

# Electrostatic interaction between non-spherical closed-shell ions with Slater Type Orbitals.

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## Abstract

We use the Silverstone and Moats's expansion of a function about a displaced center [Phys. Rev. A **16**, 1731 (1977)] and the bipolar expansion of Kay, Todd, and Silverstone for  $r_{12}^{-1}$  [J. Chem. Phys. **51**, 2359 (1969); *ibid* **51**, 2363 (1969)] to derive analytical expressions for the two-center overlap, nuclear attraction, and Coulomb integrals between real Slater type orbitals (STO) in terms of four basic one-center radial integrals  $\chi^X$  ( $X=I,II,III,IV$ ). Explicit formulas are given for  $\chi^X$  which are extremely compact and numerically stable even for nearly equal orbital exponents. Modifications of these formulas are also proposed to avoid instabilities for small internuclear distances. The derived expressions are valid for an arbitrary orientation of the two nuclei and arbitrarily high angular numbers of the STO's with  $l \leq n - 1$ , and they are easily split into long-range multipolar interactions and short-range interactions. Finally, we derive expressions for short and long-range electrostatic interactions between non-spherical closed-shell ions in terms of two-center integrals between STO.

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## I. INTRODUCTION

The computation of multi-center integrals (MI) over atom-centered basis functions is one of the fundamental problems in Quantum Chemistry. The simplicity of the calculation of MI determines to a great extent the choice of the basis functions type for molecular calculations. Thus, despite the fact that Gaussian type orbitals (GTOs) have shown wrong behavior at the nuclei and at large distances, they are by far the most widely used to perform the nowadays routine SCF Hartree–Fock–Roothaan (HFR) or Kohn–Sham (KS) calculations in molecules and solids [1] due to the ease of computation of their MI. It is generally accepted, however, that exponential type orbitals (ETOs) have an inherent greater quality than GTOs. More specifically, atomic or/and molecular orbitals expressed in terms of ETOs may give a correct asymptotic behavior at  $r \rightarrow 0$  and  $r \rightarrow \infty$ , achieve the same accuracy in bonding regions as GTO-based orbitals, and require smaller basis sets. This reduction in the number of basis functions entails important advantages in the practical implementation of the SCF segment of molecular programs. The computation of multi-center ETO molecular integrals (ETOMI) has proven to be, however, one of the most difficult tasks in Quantum–Chemistry.

All the above facts have motivated the development of a great variety of methods to evaluate ETOMI since the early days of quantum–mechanical HFR calculations. Although it is practically impossible to discuss, or even to mention, all of these methods, articles in References 2–11 collect a number of important contributions on this subject in the last years. To establish which one of the currently available algorithms is the *best one* in absolute terms is also probably utopic. At most, it can be stated that a particular method is faster, more stable or more efficient than some other method in the specific conditions of comparison. The best algebraic and computational algorithm is probably a combination of the methods published in recent years. However, Fernández Rico et al.’s integral package employing ETOs [12], the seed for a complete molecular LCAO program, deserves a special mention here.

When a closed–shell ion suffers the action of an arbitrary external potential, its electron density loses its spherical shape. However, the *Spherical Symmetry Approximation* (SSA) has been widely used to compute the electronic structure of *ions-in-crystals*, being the spatial orbitals,  $\phi_i$ , classified according to the irreducible representations (*irreps*) of the  $O_3^+$  point group. This allows every  $\phi_i$  to be expressed as the product of a spherical harmonic,

$Y_{lm}(\theta, \phi)$ , and a radial function,  $R_{nl}(r)$ , independent of the azimuthal quantum number ( $m$ ). The SSA involves some computational advantages but prevent a polarization of the electron density. In spite of this shortcoming, a large variety of atomistic simulation methods [13–20], progressively improved over the years, have provided accurate structural and thermodynamic properties for highly symmetric crystalline solids [13–18, 21]. Nevertheless, the energetic contribution due to the polarization of the electron density is of essential importance both to compute accurate equilibrium geometrical parameters and to predict the stable crystalline phase in specific conditions of pressure and temperature of low-symmetry crystals [22]. Neglecting polarization effects is probably also the responsible for the inaccurate prediction of the elastic behaviour of ionic solids [23].

All the above facts stress the relevance of taking into account properly, not only the radial relaxation, but also the polarization of the electron density for the ions in arbitrary external potentials. In that case, every  $\phi_i$  transforms according to one of the *irreps* of the true symmetry point group for the ion and should be expressed as a linear combinations of appropriate *Symmetry Adapted Functions* (SAF). The relaxation of the point group allows for the mixing of SAF belonging to different atomic symmetries and also the splitting of the atomic levels in so many sub-levels as required by the point group of the ion.

Martín Pendás and Francisco have developed algorithms to compute spherical averages of two-center nuclear attraction, Coulomb, and projection operator integrals [24] between Slater type orbitals (STOs) (the most widely used ETOs in molecular and solid state calculations) using the Silverstone and Moats (SM) expansion of a function about a displaced center [25]. These averages are the only ones required in the *ab initio* Perturbed Ion (*ai*PI) model [19, 20], a localized quantum-mechanical scheme that solves the Hartree-Fock equations for an *ion-in-a-crystal* taking as a central hypothesis the SSA. However, the generalization for ions in external potentials of arbitrary symmetry makes useless the spherical averages previously derived in Ref. 24. The present work represents an application of the SM expansion and the related Kay, Todd, and Silverstone expansion for  $r_{12}^{-1}$  [26], in order to compute the basic integrals over STOs that are necessary in the generalized (i.e. non-spherical) method. The proposed algorithms are tailored to be useful in this context, with emphasis on extracting long-range terms that have to be computed separately in infinite periodic systems. In addition, we derive analytical expressions for the *Electrostatic Interionic Energy* EIE between non-spherical ions and obtain explicit formulas for the multipolar coefficients.

The outline of the article is as follows. In Section II, some definitions are given to shorten the writing of the next Sections. In Section III, we develop compact, stable, and fast algorithms for the overlap, nuclear attraction and Coulomb integrals over STOs. In Section IV, simple expressions for the auxiliary radial functions  $\chi^X(n_1, n_2, \zeta_1, \zeta_2; R)$  are given. In Section V, some computational details and the problem of the numerical stability of the algorithm for nearly equal orbital exponents and vanishing interatomic distance are discussed. In Section VI, we define the SAF used in this work. In Section VII, we express the EIE in terms of two-center integrals between STO and divide the EIE into both short-range components and long-range or multipolar components. In Section VIII some tests are carried out with the two-center integrals. Finally, we present our conclusions in Section IX.

## II. DEFINITIONS

In this work we will use STOs  $\varphi_{plm}$ , defined as products of a radial function,  $\chi_{pl}(r)$ , and a real spherical harmonic,  $S_{lm}(\hat{r})$  ( $r$  is the modulus and  $\hat{r}$  the direction  $(\theta, \phi)$  of a vector  $\vec{r}$ ):

$$\varphi_{plm}(\vec{r}) = \chi_{pl}(r)S_{lm}(\hat{r}) = \chi_{pl}(r)\Theta_{l|m|}(\theta)\Phi_m(\phi), \quad (1)$$

where

$$\chi_{pl}(r) = N_{pl}r^{n_{pl}-1}e^{-\zeta_{pl}r}, \quad N_{pl} = \frac{(2\zeta_{pl})^{n_{pl}+\frac{1}{2}}}{\sqrt{(2n_{pl})!}}, \quad (2)$$

$$\Phi_m(\phi) = \begin{cases} \sqrt{2} \cos(m\phi) & m > 0, \\ 1 & m = 0, \\ \sqrt{2} \sin(|m|\phi) & m < 0, \end{cases} \quad (3)$$

and [27]

$$\Theta_{lm}(\theta) = N_{lm}P_l^m(\cos \theta), \quad N_{lm} = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}}, \quad (4)$$

where  $P_l^m$  is the associated Legendre function.

Some definitions and properties concerning the  $S_{lm}(\hat{r})$  functions are the following:

$$\begin{aligned} d_{l_1 m_1 l_2 m_2}^{l_3 m_3} &= \langle S_{l_3 m_3} | S_{l_1 m_1} | S_{l_2 m_2} \rangle \\ &= \int_{\Omega} S_{l_3 m_3}(\hat{r}) S_{l_1 m_1}(\hat{r}) S_{l_2 m_2}(\hat{r}) d\hat{r}, \end{aligned} \quad (5)$$

is the Gaunt coefficient between real spherical harmonics, that can be fast and straightforwardly computed using, for instance, the algorithm in Ref. 28.  $T_{l_1 m_1 l_2 m_2}^{l_3 m_3}(\hat{r})$  is the angular

coefficient given by

$$T_{l_1 m_1 l_2 m_2}^{l_3}(\hat{r}) = \sum_{m_3=-l_3}^{l_3} d_{l_1 m_1 l_2 m_2}^{l_3 m_3} S_{l_3 m_3}(\hat{r}), \quad (6)$$

and, finally, the product of two different  $S_{lm}$  is

$$S_{l_1 m_1}(\hat{r}) S_{l_2 m_2}(\hat{r}) = \sum_{l_3=|l_1-l_2|}^{l_1+l_2} T_{l_1 m_1 l_2 m_2}^{l_3}(\hat{r}) \quad (7)$$

Two atomic centers are labeled by  $R$  and  $S$ , their nuclei having vector positions  $\vec{r}^R$  and  $\vec{r}^S$ , respectively.

### III. TWO-CENTER INTEGRALS BETWEEN SLATER TYPE FUNCTIONS

#### A. Overlap integral

The basic two-center overlap integral is

$$S_{pm_p am_a}^{RS} = \langle \varphi_{pl_p m_p}^R(\vec{r} - \vec{r}^R) | \varphi_{al_a m_a}^S(\vec{r} - \vec{r}^S) \rangle. \quad (8)$$

The quantum numbers and orbital exponents of the STOs centered at  $R$  and  $S$  are  $(n_p, l_p, m_p, \zeta_p)$  and  $(n_a, l_a, m_a, \zeta_a)$ , respectively. Defining  $\vec{r}_X = \vec{r} - \vec{r}^X$  and using Eq. 1, we have

$$S_{pm_p am_a}^{RS} = \int \chi_p^R(r_R) S_{l_p m_p}(\hat{r}_R) \chi_a^S(r_S) S_{l_a m_a}(\hat{r}_S) d\tau. \quad (9)$$

Using the SM expansion [25] of the S-centered function about the R-center in terms of real spherical harmonics,  $S_{pm_p am_a}^{RS}$  results in

$$\begin{aligned} S_{pm_p am_a}^{RS} &= \int_0^\infty dr_R \chi_p^R(r_R) \int_0^\infty dr_S \chi_a^S(r_S) (-1)^{l_p} r_R^2 r_S^2 \\ &\times \sum_{l_3=|l_p-l_a|}^{l_p+l_a} T_{l_p m_p l_a m_a}^{l_3}(\hat{R}) O_{l_p l_a l_3}(r_R, r_S, R), \end{aligned} \quad (10)$$

where  $\vec{R} = \vec{r}^S - \vec{r}^R$ , the sum over  $l_3$  is for  $l_3 + l_p + l_a = \text{even}$ , and the function  $O$  is defined as

$$O_{l_1 l_2 l_3}(r_1, r_2, r_3) = 4(-1)^{\lambda/2} \int_{-\infty}^{\infty} dk k^2 j_{l_1}(kr_1) j_{l_2}(kr_2) j_{l_3}(kr_3), \quad (11)$$

where  $\lambda = l_1 + l_2 + l_3$  is always even and  $j_l(x)$  is the first class Bessel function of order  $l$

$$j_l(x) = (-1)^l x^l \left( \frac{1}{x} \frac{d}{dx} \right)^l \frac{\sin(x)}{x}. \quad (12)$$

$O_{l_1 l_2 l_3}(r_1, r_2, r_3)$  is equivalent to the integral  $\mathcal{L}_{l_1 l_2 l_3}^{(1)}(r_1, r_2, r_3)$  defined by Hierse and Oppeneer in Ref. 11. Owing to the restricted allowed values of  $l_3$  in Equation 10, the relevant contribution of  $O_{l_1 l_2 l_3}(r_1, r_2, r_3)$  can be written as [29]

$$O_{l_1 l_2 l_3}(r_1, r_2, r_3) = 2\pi \sum_{s=0}^{\lambda/2} \sum_{t=0}^{\lambda/2-s} D_{l_1 l_2 l_3 \frac{\lambda}{2} st} \left[ r_1^{2s-l_1-1} r_2^{2t-l_2-1} r_3^{\lambda-2s-2t-l_3-1} \right]^{\text{IV}} \quad (13)$$

where the superscript IV stands for the region IV of Fig. 1, characterized by  $|r_1 - r_3| \leq r_2 \leq (r_1 + r_3)$ , and  $D_{l_1 l_2 l_3 \frac{\lambda}{2} st}$  is given by

$$D_{l_1 l_2 l_3 st} = [(2s - 2l_1 - 1)!!(2t - 2l_2 - 1)!!(2l - 2s - 2t - 2l_3 - 1)!! \times (2s)!!(2t)!!(2l - 2s - 2t)!!]^{-1}. \quad (14)$$

