Efficient evaluation of molecular electrostatic potential in large systems.
Supplementary material

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1 Piecewise representation of atomic radial factors

Atomic radial factors, $\rho^A_{lm}(r_A)$, appear in the expansion of density in terms of spherical harmonics of the regular solid (*regular harmonics* henceforth) placed at the nuclei:

$$\rho^A(\mathbf{r}_A) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} z_l^m(\mathbf{r}_A)\ \rho^A_{lm}(r_A) \tag{1}$$

In order to get sufficient accuracy in the density and its related properties, these factors are piecewise fitted in terms of Chebyshev T polynomials of variable:

$$t \equiv 2\ \frac{r - \lambda_{i-1}}{\lambda_i - \lambda_{i-1}} - 1 \tag{2}$$

where λ_i are interval boundaries that have been fixed, based on experience, in the following values:

$$\{\lambda_i\}_{i=0}^{30} = \{0, 0.01, 0.03, 0.05, 0.07, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9., \\ 1, 1.5, 2, 2.5, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 20\}$$

To carry out the fitting, $\rho^A_{lm}(r_A)$ is tabulated for a set of values of r in each interval. The process is decribed in section 8.

2 Recurrence relations of regular harmonics

Regular harmonics (unnormalized) are defined as:

$$z_l^m(\mathbf{r}) = (-1)^m\ r^l\ P_l^{|m|}(\cos\theta)\ \begin{cases} \cos m\phi & (m \geq 0) \\ \sin |m|\phi & (m < 0) \end{cases} \tag{3}$$

Where $P_l^{|m|}(\cos\theta)$ are associated Legendre functions of the first type (see ref [1] 8.7-8.8). They can be efficiently computed by the recurrence relations[2]:

$$z_{l+1}^{l+1}(\mathbf{r}) = (2l+1)\ [x\ z_l^l(\mathbf{r}) - y\ z_l^{-l}(\mathbf{r})] \tag{4}$$

$$z_{l+1}^{-(l+1)}(\mathbf{r}) = (2l+1)\ [y\ z_l^l(\mathbf{r}) + x\ z_l^{-l}(\mathbf{r})] \tag{5}$$

$$z_{l+1}^{l}(\mathbf{r}) = (2\,l+1)\ z\ z_l^l(\mathbf{r}) \tag{6}$$

$$z_{l+1}^{-l}(\mathbf{r}) = (2\,l+1)\ z\ z_l^{-l}(\mathbf{r}) \tag{7}$$

and

$$z_{l+1}^{m}(\mathbf{r}) = \frac{1}{l-|m|+1}\ [(2l+1)\ z\ z_l^m(\mathbf{r}) - (l+|m|)\ r^2\ z_{l-1}^m(\mathbf{r})] \qquad -(l-1) \le m \le l-1 \tag{8}$$

The derivatives of regular harmonics can be obtained also in terms of regular harmonics by[3]:

$$\frac{\partial}{\partial x}\ z_l^{\pm m}(\mathbf{r}) = \frac{1}{2}\ \left[(1-\delta_{-1,\pm m})\ (l+m)\ (l+m-1)\ z_{l-1}^{\pm(m-1)}(\mathbf{r}) - z_{l-1}^{\pm(m+1)}(\mathbf{r})\right] \tag{9}$$

$$\frac{\partial}{\partial y}\ z_l^{\pm m}(\mathbf{r}) = \mp\frac{1}{2}\ \left[(1-\delta_{1,\pm m})\ (l+m)\ (l+m-1)\ z_{l-1}^{\mp(m-1)}(\mathbf{r}) + z_{l-1}^{\mp(m+1)}(\mathbf{r})\right] \tag{10}$$

$$\frac{\partial}{\partial z}\ z_l^{\pm m}(\mathbf{r}) = (l+m)\ z_{l-1}^{\pm m}(\mathbf{r}) \tag{11}$$

with $m > 0$ for eqs (9) and (10), and $m \ge 0$ for eq (11). For $m = 0$, derivatives with respect to x and y result:

$$\frac{\partial}{\partial x}\ z_l^0(\mathbf{r}) = -z_{l-1}^1(\mathbf{r}) \tag{12}$$

$$\frac{\partial}{\partial y}\ z_l^0(\mathbf{r}) = -z_{l-1}^{-1}(\mathbf{r}) \tag{13}$$

For second derivatives, eqs (9) to (13) are applied twice.

3 Decomposition of products of regular harmonics

The products of two (unnormalized) regular harmonics placed at one center can be decomposed in terms of regular harmonics placed in the same center as:

$$z_L^M(\mathbf{r})\ z_{L'}^{M'}(\mathbf{r}) = \sum_{k=0}^{E[(L+L')/2]} a_{L+L'-2k}^{LML'M'}\ r^{2k}\ z_{L+L'-2k}^{M^+}(\mathbf{r}) + \sum_{k=0}^{E[(L+L')/2]} b_{L+L'-2k}^{LML'M'}\ r^{2k}\ z_{L+L'-2k}^{M^-}(\mathbf{r}) \tag{14}$$

where $E(\nu)$ stands for the integer part of ν. The values of M^+ and M^-, for a given pair M, M' are:

$$\begin{aligned} M^+ &= \mathrm{sgn}(M)\ \mathrm{sgn}(M')\ (M+M') \\ M^- &= \mathrm{sgn}(M)\ \mathrm{sgn}(M')\ |M-M'| \end{aligned} \tag{15}$$

where sgn(ν) stands for the sign of ν, and the coefficients $a^{LML'M'}_{L+L'-2l}$ and $b^{LML'M'}_{L+L'-2k}$ can be easily obtained in terms of integrals involving products of three real spherical harmonics. These M^+ and M^- values, and a and b coefficients are computed at the beginning of the calculation, and stored to be used when required.
In the particular case of $M = 0$ or $M' = 0$, only the first sum in eq (14) remains:

$$z^0_L(\mathbf{r})\; z^{M'}_{L'}(\mathbf{r}) = \sum_{k=0}^{E[(L+L')/2]} a^{L0L'M'}_{L+L'-2k}\; r^{2k}\; z^{M'}_{L+L'-2k}(\mathbf{r}) \tag{16}$$

4 Expansion of one-center distributions

One center distributions of pairs of CGTOs $\chi^A_a(\mathbf{r}_A)$, $\chi^A_{a'}(\mathbf{r}_A)$ are entirely assigned to their center, A, and expanded as:

$$\chi^A_a(\mathbf{r}_A)\; \chi^A_{a'}(\mathbf{r}_A) = \sum_l \sum_m f^{L_a,M_a;L_{a'},M_{a'}}_{lm}(r_A)\; z^m_l(\mathbf{r}_A) \tag{17}$$

