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Convergence of the multipole expansion for 1,2 Coulomb interactions: The modified multipole shifting algorithm

C. J. F. Solano,[1] A. Martín Pendás,[1,a)] E. Francisco,[1] M. A. Blanco,[1] and P. L. A. Popelier[2,b)]

[1]*Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, E-33006-Oviedo, Spain*
[2]*Manchester Interdisciplinary Biocentre (MIB), 131 Princess Street, Manchester M1 7DN, United Kingdom and School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom*

A force field that accounts for the quantum chemical reality of interacting atoms must include Coulomb interactions between bonded atoms. The short-range nature of such 1,2 interactions necessitates atomic multipole moments in addition to point charges. However, the close proximity of bonded atoms would normally lead to a divergent multipolar expansion. A special algorithm presented here, within the scope of the previously presented multipole shifting method [M. Rafat and P. L. A. Popelier, J. Chem. Phys. **124**, 144102 (2006)], shows that convergence can nevertheless be achieved by a suitable selection of multipole displacements. The algorithm is applied to improve the convergence of the multipolar expansion within the quantum theory of atoms in molecules approach. © *2010 American Institute of Physics*. [doi:10.1063/1.3430523]

I. INTRODUCTION

The basic concepts used by chemists—atoms, bonds, functional groups—are based on the hypothesis of the existence of separable and transferable objects in physical three-dimensional (3D) space. At the same time, the quantum concepts use state vectors defined in an infinite dimensional Hilbert space. The quantum theory of atoms in molecules (QTAIM) (Ref. 1) allows a generalization of quantum mechanics to finite space regions, bringing it closer to the usual chemical language. The use of the topology induced by the electron density is justified under the QTAIM. It allows an exhaustive partition of 3D space, such that the systems are divided in *topological atoms* and the contacts between these atoms are associated with traditional chemical bonds. An important empirical result is that topological atoms are transferable in situations with similar chemical bonding. Note that Quantum Chemical Topology (QTAIM) is part of a wider research program called quantum chemical topology that uses the concept of a gradient vector field as a means to partition quantum chemical functions.[2]

The transferability mentioned above is very important for the generation of new force fields. In atomistic simulations of biomolecules, such as proteins, the use of force fields is widespread. These are constructed on the assumption that the molecules are formed by transferable structural units, which are called *atom types*.[3] In general, the potential energy surface of a force field has contributions of two main types: (a) bonded interactions, which include energy contributions related to bonds deviating from their equilibrium configurations; and (b) nonbonded interactions, based on intermolecular interactions. The bonded contributions can be further divided into contributions due to: (i) bond stretching, between atoms directly linked (1,2 interactions), depending on the bond lengths; (ii) bond bending, between atoms separated by two bonds (1,3 interactions), depending on the bond angles; and (iii) bond torsion, between atoms separated by three bonds (1,4 interactions), depending on the dihedral angles. The nonbonded contributions are assumed to occur between atoms separated by four or more bonds, and they comprise: (i) the van der Waals energy; and (ii) the electrostatic energy, which is usually obtained from model point atomic charges.

The main limitations of force fields are as follows: (a) the dichotomy between bonded and nonbonded interactions (which may seem natural and justified by chemical intuition, even as a result of historical development) is arbitrary and is not based on quantum mechanics; and (b) the lack of a rigorous description of the electrostatic interaction. The latter is one of the major problems to be faced by existing force fields.

In force field construction, electrostatic point charges are traditionally fitted in order to reproduce *ab initio* energies and forces,[4] liquid state bulk properties,[5] or an exact *ab initio* electrostatic potential,[6] to mention a few examples. The resulting charges are then mere numbers appearing in the familiar expression of Coulomb energy. Because they are fitted, and not obtained directly from the electron density, they may not be transferable. In this work, atomic charges are directly sampled from the electron density, securing control of transferability.[7,8] However, in order to guarantee an accurate description of electrostatic interaction at short range, high-rank atomic multipole moments are necessary, such as dipole, quadrupole, and octupole moments. Multipole moments enable that the Coulomb energy between any two atoms can be rapidly and accurately calculated, provided the corresponding multipole expansion converges. Consequently,

a)Electronic mail: angel@fluor.quimica.uniovi.es.
b)Electronic mail: pla@manchester.ac.uk.

one obtains a route to address both the challenge of transferability and short-range interaction. This route proposes to calculate the Coulomb energy between any two atoms, and only fit remaining types of interaction (e.g., dispersion). Coulomb interaction is then introduced in the force field for both bonded and nonbonded interactions. In principle, this approach is closer to the underlying quantum reality than the traditional treatment of current force fields. More details on this strategy of force field design can be found in full elsewhere.[9,10]

Some time ago one of us embarked on a project that aims at constructing a force field based on topological atoms.[11,12] One can calculate different atomic properties for the topological atoms, in particular the QTAIM *multipole moments*. From these and the *multipolar expansion* (ME), largely studied for intermolecular interactions,[13] electrostatic interactions in the force field can be rigorously introduced. The price paid for the convenience of the ME is a possible lack of convergence. We can summarize this problem as follows: the smaller the distance between the nuclei of the interacting atoms, the more likely the expansion will diverge, and hence become useless. Traditionally, the ME is expected to converge for $1, n$ interactions where n is strictly larger than 4.