$D_{l_1 l_2 l_3 st}$  is a generalization of the  $D_{l_2 l_3 l_1 st}$  coefficient defined by Pendás and Francisco [24], i.e.  $D_{l_2 l_3 l_1 st} = D_{l_1 l_2 l_3 (\frac{\lambda}{2}) st}$ . Substituting Equation 13 in Equation 10, we finally obtain

$$S_{pm_p am_a}^{RS} = (-1)^{l_p} 2\pi N_p N_a R^{l_p + l_a - 1} \sum_{l_3=|l_p-l_a|}^{l_p+l_a} T_{l_p m_p l_a m_a}^{l_3}(\hat{R}) \mathcal{A}^{(0)}(l_3; n_p, l_p, \zeta_p, n_a, l_a, \zeta_a; R), \quad (15)$$

where  $\mathcal{A}^{(0)}$  ( $\mathcal{A}$  in Ref. 24) is a particular case of the more general  $\mathcal{A}^{(m)}$  one-center radial integral

$$\mathcal{A}^{(m)}(l_3; n_1, l_1, \zeta_1, n_2, l_2, \zeta_2; R) = \sum_{s=0}^{s_m} \sum_{t=0}^{s_m-s} D_{l_1 l_2 l_3 s_m st} R^{-2s-2t} \times \chi^{\text{IV}}(n_1 - l_1 + 2s, n_2 - l_2 + 2t, \zeta_1, \zeta_2; R), \quad (16)$$

with  $s_m = \left(\frac{\lambda+2m}{2}\right)$ , and

$$\chi^{\text{IV}}(n_1, n_2, \zeta_1, \zeta_2; R) = \int_0^\infty dr_1 r_1^{n_1} e^{-\zeta_1 r_1} \int_{|r_1-R|}^{r_1+R} dr_2 r_2^{n_2} e^{-\zeta_2 r_2}. \quad (17)$$

## B. Coulomb integral

The two-center Coulomb integral is defined by

$$C_{pm_p am_a, qm_q bm_b}^{RS} = \left\langle \varphi_{pl_p m_p}^R(\vec{r}_R) \varphi_{al_a m_a}^S(\vec{r}_S) \middle| r_{12}^{-1} \middle| \varphi_{ql_q m_q}^R(\vec{r}_R) \varphi_{bl_b m_b}^S(\vec{r}_S) \right\rangle, \quad (18)$$

where  $\vec{r}_R = \vec{r}_1 - \vec{r}^R$  and  $\vec{r}_S = \vec{r}_2 - \vec{r}^S$ . Expressing the STOs in angular and radial parts, using  $\vec{r}_{12} = \vec{r}_R - \vec{r}_S - \vec{R}$ , the definitions

$$\chi_1^R(r_R) = \chi_p^R(r_R) \chi_q^R(r_R) = N_1 r_R^{n_1-2} e^{-\zeta_1 r_R} \quad (19)$$

$$\chi_2^S(r_S) = \chi_a^S(r_S) \chi_b^S(r_S) = N_2 r_S^{n_2-2} e^{-\zeta_2 r_S}, \quad (20)$$

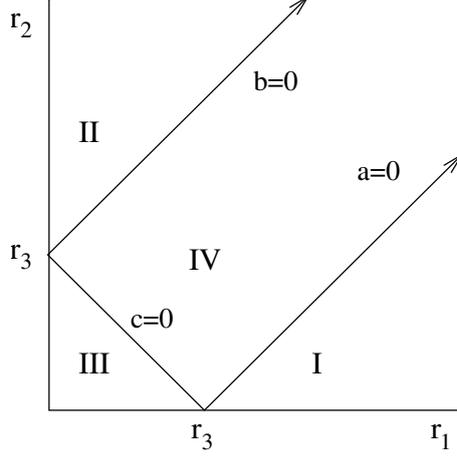


FIG. 1: The four regions in which the  $(r_1, r_2)$  plane is divided.  $a = r_1 - r_2 - r_3$ ,  $b = r_2 - r_3 - r_1$ ,  $c = r_3 - r_1 - r_2$ .

with  $n_1 = n_p + n_q$ ,  $n_2 = n_a + n_b$ ,  $\zeta_1 = \zeta_p + \zeta_q$ ,  $\zeta_2 = \zeta_a + \zeta_b$ ,  $N_1 = N_p N_q$ ,  $N_2 = N_a N_b$ , and using Eq. 7, Equation 18 transforms into

$$C_{pm_p am_a, qm_q bm_b}^{RS} = \sum_{l_1=|l_p-l_q|}^{l_p+l_q} \sum_{l_2=|l_a-l_b|}^{l_a+l_b} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} d_{l_p m_p l_q m_q}^{l_1 m_1} d_{l_a m_a l_b m_b}^{l_2 m_2} 4\pi C_{12}^{RS} \quad (21)$$

where  $C_{12}^{RS}$  is the Coulomb integral between the charge distributions  $\chi_1$  and  $\chi_2$ ,

$$C_{12}^{RS} = \frac{1}{4\pi} \int_{\tau_R} d\tau_R \int_{\tau_S} d\tau_S \frac{\chi_1^R(r_R) S_{l_1 m_1}(\hat{r}_R) \chi_2^S(r_S) S_{l_2 m_2}(\hat{r}_S)}{|\vec{r}_R - \vec{r}_S - \vec{R}|}. \quad (22)$$

Using the bipolar expansion of Kay, Todd, and Silverstone [26] for  $r_{12}^{-1} = |\vec{r}_R - \vec{r}_S - \vec{R}|^{-1}$ ,  $C_{12}^{RS}$  can be written as

$$C_{12}^{RS} = \int_0^\infty dr_R \int_0^\infty dr_S (-1)^{l_1} r_R^2 \chi_1^R(r_R) r_S^2 \chi_2^S(r_S) \times \sum_{l_3=|l_1-l_2|}^{l_1+l_2} T_{l_1 m_1 l_2 m_2}^{l_3}(\hat{R}) \times V_{l_1 l_2 l_3}(r_R, r_S, R), \quad (23)$$

where we have defined

$$V_{l_1 l_2 l_3}(r_1, r_2, r_3) = 4(-1)^{\lambda/2} \int_{-\infty}^\infty dk j_{l_1}(kr_1) j_{l_2}(kr_2) j_{l_3}(kr_3), \quad (24)$$

which is equivalent to  $\mathcal{L}_{l_1 l_2 l_3}^{(0)}(r_1, r_2, r_3)$  in the notation of Hiersse and Oppeneer [11]. Using Equation 12 and the definition

$$\hat{O}_i = r_i^{l_i} \left( \frac{1}{r_i} \frac{d}{dr_i} \right)^{l_i}, \quad (25)$$

with the property

$$\hat{O}_i r_i^m = \begin{cases} \frac{m!}{(m-2l_i)!} r_i^{m-l_i} & (m \text{ odd}) \text{ or } (m \geq 2l_i \text{ and even}), \\ 0 & (m < 2l_i \text{ and even}), \end{cases} \quad (26)$$

it is possible to show that  $V_{l_1 l_2 l_3}(r_1, r_2, r_3)$  can be written as [29]

$$V_{l_1 l_2 l_3}(r_1, r_2, r_3) = V_{l_1 l_2 l_3}^a(r_1, r_2, r_3) + V_{l_1 l_2 l_3}^b(r_1, r_2, r_3), \quad (27)$$

with

$$V_{l_1 l_2 l_3}^a(r_1, r_2, r_3) = -2\pi \sum_{s=0}^{s_1} \sum_{t=0}^{s_1-s} D_{l_1 l_2 l_3 s_1 s t} \left[ r_1^{2s-l_1-1} r_2^{2t-l_2-1} r_3^{2s_1-2s-2t-l_3-1} \right]^{\text{IV}}, \quad (28)$$

where  $s_1 = s_m(m=1) = \frac{\lambda}{2} + 1$ , and

$$V_{l_1 l_2 l_3}^b(r_1, r_2, r_3) = 2 \left( F_1^{\text{I}} + F_2^{\text{II}} + F_3^{\text{III}} \right) + \left( F_1^{\text{IV}} + F_2^{\text{IV}} + F_3^{\text{IV}} \right). \quad (29)$$

In this equation  $F_i^{\text{X}}(r_1, r_2, r_3)$  is defined by:

$$F_i^{\text{X}}(r_1, r_2, r_3) = 2\pi \Delta_{l_j l_k} \left[ \frac{r_j^{l_j} r_k^{l_k}}{r_i^{l_i+1}} \right]^{\text{X}} \delta_{l_i, l_j+l_k}, \quad (30)$$

where  $i = 1, j = 2$ , and  $k = 3$ , and cyclic permutations, the superscript X stands for the regions I, II, III, or IV of Fig. 1 in which  $F_i^{\text{X}}(r_1, r_2, r_3)$  is defined, and

$$\Delta_{l_j l_k} = \Delta_{l_k l_j} = (-1)^{l_j+l_k} \frac{(2l_j + 2l_k)! l_j! l_k!}{(l_j + l_k)! (2l_j + 1)! (2l_k + 1)!}. \quad (31)$$

Using Equations 28 and 29 in Equation 23, we obtain for  $C_{12}^{RS}$

$$C_{12}^{RS} = (-1)^{l_1} 2\pi N_1 N_2 \left[ C_a + 2C_1^1 + 2C_{\text{II}}^2 + 2C_{\text{III}}^3 + C_{\text{IV}}^1 + C_{\text{IV}}^2 + C_{\text{IV}}^3 \right], \quad (32)$$

where

$$C_a = -R^{(l_1+l_2+1)} \sum_{l_3=|l_1-l_2|}^{l_1+l_2} T_{l_1 m_1 l_2 m_2}^{l_3}(\hat{R}) \times \mathcal{A}^{(1)}(l_3; n_1 - 1, l_1, \zeta_1, n_2 - 1, l_2, \zeta_2; R), \quad (33)$$

$$C_{\text{X}}^1 = \Delta_{l_2|l_1-l_2} R^{|l_1-l_2|} \chi^{\text{X}}(n_1 - l_1 - 1, n_2 + l_2, \zeta_1, \zeta_2; R) \times T_{l_1 m_1 l_2 m_2}^{|l_1-l_2|}(\hat{R}) \delta_{l_1-l_2, |l_1-l_2|}, \quad (34)$$

$$C_{\text{X}}^2 = \Delta_{l_1|l_1-l_2} R^{|l_1-l_2|} \chi^{\text{X}}(n_1 + l_1, n_2 - l_2 - 1, \zeta_1, \zeta_2; R) \times T_{l_1 m_1 l_2 m_2}^{|l_1-l_2|}(\hat{R}) \delta_{l_2-l_1, |l_1-l_2|}, \quad (35)$$

and

$$C_{\text{X}}^3 = \Delta_{l_1 l_2} R^{-(l_1+l_2+1)} \chi^{\text{X}}(n_1 + l_1, n_2 + l_2, \zeta_1, \zeta_2; R) \times T_{l_1 m_1 l_2 m_2}^{l_1+l_2}(\hat{R}). \quad (36)$$

In the above four expressions, we have generalized the  $\chi^{\text{IV}}$  integral to other regions of the  $(r_1, r_2)$  plane, i.e.

$$\chi^{\text{X}}(n_1, n_2, \zeta_1, \zeta_2; R) = \int \int_{\text{X}} dr_1 dr_2 r_1^{n_1} r_2^{n_2} e^{-\zeta_1 r_1} e^{-\zeta_2 r_2}, \quad \text{X} = \text{I, II, III, IV}. \quad (37)$$

### C. Nuclear attraction integral

This integral is defined as

$$Z_{pm_p, qm_q}^{RS} = -Z^S \left\langle \varphi_{pl_p m_p}^R(\vec{r}_R) \left| r_S^{-1} \right| \varphi_{ql_q m_q}^R(\vec{r}_R) \right\rangle. \quad (38)$$

Transforming the operator as  $r_S^{-1} = |\vec{r} - \vec{r}^S|^{-1} = |\vec{r}_R - \vec{R}|^{-1}$ , so that the variable  $\vec{r}$  is referred to the same center as  $\varphi_{pl_p m_p}^R$  and  $\varphi_{ql_q m_q}^R$ , and using the Laplace expansion

$$|\vec{r}_R - \vec{R}|^{-1} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r_{<}^k}{r_{>}^{k+1}} \sum_{m=-k}^k S_{km}(\hat{r}_R) S_{km}(\hat{R}), \quad (39)$$

the angular and radial parts can be integrated separately, giving

$$Z_{pm_p, qm_q}^{RS} = -Z^S \sum_{k=|l_p-l_q|}^{l_p+l_q} \frac{4\pi}{2k+1} \times T_{l_p m_p l_q m_q}^k(\hat{R}) \times I_{k pq}^R(R), \quad (40)$$

where the selection rules of the Gaunt coefficients have been taken into account and  $I_{k pq}^R(R)$  is the radial integral

$$I_{k pq}^R(R) = \int_0^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} \chi_p^R(r_R) \chi_q^R(r_R) r_R^2 dr_R. \quad (41)$$

Separating the integral in two domains  $[0, R] + [R, \infty]$ , it can be easily expressed in terms of the  $\mu_n(x)$  function considered in the next Section. The resulting expression is

$$I_{k pq}^R(R) = N_1 \frac{(n_1 + k)!}{\zeta_1^{n_1+k+1}} R^{-k-1} - N_1 R^{n_1} \mu_{n_1+k}(\zeta_1 R) + N_1 R^{n_1} \mu_{n_1-k-1}(\zeta_1 R), \quad (42)$$

using  $N_1$ ,  $n_1$ , and  $\zeta_1$  definitions from the previous Subsection.