To compute the radial factors it is necessary to decompose the products of regular harmonics appearing in functions $\chi^A_a(\mathbf{r}_A)$ and $\chi^A_{a'}(\mathbf{r}_A)$ in regular harmonics. This can be readily done as described in section 3, and leads to:

$$\begin{aligned}
\chi^A_a(\mathbf{r}_A)\; \chi^A_{a'}(\mathbf{r}_A) \;&=\; \left[\sum_i^{NG_a}\sum_j^{NG_{a'}} c_i\; c_j\; \mathcal{N}^r_{\xi_i}\; \mathcal{N}^r_{\xi_j} e^{(\xi^a_i+\xi^{a'}_j)r^2_A}\right]\; \mathcal{N}^\Omega_{L_aM_a}\; \mathcal{N}^\Omega_{L_{a'}M_{a'}} \\
&\times\; \left[\sum_{k=0}^{E[(L_a+L_{a'})/2]} a^{L_aM_aL_{a'}M_{a'}}_{L_a+L_{a'}-2k}\; r^{2k}_A\; z^{M^+}_{L_a+L_{a'}-2k}(\mathbf{r}_A)\right. \\
&+\; \left.\sum_{k=0}^{E[(L_a+L_{a'})/2]} b^{L_aM_aL_{a'}M_{a'}}_{L_a+L_{a'}-2k}\; r^{2k}_A\; z^{M^-}_{L_a+L_{a'}-2k}(\mathbf{r}_A)\right]
\end{aligned} \tag{18}$$

The radial factors of eq (17) can be obtained by comparing both equations::

$$f^{L_a,M_a;L_{a'},M_{a'}}_{L_a+L_{a'}-2k\; M^+}(r_A) = \left[\sum_i^{NG_a}\sum_j^{NG_{a'}} c_i\; c_j\; \mathcal{N}^r_{\xi_i}\; \mathcal{N}^r_{\xi_j} e^{(\xi^a_i+\xi^{a'}_j)r^2_A}\right]\; \mathcal{N}^\Omega_{L_aM_a}\; \mathcal{N}^\Omega_{L_{a'}M_{a'}}\; a^{L_aM_aL_{a'}M_{a'}}_{L_a+L_{a'}-2k}\; r^{2k}_A \tag{19}$$

and, if both M_a and $M_{a'}$ are not zero:

$$f^{L_A,M_A;L'_A,M'_A}_{L_a+L_{a'}-2k\; M^-}(r_A) = \left[\sum_i^{NG_a}\sum_j^{NG_{a'}} c_i\; c_j\; \mathcal{N}^r_{\xi_i}\; \mathcal{N}^r_{\xi_j} e^{(\xi^a_i+\xi^{a'}_j)r^2_A}\right]\; \mathcal{N}^\Omega_{L_aM_a}\; \mathcal{N}^\Omega_{L_{a'}M_{a'}}\; b^{L_aM_aL_{a'}M_{a'}}_{L_a+L_{a'}-2k}\; r^{2k}_A \tag{20}$$

5 One-center expansion of two-center fragments

According to the DAM partition criterion, two-center fragments coming from products of two CGTOs, $\chi_a^A(\mathbf{r}_A)$, $\chi_b^B(\mathbf{r}_B)$, centered at A and B are defined by:

$$d_{ab}^A = \sum_i^{NG_a} \sum_j^{NG_b} \Theta(\xi_i^a - \xi_j^b)\; c_i\; c_j\; g_i^a(\xi_i^a, \mathbf{r}_A)\; g_j^b(\xi_j^b, \mathbf{r}_B) \tag{21}$$

where $g(\xi, \mathbf{r})$ are primitive gaussian functions, and $\Theta(x)$ is the step function:

$$\Theta(x) = \begin{cases} 0 & x < 0 \\ 1/2 & x = 0 \\ 1 & x > 0 \end{cases} \tag{22}$$

These fragments are to be expanded on center A in terms of regular spherical harmonics times radial factors:

$$d_{ab}^A = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathscr{F}_{lm}^{ab}(r_A)\; z_l^m(\mathbf{r}_A) \tag{23}$$

The radial factors, $\mathscr{F}_{lm}^{ab}(r_A)$, can be obtained in terms of the $f_{lm}(r_A)$ corresponding to the expansion of the products of primitives, $g_i^a(\xi_i^a, \mathbf{r}_A)$, $g_j^b(\xi_j^b, \mathbf{r}_B)$, entering eq(21).
As the rest of the section is applicable to every pair of primitives, hereafter we will suppress the i and j labels, and introduce the L and M quantum numbers corresponding to the contractions. Furthermore, we will replace the pairs of specific exponents ξ_i, ξ_j, by generic ones ξ_A, ξ_B, to make more clear the equations. With this convention, the product of two primitives in A and B is expanded as:

$$g_{L_AM_A}^A(\xi_A, \mathbf{r}_A)\; g_{L_BM_B}^B(\xi_B, \mathbf{r}_B) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} f_{lm}^{L_AM_A;L_BM_B}(r_A)\; z_l^m(\mathbf{r}_A) \tag{24}$$

To compute the radial factors, $f_{lm}^{L_AM_A;L_BM_B}(r_A)$, in a set of values of r_A, we start with the expansion corresponding to pairs of s-type primitives:

$$g_{00}^A(\xi_A, \mathbf{r}_A)\; g_{00}^B(\xi_B, \mathbf{r}_B) = \sum_{l=0}^{\infty} f_{lm}^{00;00}(r_A)\; z_l^m(\mathbf{r}_A) \tag{25}$$

Working in an aligned frame (A placed at the origin and B lying on z axis), so that $(r_A, \theta_A, \phi_A) \equiv (r, \theta, \phi)$, the expansion reads[4]:

$$\begin{aligned} g_{00}^A(\xi_A, \mathbf{r}_A)\; g_{00}^B(\xi_B, \mathbf{r}_B) &= e^{-\xi_A r_A^2}\; e^{-\xi_B (r_A^2 + R_B^2)} \sum_{l=0}^{\infty} (-1)^l\; (2l+1) \\ &\times \sqrt{\frac{\pi}{4\,\xi_B\, r_A\, R_B}}\; I_{l+1/2}(2\xi_B r_A R_B)\; P_l(\cos\theta) \\ &\equiv f_{l0}^{00;00}(r_A)\; z_l^0(\mathbf{r}_A) \end{aligned} \tag{26}$$

which yields:

$$f_{l0}^{00;00}(r_A) = e^{-\xi_A\, r_A^2}\; e^{-\xi_B\,(r_A^2+R_B^2)}\; \frac{(2l+1)}{r_A^l}\; \sqrt{\frac{\pi}{4\,\xi_B\, r_A\, R_B}}\; I_{l+1/2}(2\xi_B r_A R_B) \qquad (27)$$

$I_{l+1/2}(z)$ are the corresponding Bessel functions (see [1] 8.467) which can be computed by the stable recursion as shown in section 6

To increase the quantum numbers L_A, M_A, the product of regular spherical harmonics on A coming from expansion (27) and from function $g^A_{L_AM_A}(\xi_A, \mathbf{r}_A)$ is decomposed in regular spherical harmonics according to eq (16).

