Further use of these bounds allows the convergence properties to be analysed.

The overlap integral $S_{ij} = \int dV\, \chi_i^* \chi_j$ can be approximated as

$$\begin{aligned}S_{ij} &= \sum_q C^{ij}_q \int_{r<a} dV\, U_q(r) \\ &= \sum_{lmn} C^{ij}_{lmn} \int d\Omega\, Y_{lm}(\Omega) \int_0^a dr\, r^2 B_{ln} R_{ln}(r) \\ &= \sum_{lmn} C^{ij}_{lmn} (4\pi)^{1/2} \delta_{m0}\delta_{l0} (2/\pi k_{0n})^{1/2} B_{ln} \int_0^a dr\, r \cdot \sin(k_{0n} r) \\ &= \sum_{lmn} C^{ij}_{lmn} (4\pi)^{1/2} \delta_{m0}\delta_{l0} (2/\pi k_{0n})^{1/2} \\ &\quad \times 2^{1/2} [a J_{l+1/2}(k_{ln} a)]^{-1} \int_0^a dr\, r \cdot \sin(k_{0n} r) \\ &= \sum_{lmn} C^{ij}_{lmn} \delta_{m0}\delta_{l0} (4\pi^{1/2}/[(2a)^{1/2} k^2_{0n}]),\end{aligned} \tag{29}$$

where, the angular part of the integral renders $\delta_{m0}\delta_{l0}$, the expression of the normalization factor B_{ln} is taken into account and the radial part has been evaluated explicitly.

The monoelectronic part of the LCAO-SCF calculation [29]:

$$h_{ij} = \int dV \chi_i^*(r) \left[-\tfrac{1}{2} \nabla^2 - \sum_N \frac{Z_N}{|r - R_N|} \right] \chi_j(r) \tag{30}$$

gives matrix elements which can be easily computed, except for the kinetic energy part that requires special treatment. However, when hydrogen-like

atomic orbitals are used, from Eq. (7), the following closed expression is obtained:

$$h_{ij} = \int \mathrm{d}V\, \chi_i^*(\boldsymbol{r}) \left[\varepsilon_j + (\xi_j/|\boldsymbol{r} - \boldsymbol{R}_{Nj}|) - \sum_N (Z_N/|\boldsymbol{r} - \boldsymbol{R}_N|) \right] \chi_j(\boldsymbol{r})$$

$$= \varepsilon_j S_{ij} + 4\pi\xi_j \sum_q \frac{C_q^{ij} U_q(\boldsymbol{R}_{Nj})}{k_{ln}^2} - 4\pi \sum_N \sum_q \frac{Z_N C_q^{ij} U_q(\boldsymbol{R}_N)}{k_{ln}^2}, \tag{31}$$

where ε_j and ξ_j are respectively the energy and orbital exponent associated to the hydrogen-like AO $\chi_j(\boldsymbol{r})$, N is the nucleus where the AO is centered and $\boldsymbol{R}_N$ is the position vector of nucleus N.

2.3 Calculation of the expansion coefficients

Direct evaluation of the coefficients C_{lmn}^{ij} from Eq. (22) requires some rather involved analysis. Thus, it is convenient to extend the integration interval to infinity. Even though this introduces a further source of error, it allows the powerful methods already extensively investigated in the literature to be explicitly applied to the present problem.

It is always possible to express the coefficients C_{lmn}^{ij} as follows:

$$C_{lmn}^{ij} = \int_{r<a} \mathrm{d}V\, \chi_i^*(\boldsymbol{r}) \chi_j(\boldsymbol{r})\, U_{lmn}^*(\boldsymbol{r})$$

$$\equiv \int_{r<\infty} \mathrm{d}V\, \chi_i^*(\boldsymbol{r}) \chi_j(\boldsymbol{r})\, U_{lmn}^*(\boldsymbol{r}) - \int_{r>a} \mathrm{d}V\, \chi_i^*(\boldsymbol{r}) \chi_j(\boldsymbol{r})\, U_{lmn}^*(\boldsymbol{r}) \tag{32}$$

$$\equiv \mathscr{C}_{lmn}^{ij} - \varepsilon_{lmn}^{ij},$$

where the AOs χ_i, χ_j can be centered on different nuclei.

By using a similar argument to that outlined in Appendix I, it can be proved that the error ε_{lmn}^{ij} decreases exponentially when a increases.

Of all possible alternative methods for the calculation of $\mathscr{C}_{lmn}^{ij}$, the one of Shavitt et al. [6] can be considered particularly useful.

Thus, firstly, it is necessary to obtain the integrals corresponding to two Slater type $1s$ orbitals on different centers located at $\boldsymbol{A}$ and $\boldsymbol{B}$ (if they are located on the same center an analytical expression can be obtained quite straightforwardly along similar lines).

The coefficients are denoted by $\mathscr{C}_{lmn}^{IJ}$, where $I = 1s_A$ and $J = 1s_B$. General coefficients corresponding to the $2s$, $2p$, ... orbitals can similarly be generated by applying the following operators to $\mathscr{C}_{lmn}^{IJ}$, such as described in Ref. [6]:

$$\hat{O}_{\alpha i} = -\frac{\partial}{\partial\alpha}[\alpha^{-1}]\frac{\partial}{\partial A_i},$$

$$\hat{O}_{1\alpha} = \frac{\partial}{\partial\alpha}[\alpha^{-1}], \tag{33}$$

$$\hat{D} = \frac{\partial}{\partial\alpha}.$$

This fact is easy to show taking into account that orbitals distinct from 1*s* ones can be expressed as

$$r_A^n e^{-\alpha r_A} = (-1)^{n+1} \hat{D}^n [e^{-\alpha r_A}] \tag{34}$$

$$(r_i - A_i)^n \, \mathrm{e}^{-\alpha r_A} = \hat{O}_{\alpha i}[(r_i - A_i)^{n-1} \, \mathrm{e}^{-\alpha r_A}] + (-1)^{n+1}(n-1)\hat{O}_{1\alpha}[(r_i - A_i)^{n-2} \, \mathrm{e}^{-\alpha r_A}], \tag{35}$$

where $i = x, y, z$, $r_A = |\boldsymbol{r} - \boldsymbol{A}|$ and $n \geqslant 2$. Thus, the remaining coefficients can be obtained as linear combinations of partial derivatives of $\mathscr{C}_{lmn}^{IJ}$ with respect to the Slater exponents α and β, and the cartesian components of $\boldsymbol{A}$ and $\boldsymbol{B}$.