In Ref. [14], the *multipole shifting* (MS) method was presented, which improved the convergence of the ME for 1,3 and 1,4 interactions. However, its implementation does not work for interactions between atoms directly bonded to each other, that is, 1,2 interactions. In this paper we present a new implementation for this method, the *modified multipole shifting* (MMS) algorithm, which extends its validity to all electrostatic interactions between topological atoms.

Section II presents the general characteristics of the MS method for the calculation of the electrostatic interaction between topological atoms in terms of the ME and the QTAIM multipole moments. The problems found in 1,2 interactions and the new MMS algorithm devised to overcome them are presented together in Sec. III. We include some numerical results and discuss the validity of the MMS algorithm in Section IV, finishing with some conclusions in Sec. V.

II. THE MULTIPOLE SHIFTING METHOD FOR THE MULTIPOLAR EXPANSION OF THE QTAIM COULOMB ENERGY

In this paper, we will use the MS method, already introduced in Ref. [15] to obtain the QTAIM Coulomb energy between any two *topological atoms* by means of a ME. The MS method improves the convergence of the ME in bonded Coulomb interactions by shifting the positions of the expansion centers involved in the ME; we will present here a very brief recount of the method, leaving for an Appendix, the whole framework of the current reimplementation.

The Coulomb energy interaction between two QTAIM atoms is

$$E_{\text{elec}}(A,B) = \int_{\Omega_A} d\vec{r}_A \int_{\Omega_B} d\vec{r}_B \frac{\rho_A^{\text{tot}}(\vec{r}_A)\rho_B^{\text{tot}}(\vec{r}_B)}{r_{12}}, \quad (1)$$
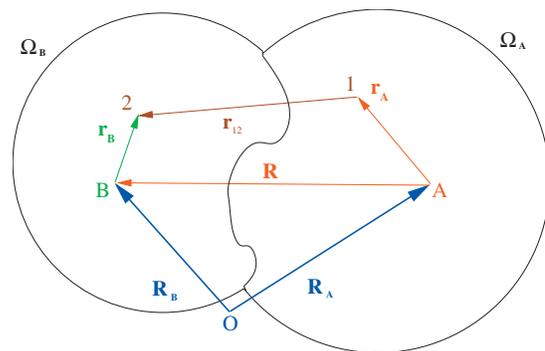
FIG. 1. Global coordinate system used in the description of the electrostatic interaction between atomic basins Ω_A and Ω_B.

where Ω_A and Ω_B label the two *atomic basins* of the topological atoms (see Fig. 1) and

$$\rho_A^{\text{tot}}(\vec{r}_A) = Z_{\Omega_A}\delta(\vec{r}_A) - \rho(\vec{r}_A + \vec{R}_A), \quad (2)$$

$$\rho_B^{\text{tot}}(\vec{r}_B) = Z_{\Omega_B}\delta(\vec{r}_B) - \rho(\vec{r}_B + \vec{R}_B), \quad (3)$$

are charge densities with origin in the A and B centers, respectively. Note that Z_Ω is a nuclear charge and $\delta(\vec{r})$ is the (three-dimensional) Dirac delta function.

Topological atoms typically have complex shapes in real space. Therefore, the integrals present in Eq. (1) are extremely difficult to solve analytically. Traditionally, these integrals have been approximated by a ME; using this, only the much simpler QTAIM multipole moments are required to compute an ME approximated Coulomb energy between topological atoms,

$$E_{\text{elec}}(A,B) = \sum_{l_A m_A} \sum_{l_B m_B} Q_{l_A m_A}(\Omega_A) T_{l_A m_A l_B m_B}(\vec{R}) Q_{l_B m_B}(\Omega_B), \quad (4)$$

where $T_{l_A m_A l_B m_B}(\vec{R})$ is an interaction tensor (see Appendix) that can also be obtained from stable recurrence relations.[16] The real QTAIM multipole moments, which include the nuclear charges, are defined as

$$Q_{l_A m_A}(\Omega_A) = \int_{\Omega_A} \rho_A^{\text{tot}}(\vec{r}_A) R_{l_A m_A}(\vec{r}_A) d\vec{r}_A, \quad (5)$$

$$Q_{l_B m_B}(\Omega_B) = \int_{\Omega_B} \rho_B^{\text{tot}}(\vec{r}_B) R_{l_B m_B}(\vec{r}_B) d\vec{r}_B, \quad (6)$$

where $R_{lm}(\vec{r})$ are the real regular spherical harmonics (see Appendix). Notice that in the above expressions, $m_A = -l_A, \ldots, l_A$ $(m_B = -l_B, \ldots, l_B)$ and $l_A = 0, \ldots, \infty$ $(l_B = 0, \ldots, \infty)$ so that ME leads to infinite series, although they would generally be truncated.

The main advantages[17] of the expressions for the Coulomb energy between topological atoms using both the QTAIM multipole moments and the ME are as follows: (a) the QTAIM multipole moments are computed and transferred from an arbitrary local coordinate system and it is not necessary to compute them once again for every possible atomic configuration (see Appendix); (b) the QTAIM multi-

pole moments are transferable in similar environments; (c) the finite size of the topological atoms makes exact convergence possible, in principle; and (d) in view of the absence of penetration energy, there is no need for damping functions.