### IV. EVALUATION OF THE INTEGRALS $\chi^X(n_1, n_2, \zeta_1, \zeta_2; R)$

The basic integrals appearing in the Coulomb and Overlap integrals,

$$\chi^X(n_1, n_2, \zeta_1, \zeta_2; R) = \int \int_X dr_1 dr_2 r_1^{n_1} r_2^{n_2} e^{-\zeta_1 r_1} e^{-\zeta_2 r_2}, \quad X = \text{I, II, III, IV}, \quad (43)$$

where X stands for one of the four regions of Fig. 1, can be computed from  $\chi^X(0, 0, \zeta_1, \zeta_2; R)$  using the relation

$$\chi^X(n_1, n_2, \zeta_1, \zeta_2; R) = \left( -\frac{\partial}{\partial \zeta_1} \right)^{n_1} \left( -\frac{\partial}{\partial \zeta_2} \right)^{n_2} \chi^X(0, 0, \zeta_1, \zeta_2; R). \quad (44)$$

For  $\chi^I(0, 0, \zeta_1, \zeta_2; R)$  and  $\chi^{II}(0, 0, \zeta_1, \zeta_2; R)$  we obtain

$$\chi^I(0, 0, \zeta_1, \zeta_2; R) = \frac{e^{-\zeta_1 R}}{\zeta_1(\zeta_1 + \zeta_2)}, \quad (45)$$

$$\chi^{II}(0, 0, \zeta_1, \zeta_2; R) = \frac{e^{-\zeta_2 R}}{\zeta_2(\zeta_1 + \zeta_2)}, \quad (46)$$

and, using Eq. 44,

$$\chi^I(n_1, n_2, \zeta_1, \zeta_2; R) = R^{n_1+n_2+2} \sum_{u=0}^{n_1} \binom{n_1}{u} \frac{N_u! \mu_u(\zeta_1 R)}{(2\alpha)^{N_u+1}}, \quad (47)$$

$$\chi^{II}(n_1, n_2, \zeta_1, \zeta_2; R) = R^{n_1+n_2+2} \sum_{u=0}^{n_2} \binom{n_2}{u} \frac{N_u! \mu_u(\zeta_2 R)}{(2\alpha)^{N_u+1}}, \quad (48)$$

where  $\alpha = \frac{1}{2}(\zeta_1 + \zeta_2)R$ ,  $N_u = n_1 + n_2 - u$ , and the  $\mu$  function is defined as

$$\mu_n(x) = \left(-\frac{d}{dx}\right)^n \frac{e^{-x}}{x} = \sum_{s=0}^n \frac{n!}{(n-s)!} \frac{e^{-x}}{x^{s+1}}. \quad (49)$$

In the case of  $\chi^{III}(0, 0, \zeta_1, \zeta_2; R)$ , we have

$$\chi^{III}(0, 0, \zeta_1, \zeta_2; R) = \frac{1}{\zeta_1 \zeta_2} + \frac{e^{-\zeta_1 R}}{\zeta_1(\zeta_1 - \zeta_2)} + \frac{e^{-\zeta_2 R}}{\zeta_2(\zeta_2 - \zeta_1)}, \quad (50)$$

and, applying Eq. 44, we obtain after some algebraic manipulation

$$\begin{aligned} \chi^{III}(n_1, n_2, \zeta_1, \zeta_2; R) &= \frac{n_1! n_2!}{\zeta_1^{n_1+1} \zeta_2^{n_2+1}} + (-1)^{n_2} R^{n_1+n_2+2} \left[ \sum_{u=0}^{n_1} \binom{n_1}{u} \frac{N_u! \mu_u(\zeta_1 R)}{(2\beta)^{N_u+1}} \right. \\ &\quad \left. - \sum_{u=0}^{n_2} \binom{n_2}{u} (-1)^u \frac{N_u! \mu_u(\zeta_2 R)}{(2\beta)^{N_u+1}} \right], \end{aligned} \quad (51)$$

where  $\beta = \frac{1}{2}(\zeta_1 - \zeta_2)R$ .

To compute  $\chi^{IV}(n_1, n_2, \zeta_1, \zeta_2; R)$ , we use the symmetrical method developed by Hierse and Oppeneer [11]. The final result is

$$\chi^{IV}(n_1, n_2, \zeta_1, \zeta_2; R) = R^{n_1+n_2+2} \sum_{u=0}^{n_1+n_2} C_{n_1 n_2 u} \times \mu_{n_1+n_2-u}(\alpha) \times \nu_u(\beta), \quad (52)$$

where the  $\nu$  function is defined as

$$\nu_n(x) = \left(\frac{d}{dx}\right)^n \frac{\sinh x}{x}, \quad (53)$$

and  $C_{n_1 n_2 u}$  is given by

$$C_{n_1 n_2 u} = \frac{1}{2^{n_1+n_2}} \sum_{s=\max(u-n_2, 0)}^{\min(u, n_1)} (-1)^s \binom{n_1}{s} \binom{n_2}{u-s}. \quad (54)$$

The  $C_{n_1 n_2 u}$  coefficients satisfy the following recurrence relations that are useful for their computation [11]

$$C_{n_1 n_2 u} = (-1)^u C_{n_2 n_1 u} \quad (55)$$

$$2C_{(n_1+1)n_2 u} = C_{n_1 n_2 u} - C_{n_1 n_2 (u-1)} \quad (56)$$

$$2C_{n_1(n_2+1)u} = C_{n_1 n_2 u} + C_{n_1 n_2 (u-1)}. \quad (57)$$

Some of the previously available algorithms for the computation of two-center ETOMI become numerically unstable for nearly equal orbital exponents. In our expressions, this would be the case with the basic integral  $\chi^{\text{III}}$ , that is divergent when  $|\zeta_1 - \zeta_2| \rightarrow 0$ . The formalism we have developed, however, has the property

$$\sum_{i=I}^{IV} \chi^i(n_1, n_2, \zeta_1, \zeta_2; R) = \frac{n_1! n_2!}{\zeta_1^{n_1+1} \zeta_2^{n_2+1}} = F(n_1, n_2, \zeta_1, \zeta_2). \quad (58)$$

Thus, the  $\chi^{\text{III}}$  integral can be computed in all the cases using  $\chi^{\text{III}} = F - \chi^{\text{I}} - \chi^{\text{II}} - \chi^{\text{IV}}$ , that is completely stable for  $|\zeta_1 - \zeta_2| \rightarrow 0$ . When  $\zeta_1 = \zeta_2 = \zeta$ , the formula for  $\chi^{\text{III}}$  reduces to

$$\chi^{\text{III}}(n_1, n_2, \zeta, \zeta; R) = F(n_1, n_2, \zeta, \zeta) - \frac{n_1! n_2! R^{n_1+n_2+2} \mu_{n_1+n_2+1}(\zeta R)}{(n_1 + n_2 + 1)!}. \quad (59)$$

It is interesting to notice that all the  $\chi^{\text{X}}$  integrals except  $\chi^{\text{III}}$  decay exponentially with  $R$  due to the presence of the  $\mu(x)$  function in their expressions. On the other hand, the  $F(n_1, n_2, \zeta_1, \zeta_2)$  contribution to  $\chi^{\text{III}}$  (see the leading term in Eq. 51) is the only one being  $R$ -independent, all other  $\chi^{\text{X}}$  contributions decaying exponentially with  $R$ . This  $F(n_1, n_2, \zeta_1, \zeta_2)$  contribution is absent from overlap integrals, which only depend on  $\chi^{\text{IV}}$  and thus decay exponentially.  $F(n_1, n_2, \zeta_1, \zeta_2)$  is, on the other hand, present in Coulomb integrals, and through Eqs. 21, 32, and 36, it can be seen that it leads to a  $R^{-(l_1+l_2+1)}$  dependence, quite similar to the  $R^{-k-1}$  one in nuclear attraction integrals (see Eq. 42). These two terms can be labelled as long range terms, in opposition to the exponential decay of the rest, and they lead to the multipolar (i.e., charge-charge, multipole-charge, and multipole-multipole) interaction energies in ionic systems as discussed in Section VII.

## V. COMPUTATIONAL DETAILS AND NUMERICAL STABILITY

It is first worthwhile to remark that the computation of the  $\mathcal{A}^{(m)}$  integral (see Eq. 16) can be sped up by reducing the number of loops in the following way: Substituting Eq. 52

in Eq. 16 we have

$$\begin{aligned} \mathcal{A}^{(m)}(l_3; n_1, l_1, \zeta_1; n_2, l_2, \zeta_2; R) &= R^{N_{\max}+2} \sum_{s=0}^{s_m} \sum_{t=0}^{s_m-s} D_{l_1 l_2 l_3 s_m s t} \\ &\times \sum_{u=0}^{N_{\max}+2s+2t} C_{(n_1+2s-l_1)(n_2+2t-l_2)u} \times \mu_{N_{\max}+2s+2t-u}(\alpha) \times \nu_u(\beta), \end{aligned} \quad (60)$$

where  $N_{\max} = n_1 + n_2 - l_1 - l_2$ . The double sum over  $s$  and  $t$ , that runs over the left top triangle of a  $s_m \times s_m$  square matrix, can be also written as an external loop extended to  $r = s + t$ , and an internal one running over the values of  $s$  compatible with the value of  $r$  (i.e.  $s = 0, \dots, r; t = r - s$ ). Developing the expression of the  $D_{l_1 l_2 l_3 s_m s t}$  coefficient, the  $\mathcal{A}^{(m)}$  integral can be put as

$$\begin{aligned} \mathcal{A}^{(m)}(l_3; n_1, l_1, \zeta_1; n_2, l_2, \zeta_2; R) &= \sum_{r=0}^{s_m} R^{N_{\max}+2} D_{(s_m-r)l_3} \\ &\times \sum_{u=0}^{N_{\max}+2r} \mu_{N_{\max}+2r-u}(\alpha) \times \nu_u(\beta) \times E(l_1, n_1 - l_1, l_2, n_2 - l_2, r, u), \end{aligned} \quad (61)$$

where the coefficients  $E$ , given by

$$E(l_1, n_1, l_2, n_2, r, u) = \sum_{s=0}^r C_{(n_1+2s)(n_2+2r-2s)u} D_{sl_1} D_{(r-s)l_2}, \quad (62)$$

with

$$D_{ab} = [(2a)!!(2a - 2b - 1)!!]^{-1}, \quad (63)$$

only depend on natural numbers, and are independent of  $\zeta_1$  and  $\zeta_2$ . We have found that  $E(l_1, n_1, l_2, n_2, r, u)$  is zero when  $u < 2r - l_1 - l_2$  and  $s_m \leq l_1 + l_2$ . So, the lower limit of  $u$  in Eq. 61 can be put as  $u_{\min} = \max(2r - l_1 - l_2, 0)$  when  $s_m \leq l_1 + l_2$ . This is the case of the overlap integral ( $m = 0$ ), where the maximum value of  $s_m$  is  $l_1 + l_2$ . In the Coulomb integrals ( $m = 1$ ), the lower limit of  $u$  in Eq. 61 must be 0 only when  $r = s_m = l_1 + l_2 + 1$ , that, in turn, can only happen if  $l_3 = l_1 + l_2$ .