Numerical evaluation of $\mathscr{C}_{lmn}^{IJ}$ can be reduced to that of a one-dimensional integral as follows. On writing $\mathscr{C}_{lmn}^{IJ}$ as

$$\mathscr{C}_{lmn}^{IJ} = N_A N_B \int_{r<\infty} \mathrm{d}V \exp(-\alpha r_A - \beta r_B) \, U_{lmn}^*(\boldsymbol{r}) \tag{36}$$

using the integral representation [6]

$$\begin{aligned} \exp(-\alpha r_A - \beta r_B) &= (\alpha\beta/4\pi) \int_0^\infty \mathrm{d}s \int_0^\infty \mathrm{d}t (st)^{-3/2} \\ &\quad \times \exp\{-(\alpha^2/4s) - (\beta^2/4t) - s r_A^2 - t r_B^2\} \\ &= (\alpha\beta/4\pi) \int_0^\infty \mathrm{d}s \int_0^\infty \mathrm{d}t (st)^{-3/2} \exp\{-(\alpha^2/4s) - (\beta^2/4t)\} \\ &\quad \times \exp\{-(s+t)|\boldsymbol{r} - \boldsymbol{P}|^2 - (st/s+t)|\boldsymbol{A} - \boldsymbol{B}|^2\}, \end{aligned} \tag{37}$$

where $\boldsymbol{P} = (s\boldsymbol{A} + t\boldsymbol{B})/(s+t)$; in conjunction with the expansion ([30] p. 227):

$$\exp(\delta \cos\gamma) = (\pi/2\delta)^{1/2} \sum_{l=0}^{\infty} (2l+1) \, P_l(\cos\gamma) \, I_{l+1/2}(\delta), \tag{38}$$

(where $\delta = 2(s+t)Pr$ and γ is the angle between $\boldsymbol{P}$ and $\boldsymbol{r}$, and $I_{l+1/2}(\delta)$ are the modified Bessel functions of fractional order ([31] p. 967)), as well as the following identity ([31] p. 718):

$$\int_0^\infty \mathrm{d}r \, r J_{l+1/2}(\gamma r) I_{l+1/2}(\beta r) \exp(-\alpha r^2) = \frac{1}{2\alpha} J_{l+1/2}(\beta\gamma/2\alpha) \exp\left(\frac{\beta^2 - \gamma^2}{4\alpha}\right) \tag{39}$$

and the addition theorem for spherical harmonics, the integration over all spatial variables can be carried out.

In order to perform the integration over s and t, the following change of variables is useful [6]:

$$u = s/(s+t)$$

$$v = s + t,$$

thus leading to the following expression for the $\mathscr{C}_{lmn}^{IJ}$:

$$\begin{aligned} \mathscr{C}_{lmn}^{IJ} &= N_A N_B \alpha\beta \, (\pi/16)^{1/2} \int_0^1 \mathrm{d}u \int_0^\infty \mathrm{d}v \, v^{-7/2} [u(1-u)]^{-3/2} \cdot \\ &\quad \times U_{lmn}^*(\boldsymbol{P}) \exp(-k_{ln}^2/4v) \exp[-\alpha^2/4uv \\ &\quad - \beta^2/4(1-u)v - u(u-1)|\boldsymbol{A} - \boldsymbol{B}|^2]. \end{aligned} \tag{40}$$

The integration over v yields

$$\mathscr{C}^{IJ}_{lmn} = N_A N_B (8\pi)^{1/2} \alpha\beta |\bar{A} - \bar{B}|^5 \int_0^1 du\, u(u-1)\, U^*_{lmn}(\boldsymbol{P}) K_{5/2}(z) z^{-5/2}, \quad (41)$$

where $z = (|\boldsymbol{A} - \boldsymbol{B}|)[k^2_{ln} u(1-u) + (1-u)\alpha^2 + u\beta^2]^{1/2}$, $\boldsymbol{P} = u\boldsymbol{A} + (1-u)\boldsymbol{B}$ and $K_{5/2}(z)$ is the modified Bessel function of degree 5/2 ([25] p. 444). Thus, the evaluation of $\mathscr{C}^{IJ}_{lmn}$ has been reduced to a one-dimensional integral.

When gaussian-type orbitals are used, a similar scheme can be followed [32] to generate the remaining coefficients starting from $\mathscr{C}^{IJ}_{lmn}$:

$$\mathscr{C}^{IJ}_{lmn} = N_A N_B B_{ln} \int_0^\infty dr\, r^{3/2} \int_\Omega d\Omega \exp(-\alpha r_A^2 - \beta r_B^2)\, Y^*_{lm}(\Omega)\, J_{l+1/2}(k_{ln} r). \quad (42)$$

In this particular case, the method outlined above leads to an analytical closed form for this coefficient:

$$\mathscr{C}^{IJ}_{lmn} = N_A N_B B_{ln} \left(\frac{\pi}{\alpha+\beta}\right)^{3/2} P^{-1/2}\, Y^*_{lm}(\Omega_P)\, J_{l+1/2}(k_{ln} P) \cdot \times \exp[-[\alpha\beta/(\alpha+\beta)]|\boldsymbol{A} - \boldsymbol{B}|^2 - [k^2_{ln}/4(\alpha+\beta)]], \quad (43)$$

where it has been used that a product of GTOs can always be expressed as a GTO centered on another point $\boldsymbol{P} = (\alpha\boldsymbol{A} + \beta\boldsymbol{B})/(\alpha+\beta)$.

2.4 Connection between the present approach and the Fourier-transform method

The present approach is closely related to the Fourier transform method [15]. To prove this equivalence, the parameter a is allowed to go to infinity in the bielectronic integral expression:

$$B = 4\pi \sum_l \sum_m \sum_n (B^2_{ln}/k^2_{ln}) \left\{ \int_{r<a} dV\, \rho_1(\boldsymbol{r}) \frac{J_{l+1/2}(k_{ln} r)}{r^{1/2}} Y^*_{lm}(\Omega) \times \int_{r'<a} dV'\, \rho_2(\boldsymbol{r}') \frac{J_{l+1/2}(k_{ln} r')}{r'^{1/2}} Y^*_{lm}(\Omega) \right\} + \varepsilon(a). \quad (44)$$

$\varepsilon(a)$ is the error discussed in Appendix I and thus $\varepsilon(a) \to 0$ as $a \to \infty$ and B_{ln} is the normalization factor in Eq. (8).

An appropriate limiting procedure such as described in Ref. [27] p. 264 allows the sum over n to be transformed into the following integral over the continuous parameter k:

$$B = 4\pi \sum_{lm} \left\{ \int_0^\infty dk\, k^{-1} \int_{\forall r} dV \rho_1(\boldsymbol{r}) \frac{J_{l+1/2}(kr)}{r^{1/2}} Y^*_{lm}(\Omega) \times \int_{\forall r'} dV' \rho_2(\boldsymbol{r}') \frac{J_{l+1/2}(kr')}{r'^{1/2}} Y^*_{lm}(\Omega') \right\}. \quad (45)$$

The expression for the bielectronic integral in the Fourier transform method [15] is

$$B = (1/2\pi^2) \int_0^\infty d^3k\, k^{-2} \int_{\forall r} dV\, \rho_1(\boldsymbol{r}) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \cdot \int_{\forall r'} dV'\, \rho_2(\boldsymbol{r}') e^{i\boldsymbol{k}\cdot\boldsymbol{r}'} \quad (46)$$

From this expression, Eq. (45) is obtained if each $e^{ik\cdot r}$ factor is replaced by its expansion in spherical Bessel functions and the integration over the angular variables in the $\{k\}$ domain is carried out explicitly.