The main limitation is that the ME has restrictions in its convergence. It is important to realize that this expansion formally converges provided $|\vec{r}_A - \vec{r}_B| < |\vec{R}|$.[18] For two finite atomic basins Ω_A and Ω_B, the ME is strictly convergent (independently of the relative orientations) if $R_A + R_B \leq |\vec{R}| = R$, where R_A is the maximum value of the radial coordinate still within Ω_A, called the *convergence radius* for topological atom A, with an equivalent definition for R_B;[19] these are the extents of their *convergence spheres*. Two atoms are called nonoverlapping if their convergence spheres do not overlap and overlapping otherwise. The ME convergence is guaranteed only between nonoverlapping atoms, that is, for interactions between atoms not directly bonded (i.e., diverge only for 1,2 interactions), although the divergence may (and does) extend to further $1,n$ interactions if the convergence radius is large (open atoms). Consequently, it should only be the electrostatic component of *long range* interactions that could be modeled with confidence and sufficient accuracy, the ME generally failing for bonded interactions in the force field sense (i.e., 1,2 to 1,4 interactions).

However, it is known that the inclusion of the electrostatic contribution from bonded interactions would substantially improve the accuracy of the force fields.[20] In addition, the arbitrary partition between bonded and nonbonded interactions would vanish. Therefore, we present here the basics of the original MS method, already introduced in Ref. 15, within the framework of the current reimplementation (see Appendix). Its aim is to improve the convergence of the ME in bonded Coulomb interactions by shifting the position of the expansion centers involved in the ME; thus reducing or avoiding the overlap between the convergence spheres through translation in the local reference systems of each atom.

If one shifts by $\vec{c}$ the origin of the local coordinate system associated with a topological atom, its shifted real multipole moments $Q_{lm}^{\vec{c}}(\Omega)$ can be obtained from

$$Q_{lm}^{\vec{c}}(\Omega) = \sum_{l'=0}^{l} \sum_{m'=-l'}^{l'} Q_{l'm'}^{\vec{0}}(\Omega) W_{l'm',lm}(\vec{c}), \tag{7}$$

where the $W_{l'm',lm}(\vec{c})$ is a real MS matrix fully described in the Appendix, the $Q_{lm}^{\vec{0}}(\Omega)$ are the original multipole moments, $l' = 0, \ldots, l$, and $m' \leq |l'|$. Note that only $l' \leq l$ multipole moments are needed to obtain $Q_{lm}^{\vec{c}}(\Omega)$, so shifting is a finite process for a given l, but also that low-order multipole moments in the original frame (l' low) generate higher-order shifted multipole moments (l higher). In other words, a shifted moment of arbitrary rank l includes contributions from all original moments of lower rank l', in general. Because this arbitrary rank l is unbounded the (finite) set of original moments gives rise in general to an unbounded (i.e., infinite) number of shifted moments.

The MS method has two main limitations: (a) if the shift vector $\vec{c}$ has a large modulus, the shifted multipole moments

will be unacceptably large; and (b) as seen with Eq. (A10), shifting can reduce the symmetry in the original multipole moments, such that a topological atom perfectly described by a reduced number of multipole moments may need a large number of shifted multipoles when its origin is displaced. For example, a spherical atom centered on origin $\vec{0}$ is fully described by a monopole moment only. Describing this atom from an alternative origin $\vec{c}$ would require a huge number of higher moments. To mitigate the effects of the reduction of symmetry, it is essential to use β-spheres. The β-spheres are usually centered at the nuclei, and have an arbitrary radius such that they are fully included in the atomic basin for the topological atoms considered. In our experience, using the largest possible β-sphere radii provides the optimum performance. Thus, the atomic basins are divided into β-spheres and the outer atomic regions that complete them. The QTAIM multipole moments are correspondingly divided into two contributions

$$Q_{lm}(\Omega) = Q_{lm}^{\beta}(\Omega) + Q_{lm}^{\text{out}}(\Omega), \tag{8}$$

where $Q_{lm}^{\beta}(\Omega)$ are multipole moments associated with the β-spheres and $Q_{lm}^{\text{out}}(\Omega)$ are multipole moments associated with the remaining regions. Consequently, the Coulomb energy between topological atoms is split into four contributions

$$E_{\text{elec}}(A,B) = \sum_{\eta,\chi=\{\beta,\text{out}\}} E_{\text{elec}}^{\eta\chi}(A,B), \tag{9}$$

where

$$E_{\text{elec}}^{\eta\chi}(A,B) = \sum_{l_A m_A} \sum_{l_B m_B} Q_{l_A m_A}^{\eta}(\Omega_A) T_{l_A m_A l_B m_B}(\vec{R}) Q_{l_B m_B}^{\chi}(\Omega_B). \tag{10}$$

The important point here is that it is only necessary to shift the residual $Q_{lm}^{\text{out}}(\Omega)$ multipoles, since the β-spheres never overlap and hence the ME is exact for them.

The convergence of the ME in the Coulomb energy between topological atoms can be improved, in principle, using shifted QTAIM multipole moments as described in Refs. 14 and 15. However, one has to consider two main issues related to the efficiency of the MS method. First, the selected displacements for the MS method must reduce the overlap between the convergence spheres of the topological atoms, but the shifted multipole moments cannot become unacceptably large. Second, the Coulomb energy ME described in Eqs. (9) and (10) has to be truncated in some way that guarantees convergence of the ME. The original implementation of the MS method introduced in Ref. 14 was able to provide reasonable energies for 1,3 and 1,4 interactions. However, this implementation did not work for 1,2 interactions, since it was unable to select multipole shifts providing ME convergence in this case, motivating the search for the new algorithm presented in Sec. III.