As mentioned in section 3, the coefficients a^{l0LML}_{l+L-2k} have been previously tabulated and stored. Thus the radial factors $f_{l0}^{L_AM_A;00}(r_A)$ are obtained by accumulating factors $f_{l0}^{00;00}(r_A)$ multiplied by suitable coefficients a^{l0LML}_{l+L-2k} and powers of r^2:

$$\begin{aligned} f_{l0}^{00;00}(r_A)\; z_l^0(\mathbf{r}_A)\; z_{L_A}^{M_A}(\mathbf{r}_A) &= \sum_{k=0}^{E[(l+L_A)/2]} a^{l0L_AM_A}_{l+L_A-2k}\; r_A^{2k}\; f_{l0}^{00;00}(r_A)\; z^{M_A}_{l+L_A-2k}(\mathbf{r}_A) \\ &\equiv \sum_{l'} f_{l'M_A}^{L_AM_A;00}(r_A)\; z_{l'}^{M_A}(\mathbf{r}_A) \end{aligned} \qquad (28)$$

with $l' = l + L_A - 2k$, leads to:

$$f_{l'M_A}^{L_AM_A;00}(r_A) \leftarrow a^{l0L_AM_A}_{l'}\; r_A^{l+L_A-l'}\; f_{l0}^{00;00}(r_A) \qquad (29)$$

where the arrow indicates that the r.h.s. term is accumulated on the l.h.s. This is so because different decompositions (16) may contain the same regular harmonic.

Next, when the quantum numbers L_B, M_B are not zero, the translation of regular harmonics along the z axis in the aligned frame[5]:

$$z_l^m(\mathbf{r}-\mathbf{R}) = \sum_{k=|m|}^{l} \binom{l+|m|}{k+|m|}\; (-R)^{l-k}\; z_k^m(\mathbf{r}) \qquad (30)$$

is combined with the decomposition of the resultant products of regular harmonics with eq (14). Thus, the radial factors $f_{lm}^{L_AM_A;L_BM_B}(r_A)$ are computed by accumulating factors $f_{l0}^{L_AM_A;00}(r_A)$ multiplied by suitable coefficients $a^{LML'0}_{L+L'-2l}$ and $b^{LML'M'}_{L+L'-2k}$ and powers of r^2:

$$\begin{aligned} f_{lM_A}^{L_AM_A;00}(r_A)\; z_l^{M_A}(\mathbf{r}_A)\; z_{L_B}^{M_B}(\mathbf{r}_B) &= f_{lM_A}^{L_AM_A;00}(r_A)\; z_l^{M_A}(\mathbf{r}_A) \sum_{k=|M_B|}^{L_B} \binom{L_B+|M_B|}{k+|M_B|} \\ &\times\; (-R_B)^{L_B-k}\; z_k^{M_B}(\mathbf{r}_A) \\ &= \sum_{k=|M_B|}^{L_B} \binom{L_B+|M_B|}{k+|M_B|}\; (-R_B)^{L_B-k}\; f_{lM_A}^{L_AM_A;00}(r_A) \\ &\times \left[\sum_{n=0}^{E[(l+k)/2]} a^{lM_AkM_B}_{l+k-2n}\; r^{2n}\; z^{M^+}_{l+k-2n}(\mathbf{r}) + \sum_{n=0}^{E[(l+k)/2]} b^{lM_AkM_B}_{l+k-2n}\; r^{2n}\; z^{M^-}_{l+k-2n}(\mathbf{r}) \right] \\ &\equiv \sum_{l'} \sum_{m=-l'}^{l'} f_{l'm}^{L_AM_A;L_BM_B}(r_A)\; z_{l'}^m(\mathbf{r}_A) \end{aligned} \qquad (31)$$

$$f^{L_A M_A;L_B M_B}_{l+k-2n\,M^+}(r_A) \leftarrow \binom{L_B+|M_B|}{k+|M_B|}\,(-R_B)^{L_B-k}\; a^{lM_AkM_B}_{l+k-2n}\; r^{2n}\; f^{L_A M_A;00}_{lM_A}(r_A) \tag{32}$$

$$f^{L_A M_A;L_B M_B}_{l+k-2n\,M^-}(r_A) \leftarrow \binom{L_B+|M_B|}{k+|M_B|}\,(-R_B)^{L_B-k}\; b^{lM_AkM_B}_{l+k-2n}\; r^{2n}\; f^{L_A M_A;00}_{lM_A}(r_A) \tag{33}$$

with the same meaning of the arrow as in eq (29).

6 Recurrence of Bessel I functions

Bessel $I_\nu(z)$ functions can be accurately computed by the stable relation (see ref [1] 8.486.1):

$$I_{\nu-1}(z) = I_{\nu+1} + \frac{2\nu}{z}\, I_\nu(z) \tag{34}$$

The recursion must be started from two functions, namely $I_{l_{max}+\frac{1}{2}}(z)$ and $I_{l_{max}-\frac{1}{2}}(z)$, which are computed *for large values of the argument* with the closed formula (ibid 8.467):

$$I_{l+1/2}(z) = \frac{1}{\sqrt{2\,\pi\,z}}\,\left[e^z\,\sum_{k=0}^{l}\frac{(-1)^k\,(l+k)!}{k!\,(l-k)!\,(2z)^k} + (-1)^{l+1}\,e^{-z}\,\sum_{k=0}^{l}\frac{(l+k)!}{k!\,(l-k)!\,(2z)^k}\right] \tag{35}$$

which for $z > 3\,\max(10, l_{max})$ can be accurately reduced to the first sum in the bracket;

$$I_{l+1/2}(z) \simeq \frac{1}{\sqrt{2\,\pi\,z}}\,e^z\,\sum_{k=0}^{l}\frac{(-1)^k\,(l+k)!}{k!\,(l-k)!\,(2z)^k} \tag{36}$$