Regarding the computation of the auxiliary functions,  $\mu_n(x)$  can be computed for any  $x > 0$  using the stable ascending recurrence formula

$$\mu_{n+1}(x) = \frac{1}{x} \left[ (n+1)\mu_n(x) + e^{-x} \right], \quad (64)$$

with  $\mu_0(x) = e^{-x}/x$ .

The  $\nu$  function has a closed formula. To avoid numerical instabilities, however, it is convenient to use an algorithm based on the recurrence relations given by Hierse and Oppeneer [11] on its computation. If the index of the function is smaller than  $|\beta|$ , the ascending

recurrence

$$\nu_u(\beta) = \frac{1}{\beta} [\cosh \beta - u\nu_{u-1}(\beta)], \quad (65)$$

$$\nu_{u+1}(\beta) = \frac{1}{\beta} [\sinh \beta - (u+1)\nu_u(\beta)], \quad (66)$$

with  $u = \text{odd}$ , is stable, and the starting point of the recursion is  $\nu_0(\beta) = \sinh \beta / \beta$ . For values of the index greater than  $|\beta|$ , the stable recurrence formula is the descending one

$$\nu_u(\beta) = \frac{1}{u+1} [\cosh \beta - \beta\nu_{u+1}], \quad (67)$$

$$\nu_{u-1}(\beta) = \frac{1}{u} [\sinh \beta - \beta\nu_u], \quad (68)$$

with  $u = \text{even}$ . The reference value will be that corresponding to the greatest necessary index,  $m$ , that is computed using

$$\nu_m(\beta) = \begin{cases} \cosh \beta u_m^{(1)}(\beta) - \sinh \beta u_m^{(2)}(\beta) & m \text{ even,} \\ \sinh \beta u_m^{(1)}(\beta) - \cosh \beta u_m^{(2)}(\beta) & m \text{ odd,} \end{cases} \quad (69)$$

where

$$u_m^{(1)}(\beta) = \sum_{j=0}^{\infty} \frac{m!}{(m+2j+1)!} \beta^{2j}, \quad (70)$$

$$u_m^{(2)}(\beta) = \sum_{j=0}^{\infty} \frac{m!}{(m+2j+2)!} \beta^{2j+1}, \quad (71)$$

are two convergent series provided that  $m \geq |\beta|$ . The loss in precision using this scheme is negligible in double precision (8 bytes) arithmetics: the relative error is below  $10^{-15}$  for a certain range about the  $u \simeq |\beta|$  turnover value for both the ascending and descending recurrences, as seen in Figure 2. For  $u = 0$  the ascending recurrence is stable for  $\beta > 0.02$ , while the descending one is essentially exact for  $\beta < 3$ ; for  $u = 7$  their ranges are  $\beta > 5$  and  $\beta < 9$ , while for  $u = 23$  they are  $\beta > 21$  and  $\beta < 29$ , respectively. It should be remarked that the descending recurrence does not introduce further errors from those already in the infinite series involved on its starting value, Eq. 69: using these series and Eq. 69 for  $u = m = 7$  (dotted line) has a performance similar to using it for  $m = 32$  and then use the descending recurrence up to  $u = 7$  (dashed line).

On the other hand, care should be taken with extreme values of  $|\beta|$ . If  $\beta = 0$ , that is, either  $R \rightarrow 0$  or both orbital exponents in  $\chi^{\text{IV}}$  are equal, none of the above recursion

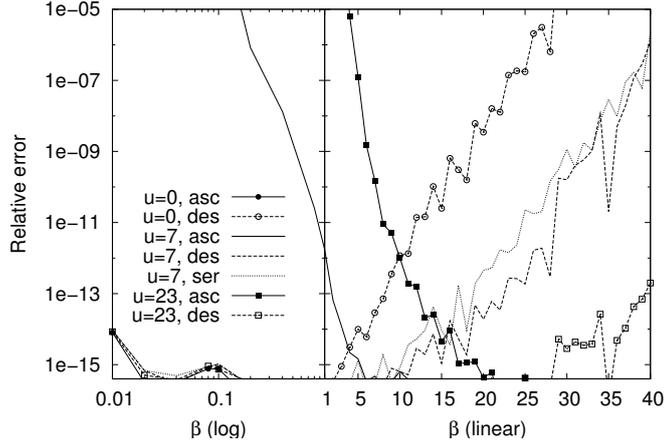


FIG. 2: Relative error (in log scale) for the different computational schemes of  $\nu_u(\beta)$ : asc corresponds to the ascending recurrence in Eqs. 65 and 66 starting from  $u = 0$ , des to the descending recurrence in Eqs. 67 and 68 starting from the  $\max(u) = m$  series in Eq. 69 (in this Figure,  $m = 32$  was selected), and ser to the series in Eq. 69 computed for the particular  $m = u$  value.  $u = 0$  (circles),  $u = 7$  (lines only), and  $u = 23$  (squares)  $\nu_u$  functions were computed as a function of  $\beta$ , ranging from 0.01 to 1 (log scale, left part) and from 1 to 40 (linear scale, right part).

formulas are valid. However, in that case

$$\nu_u(0) = \begin{cases} \frac{1}{u+1} & u \text{ even,} \\ 0 & u \text{ odd.} \end{cases} \quad (72)$$

Finally, when  $R$  is very large, the  $\beta$  values can produce overflow in the hyperbolic functions. In that case, it is convenient to transfer the factor  $e^{-\alpha}$  of the  $\mu$  function to the  $\nu$  function. With this trick, the exponentials to be evaluated will be those of  $\beta - \alpha$  and  $-\alpha - \beta$ . As  $\alpha > |\beta|$ , there is warranty that all the exponentials to be evaluated are numbers smaller than 1. At the same time, the  $\mu$  function is still convergent ( $\alpha \gg 1$  for large  $R$  values). In this way, the  $\nu$  function can be accurately computed, no matter the values of the index and the argument. All the recurrence relations are stable in this scheme, the infinite series converge very fast and the scarce overflow cases are appropriately considered.

Another divergence condition arises for  $R \rightarrow 0$  in the overlap integrals, due to the way in which we have defined the  $\mu$  function in Eq. 49. However, this divergence can be avoided just by removing the factors  $R^{l_p+l_q-1}$  and  $R^{N_{\max}+2}$  from Eqs. 15 and 61, respectively, and

redefining the  $\mu$  function as

$$\mu_n(x) = \left[ \frac{2}{\zeta_1 + \zeta_2} \right]^{n_1+n_2+1} \sum_{s=0}^n \frac{n!}{(n-s)!} x^{n_1+n_2-s} e^{-x}. \quad (73)$$

Given the selection rule for the  $E$  coefficient, the maximum value of  $n$  in the previous equation is  $n_1 + n_2$ . Thus, the minimum power of  $x$  in Eq. 73 is always 0 and the  $\mu$  function can be computed without any special care even for  $R = 0$ .

In the case of the Coulomb integrals, it is possible to redefine the  $\mu$  functions so as to make the  $C_I^1$ ,  $C_{IV}^1$ ,  $C_{II}^2$ , and  $C_{IV}^2$  contributions to  $C_{12}^{RS}$  (see Eq. 32) completely stable for  $R \rightarrow 0$ . However, the terms  $C_a$ ,  $C_{III}^3$ , and  $C_{IV}^3$  inevitably diverge in the limit  $R \rightarrow 0$ , though the individual singularities produced by these three contributions exactly cancel in this case. To avoid this instability, Hierse and Oppeneer [11] have given a simple and pragmatic solution that consists in putting  $\exp(-x)/x^n = 0$  if  $x \leq x_{\text{cutoff}}$  ( $x_{\text{cutoff}} \simeq 10^{-11}$ ). With this additional precaution, the formulas for the Coulomb integrals are stable regardless the value of  $R$ .

On the other hand, the divergence when  $R \rightarrow 0$  in the nuclear attraction basic integral given in Eq. 42 can be easily avoided using

$$I_{kpq}^R(R) = N_1 R^{n_1} \sum_{t=0}^{\infty} \frac{x^t}{t!(n_1 + k + t + 1)} + \sum_{s=0}^{n_1-k-1} \frac{(n_1 - k - 1)!}{(n_1 - k - 1 - s)!} R^{n_1-s-1} \zeta_1^{-s-1} e^{-x}, \quad (74)$$

where  $x = \zeta_1 R$ . This first sum over  $t$  converges very quickly for small values of  $x$  and the total expression is absolutely stable even for  $R = 0$ , where  $I_{kpq}^R(R = 0) = N_1 \delta_{k,0} \frac{(n_1-1)!}{\zeta_1^{n_1}}$ .

Although the above considerations in the limit  $R \rightarrow 0$  are obviously important to confer robustness to the algorithm, an interatomic distance as small as to produce instabilities in our standard formulas is, however, highly improbable in a realistic quantum-chemical calculation. For this reason, we believe more appropriate to test the value of  $R$  at the very beginning of the computer code and warn the user that the integral is in fact a mono-centric one if  $R < R_{\text{cutoff}} \simeq 0.1$  bohr. One-center formulas could be used in that case. Because the expressions we have derived could be used in solid state calculations of ionic crystals, the most difficult and relevant numerical instability in this case is when  $R \rightarrow \infty$ , and, in this limit, the algorithms developed here are perfectly stable.

## VI. SYMMETRY ADAPTED FUNCTIONS

Let us define the set  $\{\hat{A}, \dots, \hat{R}, \dots\}$  formed by the  $n_G$  (proper and improper) rotations of the symmetry point group  $\mathcal{G}$  for the ion under study, where  $n_G$  is the *group order*. If  $\hat{R}$

acts on a primitive basis function,  $\varphi_{plm}(\vec{r})$ , one obtains

$$\hat{R}\varphi_{plm}(\vec{r}) = \chi_{pl}(r)\hat{R}S_{lm}(\hat{r}) \quad (75)$$

because the point group symmetry operations do not modify the distances to the origin. In turn, when  $\hat{R}$  acts on a real spherical harmonic,  $S_{lm}(\hat{r})$ , is obeyed the following relationship:

$$\hat{R}S_{lm}(\hat{r}) = \sum_{m'=-l}^l S_{lm'}(\hat{r})\Delta_{m'm}^l(\hat{R}), \quad (76)$$

where the  $(2l+1) \times (2l+1)$  square matrix  $\Delta^l(\hat{R})$  is equivalent to the Wigner rotation matrix for the real case and can be computed using different published schemes [31, 32]. Notice that the real spherical harmonics with order  $l$  make up a basis (or a complete set) formed by  $2l+1$  orthonormal vectors. Moreover, the set formed by the  $n_{\mathcal{G}}$  matrices  $\Omega^{(\Delta)} = \{\Delta^l(\hat{A}), \dots, \Delta^l(\hat{R}), \dots\}$  is a particular representation of the symmetry point group  $\mathcal{G}$  whose dimension is  $2l+1$ .

The vector  $\sigma_l^{\Gamma\mu,k}(\hat{r})$  transforms as the subspecies of symmetry  $\mu$  belonging to the irreducible representation (*irrep*)  $\Gamma$  if it satisfies the following relationship:

$$\hat{R}\sigma_l^{\Gamma\mu,k}(\hat{r}) = \sum_{\mu'=1}^{n_{\Gamma}} \sigma_l^{\Gamma\mu',k}(\hat{r})D_{\mu'\mu}^{\Gamma}(\hat{R}), \quad (77)$$

where  $n_{\Gamma} \leq 2l+1$  is the number of subspecies of symmetry and the  $n_{\Gamma} \times n_{\Gamma}$  square matrix  $\mathbf{D}^{\Gamma}(\hat{R})$  associated to the symmetry operation  $\hat{R}$  represents the *irrep*  $\Gamma$ . The set formed by the  $n_{\Gamma}$  vectors  $\{\sigma_l^{\Gamma 1,k}, \sigma_l^{\Gamma 2,k}, \dots, \sigma_l^{\Gamma n_{\Gamma},k}\}$  is a *proper basis* for the *irrep*  $\Gamma$ , where each of these vectors are called eigenvectors or *Symmetry Adapted Functions* (SAF). The SAF only depend on the angular coordinates  $\hat{r}$  and can be obtained through

$$\sigma_l^{\Gamma\mu,k}(\hat{r}) = \sum_{m=-l}^l u_{lm}^{\Gamma\mu,k} S_{lm}(\hat{r}), \quad (78)$$

where the  $u_{lm}^{\Gamma\mu,k}$  are the *Symmetry Coefficients* (SC). Notice that the label  $k$  is a running index to differentiate SAF with a common value of  $l$ ,  $\Gamma$ , and  $\mu$ , but this only happens when the *irrep*  $\Gamma$  appears more than once included on the *direct sum* of the reducible representation  $\Omega^{(\Delta)}$ . The SC only depend on the point group of the ionic center and on the angular momentum of the SAF. Moreover, they can be efficiently determined using the *character tables* for the point groups. The SAF can be selected as an orthonormal set of vectors:

$$\langle \sigma_l^{\Gamma\mu,k} | \sigma_{l'}^{\Gamma'\mu',k'} \rangle = \delta_{\Gamma\Gamma'} \delta_{\mu\mu'} \delta_{ll'} \delta_{kk'}, \quad (79)$$

where  $(\delta_{\Gamma\Gamma'}, \delta_{\mu\mu'})$  are a result of enforcing the *great orthogonality theorem*,  $\delta_{ll'}$  is a result of the orthonormality presented by the real spherical harmonics, and  $\delta_{kk'}$  is an arbitrary election.