III. THE MODIFIED MULTIPOLE SHIFTING ALGORITHM

We propose here the MMS algorithm for selecting the multipole displacements involved in the MS method, replac-

ing the one presented in Ref. 14. We will first introduce some definitions regarding the different errors involved, using them in some examples with a whole range of possible displacements to demonstrate the problems posed by the ME for 1,2 interactions within the MS framework that motivates this new algorithm. Then, we will present the MMS selection algorithm devised to cope with them, which will be applied to this particular set of displacements in this section to better understand its inner workings.

The *real error* in the Coulomb energy between topological atoms A and B is defined as

$$\Lambda_{real}^{l_{tot},\vec{c}}(A,B) = |E_{elec}^{l_{tot},\vec{c}}(A,B) - E_{exact}(A,B)|, \quad (11)$$

where the l_{tot} angular quantum number and shift vector $\vec{c}$ labels come from $E_{elec}^{l_{tot},\vec{c}}(A,B)$, which is the Coulomb energy obtained through Eqs. (9) and (10) using the $Q_{lm}^{out}(\Omega)$ multipole moments displaced by $\vec{c}$, such that in Eq. (10) the sums on both l_A and l_B extend to l_{tot}. $E_{exact}(A,B)$ is the *exact* Coulomb energy between topological atoms A and B, which will be numerically computed through a different algorithm[21] (see below). Note that this error is computed *outside* the algorithm, and although the aim of the method is to minimize it, we are by no means doing a fit to this error: it is only the final measure of how the algorithm has performed.

The *truncation error* in the Coulomb energy between two topological atoms A and B for a given l_{tot} angular quantum number and shift vector $\vec{c}$ is defined as

$$\Lambda_{trunc}^{l_{tot},\vec{c}}(A,B) = |E_{elec}^{l_{tot},\vec{c}}(A,B) - E_{elec}^{l_{tot}-1,\vec{c}}(A,B)|. \quad (12)$$

Similarly, we introduce the *shift error* in the Coulomb energy between topological atoms A and B for a l_{tot} angular quantum number and shift vector $\vec{c}$ as

$$\Lambda_{shift}^{l_{tot},\vec{c}}(A,B) = |E_{elec}^{l_{tot},\vec{c}-\vec{c}}(A,B) - E_{elec}^{l_{tot},\vec{0}}(A,B)|, \quad (13)$$

where $E_{elec}^{l_{tot},\vec{0}}(A,B)$ is the Coulomb energy obtained through Eqs. (9) and (10) using the original (undisplaced) multipoles $Q_{lm}^{0}(\Omega)$, such that in Eq. (10) the sums on both l_A and l_B extend to l_{tot}. The symbol $E_{elec}^{l_{tot},\vec{c}-\vec{c}}(A,B)$ represents the same Coulomb energy estimation as $E_{elec}^{l_{tot},\vec{0}}(A,B)$ but obtained from the $Q_{lm}^{out}(\Omega)$ multipoles first shifted by $\vec{c}$ and then back shifted (shift by $-\vec{c}$, $Q_{lm}^{\vec{c}-\vec{c}}$) to the initial origin, introducing possibly large rounding errors. To conclude these definitions, the *total error* in the Coulomb energy between two topological atoms A and B for a l_{tot} angular quantum number and shift vector $\vec{c}$ is obtained through

$$\Lambda_{total}^{l_{tot},\vec{c}}(A,B) = \Lambda_{trunc}^{l_{tot},\vec{c}}(A,B) + \Lambda_{shift}^{l_{tot},\vec{c}}(A,B). \quad (14)$$

This is an estimate of the real error, which of course cannot be computed on production runs. However, we can check how good our estimate is in the present test cases, seeing whether minima of the total error correspond to minima of the real error.

Figures 2–4 show the real and total errors in the Coulomb energy for 1,2 interactions in H_2, LiH, and H_2O, respectively, for a large trial set of $\vec{c}$ shift vectors spaced $0.1a_0$. All total errors have minima at various displacements of the local coordinate systems. However, the lowest minimum for the total error does not usually coincide with the lowest
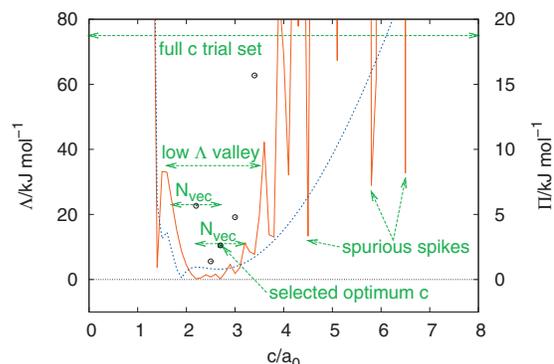
FIG. 2. $\Lambda_{total}^{10,\vec{c}}(H,H)$ (solid line) and $\Lambda_{real}^{10,\vec{c}}(H,H)$ (dashed line) vs $c=|\vec{c}|$ for the H_2 molecule [$d_{H-H}=1.40a_0$ and $E_{exact}(H,H)=111.51$ kJ/mol] are represented in the main axes; the right y axis is used for $\Pi^{10,\vec{c}}(H,H)$ (circles) vs c computed at the total error minima, with the parameter $N_{vec}=10$. The shift vectors for each of the two topological atoms stand along the internuclear axis and face in opposite directions. Explanatory labels have been added, see text.