In the remaining cases (i.e. for $z \leq 3 * \max(10, l_{max})$), the following expansion is used (ibid 8.445):

$$I_{l+1/2}(z) = \sum_{k=0}^{\infty}\frac{1}{k!\,\Gamma(l+k+3/2)}\,\left(\frac{z}{2}\right)^{l+2k+1/2} \tag{37}$$

or alternatively:

$$I_{l+1/2}(z) = \left(\frac{z}{2}\right)^{l+1/2}\,\frac{1}{(l+1/2)!}\;{}_0F_1(l+3/2; z^2/4) \tag{38}$$

where the hypergeometric ${}_0F_1$ is first computed for a sufficiently large l, namely Λ ($> l_{max}$), and for $\Lambda - 1$, either by applying its definition:

$${}_0F_1(l; z) = \sum_{k=0}^{\infty}\frac{1}{(l)_k}\,\frac{z^k}{k!} \tag{39}$$

where $(l)_k$ stands for the Pochhammer symbol: $(l)_k = (l+k-1)!/(l-1)!$, $(l)_0 = 1$, or as a continued fraction:

$$
{}_0F_1(l;z) = 1 + \cfrac{z/l}{1 + \cfrac{-z/2(1+l)}{1 + z/2(1+l) + \cfrac{-z/3(2+l)}{1 + z/3(2+l) + \cfrac{-z/4(3+l)}{1 + z/4(3+l) + \cfrac{-z/5(4+l)}{1 + z/5(4+l) + ...}}}}}
\tag{40}
$$

using the algorithm reported in [6]. Next, downwards recursion is applied to reach l_{max} and $l_{max} - 1$:

$$
{}_0F_1(l-1,z) = {}_0F_1(l,z) + \frac{z}{l\,(l-1)}\ {}_0F_1(l+1,z) \tag{41}
$$

7 Rotations

The algorithm reported requires the transformation of density matrix elements and radial factors between the molecular frame and aligned systems, in which one center A is placed at the origin and another center B is lying on the z axis, i.e. $\mathbf{R}_A = (0,0,0)$, $\mathbf{R}_B = (0,0,R_B)$. These transformations are related to rotations of regular harmonics which are carried out by means of rotation matrices, $\boldsymbol{D}^l$, as:

$$
(\boldsymbol{\mathcal{Z}}^l)^t = (\hat{\boldsymbol{\mathcal{Z}}}^l)^t\ \boldsymbol{D}^l \tag{42}
$$

where $\boldsymbol{\mathcal{Z}}^l$ is a column vector containing the angular-normalized regular harmonics in the molecular frame, $\mathcal{Z}^l_m = \mathcal{N}^\Omega_{lm}\ z^m_l(\mathbf{r})$, whereas $\hat{\boldsymbol{\mathcal{Z}}}^l$ is a column vector with the corresponding harmonics in an arbitrary frame. In both vectors, regular harmonics are arranged in canonical order:

$$
(\boldsymbol{\mathcal{Z}}^l)^t = \left(z^{-l}_l, z^{-l+1}_l, ..., z^l_l\right) \tag{43}
$$

and the rotation matrices, $\boldsymbol{D}^l$, can be efficiently computed by recursion[7].
As discussed in section 5, the partition of two-center charge distributions, $\chi^A_r(\mathbf{r}_A)\chi^B_s(\mathbf{r}_B)$, is carried out in an aligned system. In order to accumulate the contributions to the fragment A coming from all the basis functions in a pair of centers (A,B) and weighted with the pertaining elements of the density matrix, it is necessary to rotate the ρ^{AB} block of this matrix from the molecular frame, in which it is computed, to this aligned system. This operation is carried out in terms of sub-blocks of ρ^{AB} corresponding to pairs of shells of basis functions. Each shell contains all functions that have the same radial part and l quantum number, and only differ in the value of their m quantum number. Thus, the part of the electron density associated to each sub-block that has to be partitioned is given by:

$$
\boldsymbol{\rho}^{AB}_{ll'}(r_A, r_B) = (\boldsymbol{\chi}^A_l)^t\ \boldsymbol{\rho}^{AB}_{ll'}\ \boldsymbol{\chi}^B_{l'} \tag{44}
$$

where $\boldsymbol{\chi}^A_l$ and $\boldsymbol{\chi}^B_{l'}$ are column vectors containing angular normalized basis functions on A and B, with angular quantum numbers l and l', and $\boldsymbol{\rho}^{AB}_{ll'}$ is the pertaining block of density matrix.

Since the radial part is common to all functions in $\boldsymbol{\chi}_A$, and the same holds for $\boldsymbol{\chi}_B$, the rotation matrices that transform the basis functions from the molecular frame to the aligned system are the transpose of the $\boldsymbol{D}^l$, and according to eq (42):

$$(\hat{\boldsymbol{\chi}}_l)^t = (\boldsymbol{\chi}_l)^t \; (\boldsymbol{D}^l)^t \tag{45}$$

where $\boldsymbol{\chi}_l$ contains the angular-normalized basis functions of the block in the molecular frame, and $\hat{\boldsymbol{\chi}}_l$ contains the same functions in the aligned frame.
Taking into account that $(\boldsymbol{D}^l)^t \; \boldsymbol{D}^l = \boldsymbol{D}^l \; (\boldsymbol{D}^l)^t = \mathbf{1}$ eq (44) can be transformed as:

$$\begin{aligned} \boldsymbol{\rho}^{AB}_{ll'}(r_A, r_B) &= (\boldsymbol{\chi}^A_l)^t \; (\boldsymbol{D}^l)^t \; \boldsymbol{D}^l \; \boldsymbol{\rho}^{AB}_{ll'} \; (\boldsymbol{D}^l)^t \; \boldsymbol{D}^l \; \boldsymbol{\chi}^B_{l'} \\ &\equiv (\hat{\boldsymbol{\chi}}^A_l)^t \; \hat{\boldsymbol{\rho}}^{AB}_{ll'} \; \hat{\boldsymbol{\chi}}^B_{l'} \end{aligned} \tag{46}$$

Therefore, the rotated block of the density matrix is computed by:

$$\hat{\boldsymbol{\rho}}^{AB}_{ll'} = \boldsymbol{D}^l \; \boldsymbol{\rho}^{AB}_{ll'} \; (\boldsymbol{D}^{l'})^t \tag{47}$$