The *Symmetry Basis Functions* (SBF) can be obtained through

$$\lambda_{pl}^{\Gamma\mu,k}(\vec{r}) = \chi_{pl}(r)\sigma_l^{\Gamma\mu,k}(\hat{r}). \quad (80)$$

Using Eq. 78 in Eq. 80 we have

$$\lambda_{pl}^{\Gamma\mu,k}(\vec{r}) = \sum_{m=-l}^l u_{lm}^{\Gamma\mu,k} \varphi_{plm}(\vec{r}). \quad (81)$$

Therefore, the SBF are linear combination of the primitive basis functions and their coefficients match up with the SC.

The spatial orbitals of the ion,  $\phi$ , are expressed in terms of the  $\lambda_{pl}^{\Gamma\mu,k}(\vec{r})$ , as

$$\phi_i^{\Gamma\mu}(\vec{r}) = \sum_{plk} c_{iplk}^{\Gamma} \lambda_{pl}^{\Gamma\mu,k}(\vec{r}), \quad (82)$$

where, as usually, the orbital coefficients  $c_{iplk}^{\Gamma}$  are  $\mu$ -independent and  $i$  is an ordinal number within the complete set of  $\phi_i$  functions corresponding to the  $\Gamma$  *irrep*.

In general,  $\phi_i^{\Gamma\mu}(\vec{r})$  can not be factorized in an angular and a radial part. If we substitute Eq. 80 in Eq. 82, we obtain

$$\phi_i^{\Gamma\mu}(\vec{r}) = \sum_{plk} c_{iplk}^{\Gamma} \chi_{pl}(r) \sigma_l^{\Gamma\mu,k}(\hat{r}) = \sum_{lk} R_{ilk}^{\Gamma}(r) \sigma_l^{\Gamma\mu,k}(\hat{r}), \quad (83)$$

where the radial functions  $R_{ilk}^{\Gamma}(r)$  are

$$R_{ilk}^{\Gamma}(r) = \sum_p c_{iplk}^{\Gamma} \chi_{pl}(r). \quad (84)$$

Therefore, the angular part cannot be separated as a common factor in Eq. 83 because SAF with different  $l$  and  $k$  values can, in principle, contribute to  $\phi_i^{\Gamma\mu}(\vec{r})$ . This separation is only possible when the point symmetry group is  $O_3^+$  (spherical symmetry).

To simplify the notation in the following sections, the  $p$ ,  $l$  and  $k$  indices will be collected in a single index  $p$  that runs over all the functions corresponding to a given value of  $\mu$  and  $\Gamma$ . In this way,  $\phi_i^{\Gamma\mu}$  can be written as

$$\phi_i^{\Gamma\mu}(\vec{r}) = \sum_p c_{ip}^{\Gamma} \lambda_p^{\Gamma\mu}(\vec{r}) = \sum_p c_{ip}^{\Gamma} \sum_m u_{l_p m}^{\Gamma\mu, k_p} \varphi_{pl_p m}(\vec{r}), \quad (85)$$

where  $l_p$  is the  $l$  value of the  $p^{th}$  SBF and  $k_p$  is the index of the function within the set of SAF with angular momentum  $l$  that transform according to  $\Gamma$  and  $\mu$ .

## VII. ELECTROSTATIC INTERACTION ENERGY

In this Section, we will derive analytical expressions for the *Electrostatic Interaction Energy* (EIE),  $V^{RS}$ , between two ions  $R$  (point group  $\mathcal{G}$ ) and  $S$  (point group  $\mathcal{G}'$ ) in terms of basic integrals between SBF centered at both ions. Let  $\vec{r}^R$  and  $\vec{r}^S$  the vector positions of the  $R$  and  $S$  nuclei, respectively.  $V^{RS}$  is given by

$$V^{RS} = -Z^R \hat{V}_{\text{loc}}^S(\vec{r}^R) + 2 \sum_{\Gamma\mu} \sum_i \sum_{p,q=1}^{N^{R,\Gamma}} c_{ip}^{R,\Gamma} c_{iq}^{R,\Gamma} \langle \lambda_p^{R,\Gamma\mu} | \hat{V}_{\text{loc}}^S | \lambda_q^{R,\Gamma\mu} \rangle, \quad (86)$$

where the index  $i$  runs on occupied orbitals of the closed-shell ion  $R$  belonging to the  $\Gamma$  irrep,  $N^{R,\Gamma}$  is the number of the SBF in the  $\Gamma$  irrep, and the (classical) local potential created by the ion  $S$

$$\hat{V}_{\text{loc}}^S = \hat{U}^S + \hat{J}^S \quad (87)$$

is formed by the nuclear potential  $\hat{U}^S$  and the Coulomb operator  $\hat{J}^S$ . The first term in Eq. 86 is the interaction energy between  $R$  nucleus and the  $S$  nucleus+electrons, while the second term is the interaction energy between  $R$  electrons and the  $S$  nucleus+electrons.

### A. Nuclear attraction interaction

The nuclear potential created by the ion  $S$  at  $\vec{r}_1$  is

$$\hat{U}^S(\vec{r}_1) = -\frac{Z^S}{|\vec{r}_1 - \vec{r}^S|}. \quad (88)$$

Let us define the average integrals  $(V_{\text{nuc}}^{RS})_{\Gamma pq}$  as

$$(V_{\text{nuc}}^{RS})_{\Gamma pq} = \frac{1}{n_\Gamma} \sum_\mu \langle \lambda_p^{R,\Gamma\mu} | \hat{U}^S(\vec{r}_1) | \lambda_q^{R,\Gamma\mu} \rangle, \quad (89)$$

where  $\Gamma pq$  is a complex index, called *density charge*, which runs over all *irreps* and, for each of them, over all possible pairs of SBF. Thus, the average integrals  $(V_{\text{nuc}}^{RS})_{\Gamma pq}$  are one-dimensional arrays or *supervectors* where the matrix elements have to be stored in a similar manner to as described in Ref. [33]. Hereafter we assume that the matrices only depending on density charge are always supervectors. Using Eq. 88 and developing the SBF in terms of the primitive basis functions (Eq. 81)  $(V_{\text{nuc}}^{RS})_{\Gamma pq}$  transforms to

$$(V_{\text{nuc}}^{RS})_{\Gamma pq} = \sum_{m_p m_q} U_{m_p m_q}^{R,\Gamma pq} Z_{pm_p, qm_q}^{RS}, \quad (90)$$

where the basic nuclear attraction integrals  $Z_{pm_p, qm_q}^{RS}$  are defined in Eqs. 40 and 41 and

$$U_{m_p m_q}^{\Gamma pq} = U_{m_q m_p}^{\Gamma qp} = \frac{1}{n_\Gamma} \sum_{\mu} u_{l_p m_p}^{\Gamma \mu, k_p} u_{l_q m_q}^{\Gamma \mu, k_q} \quad (91)$$

are average symmetry coefficients.

Substituting the analytical expression for the nuclear attraction integrals in Eq. 90,  $(V_{\text{nuc}}^{RS})_{\Gamma pq}$  can be written as

$$(V_{\text{nuc}}^{RS})_{\Gamma pq} = (V_{\text{nuc,lr}}^{RS})_{\Gamma pq} + (V_{\text{nuc,sr}}^{RS})_{\Gamma pq}, \quad (92)$$

where

$$\begin{aligned} (V_{\text{nuc,lr}}^{RS})_{\Gamma pq} &= -Z^S N_{pq}^R \sum_{l=|l_p-l_q|}^{l_p+l_q} \frac{(n_{pq}^R + l)!}{(\zeta_{pq}^R)^{n_{pq}^R+l+1}} R^{-l-1} \\ &\quad \times \frac{4\pi}{2l+1} \left\{ \sum_{m_p m_q} U_{m_p m_q}^{R, \Gamma pq} T_{l_p m_p l_q m_q}^l(\hat{R}) \right\}, \\ (V_{\text{nuc,sr}}^{RS})_{\Gamma pq} &= -Z^S N_{pq}^R R^{n_{pq}^R} \sum_{l=|l_p-l_q|}^{l_p+l_q} \left[ \mu_{n_{pq}^R-l-1}(\zeta_{pq}^R R) - \mu_{n_{pq}^R+l}(\zeta_{pq}^R R) \right] \\ &\quad \times \frac{4\pi}{2l+1} \left\{ \sum_{m_p m_q} U_{m_p m_q}^{R, \Gamma pq} T_{l_p m_p l_q m_q}^l(\hat{R}) \right\}. \end{aligned} \quad (93)$$

Notice that  $\vec{R} = \vec{r}^S - \vec{r}^R$  ( $R$  is the modulus and  $\hat{R}$  the direction  $(\Theta, \Phi)$  of a vector  $\vec{R}$ ),  $N_{pq}^R = N_{qp}^R = N_{pl_p}^R N_{ql_q}^R$ ,  $n_{pq}^R = n_{qp}^R = n_{pl_p}^R + n_{ql_q}^R$ , and  $\zeta_{pq}^R = \zeta_{qp}^R = \zeta_{pl_p}^R + \zeta_{ql_q}^R$ . The real numbers  $(N_{pl_p}^R, N_{ql_q}^R)$  are the normalization constants for the radial functions  $(\chi_{pl_p}^R, \chi_{ql_q}^R)$  (see Eq. 2). In turn, the natural numbers  $(n_{pl_p}^R, n_{ql_q}^R)$  and the real numbers  $(\zeta_{pl_p}^R, \zeta_{ql_q}^R)$  are the principal quantum numbers and the orbital exponentials, respectively, for the radial functions  $(\chi_{pl_p}^R, \chi_{ql_q}^R)$ . Additionally, the angular coefficients  $T_{l_p m_p l_q m_q}^l$  and the  $\mu_n$  functions are also defined in Eqs. 6 and 64. The  $(V_{\text{nuc,lr}}^{RS})_{\Gamma pq}$  term, with a dependence  $R^{-l-1}$ , is the long-range one and decreases very slowly with  $R$ . However, the  $(V_{\text{nuc,sr}}^{RS})_{\Gamma pq}$  term is of a short-range character due to the  $\mu_n$  function.