minimum for the real error. Also, notice that there may be several minima for the total error within a given low-error valley, but there are also spurious low-error spikes outside of these valleys. From the whole set of minima of the total error, we wanted to select those in regions with smooth behavior, and to do that you have to sample each points surroundings. We thus introduce here a new variable to help us to choose among the total error minima, through their smoothness, so that they lead to a reasonable real error in the energy *without an actual knowledge* of the latter. The *merit* of the total error in the Coulomb energy between two topological atoms A and B for a l_{tot} angular quantum number and shift vector $\vec{c}$ is defined as a measure of that smoothness,

$$\Pi^{l_{tot},\vec{c}}(A,B) = \frac{\sum_{i}^{N_{vec}} |\Lambda_{total}^{l_{tot},\vec{c}}(A,B) - \Lambda_{total}^{l_{tot},\vec{c}_i}(A,B)|}{N_{vec}}. \quad (15)$$

The set of N_{vec} $\vec{c}_i$ vectors around $\vec{c}$ is selected from those in the full trial set by their proximity in modulus to $|\vec{c}|$, so that $\{\vec{c}_i\}_{i=1,...,N_{vec}}$ are the shift vectors closest to $\vec{c}$. The choice of N_{vec} should try to be low enough not to include vectors outside a given Λ_{total} valley, and large enough to discard spuri-
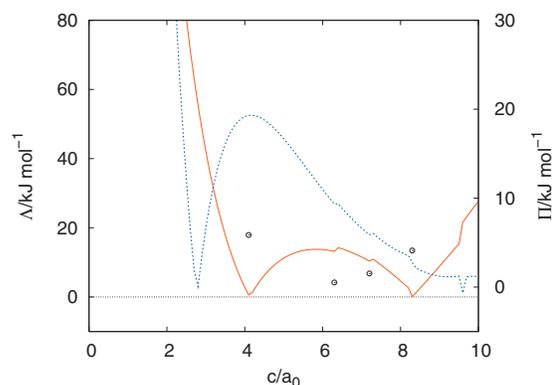
FIG. 3. $\Lambda_{total}^{10,\vec{c}}(Li,H)$ (solid line) and $\Lambda_{real}^{10,\vec{c}}(Li,H)$ (dashed line) vs $c=|\vec{c}|$ for the LiH molecule [$d_{Li-H}=3.25$ a_0 and $E_{exact}(Li,H)=-603.39$ kJ/mol] are represented in the main axes; the right y axis is used for $\Pi^{10,\vec{c}}(Li,H)$ (circles) vs c computed at the total error minima, with the parameter $N_{vec}=10$. The shift vectors for each of the two topological atoms stand along the internuclear axis and face in opposite directions.
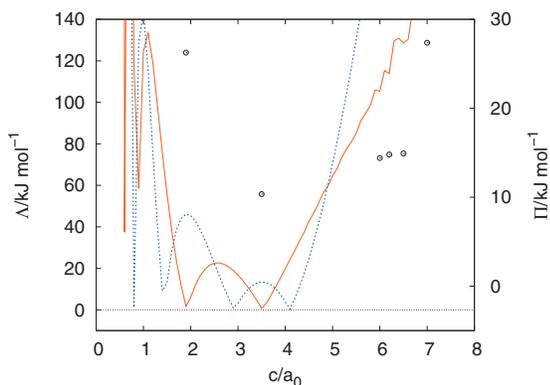
FIG. 4. $\Lambda_{total}^{10,\vec{c}}(O,H)$ (solid line) and $\Lambda_{real}^{10,\vec{c}}(O,H)$ (dashed line) vs $c=|\vec{c}|$ for the H_2O molecule $[d_{O-H}=1.78a_0$ and $E_{exact}(O,H)=-766.67$ kJ/mol] are represented in the main axes; the right y axis is used for $\Pi^{10,\vec{c}}(O,H)$ (circles) vs c computed at the total error minima, with the parameter $N_{vec}=10$. The shift vectors for each of the two topological atoms stand along the internuclear axis and face in opposite directions.

FIG. 5. $\Lambda_{total}^{10,\vec{c}}(H,H)$ (solid line) and $\Lambda_{real}^{10,\vec{c}}(H,H)$ (dashed line) vs $c=|\vec{c}|$ for the H_2O molecule $[d_{H-H}=2.85$ a_0 and $E_{exact}(H,H)=339.87$ kJ/mol] are represented in the main axes; the right y axis is used for $\Pi^{10,\vec{c}}(H,H)$ (circles) vs c computed at the total error minima, with the parameter $N_{vec}=10$. The shift vectors for each of the two topological atoms stand along the internuclear axis and face in opposite directions.

ous low-error spikes (see Fig. 2 for an example). Notice that the merit is computed only for trial points which are total error minima and hence candidates for selection by the algorithm, however, the points in the merit's N_{vec} set are not minima but just which points surround the given minimum in the full trial set, as shown by the horizontal arrows at the bottom of Fig. 2. Notice how taking a spike for the minima will lead to a N_{vec} set with a much higher total error than the actual spike, and hence to a much larger merit, which will discard it in the algorithm as nonsmooth.

Figures 2–4 include the merits computed for each $\vec{c}$ that is a total error minimum (circles, right y axis) for each of the molecules at the given geometries. As our data shows, reasonable real errors in the computed electrostatic energy may be obtained from the minimum total errors if the following requirements are fulfilled: (a) the minimum total error has a small magnitude; and (b) the merit of this minimum is small. Therefore, an efficient algorithm should take into account both requirements to the appropriate extent. It should be noticed that the large $\Lambda_{total}^{l_{tot},\vec{c}}(A,B)$ values at small displacements come mainly from the truncation error, in this case measuring the nonconvergence of the original $\vec{c}=\vec{0}$ ME, while the large $\Lambda_{total}^{l_{tot},\vec{c}}(A,B)$ values at large displacements usually signal an increase in the shift error, since the multipole moments increase in value as $|\vec{c}|^l$ and the rounding error (both while performing the displacements and while using the shifted multipole moments in the ME) can become pronounced.