Furthermore, the radial factors, $\Phi_{lm}(r_A)$, that result from the partition of all the sub-blocks $\boldsymbol{\rho}^{AB}_{ll'}(r_A, r_B)$ can be obtained multiplying the $\mathscr{F}^{ab}_{lm}(r_A)$ of eq (23) by the pertaining elements of $\boldsymbol{\rho}^{AB}_{ll'}$ and accumulating over all the functions in the centers:

$$\begin{aligned} D^A_{AB}(\mathbf{r}_A) &\equiv \sum_{a\in A}\sum_{b\in B} \hat{\rho}^{ab}_{lm} \; d^A_{ab} = \sum_{a\in A}\sum_{b\in B}\sum_{l=0}^{\infty}\sum_{m=-l}^{l} \hat{\rho}^{ab}_{lm} \; \hat{\mathscr{F}}^{ab}_{lm}(r_A) \; \hat{z}^m_l(\mathbf{r}_A) \\ &\equiv \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \hat{\Phi}_{lm}(r_A) \; \hat{z}^m_l(\mathbf{r}_A) \end{aligned} \tag{48}$$

where the *hat* symbols have been introduced to recall that these quantities are computed in the aligned system.
The radial factors $\hat{\Phi}_{lm}(r_A)$ of eq (48) must be rotated to the molecular frame, to be accumulated with those coming from other pairs of centers. Again, this rotation is achieved working by blocks of factors with the same l. Writing eq (48) as:

$$\begin{aligned} D^A_{AB}(\mathbf{r}_A) &= \sum_{l=0}^{\infty} (\hat{\boldsymbol{\mathcal{Z}}}_l)^t \; \hat{\boldsymbol{\Phi}}_l = \sum_{l=0}^{\infty} (\hat{\boldsymbol{\mathcal{Z}}}_l)^t \; \boldsymbol{D}^l \; (\boldsymbol{D}^l)^t \; \hat{\boldsymbol{\Phi}}_l \\ &\equiv \sum_{l=0}^{\infty} (\boldsymbol{\mathcal{Z}}_l)^t \; \boldsymbol{\Phi}_l \end{aligned} \tag{49}$$

the radial factors in the molecular frame, $\Phi_{lm}(r_A)$, are obtained from those in the aligned axis by:

$$\boldsymbol{\Phi}_l = (\boldsymbol{D}^l)^t \; \hat{\boldsymbol{\Phi}}_l \tag{50}$$

Notice that the set of rotation matrices is the same for all operations within a given pair of centers, i.e. for rotations of both density matrix and radial factors.

8 Expansion of atomic radial factors

Atomic radial factors are piecewise expanded in the intervals with the previously chosen boundaries, λ_i, quoted in section 1. In each interval, the expansion reads:

$$\rho_{lm}^{i,A}(r_A) \simeq e^{-\zeta_i r_A} \sum_{k=0}^{n_i} c_k^{(i)}(l,m)\, T_k(t), \qquad r_A \in [\lambda_{i-1}, \lambda_i] \tag{51}$$

with t defined by eq (2).
The exponents ζ_i are taken as:

$$\zeta_i = \frac{(\ln[f_{00}(\lambda_i)] - \ln[f_{00}(\lambda_{i-1})]}{\lambda_i - \lambda_{i-1}} \tag{52}$$

where λ_i and λ_{i-1} stand for the upper and lower bounds of r in the i-th interval. If ζ_i in eq (51) results lower than 1, it is taken as zero.
The expansion coefficients $c_k^{(i)}(l,m)$ are obtained by numerical projection of $e^{\zeta_i r}\ f_{lm}(r)$ onto Chebyshev T polynomials of variable t. For this purpose, a set of points $\{r_{j,i}\}_{j=1}^{n}$, is chosen so that their corresponding values of t are the roots of Chebyshev T polynomial of order n:

$$t_j = -\cos[\pi\ (j - 1/2)/n] \qquad j = 1, ...n \tag{53}$$

$$r_{j,i} = (\lambda_i - \lambda_{i-1})\ \frac{t_j + 1}{2} + \lambda_{i-1} \qquad j = 1, ...n \tag{54}$$

In the current implementation, $n = 30$.
The expansion coefficients of $\rho_{lm}^{A}(r_A)$ in Chebyshev T polynomials are thus obtained by (see [8] eq 6.14):

$$c_k^{(i)}(l,m) = \frac{2}{n} \sum_{j=0}^{n} e^{\zeta_i r_{j,i}}\ f_{lm}(r_{j,i})\ T_k(t_j) \qquad k < n \tag{55}$$

The Chebyshev T polynomials are accurately evaluated by recursion:

$$T_{k+1}(x) = 2x\, T_k(x) + T_{k-1}(x) \qquad k > 1 \tag{56}$$

starting with $T_0(x) = 1$ and $T_1(x) = x$.
Coefficients are computed in sequence and, at the same time that coefficient of index k in the i-th interval is computed with eq(55), the norm of the unprojected part of the radial factor is estimated by:

$$\Delta^2 \simeq \sum_{j=1}^{n} r_{j,i}^{2l+2} \left[f_{lm}(r_{j,i}) - e^{-\zeta_i r} \sum_{\kappa=0}^{k} c_\kappa^{(i)}(l,m)\, T_\kappa(t_j) \right]^2 \tag{57}$$

where the weight factor r^{2l+2} is included to take into account the radial part of the regular harmonic and the jacobian upon integration in $\mathbb{R}^3$. The expansion is truncated at the term in which Δ becomes lower than a given threshold.

9 Effective multipoles from density expansion

The DAM partition/expansion of density allows to write the molecular electrostatic potential MESP as[9]:

$$V(\mathbf{r}) = \sum_{A=1}^{N} \left\{ \frac{\zeta_A}{r_A} - \sum_{l=0}^{\infty} \sum_{m=-l}^{l} z_l^m(\mathbf{r}_A) \left[\frac{Q_{lm}^A(r_A)}{r_A^{2l+1}} + q_{lm}^A(r_A) \right] \right\} \tag{58}$$

in terms of atomic nuclei charges, ζ_A, effective multipoles, $Q_{lm}(r)$, and inverse multipoles, $q_{lm}(r)$:

$$Q_{lm}^A(r) = \frac{(l-|m|)!}{(l+|m|)!} \int_{r'<r} d\mathbf{r}' \; z_l^m(\mathbf{r}') \; \rho(\mathbf{r}') = \frac{4\,\pi}{2l+1} \int_0^r dr' \; r'^{2l+2} \; \rho_{lm}^A(r') \tag{59}$$

$$q_{lm}^A(r) = \frac{(l-|m|)!}{(l+|m|)!} \int_{r'>r} d\mathbf{r}' \; \frac{z_l^m(\mathbf{r}')}{r'^{2l+1}} \; \rho(\mathbf{r}') = \frac{4\,\pi}{2l+1} \int_r^\infty dr' \; r' \; \rho_{lm}^A(r') \tag{60}$$