## B. Coulomb interaction between electrons

The Coulomb operator can be expressed in terms of the electronic charge distribution of closed-shell ion  $S$ ,  $\rho^S(\vec{r}_2)$ , as:

$$\hat{J}^S(\vec{r}_1) = \int \frac{\rho^S(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 = 2 \sum_{\Gamma' \mu'} \sum_i \langle \phi_i^{S, \Gamma' \mu'} | r_{12}^{-1} | \phi_i^{S, \Gamma' \mu'} \rangle, \quad (94)$$

where the  $S$  superscript has been used to indicate the center to which the functions correspond. Expressing the orbitals in terms of the SBF (Eq. 85) we have

$$\begin{aligned}\hat{J}^S(\vec{r}_1) &= 2 \sum_{\Gamma'\mu'} \sum_i \sum_{a=1}^{N^{S,\Gamma'}} \sum_{b=1}^{N^{S,\Gamma'}} c_{ia}^{S,\Gamma'} c_{ib}^{S,\Gamma'} \langle \lambda_a^{S,\Gamma'\mu'} | r_{12}^{-1} | \lambda_b^{S,\Gamma'\mu'} \rangle \\ &= \sum_{\Gamma'ab} \rho_{\Gamma'ab}^S \frac{1}{n_{\Gamma'}} \sum_{\mu'} \langle \lambda_a^{S,\Gamma'\mu'} | r_{12}^{-1} | \lambda_b^{S,\Gamma'\mu'} \rangle,\end{aligned}\quad (95)$$

where  $\rho_{\Gamma'ab}^S$  is the density matrix

$$\rho_{\Gamma pq}^S = (2 - \delta_{pq}) \sum_{i \in \Gamma} M_i^{S,\Gamma} c_{ip}^{S,\Gamma} c_{iq}^{S,\Gamma}, \quad (96)$$

and  $M_i^{S,\Gamma}$  is the number of electrons of  $S$  ion which fill the  $i^{\text{th}}$  orbital of the  $\Gamma$  *irrep*. Note that  $M_i^{S,\Gamma} = 2n_\Gamma$  in closed-shell ions. Let us define the average integrals  $(V_{\text{el}}^{RS})_{\Gamma pq}$  as

$$(V_{\text{el}}^{RS})_{\Gamma pq} = \frac{1}{n_\Gamma} \sum_{\mu} \langle \lambda_p^{R,\Gamma\mu} | \hat{J}^S(\vec{r}_1) | \lambda_q^{R,\Gamma\mu} \rangle. \quad (97)$$

Using Eq. 95 in Eq. 97  $(V_{\text{el}}^{RS})_{\Gamma pq}$  becomes

$$(V_{\text{el}}^{RS})_{\Gamma pq} = \sum_{\Gamma'ab} \rho_{\Gamma'ab}^S W_{\Gamma pq, \Gamma'ab}^{RS}, \quad (98)$$

where  $W_{\Gamma pq, \Gamma'ab}^{RS}$  are the average Coulomb operator integrals

$$W_{\Gamma pq, \Gamma'ab}^{RS} = \frac{1}{n_\Gamma n_{\Gamma'}} \sum_{\mu} \sum_{\mu'} \langle \lambda_p^{R,\Gamma\mu} \lambda_a^{S,\Gamma'\mu'} | r_{12}^{-1} | \lambda_q^{R,\Gamma\mu} \lambda_b^{S,\Gamma'\mu'} \rangle. \quad (99)$$

Notice that the average Coulomb operator integrals are (two-dimensional arrays or) *supermatrices* whose elements are storing and ordering in the same way described in Ref. [33]. Hereafter we assume that the matrices whose elements are labelled by means of two charge densities are, therefore, supermatrices. Developed in terms of the basis functions of the SBF, the average Coulomb operator integrals are given by

$$\begin{aligned}W_{\Gamma pq, \Gamma'ab}^{RS} &= \frac{1}{n_\Gamma n_{\Gamma'}} \sum_{\mu} \sum_{\mu'} \sum_{m_p m_q m_a m_b} u_{l_p m_p}^{R,\Gamma\mu, k_p} u_{l_q m_q}^{R,\Gamma\mu, k_q} u_{l_a m_a}^{S,\Gamma'\mu', k_a} u_{l_b m_b}^{S,\Gamma'\mu', k_b} \\ &\times \langle \varphi_{pl_p m_p}^R \varphi_{al_a m_a}^S | r_{12}^{-1} | \varphi_{ql_q m_q}^R \varphi_{bl_b m_b}^S \rangle \\ &= \sum_{m_p m_q m_a m_b} U_{m_p m_q}^{R,\Gamma pq} U_{m_a m_b}^{S,\Gamma' ab} C_{pm_p am_a, qm_q bm_b}^{RS},\end{aligned}\quad (100)$$

where the basic bicentric Coulomb integrals  $C_{pm_p am_a, qm_q bm_b}^{RS}$  were defined in Eqs. 21 and 32.

One can reach a compact analytical expression for the  $W$  integral. However, it is necessary to introduce some alternative definitions related to the  $\chi$  and  $\mathcal{A}$  basic integrals previously defined. Thus, we define the basic integrals

$$\omega^X(n_1, n_2, \zeta_1, \zeta_2; R) = \frac{\chi^X(n_1, n_2, \zeta_1, \zeta_2; R)}{R^{n_1+n_2+2}}, \quad (101)$$

where  $X = \text{I,II,IV}$ . On other hand, only the  $\chi^{\text{III}}$  integral has long-range contribution, such as is previously discussed. Let us define

$$\begin{aligned} \omega_{\text{sr}}^{\text{III}}(n_1, n_2, \zeta_1, \zeta_2; R) = & - \left[ \omega^{\text{I}}(n_1, n_2, \zeta_1, \zeta_2; R) + \omega^{\text{II}}(n_1, n_2, \zeta_1, \zeta_2; R) \right. \\ & \left. + \omega^{\text{IV}}(n_1, n_2, \zeta_1, \zeta_2; R) \right], \quad \zeta_1 \neq \zeta_2 \end{aligned} \quad (102)$$

$$\omega_{\text{sr}}^{\text{III}}(n_1, n_2, \zeta, \zeta; R) = -\frac{n_1!n_2!\mu_{n_1+n_2+1}(\zeta R)}{(n_1+n_2+1)!}, \quad (103)$$

$$\omega_{\text{lr}}^{\text{III}}(n_1, n_2, \zeta_1, \zeta_2) = F(n_1, n_2, \zeta_1, \zeta_2) = \frac{n_1!n_2!}{\zeta_1^{n_1+1}\zeta_2^{n_2+1}}, \quad (104)$$

where  $\omega_{\text{sr}}^{\text{III}}$  and  $\omega_{\text{lr}}^{\text{III}}$  are short-range and long-range contributions, respectively. Finally, we define the one-center radial integral

$$\mathcal{A}(l_3; n_1, l_1, \zeta_1; n_2, l_2, \zeta_2; R) = \frac{\mathcal{A}^{(1)}(l_3; n_1, l_1, \zeta_1; n_2, l_2, \zeta_2; R)}{R^{n_1+n_2-l_1-l_2+2}}. \quad (105)$$

If one uses the above definitions, the  $W$  integral can be divided into both a short-range and a long-range contribution,

$$W_{\Gamma pq, \Gamma' ab}^{RS} = W_{\Gamma pq, \Gamma' ab}^{RS, \text{sr}} + W_{\Gamma pq, \Gamma' ab}^{RS, \text{lr}}, \quad (106)$$

such that

$$\begin{aligned} W_{\Gamma pq, \Gamma' ab}^{RS, \text{sr}} = & (-1)^{l_p+l_q} 8\pi^2 N_{pq}^R N_{ab}^S R^{n_{pq}^R+n_{ab}^S+1} \sum_{l_1=|l_p-l_q|}^{l_p+l_q} \sum_{l_2=|l_a-l_b|}^{l_a+l_b} \\ & \times \left\{ \left[ - \sum_{l_3=|l_1-l_2|}^{l_1+l_2} A^{l_1 l_2 l_3}(\Gamma pq, \Gamma' ab; \hat{R}) \mathcal{A}(l_3; n_{pq}^R - 1, l_1, \zeta_{pq}^R; n_{ab}^S - 1, l_2, \zeta_{ab}^S; R) \right] \right. \\ & + A^{l_1 l_2 (l_1+l_2)}(\Gamma pq, \Gamma' ab; \hat{R}) \mathcal{B}(n_{pq}^R, l_1, \zeta_{pq}^R; n_{ab}^S, l_2, \zeta_{ab}^S; R) \\ & \left. + A^{l_1 l_2 |l_1-l_2|}(\Gamma pq, \Gamma' ab; \hat{R}) \mathcal{C}(n_{pq}^R, l_1, \zeta_{pq}^R; n_{ab}^S, l_2, \zeta_{ab}^S; R) \right\}, \end{aligned} \quad (107)$$

and

$$\begin{aligned} W_{\Gamma pq, \Gamma' ab}^{RS, \text{lr}} = & (-1)^{l_p+l_q} 16\pi^2 N_{pq}^R N_{ab}^S \sum_{l_1=|l_p-l_q|}^{l_p+l_q} \sum_{l_2=|l_a-l_b|}^{l_a+l_b} R^{-(l_1+l_2+1)} \\ & \times A^{l_1 l_2 (l_1+l_2)}(\Gamma pq, \Gamma' ab; \hat{R}) \mathcal{D}(n_{pq}^R, l_1, \zeta_{pq}^R; n_{ab}^S, l_2, \zeta_{ab}^S). \end{aligned} \quad (108)$$

In Eqs. 107 and 108 we have introduced the radial integrals

$$\begin{aligned}
\mathcal{C}(n_1, l_1, \zeta_1; n_2, l_2, \zeta_2; R) &= \delta_{l_1-l_2, |l_1-l_2|} \Delta_{l_2|l_1-l_2|} \left( 2\omega^{\text{I}}(n_1 - l_1 - 1, n_2 + l_2, \zeta_1, \zeta_2; R) \right. \\
&\quad + \omega^{\text{IV}}(n_1 - l_1 - 1, n_2 + l_2, \zeta_1, \zeta_2; R) \\
&\quad + \delta_{l_2-l_1, |l_1-l_2|} \Delta_{l_1|l_1-l_2|} \left( 2\omega^{\text{II}}(n_1 + l_1, n_2 - l_2 - 1, \zeta_1, \zeta_2; R) \right. \\
&\quad \left. \left. + \omega^{\text{IV}}(n_1 + l_1, n_2 - l_2 - 1, \zeta_1, \zeta_2; R) \right) \right), \tag{109}
\end{aligned}$$

$$\begin{aligned}
\mathcal{B}(n_1, l_1, \zeta_1; n_2, l_2, \zeta_2; R) &= \Delta_{l_1 l_2} \left( 2\omega_{\text{sr}}^{\text{III}}(n_1 + l_1, n_2 + l_2, \zeta_1, \zeta_2; R) \right. \\
&\quad \left. + \omega^{\text{IV}}(n_1 + l_1, n_2 + l_2, \zeta_1, \zeta_2; R) \right), \tag{110}
\end{aligned}$$

the angular coefficient

$$A^{l_1 l_2 l_3}(\Gamma pq, \Gamma' ab; \hat{R}) = \sum_{m_p m_q m_a m_b} U_{m_p m_q}^{R, \Gamma pq} U_{m_a m_b}^{S, \Gamma' ab} \left\{ \sum_{m_1 m_2} d_{l_p m_p l_q m_q}^{l_1 m_1} d_{l_a m_a l_b m_b}^{l_2 m_2} T_{l_1 m_1 l_2 m_2}^{l_3}(\hat{R}) \right\}, \tag{111}$$

and

$$\mathcal{D}(n_1, l_1, \zeta_1; n_2, l_2, \zeta_2) = \Delta_{l_1 l_2} \omega_{\text{lr}}^{\text{III}}(n_1 + l_1, n_2 + l_2, \zeta_1, \zeta_2). \tag{112}$$

Notice that the  $\Delta$  coefficients are defined in Eq. 31.

Substituting Eq. 106 in Eq. 98,  $(V_{\text{el}}^{RS})_{\Gamma pq}$  can be written as

$$(\mathbf{V}_{\text{el}}^{RS})_{\Gamma pq} = (\mathbf{V}_{\text{el, sr}}^{RS})_{\Gamma pq} + (\mathbf{V}_{\text{el, lr}}^{RS})_{\Gamma pq}, \tag{113}$$

where

$$(\mathbf{V}_{\text{el, sr}}^{RS})_{\Gamma pq} = \sum_{\Gamma' ab} W_{\Gamma pq, \Gamma' ab}^{RS, \text{sr}} \rho_{\Gamma' ab}^S, \tag{114}$$

$$(\mathbf{V}_{\text{el, lr}}^{RS})_{\Gamma pq} = \sum_{\Gamma' ab} W_{\Gamma pq, \Gamma' ab}^{RS, \text{lr}} \rho_{\Gamma' ab}^S. \tag{115}$$

The  $(V_{\text{el, lr}}^{RS})_{\Gamma pq}$  term, with a dependence  $R^{-l_1-l_2-1}$ , is the long-range one and decreases very slowly with  $R$ . However, the  $(V_{\text{el, sr}}^{RS})_{\Gamma pq}$  term is of a short-range character due to the presence of the  $\mu_n$  function in their expressions.  $(V_{\text{el, lr}}^{RS})_{\Gamma pq}$  will be combined in the Subsection VII D with the corresponding long-range term of the nuclear matrix element yielding an unique multipolar interaction term.