Figure 5 shows the real and total errors in the Coulomb energy for 1,3 interactions between the two H atoms in H_2O, as well as the merits of the total error minima subset. This figure allows us to understand the efficiency of the MS method between atoms that are not directly bonded. In these cases, the real and total errors present a quite similar behavior, such that there is a wide shift range available with negligible real errors in the Coulomb energy.

The MMS algorithm consists of the following steps: (a) user-specify l_{tot} for the QTAIM multipole moments of the atoms under study, and obtain the $\Lambda_{total}^{l_{tot},\vec{c}}(A,B)$ for the set of user-specified shift vectors $\vec{c}=\vec{c}_{min},\dots,\vec{c}_{max}$ with a given step of say $0.1a_0$ (note that shifts have only been implemented in
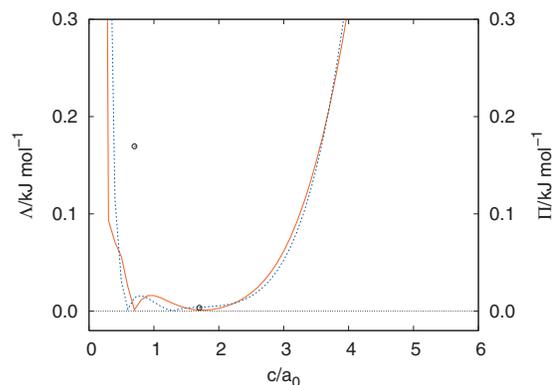
the internuclear direction and with opposite signs for each topological atom; these shifts have proven to be the overall best in improving the ME convergence); (b) determine the subset of total error minima in this full trial set; (c) obtain, for each of these minima, their merits for the user-specified N_{vec}, and also their *relative merits* $\Pi_{rel}^{l_{tot},\vec{c}}(A,B)$, defined as the ratios of the different merits and the smallest value among them; and finally (d) the $\Lambda_{final}^{l_{tot},\vec{c}}(A,B)$ $=\Pi_{rel}^{l_{tot},\vec{c}}(A,B)\Lambda_{total}^{l_{tot},\vec{c}}(A,B)$ errors are calculated for the subset of total error minima. The smallest of these final errors determines the optimal shift vector according to this algorithm, selected to improve the ME convergence in the Coulomb energy between topological atoms. Hence, notice that the electrostatic interaction between topological atoms is evaluated by means of $E_{elec}^{l_{tot},\vec{c}_{opt}}(A,B)$, where $\vec{c}_{opt}$ is the optimal shift vector selected.

In order to see how this MMS algorithm works, let us briefly analyze the most significant total error minima in Figs. 2–5. In the case of H_2, the set of minima with displacements $c=2.2, 2.5, 2.7,$ and $3.0a_0$ has $\Pi^{10,\vec{c}}(H,H)$ values several orders of magnitude smaller than the rest (which thus have relative merits larger than 10), and their corresponding $\Lambda_{final}^{10,\vec{c}}(H,H)$ values are 0.84, 0.75, 0.37, and 6.33 kJ/mol, the rest having values of 87.39 kJ/mol (for $c=3.4a_0$) or larger. Hence, outside from the total error valley for c between 2 and $3a_0$, the algorithm discards all minima; within that valley, the different displacements lead to merits and final errors that are all acceptable. Accordingly, the *real* errors in that valley are 3.81, 3.33, 3.16, and 3.92 kJ/mol, the errors being 6.91 kJ/mol (again for $c=3.4a_0$) or larger outside of the valley. What is more important, the MMS algorithm leads to a $\Lambda_{final}^{10,\vec{c}}(H,H)$ ordering that coincides with the $\Lambda_{real}^{10,\vec{c}}(H,H)$ ordering for the eight lowest-lying minima, and hence it is a good predictor for that magnitude. The fact that $c=2.7a_0$ is finally chosen is irrelevant, for any of the points in the valley leads to similar results.

In the LiH case, only four minima appear, with $c=4.1, 6.3, 7.2,$ and $8.3a_0$, with relative merits $\Pi_{rel}^{10,\vec{c}}(Li,H)=11, 1, 3,$ and 8, respectively, while their final errors are $\Lambda_{final}^{10,\vec{c}}(Li,H)=6.45, 13.17, 30.60,$ and 0.56 kJ/mol, and their

real errors are $\Lambda_{\text{real}}^{10,\vec{c}}(\text{Li},\text{H})=52.50$, 26.90, 18.01, and 10.00 kJ/mol, respectively. Again, the final error from the MMS algorithm selects the best approximation, $c=8.3a_0$, although here it does not sort all the minima in the same order of real errors.

In the O–H interaction in H_2O there is again a valley of low total (and real) errors in the $c=2-4a_0$ range; the minima there are at $c=1.9$ and 3.5, having final errors of 4.47 and 0.79 kJ/mol, while outside of that valley the final error is larger than 146 kJ/mol. The corresponding real errors are 46.10 and 13.46 kJ/mol, being larger than 200 kJ/mol outside of the valley; once again, the algorithm not only chooses the best $c=3.5a_0$ shift, but it also correctly orders the next 13 minima in increasing order of real errors.