and for long distances the effective multipoles can be accurately replaced by point multipoles:

$$Q_{lm}^A = \lim_{r\to\infty} Q_{lm}^A(r) = \frac{4\,\pi}{2l+1} \int_0^\infty dr' \; r'^{2l+2} \; \rho_{lm}^A(r') \tag{61}$$

and the inverse multipoles do vanish: $\lim_{r\to\infty} q_{lm}^A(r) = 0$.
Thus, the efficient computation of MESP lies on the computation of several auxiliary quantities related to integrals of the radial factors of MED expansion. In particular, the $Q_{lm}^A(\lambda_{i-1}, r_{j,i})$, $q_{lm}^A(\lambda_i, r_{j,i})$ $Q_{lm}^A(\lambda_i)$ and $q_{lm}^A(\lambda_i)$ defined in eqs (25) to (28) of the main body are computed from the expansions of the radial factors given in eq (16). The procedure is described in the following subsections.

9.1 Accurate and efficient computation of $Q_{lm}^A(\lambda_i)$ and $q_{lm}^A(\lambda_i)$

These quantities imply solving integrals of the form:

$$\mathscr{I}_n^\alpha = \int_a^b dr \; r^\alpha \; e^{-\zeta r} \; T_n[t(r)] \tag{62}$$

which must be evaluated for every interval in the piecewise expansion of MED radial factors. For each interval, $a = \lambda_{i-1}$ and $b = \lambda_i$ are the boundaries, and the argument of Chebyshev T polynomials, according to eq (2), is given by:

$$t \equiv 2\,\frac{r-a}{b-a} - 1 \tag{63}$$

These integrals are trivial for $\zeta = 0$. On the other hand, for $\zeta \neq 0$ they can be expressed as a combination of incomplete Gamma functions (see [1] sec 8.35), but the resultant subtractions are error prone due to pathological cancellations between large sumands. Therefore, a more elaborate algorithm is required to guarantee the stability in this case too. The algorithm proceeds as follows:

1. We start by computing the integrals $\mathscr{I}_n^0$. For this purpose, we introduce two auxiliary variables $\delta \equiv (b-a)\,\zeta/2$, and $\sigma \equiv (b+a)\,\zeta/2$ so that $r = \frac{1}{\zeta}(\delta\, t + \sigma)$, and:

$$\mathscr{I}_n^0 = \int_a^b dr\; e^{-\zeta r}\; T_n[t(r)] = \frac{\delta\; e^{-\sigma}}{\zeta} \int_{-1}^{1} dt\; e^{-\delta t}\; T_n[t] \tag{64}$$

2. To accurately compute the integrals on the r.h.s. of eq(64) for $\delta \neq 0$, we use the auxiliary integrals:

$$\mathscr{J}_{j,l}^{Leg} = \int_{-1}^{1} dt\; t^j\; e^{-\delta t}\; P_l(t) \tag{65}$$

starting with

$$\mathscr{J}_{0,l}^{Leg} = \int_{-1}^{1} dt\; e^{-\delta t}\; P_l(t) = (-1)^l \sqrt{\frac{2\pi}{\delta}}\; I_{l+1/2}(\delta) \tag{66}$$

where $I_{l+1/2}(\delta)$ are the corresponding Bessel functions, that can be computed by recursion as commented in section 6.

Next, the index j of $\mathscr{J}_{j,l}^{Leg}$, is increased applying the recurrence relation (see [1] eq 8.733.2):

$$\mathscr{J}_{j+1,l}^{Leg} = \frac{1}{2l+1}\; \left[(l+1)\; \mathscr{J}_{j,l+1}^{Leg} - l\; \mathscr{J}_{j,l-1}^{Leg}\right] \tag{67}$$

with $\mathscr{I}_{j,l}^{Leg} = 0$ for $l < 0$.

The recursion is applied as many times as required to get the integrals of powers of t as:

$$\mathscr{J}_j^{pow} \equiv \int_{-1}^{1} dt\; t^j\; e^{-\delta t} = \mathscr{J}_{j,0}^{Leg} \qquad \delta \neq 0 \tag{68}$$

3. For $\delta = 0$, the $\mathscr{J}_j^{pow}$ are computed directly as:

$$\mathscr{J}_j^{pow} = \begin{cases} 2/(l+1) & \text{if } l \text{ even} \\ 0 & \text{if } l \text{ odd} \end{cases} \qquad \delta = 0 \tag{69}$$

4. Once the $\mathscr{J}_j^{pow}$ have been computed, and taking into account the expansion of Chebyshev T polynomials in powers (see [8] eq 2.15):

$$T_n(t) = \sum_{k=0}^{E[n/2]} \left[(-1)^k \sum_{j=k}^{E[n/2]} \binom{n}{2j} \binom{j}{k}\right] t^{n-2k} \equiv \sum_{k=0}^{E[n/2]} c_k^T\; t^{n-2k} \tag{70}$$

integrals of eq(62) with $\alpha = 0$ are expressed as combinations of the $\mathscr{J}_j^{pow}$:

$$\mathscr{I}_n^0 = \sum_{k=0}^{E[n/2]} c_k^T\; \mathscr{J}_{n-2k}^{pow} \tag{71}$$

and the remaining $\mathscr{I}_n^\alpha$ are computed by the recursion with the recurrence relation obtained from $r = \frac{1}{\zeta}(\delta\ t + \sigma)$, which yields:

$$\mathscr{I}_n^{\alpha+1} = \frac{1}{\zeta}\ (\delta\ \mathscr{I}_{n+1}^\alpha + \sigma\ \mathscr{I}_n^\alpha) \tag{72}$$

5. Finally, calling $\mathscr{I}_{i,k}^\alpha$ to the $\mathscr{I}_k^\alpha$ integrals evaluated in the i-th interval, the $Q_{lm}^A(\lambda_i)$ are computed by:

$$Q_{lm}^A(\lambda_i) \equiv \frac{4\ \pi}{2l+1}\ \int_{\lambda_{i-1}}^{\lambda_i} dr'\ r'^{2l+2}\ \rho_{lm}(r') = \frac{4\ \pi}{2l+1}\ \frac{\delta\ e^{-\sigma}}{\zeta_i}\ \sum_{k=0}^{n_i} c_k^{(i)}(l,m)\ \mathscr{I}_{i,k}^{2l+2} \tag{73}$$

and the $q_{lm}^A(\lambda_i)$, by:

$$q_{lm}^A(\lambda_i) \equiv \frac{4\ \pi}{2l+1}\ \int_{\lambda_{i-1}}^{\lambda_i} dr'\ r'\ \rho_{lm}(r') = \frac{4\ \pi}{2l+1}\ \frac{\delta\ e^{-\sigma}}{\zeta_i}\ \sum_{k=0}^{n_i} c_k^{(i)}(l,m)\ \mathscr{I}_{i,k}^{1} \tag{74}$$