An alternative procedure to show the connection between both methods is by letting the spatial integrals in Eq. (46) be truncated to the domain $r < a$ (for example, by use of the approximation $\rho_i(r) \cong \rho_i(r)\theta(a - r)$). Then the following equality holds:

$$B \cong (1/2\pi^2) \int_0^\infty d^3k\, k^{-2} \int_{r<a} dV\, \rho_1(r) e^{-ik\cdot r} \cdot \int_{r'<a} dV'\, \rho_2(r') e^{ik\cdot r'}$$

$$= 4\pi \sum_{lm} \sum_{n=1}^{\infty} k_{ln}^{-2} \int_{r<a} dV \rho_1(r)\, U_{lmn}^*(r) \int_{r'<a} dV'\, \rho_2(r')\, U_{lmn}(r'). \quad (47)$$

This relation can be obtained by introducing the expansion of $e^{-i\bar{k}\cdot\bar{r}}$ in terms of the basis $\{U_{nlm}(r)\}$ within the domain $r < a$:

$$e^{-i\bar{k}\cdot\bar{r}} = \sum_{nlm} \Lambda_{nlm}(k)\, U_{nlm}(r) \quad r < a, \quad (48)$$

where

$$\Lambda_{nlm}(k) = \int_{r<a} dV\, e^{-ik\cdot r}\, U_{nlm}^*(r). \quad (49)$$

Introducing Eq. (48) and Eq. (49) in the left-hand side of Eq. (47), the integration over k can be carried out explicitly, as outlined in Appendix III, and the right-hand side of Eq. (47) is obtained. From this point of view, the present method is seen to be based on the same grounds as the Fourier transform one, with a discrete k parameter. Discretization of k is shown to be a direct consequence of the fact that the distributions $\rho_i(r)$ take negligible values for $r > a$.

3 Concluding remarks

In this work it has been shown that a discrete basis set of functions can be defined within a finite spherical domain of radius a which has special properties with respect to the operator $|r - r'|^{-1}$. Taking advantage of this feature a method to compute LCAO-SCF matrix elements can be implemented. As discussed in the previous sections, the calculation of such matrix elements is shown to be reduced to the evaluation of the expansion coefficients C_{lmn}^{ij} of AOs products $\chi_i^* \chi_j$ in terms of the basis set functions $\{U_{lmn}\}$ defined in this paper, thus requiring the computation of only three-dimensional integrals, Eq. (26). It is worth noting that once all coefficients have been computed, monoelectronic as well as bielectronic Coulomb-type integrals are straightforwardly expressed in terms of such coefficients, independently of the number of atomic centers involved. The evaluation of C_{lmn}^{ij} requires to deal at most with three-center integrals. Although finding the most efficient technique of evaluating such coefficients is up to now a matter of research, in this work a particular method is presented in which the required evaluation is reduced to a one-dimensional numerical integral for STOs, and analytical expressions are obtained for GTOs. However, other possibilities can be envisioned. All of them can be implemented if the parameter a is allowed to go to infinity in the actual calculation of the coefficients, as outlined in Sect. 2.3.

For instance, using Eq. (7), the coefficients can be expressed as

$$C_{lmn}^{ij} = (k_{ln}^2)/4\pi) \int dV' \left[\int dV \frac{\chi_i^*(r)\chi_j(r)}{|r - r'|} \right] U_{lmn}(r') \tag{50}$$

The quantity in brackets can be expanded using the schemes developed either in Refs. [7] and [8], or the ones in Refs. [10, 20, 35].

It must be emphasized that the approaches mentioned above do not have any restriction on the l, m, n atomic orbitals indices involved in the calculation. Despite the rather intrinsic computational problems which could arise, this fact ensures the flexibility of this method; thus allowing to deal with orbitals of arbitrary l ($s, p, d, f \ldots$). Further, this approach can be applied regardless of the AOs functional form, and thus could be implemented with other choices of AOs, as for instance those proposed in Ref. [35].

An important point to be discussed is the choice of the parameter a, i.e, the radius of the sphere. In principle, this parameter should be taken so that the whole molecule is included within the sphere. As shown in Appendix I, an analysis can be carried out in order to make the error due to this truncation of the space as small as desired. However, in actual applications to extended systems, this criterion may become unpractical. In such cases a different approach could be adopted. A distance d can always be defined such that bielectronic integrals involving centers that lie at a distance larger than d yield negligibly small values [36], and thus they can be systematically neglected in the calculations. If d is smaller than the dimensions of the system under study, then the value of d can be chosen to be the radius of the sphere. In this case, several spheres could be defined on different atomic centers in order to evaluate those bielectronic integrals which involve those atoms that lie at a distance smaller than d from that particular center. An approximate value of bielectronic integrals between AOs of atoms which lie out of the sphere and those within it could nevertheless be obtained following the multipole expansion technique [19]. These integrals would be expressed in terms of both the multipole moments of the distributions $\chi_i^* \chi_j$ lying out of the sphere as well as the expansion coefficients of the distribution $\chi_l^* \chi_m$ which lies within the sphere.

It should be mentioned that an analysis of the errors due to the truncation of the space and of the series expansion can be carried out. In Appendix I the error due to the truncation of the space is explicitly discussed. The error in the bielectronic integrals must take into account that the actual calculations are carried out with the approximate $\mathscr{C}_{lmn}^{ij}$ coefficients. In Appendix IIb this problem is analysed in some detail. The bounds to the error obtained in that section have the following properties: they are expressed as finite sums, i.e., their evaluation requires the same information as that used for the evaluation of the bielectronic integrals, in addition to the integrals T_{ij}. Such results are a direct consequence of the completeness of the basis set and its integral property, Eq. (24).

The rate of convergence of the series expansion involving the $\mathscr{C}_{lmn}^{ij}$ coefficients is a subject that can only be explicitly analysed in practical applications. However, from the expression of those coefficients obtained for $1s$ Slater atomic orbitals, Eq. (41), such analysis can be carried out in detail. This is done in Appendix IIc. A deeper analysis for other type of atomic orbitals can be performed in a similar way as that outlined in Ref. [15]. Expressions (41) and (43) are well suited to analyse the asymptotic behaviour of the coefficients in terms of the l, m, n indices.

Another point worth of mentioning is that the evaluation of the integrals discussed in the present work do not require to locally reproduce the charge

distribution products at each point in space in an adjusted way, as the interest is centered on integral properties. The rate of convergence of the sums found in Appendix IIc for the case of 1*s* Slater atomic orbitals centered at any point within the sphere supports this assertion. This feature of the present approach can be related to the good convergence properties of the Dini expansions. However, for more complicated charge distributions a deeper analysis is needed.

To end up, it is important to point out that the methods described in Section 2.3 for evaluating the coefficients [6, 32] make explicit use of partial derivatives of the coefficients with respect to atomic positions, thus allowing analytic gradients to be directly implemented in order to perform geometry optimizations within the present approach.