Finally, the 1,3 H–H interaction in water is much better represented by the ME than the rest; correspondingly, the scale in Fig. 5 is two orders of magnitude smaller. Here, there are just two minima, with $c=0.7$ and $1.7a_0$, relative merits of 49 and 1, final errors of <0.01 and 0.06 kJ/mol, and real errors of 0.01 and <0.01 kJ/mol, respectively. Although the algorithm does not give the correct order here, both shift values give virtually exact ME expansions, the errors being negligible.

Notice that, although the real errors at the selected $\vec{c}_{\text{opt}}$ may seem large (3.8, 8.7, and 18.3 kJ/mol for H–H, Li–H, and O–H 1,2 interactions), the Coulomb interaction energies are much larger (111.51, -603.39, and -766.67 kJ/mol, respectively), so that the percentage errors are in fact quite small (3.4%, 1.4%, and 2.4%, respectively).

IV. RESULTS

In order to test the validity of the MMS algorithm for the selection of $\vec{c}_{\text{opt}}$ in a suitable range of situations, we have studied some 1,2, 1,3, and 1,4 electrostatic interactions between topological atoms. First, we have selected H_2, LiH, and H_2O at different internuclear distances.[22] These molecules are examples of different types of bonds: covalent (H_2), polar (H_2O) and ionic (LiH). The electronic densities of these molecules were obtained by 6-311G(p,d) CASSCF calculations with the GAMESS code.[23] In addition, we have computed glycine and N-methylacetamice at the single optimized 6-311G(p,d) HF geometry (see Fig. 6) to test more real-life examples.

The topological analysis was performed using the PROMOLDEN code,[24] where we used the following computational choices: (a) the interatomic surface of the topological atoms was obtained with an accuracy of $1\times10^{-5}a_0$ and we used β-spheres to split the atomic basins;[25] (b) a two-dimensional angular Lebedev quadrature with 74 and 5810 nodes for the β-spheres and the outer regions, respectively; and (c) radial Gauss–Chebychev second-order (600 nodes) and trapezoidal (500 nodes) quadratures for the β-spheres and the outer regions, respectively. Although a numerical quadrature could be chosen directly for the radial coordinate, it is computationally more efficient to first map it onto a new finite interval $u\in[-1,+1]$ by means of the coordinate transformation $r(u)=\eta(1+u)/(1-u+a)$, where the parameter a is chosen to
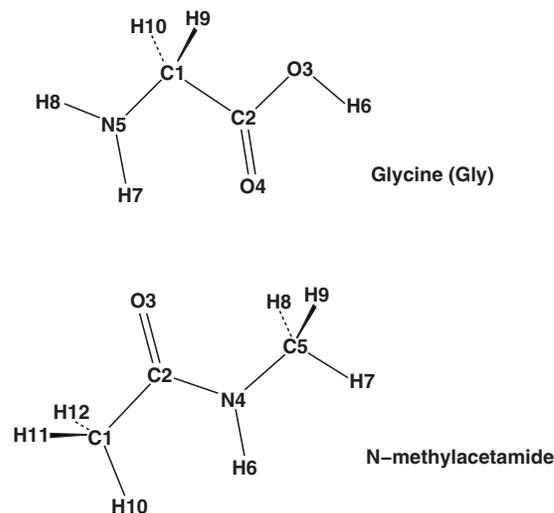
FIG. 6. Atomic numbering scheme for the glycine and N-methylacetamide molecules.

recover the initial interval and η is the Bragg–Slater radius of the atom.[21]

We have implemented our new MMS algorithm for the MS method in the RHOLM code,[26] which is tightly linked with PROMOLDEN. In the present calculations, the following parameters have been chosen: (a) the highest rank of the QTAIM multipole moments is $l_{\text{tot}}=10$; (b) the minimum and maximum shift vector modules are $c_{\text{min}}=0a_0$ and $c_{\text{max}}=10a_0$, and any two consecutive shifts in the set differ by $0.2a_0$ (51 $\vec{c}$ vectors in the full trial set); and (c) $N_{\text{vec}}=10$ to calculate the merits for the total errors in the Coulomb energy.

Tables I–III present the results obtained by the MMS

TABLE I. Relative error $[\varepsilon(\text{H},\text{H})=\Lambda_{\text{real}}^{10}(\text{H},\text{H})/|E_{\text{exact}}(\text{H},\text{H})|$ in percentage terms] in the Coulomb energy between the topological atoms of the H_2 molecule obtained by the MMS method for a wide range of internuclear distances. $d_{\text{H–H}}$ represents the internuclear distance (equilibrium is at $1.43a_0$), while $E_{\text{exact}}(\text{H},\text{H})$ is the Coulomb energy obtained by PROMOLDEN.