9.2 Accurate and efficient computation of $Q_{lm}^A(\lambda_i, r_{j,i})$ and $q_{lm}^A(\lambda_i, r_{j,i})$

The procedure exposed for computing $Q_{lm}^A(\lambda_i)$ and $q_{lm}^A(\lambda_i)$ can be used also for $Q_{lm}^A(\lambda_i, r_{j,i})$ and $q_{lm}^A(\lambda_i, r_{j,i})$, but now one has to take into account that the boundaries of integrals $\mathscr{I}_n^\alpha$ do not coincide with the boundaries of the intervals in which MED radial factors are fitted. In other words, the transformation to variable t as defined by eq(2) will not lead to integrals in the interval $[-1, 1]$.
One way to circumvent this problem consists of transforming, in every interval i, the variable t, as defined in eq(2), to a new variable in a suitable interval $[a, b]$, where $a = \lambda_{i-1}$ and $b = r_{j,i}$ for $Q_{lm}^A(\lambda_i, r_{j,i})$, and $a = r_{j,i}$, $b = \lambda_i$ for $q_{lm}^A(\lambda_i, r_{j,i})$.
The change of variable of eq (63), when applied with these definitions of a and b, leads to a new variable t' so that integral is carried out in the interval $t' \in [-1, 1]$. This variable t' is related with the variable t of eq (2) appearing in the Chebyshev T polynomials by:

$$t = \overline{\delta}\ t' + \overline{\sigma} \tag{75}$$

where

$$\overline{\delta}_Q = \frac{r_{j,i} - \lambda_{i-1}}{\lambda_i - \lambda_{i-1}} \qquad \overline{\sigma}_Q = \frac{r_{j,i} - \lambda_i}{\lambda_i - \lambda_{i-1}} \tag{76}$$

$$\overline{\delta}_q = \frac{\lambda_i - r_{j,i}}{\lambda_i - \lambda_{i-1}} \qquad \overline{\sigma}_q = \frac{r_{j,i} - \lambda_{i-1}}{\lambda_i - \lambda_{i-1}} \tag{77}$$

Next, the coefficients c_k^T that multiply powers of t in eq(70) are transformed to coefficients $c_k^{T'}$ of powers of t':

$$\sum_{k=0}^{E[n/2]} c_k^T\ t^{n-2k} = \sum_{k=0}^{E[n/2]} c_k^T\ (\overline{\delta}\ t' + \overline{\sigma})^{n-2k} \equiv \sum_{p=0}^{n} c_p^{T'}\ t'^p \tag{78}$$

Using the binomial expansion:

$$\sum_{p=0}^{n} c_p^{T'}\ t'^p = \sum_{k=0}^{E[n/2]} c_k^T \sum_{p=0}^{n-2k} \binom{n-2k}{p} \bar{\delta}^p\ \bar{\sigma}^{n-2k-p}\ t'^p \tag{79}$$

the coefficients $c_k^{T'}$ can be obtained as combinations of c_k^T by equating powers of t' in both sides of eq(79). Now the algorithm of section 9.1 can be applied by just replacing the c_k^T by the new coefficients $c_k^{T'}$.
The values of $Q_{lm}^A(\lambda_i, r)$ and $q_{lm}^A(\lambda_i, r)$ computed at points r_{ji} are used to fit these functions as combinations of Chebyshev T polynomials, very much like in case of the radial factors of MED discussed in section 8, with the difference that now no exponential factor is included. Thus, after numerical projection onto Chebyshev T polynomials, they can be efficiently computed when required by:

$$Q_{lm}^A(\lambda_i, r) \simeq \sum_{k=0}^{n_i} b_k^{(i)}(l,m)\ T_k[t(r)], \qquad r_A \in [\lambda_{i-1}, \lambda_i] \tag{80}$$

$$q_{lm}^A(\lambda_i, r) \simeq \sum_{k=0}^{n_i} d_k^{(i)}(l,m)\ T_k[t(r)], \qquad r_A \in [\lambda_{i-1}, \lambda_i] \tag{81}$$

with t given by eq (2) and in the same intervals as used for MED radial factors piecewise representation.
The efficient computation of the effective multipoles and inverse multipoles appearing in the expansion of the atomic contributions to MESP is carried out as:

$$Q_{lm}^A(r_A) = \sum_{j=0}^{i-1} Q_{lm}(\lambda_j) + \sum_{k=0}^{n_i} b_k^{(i)}(l,m)\ T_k[t(r_A)], \qquad r_A \in [\lambda_{i-1}, \lambda_i] \tag{82}$$

and

$$q_{lm}^A(r_A) = \sum_{j=i+1}^{n} q_{lm}(\lambda_j) + \sum_{k=0}^{n_i} d_k^{(i)}(l,m)\ T_k[t(r_A)], \qquad r_A \in [\lambda_{i-1}, \lambda_i] \tag{83}$$

where n in the first sum stands for the number of intervals in the piecewise expansion of the radial factors.

10 Computing MESP derivatives

According to eq (58), and using the chain rule, the first derivatives of MESP can be computed as:

$$\begin{aligned} \frac{\partial V(\mathbf{r})}{\partial x} &\equiv \sum_{A=1}^{N} \frac{\partial V^A(\mathbf{r}_A)}{\partial x_A} \\ &= \sum_{A=1}^{N} \frac{\partial}{\partial x_A} \left\{ \frac{\zeta_A}{r_A} - \sum_{l=0}^{\infty} \sum_{m=-l}^{l} z_l^m(\mathbf{r}_A)\ \left[\frac{Q_{lm}^A(r_A)}{r_A^{2l+1}} + q_{lm}^A(r_A) \right] \right\} \end{aligned} \tag{84}$$

with analogous equations for derivatives with respect to y and z. For each atomic contribution, it yields:

$$\begin{aligned}
\frac{\partial V^A(\mathbf{r}_A)}{\partial x_A} &= \frac{\partial}{\partial x_A}\,\frac{\zeta_A}{r_A} - \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left\{\frac{\partial}{\partial x_A}\,\left[\frac{z_l^m(\mathbf{r}_A)}{r_A^{2l+1}}\,Q_{lm}^A(r_A)\right]\right. \\
&+ \left.\frac{\partial}{\partial x_A}\,\left[z_l^m(\mathbf{r}_A)\,q_{lm}^A(r_A)\right]\right\} \\
&= -\frac{\zeta_A\,x_A}{r_A^3} - \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left\{Q_{lm}^A(r_A)\,\frac{\partial}{\partial x_A}\,\left[\frac{z_l^m(\mathbf{r}_A)}{r_A^{2l+1}}\right]\right. \\
&+ q_{lm}^A(r_A)\,\frac{\partial z_l^m(\mathbf{r}_A)}{\partial x_A} + \frac{z_l^m(\mathbf{r}_A)}{r_A^{2l+1}}\,\frac{\partial Q_{lm}^A(r_A)}{\partial x_A} \\
&+ \left. z_l^m(\mathbf{r}_A)\,\frac{\partial q_{lm}^A(r_A)}{\partial x_A}\right\} \qquad (85)
\end{aligned}$$