Appendix I

Consider for instance the bielectronic integral:

$$(ij|rs) = \int \mathrm{d}V \int \mathrm{d}V' \frac{\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})\chi_r^*(\boldsymbol{r}')\chi_s(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|}, \tag{a1}$$

where the AOs $\chi_i, \chi_j, \chi_r, \chi_s$ are centered on different nuclei in the most general case. The integration can be performed by partitioning the whole space as

$$\begin{aligned}(ij|rs) = &\int_{r<a} \mathrm{d}V \int_{r'<a} \mathrm{d}V' \frac{\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})\chi_r^*(\boldsymbol{r}')\chi_s(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|} \\ &+ \int_{r<a} \mathrm{d}V \int_{r'>a} \mathrm{d}V' \frac{\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})\chi_r^*(\boldsymbol{r}')\chi_s(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|} \\ &+ \int_{r>a} \mathrm{d}V \int_{r'<\infty} \mathrm{d}V' \frac{\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})\chi_r^*(\boldsymbol{r}')\chi_s(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|} \\ = &\int_{r<a} \mathrm{d}V \int_{r'<a} \mathrm{d}V' \frac{\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})\chi_r^*(\boldsymbol{r}')\chi_s(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|} + \varepsilon_1 + \varepsilon_2.\end{aligned} \tag{a2}$$

Hence, ε_1 and ε_2 represent the errors in the calculation of $(ij|rs)$ when the integration is restricted to the region inside the sphere of radius a. It can be demonstrated that both ε_1 and ε_2 decrease exponentially with increasing a. It is done here explicitly for ε_1 using the less favourable case of ETOs (a similar demonstration holds for ε_2).

Each AO product can be expressed as

$$\begin{aligned}\chi_r^*(\boldsymbol{r})\chi_s(\boldsymbol{r}) = &P(\boldsymbol{r} - \boldsymbol{R}_A)Q(\boldsymbol{r} - \boldsymbol{R}_B) \\ &\times \exp[-\alpha|\boldsymbol{r} - \boldsymbol{R}_A| - \beta|\boldsymbol{r} - \boldsymbol{R}_B|],\end{aligned} \tag{a3}$$

where $P(\boldsymbol{r} - \boldsymbol{R}_A)$ and $Q(\boldsymbol{r} - \boldsymbol{R}_B)$ represent polynomials centered on $\boldsymbol{R}_A$ and $\boldsymbol{R}_B$, the nuclei positions, respectively. By means of the triangle inequality, the AOs product can be upper bounded as

$$|\chi_r^*(\boldsymbol{r})\chi_s(\boldsymbol{r})| \leqslant \sum_{n=1}^{N} A_n r^n \exp[-\alpha(r - R_A) - \beta(r - R_B)], \tag{a4}$$

where A_n are the absolute values of the coefficients in the expansion of the product of polynomials P and Q and the absolute values of the components of $\boldsymbol{r}$ have been upper bounded by r. Thus for ε_1:

$$|\varepsilon_1| \leqslant \int_{r<a} \mathrm{d}V |\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})| \int_{r'>a} \mathrm{d}V' \times \sum_{n=1}^{N} \frac{A_n r'^n \exp\left[-\alpha(r'-R_A)-\beta(r'-R_B)\right]}{|\boldsymbol{r}'-\boldsymbol{r}|}. \tag{a5}$$

Using the well-known spherical harmonics expansion of $|\boldsymbol{r}'-\boldsymbol{r}|^{-1}$, integration over the angular variables of $\mathrm{d}V'$ leads to

$$|\varepsilon_1| \leqslant (4\pi)^{1/2} \int_{r<a} \mathrm{d}V |\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})| \int_a^{\infty} \mathrm{d}r' \times \sum_{n=1}^{N} A_n r'^{n+1} \exp\left[-\alpha(r'-R_A)-\beta(r'-R_B)\right], \tag{a6}$$

which finally results:

$$|\varepsilon_1| \leqslant \left[(4\pi)^{1/2} \int_{r<a} \mathrm{d}V |\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})| \sum_{n=1}^{N} \sum_{m=0}^{n+1} \frac{A_n(-1)^m(n+1)!\,a^m}{m!(\alpha+\beta)^{n-m+2}}\right] \times \exp\left[-\alpha(a-R_A)-\beta(a-R_B)\right] \leqslant (4\pi)^{3/2}\frac{a^3}{3}\,\mathrm{Max}(|\chi_i^*(\boldsymbol{r})\chi_j(\boldsymbol{r})|) \times R(a)\cdot\exp\left[-\alpha(a-R_A)-\beta(a-R_B)\right], \tag{a7}$$

where $R(a)$ is a polynomial of known degree evaluated on a and it is assumed that the maximum of the function lies inside the sphere. A similar demonstration can be performed for any matrix element.

Appendix II

(a) Estimate of the error in the bielectronic integrals due to the truncation of the series expansion

An upper bound to the error E due to the truncation of the series Eq. (28) to evaluate bielectronic integrals can be found as follows:

$$|E| = 4\pi \left| \sum_{l=L+1}^{\infty} \sum_{m=-l}^{l} \sum_{n=1}^{\infty} \frac{C_{lmn}^{ji*} C_{lmn}^{pq}}{k_{ln}^2} + \sum_{l=0}^{L} \sum_{m=-l}^{l} \sum_{n=N+1}^{\infty} \frac{C_{lmn}^{ji*} C_{lmn}^{pq}}{k_{ln}^2} \right|. \tag{a8}$$

Since $\{U_q(\boldsymbol{r})\}$ form an orthonormal basis set of a Hilbert space, the Cauchy inequality holds [34] and it can be used to set an upper bound to $|E|$. Defining:

$$R_{ji} = 4\pi \sum_{l=L+1}^{\infty} \sum_{m=-l}^{l} \sum_{n=1}^{\infty} \left| \frac{C_{lmn}^{ji}}{k_{ln}} \right|^2 + 4\pi \sum_{l=0}^{L} \sum_{m=-l}^{l} \sum_{n=N+1}^{\infty} \left| \frac{C_{lmn}^{ji}}{k_{ln}} \right|^2, \tag{a9}$$

the upper bound can be expressed as

$$|E| \leqslant R_{ji}^{1/2} \cdot R_{pq}^{1/2}. \tag{a10}$$

In the following, an upper bound to R_{ji} is considered. The roots of the Bessel functions satisfy:

$$k_{0,N+1} < k_{ln} \quad \forall n > N+1, \forall l$$
$$k_{L+1,1} < k_{ln} \quad \forall n, \forall l > L+1 \tag{a11}$$