### C. Local potential

The local potential  $\hat{V}_{\text{loc}}^S(\vec{r}^R)$ , defined by Eq. 87, is the potential created by ion  $S$  on the nucleus of ion  $R$ . Remembering that the Coulomb potential,  $\hat{J}^S(\vec{r}^R)$ , is given by (see Eq. 95)

$$J^S(\vec{r}^R) = \sum_{\Gamma' ab} \rho_{\Gamma' ab}^S \frac{1}{n_{\Gamma'}} \sum_{\mu'} \langle \lambda_a^{S, \Gamma' \mu'} | (|\vec{r}^R - \vec{r}'|^{-1}) | \lambda_b^{S, \Gamma' \mu'} \rangle, \tag{116}$$

and comparing this equation with the nuclear attraction interaction (Eq. 89), it is clear that  $\hat{J}^S(\vec{r}^R)$  can be also put in the form

$$J^S(\vec{r}^R) = -\frac{1}{Z^R} \sum_{\Gamma'ab} \rho_{\Gamma'ab}^S (V_{\text{nuc}}^{SR})_{\Gamma'ab}. \quad (117)$$

Adding the nuclear potential created by ion  $S$ , we have

$$V_{\text{loc}}^S(\vec{r}^R) = U^S(\vec{r}^R) + J^S(\vec{r}^R) = -\frac{Z^S}{|\vec{r}^S - \vec{r}^R|} - \frac{1}{Z^R} \sum_{\Gamma'ab} \rho_{\Gamma'ab}^S (V_{\text{nuc}}^{SR})_{\Gamma'ab}, \quad (118)$$

that can be put in the form

$$V_{\text{loc}}^S(\vec{r}^R) = V_{\text{loc,lr}}^S(\vec{r}^R) + V_{\text{loc,sr}}^S(\vec{r}^R), \quad (119)$$

where  $V_{\text{loc,sr}}^S(\vec{r}^R)$  is the short range term, given by

$$\begin{aligned} V_{\text{loc,sr}}^S(\vec{r}^R) &= -\frac{1}{Z^R} \sum_{\Gamma'ab} \rho_{\Gamma'ab}^S (V_{\text{nuc,sr}}^{SR})_{\Gamma'ab} \\ &= \sum_{\Gamma'ab} \rho_{\Gamma'ab}^S N_{ab}^S R^{n_{ab}^S} \sum_{l=|l_a-l_b|}^{l_a+l_b} \left[ \mu_{n_{ab}^S-l-1}(\zeta_{ab}^S R) - \mu_{n_{ab}^S+l}(\zeta_{ab}^S R) \right] \\ &\quad \times \frac{4\pi(-1)^l}{2l+1} \left\{ \sum_{m_a m_b} U_{m_a m_b}^{S,\Gamma'ab} T_{l_a m_a l_b m_b}^l(\hat{R}) \right\}. \end{aligned} \quad (120)$$

The coefficient  $(-1)^l$  appears because the vector involved in the integrals  $V_{\text{nuc}}^{SR}$  is  $\vec{r}^S - \vec{r}^R = -(\vec{r}^R - \vec{r}^S) = -\vec{R}$  so that  $T_{l_a m_a l_b m_b}^l(-\hat{R}) = (-1)^l T_{l_a m_a l_b m_b}^l(\hat{R})$ .  $V_{\text{loc,sr}}^S(\vec{r}^R)$  only contains interactions between the electrons of ion  $S$  and the nucleus of ion  $R$ . On the other hand, the long-range term,  $V_{\text{loc,lr}}^S(\vec{r}^R)$ , containing the rest of the interactions between the electrons of ion  $S$  and the nucleus of ion  $R$  and the internuclear repulsion, is given by

$$\begin{aligned} V_{\text{loc,lr}}^S(\vec{r}^R) &= -\frac{Z^S}{R} + \sum_{\Gamma'ab} \rho_{\Gamma'ab}^S N_{ab}^S \sum_{l=|l_a-l_b|}^{l_a+l_b} \frac{(n_{ab}^S + l)!}{\zeta_{ab}^{n_{ab}^S+l+1}} R^{-l-1} \\ &\quad \times \frac{4\pi(-1)^l}{2l+1} \left\{ \sum_{m_a m_b} U_{m_a m_b}^{S,\Gamma'ab} T_{l_a m_a l_b m_b}^l(\hat{R}) \right\}. \end{aligned} \quad (121)$$

#### D. Multipolar interactions

The EIE between two charge distributions  $\rho^R(\vec{r})$  and  $\rho^S(\vec{r})$  is given by:

$$E_e^{RS} = \int \frac{\rho^R(\vec{r}_1) \rho^S(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2. \quad (122)$$

Defining the *spherical multipolar moment*,  $Q_{lm}$ , as

$$Q_{lm} = \sqrt{\frac{4\pi}{2l+1}} \int \rho(\vec{r}) r^l S_{lm}(\hat{r}) d\vec{r}, \quad (123)$$

and assuming that  $\rho^R(\vec{r})$  and  $\rho^S(\vec{r})$  are non-overlapping,  $E_e^{RS}$  can be expressed in the form

$$E_e^{RS} = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} \frac{Q_{l_1 m_1}^R C_{l_1 m_1, l_2 m_2}(\hat{R}) Q_{l_2 m_2}^S}{R^{l_1+l_2+1}}, \quad (124)$$

where the coefficient  $C_{l_1 m_1, l_2 m_2}$ , given by

$$C_{l_1 m_1, l_2 m_2}(\hat{R}) = \frac{4\pi(-1)^{l_2}}{\sqrt{(2l_1+1)(2l_2+1)}} \frac{l_1! l_2! (2l_1+2l_2)!}{(l_1+l_2)! (2l_1)! (2l_2)!} T_{l_1 m_1 l_2 m_2}^{(l_1+l_2)}(\hat{R}), \quad (125)$$

only depends on the relative angular coordinates  $\hat{R}$  of the  $R$  and  $S$  centers. Eq. 124 is known as the *multipolar expansion* of the electrostatic interaction, and is one of the most widely used approximation in the treatment of intermolecular interactions. It involves the charge distributions  $\rho^R(\vec{r})$  and  $\rho^S(\vec{r})$  as basic magnitudes. These ionic electron densities are determined, however, by the potential acting on the electrons. The problem leads to the well known self-consistent Hartree-Fock method, yielding electron densities that are consistent with the interactions they generate. In our scheme, the final result of the SCF HFR method are the  $c_{ip}^{\Gamma}$  coefficients (see Eq. 85) or, in other words, the density matrix elements  $\rho_{\Gamma pq}$  (Eq. 96). In terms of  $\rho_{\Gamma pq}$ , the expression of  $Q_{lm}$  can be derived as follows. First,  $\rho^R(\vec{r})$  of the  $R$  closed-shell ion can be written as

$$\rho^R(\vec{r}) = 2 \sum_{\Gamma\mu} \sum_i |\phi_i^{\Gamma\mu}(\vec{r})|^2 = 2 \sum_{\Gamma\mu} \sum_i \sum_{pq} c_{ip}^{\Gamma} c_{iq}^{\Gamma} \lambda_p^{R, \Gamma\mu}(\vec{r}) \lambda_q^{R, \Gamma\mu}(\vec{r}), \quad (126)$$

where Eq. 85 is used. Taking into account Eqs. 1, 81, 91, and 96, the above equation results

$$\rho^R(\vec{r}) = \sum_{\Gamma pq} \rho_{\Gamma pq}^R \chi_p(r) \chi_q(r) \sum_{m_p m_q} U_{m_p m_q}^{R, \Gamma pq} S_{l_p m_p}(\hat{r}) S_{l_q m_q}(\hat{r}). \quad (127)$$

Introducing this electron density in the expression of  $Q_{lm}$  (Eq. 123), it is obvious that

$$\begin{aligned} Q_{lm}^R &= \sqrt{\frac{4\pi}{2l+1}} \sum_{\Gamma pq} \rho_{\Gamma pq}^R \langle \chi_p | r^{l+2} | \chi_q \rangle \\ &\times \sum_{m_p m_q} U_{m_p m_q}^{R, \Gamma pq} \langle S_{l_p m_p} | S_{lm} | S_{l_q m_q} \rangle. \end{aligned} \quad (128)$$

Solving the radial integrals and remembering the definition of the Gaunt coefficients between real spherical harmonics,  $d_{l_p m_p l_q m_q}^{lm}$  (see Eq. 5),

$$Q_{lm}^R = \sum_{\Gamma pq} \rho_{\Gamma pq}^R (Q_{lm}^R)_{\Gamma pq}, \quad (129)$$

where we have defined  $(Q_{lm}^R)_{\Gamma pq}$  as

$$(Q_{lm}^R)_{\Gamma pq} = \sqrt{\frac{4\pi}{2l+1}} N_{pq}^R \frac{(n_{pq}^R + l)!}{(c_{pq}^R)^{n_{pq}^R + l + 1}} \sum_{m_p m_q} U_{m_p m_q}^{R, \Gamma pq} d_{l_p m_p l_q m_q}^{lm}. \quad (130)$$

It is important to notice that, due to the selection rules of the Gaunt coefficient, the density charge  $\Gamma pq$  only has contributions to the multipole moments with  $|l_p - l_q| \leq l \leq l_p + l_q$  and  $l + l_p + l_q = \text{even}$ . Redefining the  $l = 0, m = 0$  multipole moments to include the nuclear charge

$$Q_{lm}^R = -Z^R \delta_{l,0} + \sum_{\Gamma pq} \rho_{\Gamma pq}^R (Q_{lm}^R)_{\Gamma pq}, \quad (131)$$

the *multipolar potential*

$$(V_{mp}^{RS})_{\Gamma pq} = (V_{\text{nuc,lr}}^{RS})_{\Gamma pq} + (V_{\text{el,lr}}^{RS})_{\Gamma pq} \quad (132)$$

can be written as

$$(V_{mp}^{RS})_{\Gamma pq} = \sum_{l_1 m_1} \sum_{l_2 m_2} \frac{(Q_{l_1 m_1}^R)_{\Gamma pq} C_{l_1 m_1, l_2 m_2}(\hat{R}) Q_{l_2 m_2}^S}{R^{l_1 + l_2 + 1}}. \quad (133)$$

On the other hand,  $V_{\text{loc,lr}}^S(\vec{r}^R)$  (Eq. 121) can be put in terms of the  $Q_{l_2 m_2}^S$ 's as

$$\begin{aligned} V_{\text{loc,lr}}^S(\vec{r}^R) &= -\frac{Z^S}{R} + \sum_{l_2 m_2} C_{00, l_2 m_2}(\hat{R}) \frac{\sum_{\Gamma' ab} \rho_{\Gamma' ab}^S (Q_{l_2 m_2}^S)_{\Gamma' ab}}{R^{l_2 + 1}} \\ &= \sum_{l_2 m_2} C_{00, l_2 m_2}(\hat{R}) \frac{Q_{l_2 m_2}^S}{R^{l_2 + 1}}. \end{aligned} \quad (134)$$

The EIE  $V^{RS}$  (see Eq. 86) can then finally written as

$$V^{RS} = E_{\text{mp}}^{RS} + E_{\text{sr}}^{RS} \quad (135)$$

where  $E_{\text{mp}}^{RS}$  is the multipolar interaction

$$E_{\text{mp}}^{RS} = \sum_{\Gamma pq} \rho_{\Gamma pq}^R (V_{\text{mp}}^{RS})_{\Gamma pq} - Z^R V_{\text{loc,lr}}^S(\vec{r}^R) \quad (136)$$

or

$$E_{\text{mp}}^{RS} = \sum_{l_1 m_1} \sum_{l_2 m_2} \frac{Q_{l_1 m_1}^R C_{l_1 m_1, l_2 m_2}(\hat{R}) Q_{l_2 m_2}^S}{R^{l_1 + l_2 + 1}}, \quad (137)$$

and  $E_{\text{sr}}^{RS}$  is the short range interaction energy due to the overlapping of the electron densities

$$E_{\text{sr}}^{RS} = \sum_{\Gamma pq} \rho_{\Gamma pq}^R \left[ (V_{\text{nuc, sr}}^{RS})_{\Gamma pq} + (V_{\text{el, sr}}^{RS})_{\Gamma pq} \right] - Z^R V_{\text{loc, sr}}^S(\vec{r}^R). \quad (138)$$

TABLE I: Test positions  $\vec{r}_1^S$ ,  $\vec{r}_2^S$  and  $\vec{r}_3^S$  of center  $S$  in the Cartesian  $(x, y, z)$  and polar  $(r, \theta, \phi)$  systems. Atomic units are used for distances, radians for angles.

Vector	$(x, y, z)$	$(r, \theta, \phi)$
$\vec{r}_1^S$	(0.05477,-0.07071,-0.04472)	(0.10000,2.03443,-0.91175)
$\vec{r}_2^S$	(-2.23607,1.00000,-1.73205)	(3.00000,2.18628,-0.42053)
$\vec{r}_3^S$	(4.12311,5.65685,7.14143)	(10.00000,0.77540,0.94096)

As the direct sum of the multipolar interactions extended to the infinite set of ionic pairs in a crystal is only conditionally convergent, special methods, such as the Ewald technique [30], must be used on its computation. In turn, the short range interaction energies can be easily computed as a direct sum extended to all the pairs of ions in the crystal up to a predetermined convergence criterion.