According to eqs (59) and (60), the last two terms in eq (85) cancel each other, giving:

$$\begin{aligned}
\frac{\partial V^A(\mathbf{r}_A)}{\partial x_A} &= -\frac{\zeta_A\,x_A}{r_A^3} - \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left\{Q_{lm}^A(r_A)\,\frac{\partial}{\partial x_A}\,\left[\frac{z_l^m(\mathbf{r}_A)}{r_A^{2l+1}}\right]\right. \\
&+ \left. q_{lm}^A(r_A)\,\frac{\partial z_l^m(\mathbf{r}_A)}{\partial x_A}\right\} \qquad (86)
\end{aligned}$$

and, for second derivatives:

$$\begin{aligned}
\frac{\partial^2 V^A(\mathbf{r}_A)}{\partial x_A^2} &= -\frac{\zeta_A}{r_A^3} + \frac{3\,\zeta_A\,x_A^2}{r_A^5} + \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left\{4\,\pi\,\frac{x_A^2}{r_A^2}\,\rho_{lm}(r_A)\,z_l^m(\mathbf{r}_A)\right. \\
&- \left. Q_{lm}^A(r_A)\,\frac{\partial^2}{\partial x_A^2}\left(\frac{z_l^m(\mathbf{r}_A)}{r_A^{2l+1}}\right) - q_{lm}^A(r_A)\,\frac{\partial^2 z_l^m(\mathbf{r}_A)}{\partial x_A^2}\right\} \qquad (87)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial^2 V^A(\mathbf{r}_A)}{\partial x_A \partial y_A} &= \frac{3\,\zeta_A\,x_A\,y_A}{r_A^5} + \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left\{\frac{4\,\pi}{2l+1}\,\frac{x_A\,y_A}{r_A^2}\,\rho_{lm}(r_A)\,z_l^m(\mathbf{r}_A)\right. \\
&- \left. Q_{lm}^A(r_A)\,\frac{\partial^2}{\partial x_A \partial y_A}\left(\frac{z_l^m(\mathbf{r}_A)}{r_A^{2l+1}}\right) - q_{lm}^A(r_A)\,\frac{\partial^2 z_l^m(\mathbf{r}_A)}{\partial x_A \partial y_A}\right\} \qquad (88)
\end{aligned}$$

Derivatives with respect to y_A and z_A can be obtained also from (86) replacing x_A by them.
The derivatives of the regular spherical harmonics can be computed with eqs (9) to (11), and those of the irregular harmonics can be obtained from those of the regular harmonics or, alternatively, by:

$$\frac{\partial}{\partial x}\frac{z_l^{\pm m}(\mathbf{r})}{r^{2l+1}} = \frac{1}{2}\left[(1-\delta_{-1,\pm m})\,(l+1-m)\,(l+2-m)\,\frac{z_{l+1}^{\pm(m-1)}(\mathbf{r})}{r^{2l+3}} - \frac{z_{l+1}^{\pm(m+1)}(\mathbf{r})}{r^{2l+3}}\right] \tag{89}$$

$$\frac{\partial}{\partial y}\frac{z_l^{\pm m}(\mathbf{r})}{r^{2l+1}} = \mp\frac{1}{2}\left[(1-\delta_{1,\pm m})\,(l+1-m)\,(l+2-m)\,\frac{z_{l+1}^{\mp(m-1)}(\mathbf{r})}{r^{2l+3}} + \frac{z_{l+1}^{\mp(m+1)}(\mathbf{r})}{r^{2l+3}}\right] \tag{90}$$

$$\frac{\partial}{\partial z}\frac{z_l^{\pm m}(\mathbf{r})}{r^{2l+1}} = -(l+1-m)\,\frac{z_{l+1}^{\pm m}(\mathbf{r})}{r^{2l+3}} \tag{91}$$

with $m > 0$ for eqs (89) and (90), and $m \geq 0$ for eq (91). For $m = 0$, derivatives with respect to x and y result:

$$\frac{\partial}{\partial x}\frac{z_l^{0}(\mathbf{r})}{r^{2l+1}} = -\frac{z_{l+1}^{1}(\mathbf{r})}{r^{2l+3}} \tag{92}$$

$$\frac{\partial}{\partial y}\frac{z_l^{0}(\mathbf{r})}{r^{2l+1}} = -\frac{z_{l+1}^{-1}(\mathbf{r})}{r^{2l+3}} \tag{93}$$

Second derivatives can be computed by applying twice these relations.

11 Precision of MESP calculation

Table 1 collects the precision in the results attained for MESP computation of benzene in a set of equally spaced points corresponding to a 129x129x129 grid in the octant defined by $x, y, z \in [0, 20]$ (length in bohr).

Table 1: Precision of MESP computed with the current algorithm

l_{max}	5	10	15	20
n	precision[a]			
0	0	0	0	0
1	0	0	0	0
2	357	0	0	0
3	19455	0	0	0
4	49760	159	0	0
5	134595	14007	0	0
6	342895	42247	168	1
7	746059	105848	8735	42
8	668487	147250	33499	866
9	166413	227734	60948	22451
10	16706	286921	38251	19208
11	1302	83381	8519	6731
12	660	1239142	1996569	2097390

[a] Number of grid points with n coincident decimal figures.

Reference values are computed in terms of the elements of electron density matrix, ρ_{rs}, and integrals involving basis set functions, χ_r, by means of:

$$V^{exact}(\mathbf{r}_C) = \sum_{r=1}^{nbasis} \sum_{s=1}^{r} (2 - \delta_{rs})\ \rho_{rs} \int d\mathbf{r}\ \frac{\chi_r(\mathbf{r})\ \chi_s(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_C|} \tag{94}$$

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