These properties can be used to extract the factors k_{ln} from the sums, setting an upper bound to its value, i.e.,

$$R_{ji} \leqslant \frac{4\pi}{(k_{L+1,1})^2} \sum_{l=L+1}^{\infty} \sum_{m=-l}^{l} \sum_{n=1}^{\infty} |C_{lmn}^{ji}|^2 + \frac{4\pi}{(k_{0,N+1})^2} \sum_{l=0}^{L} \sum_{m=-l}^{l} \sum_{n=N+1}^{\infty} |C_{lmn}^{ji}|^2$$
$$\leqslant 4\pi \left(\frac{1}{(k_{L+1,1})^2} + \frac{1}{(k_{0,N+1})^2} \right) \left\{ \sum_{l=L+1}^{\infty} \sum_{m=-l}^{l} \sum_{n=1}^{\infty} |C_{lmn}^{ji}|^2 \right.$$
$$\left. + \sum_{l=0}^{L} \sum_{m=-l}^{l} \sum_{n=N+1}^{\infty} |C_{lmn}^{ji}|^2 \right\}. \tag{a12}$$

In the last step a very convenient expression is obtained since it involves only the expansion coefficients in the sums. It can be directly related to the charge distribution product $\chi_i^* \chi_j$. Using the relation:

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{n=1}^{\infty} |C_{lmn}^{ji}|^2 = \int_{r<a} dV |\chi_j \chi_j^*|^2 \leqslant \int_{r<\infty} dV |\chi_i \chi_j^*|^2 \equiv T_{ji} \tag{a13}$$

and splitting the sum, the last inequality can be expressed as

$$\sum_{l=L+1}^{\infty} \sum_{m=-l}^{l} \sum_{n=1}^{\infty} |C_{lmn}^{ij}|^2 + \sum_{l=0}^{L} \sum_{m=-l}^{l} \sum_{n=N+1}^{\infty} |C_{lmn}^{ij}|^2 \leqslant T_{ji} - t_{ji}, \tag{a14}$$

where t_{ji} is given by

$$t_{ji} = \sum_{l=0}^{L} \sum_{m=-l}^{l} \sum_{n=1}^{N} |C_{lmn}^{ij}|^2 \tag{a15}$$

Inserting inequalities (a12), (a13), and (a14) valid for both charge distributions in Eq. (a10), the following upper bound to the error E is found:

$$|E| \leqslant 4\pi \left(\frac{1}{(k_{L+1,1})^2} + \frac{1}{(k_{0,N+1})^2} \right) (T_{ji} - t_{ji})^{1/2} (T_{pq} - t_{pq})^{1/2}. \tag{a16}$$

Using the well-known properties of the roots of Bessel functions ([25] p. 371):

$$k_{L+1,1} \xrightarrow[L \to \infty]{} L\pi/a,$$

$$k_{0,N+1} \xrightarrow[N \to \infty]{} N\pi/a.$$

Eq. (a16) can be estimated as

$$|E| \leqslant \frac{4a^2}{\pi} \left(\frac{1}{L^2} + \frac{1}{N^2} \right) (T_{ji} - t_{ji})^{1/2} (T_{pq} - t_{pq})^{1/2} \tag{a17}$$

(b) Corrections to the result in (a) introduced by the use of the approximate coefficients $\mathscr{C}_{lmn}^{ij}$ defined in Eq. (32)

However, a practical estimate of the error should taken into account the use of the approximate coefficients $\mathscr{C}^{ij}_{lmn}$. In terms of the parameters ε^{ij}_{lmn} defined in Eq. (32), an error which takes into account these facts is defined as

$$\varepsilon = (ij|pq)_a - \sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}\frac{\mathscr{C}^{ij*}_{lmn}\mathscr{C}^{pq}_{lmn}}{k^2_{ln}} = E - T_1, \tag{a18}$$

where $(ij|pq)_a$ is the bielectronic integral limiting the integration volume to the region inside the sphere of radius a, T_1 is defined by

$$T_1 = \sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}\frac{G^{ijpq}_{lmn}}{k^2_{ln}}, \tag{a19}$$

with

$$G^{ijpq}_{lmn} = C^{ij*}_{lmn}\,\varepsilon^{pq}_{lmn} + C^{pq}_{lmn}\,\varepsilon^{ij*}_{lmn} + \varepsilon^{ij*}_{lmn}\,\varepsilon^{pq}_{lmn}. \tag{a20}$$

Using Eq. (a16), ε satisfies:

$$|\varepsilon| \leqslant T_1 + (T^{ij}_2 + T^{ij}_3)^{1/2}(T^{pq}_2 + T^{pq}_3)^{1/2}, \tag{a21}$$

where

$$T^{ij}_2 = 4\pi\,(k^{-2}_{L+1,1} + k^{-2}_{0,N+1})\left(T_{ij} - \sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}|\mathscr{C}^{ij}_{lmn}|^2\right), \tag{a22}$$

$$T^{ij}_3 = 4\pi\,(k^{-2}_{L+1,1} + k^{-2}_{0,N+1})\sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}G^{ijij}_{lmn} \tag{a23}$$

T_1 and T^{ij}_3 contain the quantities ε^{ij}_{lmn} which are exponentially decreasing functions of a. In the following, it is shown that these sums can be bounded under suitable assumptions. On the other hand, T^{ij}_2 cannot be made arbitrarily small by increasing a unless N and L are sufficiently large.

In order to obtain a bound to T_1 and T^{ij}_3 which contain sums over G^{ijpq}_{lmn} it must be observed that:

$$\left|\sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}G^{ijpq}_{lmn}\right| \leqslant \left|\sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}C^{ij*}_{lmn}\,\varepsilon^{pq}_{lmn}\right| + \left|\sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}C^{pq}_{lmn}\,\varepsilon^{ij*}_{lmn}\right| + \left|\sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}\varepsilon^{ij*}_{lmn}\,\varepsilon^{pq}_{lmn}\right|. \tag{a24}$$

Each term on the right-hand side of Eq. (a24) can be upperbounded using the Schwarz inequality:

$$\left|\sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}A^{*}_{lmn}B_{lmn}\right|^2 \leqslant \left[\sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}|A_{lmn}|^2\right]\left[\sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}|B_{lmn}|^2\right]. \tag{a25}$$

Since C^{ij}_{lmn} stand for the original coefficients within the sphere they satisfy:

$$\sum_{l=0}^{L}\sum_{n=1}^{N}\sum_{m=-l}^{l}|C^{ij}_{lmn}|^2 \leqslant T_{ij}. \tag{a26}$$

From Eqs. (a24), (a25) and (a26) it is concluded that in order to find proper bounds to T_1 and T_3^{ij} it is necessary to investigate the behaviour of the sums:

$$\sum_{l=0}^{L} \sum_{n=1}^{N} \sum_{m=-l}^{l} |\varepsilon_{lmn}^{ij}|^2, \tag{a27}$$

where ε_{lmn}^{ij} take the explicit expression:

$$\varepsilon_{lmn}^{ij} = \mathscr{C}_{lmn}^{ij} - C_{lmn}^{ij} = B_{ln}(2k_{ln}/\pi)^{1/2} \int_a^\infty r^2 \, \mathrm{d}r j_l(k_{ln}r) \int \mathrm{d}\Omega \; Y_{lm}^*(\Omega) \rho_{ij}(\boldsymbol{r}). \tag{a28}$$