### VIII. NUMERICAL TESTS

We have generated simple Fortran codes that calculate the two-center integrals considered in this paper by means of the algorithms described in previous Sections. Double precision (8 bytes, approximately 15 significant figures) has been used as our main choice for real variables; however, a quadruple precision (16 bytes, about 34 significant figures) version has been prepared, to test truncation error issues.

For our test integrals, we have selected the STOs  $1s \equiv \chi_{1s}S_{00}$ ,  $2p_z \equiv \chi_{2p}S_{10}$ ,  $4d_{z^2} \equiv \chi_{4d}S_{20}$  and  $3d_{xy} \equiv \chi_{3d}S_{2-2}$  with orbital exponents 56.114521, 0.408310, 10.940400 and 5.538740, respectively. In comparing our approach with other methods, our formulas are not restricted to orbitals whose centers are aligned along the  $z$ -axis (Mulliken orientation). Therefore, there is no need for subsequent multiplications with rotation matrices even for general orientations. Hence, we have selected different orientations of the orbital centers with the center  $R$  fixed in the origin, while the position of the center  $S$  varies as indicated in Table I.

One of the worries often found in developing algorithms to compute ETOMI is the analysis of the results. The common practice is to compare the results provided by the trial algorithm with the values found in the literature for some particular integrals. However, when multi-

TABLE II: Coulomb integrals obtained using the algorithms described in Section III for the different STOs and center  $S$  positions.

Integral	$\vec{r}_1^S$	$\vec{r}_2^S$	$\vec{r}_3^S$
$C_{1s1s,1s1s}^{RS}$	9.9919736083225	0.3333332176408	0.0999999948025
$C_{1s1s,2p_z2p_z}^{RS}$	0.2041368026457	0.1909127293863	0.1026745438956
$C_{1s1s,4d_{z^2}4d_{z^2}}^{RS}$	2.7129383373309	0.3333095179182	0.1000141685427
$C_{2p_z2p_z,2p_z2p_z}^{RS}$	0.1597987934947	0.1472557745713	0.0953473807448
$C_{2p_z2p_z,4d_{z^2}4d_{z^2}}^{RS}$	0.2045681364834	0.1905762508091	0.1026485981662
$C_{4d_{z^2}4d_{z^2},4d_{z^2}4d_{z^2}}^{RS}$	2.3071008129045	0.3332606626520	0.1000282727447
$C_{1s1s,1s4d_{z^2}}^{RS}$	-0.0023871573922	-0.0000000000007	0.0000000065601
$C_{1s2p_z,4d_{z^2}3d_{xy}}^{RS}$	-0.0000002687124	-0.0000000024077	-0.0000000000226

center integrals are considered, the number of available comparison values is rather small and, in many cases, the accuracy of these values is not sufficient for an adequate evaluation of the trial algorithm performance. Therefore, it seems desirable for testing purposes to have a procedure that enables the computation of any arbitrary integral with sufficient accuracy. The **STNGINT** program by Fernández Rico *et al* [12], that calculates the ETOMI using STOs, provides a quite suitable reference. In this code, each STO is expanded in terms of a very large number of GTOs ( $\simeq 30$ ), and the integrals attain an accuracy of at least ten decimal places with the penalty of a quite expensive fitting procedure. In what follows, we will use the **STNGINT** program to compare the accuracy of the Coulomb integrals obtained by our algorithms. Unfortunately, we have not found alternative algorithms that could allow us to compare the accuracy of overlap and nuclear attraction integrals.

Table II presents the results for the Coulomb integrals obtained by our algorithms. In turn, Table III presents the absolute difference between the Coulomb integrals obtained by our algorithms and by those implemented in the **STNGINT** code. This absolute difference is always less than  $1 \times 10^{-7}$ . It can be seen as the greatest loss of accuracy (and precision) generally occurs for small distance between the STO centers (0.1 bohr). Regarding this, one should note that our two-center integral Fortran codes do not take into account the considerations for the limit  $R \rightarrow 0$  presented in Section V. For such small distances, usually

TABLE III: Absolute difference between the Coulomb integral obtained through the algorithms described in Section III and the algorithms implemented in STNGINT program. Numbers in parentheses correspond to absolute differences between values obtained using quadruple-precision and double-precision real variables, when these values do not match.

Integral	$\vec{r}_1^S$	$\vec{r}_2^S$	$\vec{r}_3^S$
$C_{1s1s,1s1s}^{RS}$	$< 1 \times 10^{-13}$	$< 1 \times 10^{-13}$	$< 1 \times 10^{-13}$
$C_{1s1s,2p_z2p_z}^{RS}$	$1.8 \times 10^{-12}$ ( $2.7 \times 10^{-12}$ )	$2.8 \times 10^{-12}$	$7.4 \times 10^{-12}$
$C_{1s1s,4d_{z^2}4d_{z^2}}^{RS}$	$1.1 \times 10^{-12}$ ( $0.8 \times 10^{-12}$ )	$< 1 \times 10^{-13}$	$< 1 \times 10^{-13}$
$C_{2p_z2p_z,2p_z2p_z}^{RS}$	$1.70194 \times 10^{-8}$ ( $2.0 \times 10^{-12}$ )	$1.9 \times 10^{-12}$	$1.8 \times 10^{-12}$
$C_{2p_z2p_z,4d_{z^2}4d_{z^2}}^{RS}$	$3.36147 \times 10^{-8}$ ( $0.1 \times 10^{-12}$ )	$5.28 \times 10^{-9}$ ( $0.1 \times 10^{-12}$ )	$8.68490 \times 10^{-8}$ ( $2.4 \times 10^{-12}$ )
$C_{4d_{z^2}4d_{z^2},4d_{z^2}4d_{z^2}}^{RS}$	$8.0035 \times 10^{-9}$ ( $0.5 \times 10^{-12}$ )	$< 1 \times 10^{-13}$	$0.1 \times 10^{-12}$
$C_{1s1s,1s4d_{z^2}}^{RS}$	$2.9 \times 10^{-12}$	0	0
$C_{1s2p_z,4d_{z^2}3d_{xy}}^{RS}$	$2.9 \times 10^{-12}$	$0.1 \times 10^{-12}$	0

corresponding to highly unstable configurations, we can assume these errors as harmless. On the other hand, an important advantage of the implemented algorithms, without the  $R \rightarrow 0$  considerations, is their efficiency. In fact, when calculating a high number of integrals and computing their CPU times, the results for our algorithms can be about 1000 times faster than STNGINT ones.

Tables IV and V present the results obtained for the overlap and nuclear attraction integrals calculations. The sign of the overlap integrals depends on the relative signs of the two basis functions and on their relative orientation and separation in space. As already mentioned, we do not have alternative implemented algorithms to compare them with these integrals. Nevertheless, using our algorithms in a test code gives correct results for systems with no symmetry splitting of the spherical averages (for instance NaCl, with no splitting

TABLE IV: Overlap integrals obtained through the algorithms described in Section III for the different STOs and center  $S$  positions. The results obtained with quadruple-precision real variables coincide in all presented figures with these double-precision results, except for the integral marked with †, whose quadruple-precision result is  $-0.0000134013088$ .

Integral	$\vec{r}_1^S$	$\vec{r}_2^S$	$\vec{r}_3^S$
$S_{1s1s}^{RS}$	0.0625470618575	$< 1 \times 10^{-13}$	$< 1 \times 10^{-13}$
$S_{1s2p_z}^{RS}$	0.0000862323629	0.0010314017092	-0.0002440452531
$S_{1s4d_{z^2}}^{RS}$	-0.0068800772878	$< 1 \times 10^{-13}$	$< 1 \times 10^{-13}$
$S_{2p_z2p_z}^{RS}$	0.9997666495955	0.7858718212100	-0.0304085882522
$S_{2p_z4d_{z^2}}^{RS}$	0.0001818443606	0.0005568015453	$-0.0000134013091^\dagger$
$S_{4d_{z^2}4d_{z^2}}^{RS}$	0.9033740735665	-0.0000000302005	$< 1 \times 10^{-13}$

of the  $\text{Na}^+$  and  $\text{Cl}^-$   $p$  orbitals, is computed with results coincident with those from  $aiPI$  up to the convergence criterion of the SCF procedure). The nuclear attraction integrals were calculated using a nuclear charge equal to  $+1$ , so that the integrals depend exclusively on the STOs. The integrals between identical STOs have a simple physical interpretation, since they are the interactions between an electron, described by the orbital, and the nuclear charge. Therefore, this interaction should always be attractive (negative sign). Again, one should see a loss of precision for small distances between the centers, as computed comparing our double- and quadruple-precision implementations. However, there are two fundamental differences with the Coulomb integrals: (a) there are fewer situations where precision is lost when one uses double-precision real variables, and (b) the loss of precision is usually smaller.

## IX. CONCLUSIONS

The Silverstone and Moats's expansion of a function about a displaced center [25] and the bipolar expansion of Kay, Todd, and Silverstone for  $r_{12}^{-1}$  [26] have been used to develop extremely compact and numerically stable formulas for the two-center overlap, nuclear attraction and Coulomb integrals between Slater type orbitals. Since there is no restriction in the angular numbers of the STO's, the derived expressions are valid for atoms with an

TABLE V: Nuclear attraction integrals obtained through the algorithms described in Section III for the different STOs and center  $S$  positions. The results obtained with quadruple-precision real variables coincide in all presented figures with these double-precision results, except for the integrals marked with † and ‡, whose quadruple-precision results are  $-0.2041368174305$  and  $-2.7131314621086$ , respectively.

Integral	$\vec{r}_1^S$	$\vec{r}_2^S$	$\vec{r}_3^S$
$Z_{1s1s}^{RS}$	-9.9993484831756	-0.3333332176408	-0.0999999947803
$Z_{1s2p_z}^{RS}$	0.0000934616199	0.0000001593362	-0.0000000177380
$Z_{1s4d_{z^2}}^{RS}$	0.0027543920296	0.0000000000007	-0.0000000065601
$Z_{2p_z2p_z}^{RS}$	$-0.2041368174296^\dagger$	-0.1909145956536	-0.1026746483376
$Z_{2p_z4d_{z^2}}^{RS}$	0.0018062329331	0.0003879624795	-0.0000443348506
$Z_{4d_{z^2}4d_{z^2}}^{RS}$	$-2.7131314621083^\ddagger$	-0.3333095179182	-0.1000141685427

arbitrary number of symmetries. In developing the final formula for the basic one-center radial integral  $\chi^{\text{III}}$ , we avoid deliberately the use of the parameter  $\beta = \frac{1}{2}(\zeta_1 - \zeta_2)$ . Then, all the integrals are absolutely stable for nearly equal orbital exponents and no asymptotic formulas are required. Moreover, the singularities produced for very small interatomic distances can be easily bypassed in the overlap and nuclear attraction integrals by introducing all the powers of  $R$  inside the innermost loop of the expressions. Although this trick does not work for the Coulomb integrals, we want to stress here that a value of  $R$  so small as to produce instabilities in this integral cannot take place in realistic molecular and solid state calculations. On the other hand, all integrals are stable with respect to the  $R \rightarrow \infty$ ; in addition, it has been shown that only Coulomb and nuclear attraction integrals have a long-range term that decays as  $R^{-(l_1+l_2+1)}$ , while most of the terms in those integrals as well as all of the terms in the overlap integrals decay exponentially with distance. The separation of these long-range terms is crucial for infinite periodic systems, as they have to be summed up by special algorithms, and they lead to multipolar interactions. Another relevant property of the algorithm given here is that the two nuclei involved in the integrals are not restricted to be aligned along the  $z$  axis (Mulliken orientation). In the same way, as the only dependence of the integrals on angular variables is through the  $T_{l_1 m_1 l_2 m_2}^{l_3}$  coefficient,

their computation can be made for as many orientations as desired with the only extra cost of recomputing  $T_{l_1 m_1 l_2 m_2}^{l_3}$  each time. This fact makes the algorithm very attractive in solid state calculations, where each atom is surrounded by shells of equivalent atoms at the same  $R$  distance but with different orientations.

From formulas deduced for two-center integrals between STO, we demonstrate as the EIE between non-spherical closed-shell ions can be divided into short-range interaction energy and multipolar interaction, where this multipolar interaction is equivalent to multipolar expansion of the electrostatic interaction.

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