Defining the function $f_{ln}^{ij}(\Omega)$ as

$$f_{ln}^{ij}(\Omega) = B_{ln}(2k_{ln}/\pi)^{1/2} \int_a^\infty r^2 \, \mathrm{d}r \, j_l(k_{ln}r) \rho_{ij}(\boldsymbol{r})$$

$$= B_{ln} \int_a^\infty r^{3/2} \, \mathrm{d}r \, J_{l+1/2}(k_{ln}r) \, \rho_{ij}(\boldsymbol{r}), \tag{a29}$$

ε_{lmn}^{ij} satisfies:

$$\varepsilon_{lmn}^{ij} = \int f_{ln}^{ij}(\Omega) \; Y_{lm}^*(\Omega) \, \mathrm{d}\Omega, \tag{a30}$$

i.e., ε_{lmn}^{ij} can be seen as the projection of $f_{ln}^{ij}(\Omega)$ on the spherical harmonic $Y_{lm}(\Omega)$. The following expression (for fixed l):

$$\sum_{m=-l}^{l} |\varepsilon_{lmn}^{ij}|^2 \tag{a31}$$

is the projection of $f_{ln}^{ij}(\Omega)$ on the subspace spanned by the set $\{Y_{lm}, m = -l, \ldots, l\}$ and consequently it satisfies:

$$\sum_{m=-l}^{l} |\varepsilon_{lmn}^{ij}|^2 \leqslant \| f_{ln}^{ij}(\Omega) \|^2 = \int |f_{ln}^{ij}(\Omega)|^2 \, \mathrm{d}\Omega \equiv F_{ln}^{ij}. \tag{a32}$$

This is a bound for the summation over m for each value of l, n. Thus it holds

$$\sum_{l=0}^{L} \sum_{n=1}^{N} \sum_{m=-l}^{l} |\varepsilon_{lmn}^{ij}|^2 \leqslant \sum_{l=0}^{L} \sum_{n=0}^{N} F_{ln}^{ij}. \tag{a33}$$

An upper bound to F_{ln}^{ij} is obtainable from:

$$F_{ln}^{ij} \leqslant 4\pi \, |f_{ln}^{ij}(\Omega_M)|^2, \tag{a34}$$

where Ω_M is such that $|f_{ln}^{ij}(\Omega)|$ is maximum for $\Omega = \Omega_M$.

A general expression for a bound to $|f_{ln}^{ij}(\Omega_M)|$ can be obtained. In the region $r > a$ all AOs can be considered to take small values and to be decreasing functions of r, thus allowing to write:

$$r^{3/2} \rho_{ij}(r, \Omega_M) = \sum_{\mu} A_{\mu}^{ij}(\Omega_M) \, g_{\mu}^{ij}(r, \Omega_M), \tag{a35}$$

with $g_{\mu}^{ij}(r, \Omega_M)$ positive decreasing functions of r for $r > a$. With this decomposition it holds

$$|f_{ln}^{ij}(\Omega)| \leqslant \sum_{\mu} |A_{\mu}^{ij}(\Omega_M)| \cdot \left| \int_a^\infty g_{\mu}^{ij}(r, \Omega_M) B_{ln} J_{l+1/2}(k_{ln}r) \, \mathrm{d}r \right|, \tag{a36}$$

B_{ln} is the normalization factor. The following property of Bessel functions described in Ref. [26] p. 595 is useful. For $f(r)$ a positive decreasing function of r, there exists $\xi \in (a, s)$ such that

$$\left| \int_a^s f(r)\, J_{l+1/2}(kr)\, \mathrm{d}r \right| = \left| f(a) \int_a^{\xi} J_{l+1/2}(kr)\, \mathrm{d}r + f(s) \int_{\xi}^{s} J_{l+1/2}(kr)\, \mathrm{d}r \right|. \quad \text{(a37)}$$

This property, when applied to the integrals in Eq. (a36) allows to write:

$$\begin{aligned} I_{\mu}^{ij} &= \left| \int_a^{\infty} g_{\mu}^{ij}(r, \Omega_M) B_{ln} J_{l+1/2}(k_{ln} r)\, \mathrm{d}r \right| \\ &= |B_{ln} g_{\mu}^{ij}(a, \Omega_M)| \cdot \left| \int_a^{\xi} J_{l+1/2}(k_{ln} r)\, \mathrm{d}r \right|, \end{aligned} \quad \text{(a38)}$$

where it has been used that $g_{\mu}^{ij}(s, \Omega_M) \to 0$ as $s \to \infty$ and that the function:

$$I_{\nu}(u_1, u_2) = \left| \int_{u_1}^{u_2} J_{\nu}(u)\, \mathrm{d}u \right| \quad \text{(a39)}$$

is finite for any value of $u_1, u_2 \geqslant 0$. An upper bound to $I_{\nu}(u_1, u_2)$ can be set independent of u_1, u_2 and ν:

$$I_{\mathrm{MAX}} = \int_0^{x_{1/2,1}} J_{1/2}(x)\, \mathrm{d}x, \quad \text{(a40)}$$

where $x_{1/2,1}$ is the first root of $J_{1/2}(x)$. Consequently,

$$\begin{aligned} \left| \int_a^{\infty} g_{\mu}^{ij}(r, \Omega_M) B_{ln} J_{l+1/2}(k_{ln} r)\, \mathrm{d}r \right| &\leqslant g_{\mu}^{ij}(a, \Omega_M) k_{ln}^{-1} I_{\mathrm{MAX}} B_{ln} \\ &\sim g_{\mu}^{ij}(a, \Omega_M) I_{\mathrm{MAX}} \frac{k_{ln}^{-1/2}}{a^{1/2}}, \end{aligned} \quad \text{(a41)}$$

where it has been used that

$$|B_{ln}| = |2^{1/2}/(a J_{l+1/2}(k_{ln} a))| \sim k_{ln}^{1/2}. \quad \text{(a42)}$$

Equations (a41), (a36), (a34) and (a32), together with the assumption that $L \sim N$, allow to obtain exponentially decreasing and convergent upper bounds for the T_1 and T_3^{ij} sums. Even though it is not a simple matter to calculate such bounds, it is interesting to remark that they are expressed as finite sums and there is no need to compute any quantity involving values of l, n larger than L and N.

It can be shown in a simple application that the sums involved in these calculations have a good rate of convergence. This can be done by assuming that $\rho_{ij}(r, \Omega_M)$ is an exponentially decreasing function of r, i.e.,

$$g_{\mu}^{ij}(r, \Omega_M) = A r^{3/2} \mathrm{e}^{-\alpha r}, \quad \text{(a43)}$$

where A is a normalization factor. This functional dependence can be used to estimate the integral in Eq. (a36) in an alternative way. Assuming that n, l take large values and $n \cong l$, the Bessel function in Eq. (a36) can be replaced by its asymptotic

expansion to carry out the integration, in order to analyze the dependence of the integral on the l, n indices:

$$I_{\mu}^{ij} = \int_a^{\infty} g_{\mu}^{ij}(r, \Omega_M) B_{ln} J_{l+1/2}(k_{ln} r)\, \mathrm{d}r$$

$$\cong A \int_a^{\infty} r^{3/2} \mathrm{e}^{-\alpha r} B_{ln} \cos(k_{ln} r - \phi_l)(k_{ln} r)^{-1/2} \mathrm{d}r. \tag{a44}$$

where $\phi_l = (l + 1)\pi/2$. This expression is valid for large values of k_{ln}. The integration can be carried out explicitly:

$$I_{\mu}^{ij} \cong A(\alpha^2 + k_{ln}^2)^{-1} k_{ln}^{-1/2} \mathrm{e}^{-\alpha a} [D_1 \cos(k_{ln} a - \phi_l) - D_2 \sin(k_{ln} a - \phi_l)], \tag{a45}$$

$$\text{with } D_1 = \alpha a + (\alpha^2 - k_{ln}^2)/(\alpha^2 + k_{ln}^2)$$

$$\text{and } D_2 = k_{ln}[a + \{2\alpha/(\alpha^2 + k_{ln}^2)\}]. \tag{a46}$$

The values $k_{ln} a = x_{ln}$ are the roots of $J_{l-1/2}(kr)$. For fixed l and large n values it holds ([25] p. 371):

$$x_{ln} \to \phi_{l-1} + (2n + 1)\pi/2 \tag{a47}$$

and

$$|\cos(k_{ln} a - \phi_1)| \cong 1 \tag{a48}$$

$$\sin(k_{ln} a - \phi_1) \cong O(1/k_{ln}). \tag{a49}$$

Thus, the product $D_2 \sin(k_{ln} a - \phi_1)$ remains finite as k_{ln} goes to infinity. Consequently it is found that I_{μ}^{ij} decrease as k_{ln}^{-2} and thus the general term in F_{ln}^{ij} in Eq. (a32) decreases as k_{ln}^{-4} for large values of k_{ln}. Equation (a45) also shows explicitly the exponential decay of F_{ln}^{ij} with increasing a.

From the previous results the following conclusions can be drawn. The errors T_1 and T_3^{ij} can be estimated for an initial choice of the values of N and L, and they can be made arbitrarily small by a proper choice of the parameter a. On the other hand, T_2^{ij} depends on the convergence properties of the sums involved in the calculations, i.e., it may be necessary to increase the values of N and L in order to make T_2^{ij} smaller than a desired threshold. The fact that the sums involved in T_1 and T_3^{ij} have a good rate of convergence suggests that their values are almost unaffected by this increase of N and L.

(c) Convergence analysis in the case of 1s Slater-type orbitals

The explicit expressions for the coefficients $\mathscr{C}_{lmn}^{ij}$ corresponding to $1s$ Slater-type orbitals defined in Eq. (36) allow to analyze in this specific case the important question of the rate of convergence of the sums involving the expansion coefficients. The coefficient which corresponds to two $1s$ Slater orbitals centered on the same nucleus is:

$$\mathscr{C}_{lmn}^{ii} = \frac{\alpha_i^4 U_{lmn}^*(\boldsymbol{R}_i)}{(\alpha^2 + k_{ln}^2/4)^2}, \tag{a50}$$

where i stands for the $1s$ orbital. The quantities appearing in all calculations are of the form

$$\sum_n^N \sum_l^L \sum_{m=-l}^{l} |\mathscr{C}_{lmn}^{ij}|^2. \tag{a51}$$

Taking into account the relations in Eqs. (a42) ([25] p. 364), Eq. (a52) ([25] p. 371), and Eq. (a53) ([31] p. 1015):

$$|J_{l+1/2}(k_{ln}r)| \leqslant J_{l+1/2}(r'_{l1}) \sim (l+1/2)^{-1/3} \tag{a52}$$

$$\left| \sum_{m=-l}^{l} Y^*_{lm}(\hat{R}_i)\, Y_{lm}(\hat{R}_i) \right| = |P_l(1)|(2l+1)/4\pi = (2l+1)/4\pi, \tag{a53}$$

where r'_{l1} is the first root of $J'_{l+1/2}$, the following bound can be established:

$$\begin{aligned} \sum_{m=-l}^{l} |\mathscr{C}^{ii}_{lmn}|^2 &\leqslant \left[\alpha_i^2 \Big/ \left(\alpha_i^2 + \frac{k_{ln}^2}{4} \right)^2 \right]^2 \\ &\quad \times B_{ln}^2 \left[\frac{J_{l+1/2}(k_{ln}R_i)}{R_i^{1/2}} \right]^2 \left| \sum_{m=-l}^{l} Y^*_{lm}(\hat{R}_i)\, Y_{lm}(\hat{R}_i) \right| \\ &\leqslant \left[\alpha_i^2 \Big/ \left(\alpha_i^2 + \frac{k_{ln}^2}{4} \right)^2 \right]^2 (k_{ln}/a)[(l+1/2)^{-1/3}]^2\,(2l+1)/4\pi R_i, \end{aligned} \tag{a54}$$

where $\hat{R}_i$ represents the angular coordinates of $\boldsymbol{R}_i$. From this last relation, it is easily shown that the asymptotic behavior of the resulting sum in n and l goes at least as $k_{ln}^{-7}\, l^{1/3}$.

When the $1s$ orbitals are centered on different nuclei, the following relation is found, taking into account Eq. (36):

$$\begin{aligned} \sum_{m=-l}^{l} |\mathscr{C}^{ij}_{lmn}|^2 &\leqslant (N_A N_B)^2 B_{ln}^2 ((2l+1)/4\pi)(l+1/2)^{-2/3}\, P_{\min}^{-1} \\ &\quad \cdot \left\{ \int_0^1 \mathrm{d}x\, x(1-x) K_{5/2}(z(x))\, z^{-5/2}(x) \right\}^2 \\ &\leqslant \left[\frac{N_A N_B}{2} \right]^2 k_{ln}(l+1/2)^{1/3}(1 + 3/z_{\min} + 3/z_{\min}^2)^2 (R_{AB}k_{ln})^{-6} C^2 P_{\min}^{-1} \end{aligned} \tag{a55}$$

where C is a constant, P is assumed to be positive, z is defined as in Eq. (36) and the following relations were used:

$$z(x) \geqslant z_{\min} = R_{AB}\alpha \tag{a56}$$

$$K_{5/2}(z) \leqslant (\pi/2)^{1/2}(1 + 3/z_{\min} + 3/z_{\min}^2)\, \mathrm{e}^{-z}/z^{1/2} \tag{a57}$$

$$z(x) > R_{AB}k_{ln}[x(1-x)]^{1/2}, \tag{a58}$$

With these relations the following bound can be set to the integral in Eq. (a55):

$$\begin{aligned} \int_0^1 \mathrm{d}x\, x(1-x) K_{5/2}(z(x))\, z^{-5/2}(x) &\leqslant (\pi/2)^{1/2}(1 + 3/z_{\min} + 3/z_{\min}^2 k_{ln}) \\ &\quad \times (R_{AB}k_{ln})^{-3} \int_0^1 \mathrm{d}x\, \frac{\exp[-(R_{AB}k_{ln})(x(1-x))^{1/2}]}{[x(1-x)]^{1/2}}. \end{aligned} \tag{a59}$$

As in the previous case, it can be seen from Eq. (a55) that the asymptotic behavior is at least like $k_{ln}^{-5}\, l^{1/3}$.

Appendix III

In this appendix the way in which the integration over $\boldsymbol{k}$ is carried out in Eq. (47) is shown. The $\Lambda_{nlm}(\boldsymbol{k})$ functions defined in Eq. (48) take the explicit expression:

$$\Lambda_{nlm}(\boldsymbol{k}) = \int \mathrm{dV} \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}) U^*_{nlm}(\boldsymbol{r}) = 4\pi(\pi/2)^{1/2} i^l Y^*_{lm}(\hat{k}) B_{ln} \cdot \times \int_0^a \mathrm{d}r\, r J_{l+1/2}(k_{ln} r) J_{l+1/2}(kr). \tag{a60}$$

The integration over r can be carried out explicitly ([25] p. 484), Eq. 11.3.29):

$$\Lambda_{nlm}(\boldsymbol{k}) = 4\pi(\pi/2)^{1/2} i^l Y^*_{lm}(\hat{k}) \frac{a B_{ln}}{(k^2 - k_{ln}^2)} \times [k J_{\nu+1}(ka) J_\nu(k_{ln} a) - k_{ln} J_\nu(ka) J_{\nu+1}(k_{ln} a)] \tag{a61}$$

where $\nu = l + 1/2$. When the expansion Eq. (48) is inserted in Eq. (47) the bielectronic integral is expressed:

$$B \cong (1/2\pi^2) \sum_{q_1, q_2} C_{q_1} C^*_{q_2} \int \frac{d^3k}{k^2} \Lambda^*_{q_1}(\boldsymbol{k}) \Lambda_{q_2}(\boldsymbol{k}). \tag{a62}$$

The integration over $\boldsymbol{k}$ is carried out inserting Eq. (a61) and using the recurrence relations Eqs. (14) and (15) to obtain

$$\int \frac{d^3k}{k^2} \Lambda^*_{q_1}(\boldsymbol{k}) \Lambda_{q_2}(\boldsymbol{k}) = 8\pi^3 \delta_{l_1 l_2} \delta_{m_1 m_2} B_{l_1 n_1} B_{l_2 n_2} J_\nu(k_1 a) J_\nu(k_2 a) a^2 \cdot \times \int_0^\infty \frac{\mathrm{d}k\, k J^2_{\nu-1}(ka)}{(k^2 - k_1^2)(k^2 - k_2^2)}, \tag{a63}$$

where k_i stand for $k_{l_i n_i}$.

In order to integrate over k the following representations of the Bessel functions are used ([31] p. 671 and p. 952):

$$J^2_{l-1/2}(ka) = (2/\pi) \int_0^{\pi/2} \mathrm{d}\theta\, J_{(2l-1)}(2ka\cos\theta), \tag{a64}$$

$$J_{(2l-1)}(x) = (1/\pi) \int_0^\pi \mathrm{d}\varphi \sin[(2l-1)\varphi] \sin(x \sin\varphi). \tag{a65}$$

Thus, the integral in the right-hand side of Eq. (a63) assumes the form

$$Y = (2/\pi^2) \int_0^{\pi/2} \mathrm{d}\theta \int_0^\pi \mathrm{d}\varphi \sin[(2l-1)\varphi] \int_0^\infty \mathrm{d}k \frac{k \sin(sk)}{(k^2 - k_1^2)(k^2 - k_2^2)}, \tag{a66}$$

where $s = 2a\cos\theta\sin\varphi$ ($s > 0$).

The integration over k can now be evaluated using standard complex techniques and yields

$$Y = (2/\pi^2) \int_0^{\pi/2} \mathrm{d}\theta \int_0^\pi \mathrm{d}\varphi \sin[(2l-1)\varphi] \cdot \left[(1/2) \frac{\pi}{k_1 + k_2} \frac{\cos(sk_2) - \cos(sk_1)}{k_2 - k_1} \right]. \tag{a67}$$

In order to integrate over θ and φ, the case $k_1 \neq k_2$ is first considered. In this case:

$$Y = Y_1 + Y_2, \text{ with} \tag{a68}$$

$$Y_j = \frac{(-1)^j}{\pi(k_2^2 - k_1^2)} \int_0^{\pi/2} d\theta \int_0^{\pi} d\varphi \sin[(2l-1)\varphi] \cos(2k_j a \sin\varphi \cos\theta) \tag{a69}$$

The integration over θ yields ([31] p. 402):

$$Y_j = \frac{(-1)^j}{\pi(k_2^2 - k_1^2)} \int_0^{\pi} d\varphi \sin[(2l-1)\varphi] J_0(2k_j a \sin\varphi), \tag{a70}$$

which finally yields ([31] p. 739):

$$Y_j = (\pi/2) \sin[(l-1/2)\pi] J_{-(l-1/2)}(k_j a) J_{(l-1/2)}(k_j a) = 0 \tag{a71}$$

by virtue of Eq. (16).

In the case $k_2 = k_1$ Y becomes

$$Y = -(a/\pi k_1) \int_0^{\pi/2} d\theta \int_0^{\pi} d\phi \sin[(2l-1)\phi] \times \sin\phi \cos\theta \sin(2k_1 a \sin\phi \cos\theta). \tag{a72}$$

The integration over θ can be carried out as indicated in Ref. [31] p. 402, Eq. (14) for the case of $n = 0$ and yields

$$Y = -\frac{a}{2k_1} \int_0^{\pi} d\phi \sin[(2l-1)\phi] \sin\phi J_1(2k_1 a \sin\phi). \tag{a73}$$

On using that

$$\sin[(2l-1)\phi] \sin\phi = \tfrac{1}{2}\{\cos[2(l-1)\phi] - \cos(2l\phi)\} \tag{a74}$$

the results of Ref. [31] p. 739, Eq. 9 and [26] p. 46, Eq. 7 can be used to obtain:

$$Y = \frac{a}{4k_1} \pi \cos(l\pi) \frac{2\sin[(l+1/2)\pi]}{\pi k_1 a} = \frac{1}{2k_1^2}. \tag{a75}$$

Inserting this last relation and using the explicit expression of the normalization factors B_{ln}, Eq. (a63) yields

$$\int \frac{d^3k}{k^2} \Lambda_{q_1}^*(\boldsymbol{k}) \Lambda_{q_2}(\boldsymbol{k}) = 8\pi^3 \delta_{q_1 q_2}/k_1^2. \tag{a76}$$

When this result is inserted in Eq. (a62), Eq. (28) is reobtained.

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