$d_{\text{H–H}}/a_0$	$E_{\text{exact}}(\text{H},\text{H})$ (kJ mol^{-1})	$\varepsilon(\text{H},\text{H})$
0.60	1144.63	0.18
0.80	584.93	3.46
1.00	322.66	1.63
1.20	186.88	2.40
1.40	111.51	3.42
1.60	67.93	3.13
1.80	41.88	3.08
1.90	33.08	2.94
2.00	26.12	2.88
2.20	16.41	2.44
2.30	13.01	2.16
2.40	10.38	1.86
2.50	8.27	1.53
2.80	4.25	0.62
3.00	2.77	0.05
3.20	1.81	0.28
3.60	0.80	0.29
4.00	0.35	2.72

TABLE II. Relative error $[\varepsilon(\mathrm{Li,H})=\Lambda_{\mathrm{real}}^{10}(\mathrm{Li,H})/|E_{\mathrm{exact}}(\mathrm{Li,H})|$ in percentage terms] in the Coulomb energy between the topological atoms of the LiH molecule obtained by the MMS method for a wide range of internuclear distances. $d_{\mathrm{Li-H}}$ represents the internuclear distance (equilibrium is at $3.09a_0$), while $E_{\mathrm{exact}}(\mathrm{Li,H})$ is the Coulomb energy obtained by PROMOLDEN.

$d_{\mathrm{Li-H}}/a_0$	$E_{\mathrm{exact}}(\mathrm{Li,H})$ (kJ mol^{-1})	$\varepsilon(\mathrm{Li,H})$
2.50	−664.67	7.64
2.75	−652.59	4.62
3.00	−630.17	3.08
3.25	−603.39	1.38
3.50	−573.56	0.56
3.75	−540.72	0.01
4.00	−505.47	0.43
4.25	−467.28	1.39
4.50	−424.77	0.93
4.75	−377.62	0.99
5.00	−325.00	0.43
5.25	−266.31	0.50
5.50	−202.80	0.20
5.75	−135.55	0.31
6.00	−75.11	0.30
6.25	−43.12	0.03
6.50	−25.26	0.63
6.75	−14.67	0.66
7.00	−8.46	1.48
7.25	−4.89	2.28
7.50	−2.85	2.95

TABLE III. Relative error $[\varepsilon(\mathrm{O,H})=\Lambda_{\mathrm{real}}^{10}(\mathrm{O,H})/|E_{\mathrm{exact}}(\mathrm{O,H})|$ in percentage terms] in the Coulomb energy between the O and H topological atoms of the H_2O molecule obtained by the MMS method for a wide range of O–H internuclear distances ($d_{\mathrm{O-H}}$) but fixing the opposite O–H distance and the $\widehat{\mathrm{HOH}}$ angle [equilibrium has $d_{\mathrm{O-H}}=1.82a_0$]. $E_{\mathrm{exact}}(\mathrm{O,H})$ is the Coulomb energy obtained by PROMOLDEN.

$d_{\mathrm{O-H}}/a_0$	$E_{\mathrm{exact}}(\mathrm{O,H})$ (kJ mol^{-1})	$\varepsilon(\mathrm{O,H})$
1.51	−846.26	5.34
1.70	−797.21	3.05
1.78	−766.67	2.39
1.89	−644.13	0.65
2.08	−515.35	0.28
2.27	−407.07	0.76
2.46	−305.97	0.93
2.83	−156.84	0.85
3.21	−83.29	0.60
3.40	−61.98	0.47
3.59	−46.46	0.36
3.78	−34.93	0.35
3.97	−26.40	0.16
4.16	−20.07	0.11
4.35	−15.36	0.06
4.54	−11.93	0.05
4.72	−9.32	0.08
5.10	−5.86	0.07
5.67	−3.05	0.11

algorithm for 1,2 interactions in the different molecules. The exact Coulomb energy between two topological atoms (shown here and used in computing the real errors in Figs. 2–5) is numerically computed using the Kay, Todd, and Silverstone bipolar expansion (KTSBE),[27,28] which has excellent convergence properties and has been successfully implemented in the PROMOLDEN code.[21] This implementation of the KTSBE has no restrictions on its convergence, so any electrostatic interaction between topological atoms (i.e., bonded and nonbonded interactions) can be obtained. However, the QTAIM multipole moments defined by the KTSBE are r-dependent functions. Thus, one cannot obtain expressions similar to Eq. (4) for electrostatic interactions between atoms, where the integrals of Eq. (1) are independently calculated in each atomic basin. As shown in these tables, the $\varepsilon(A,B)=\Lambda_{\mathrm{real}}^{10}(A,B)/|E_{\mathrm{exact}}(A,B)|$ relative errors have reasonable values, appropriate for their use in obtaining the 1,2 interactions. In fact, these errors never exceed an 8% threshold value, and they are generally below 4% for geometries close to equilibrium. There is also a slight increase at very large distances probably due to the residual numerical error present in the KTSBE E_{exact}, on the order of 1 kJ/mol which is close to its total value.

Table IV presents the results obtained by the MMS algorithm for the 1,3 H–H interaction in the H_2O molecule. As shown in this table, the relative errors are negligible in this kind of interaction. Furthermore, these errors are well below those obtained by the algorithm described in Ref. 14.[29]

Table V contains the results for 1,2 interactions and selected 1,3 and 1,4 interactions in glycine. All 1,2 interac-

tions, ranking even in the thousands of kJ/mol, are reproduced within 5% or even less with the only exception of the C1–H9 interaction. This is a particular problem of the C–H interaction: it has a very close range, and its interatomic

TABLE IV. Relative error $[\varepsilon(\mathrm{H,H})=\Lambda_{\mathrm{real}}^{10}(\mathrm{H,H})/|E_{\mathrm{exact}}(\mathrm{H,H})|$ in percentage terms] in the Coulomb energy between the two H topological atoms of the H_2O molecule obtained by the MMS method for the same set of configurations employed in Table III. $d_{\mathrm{H-H}}$ represents the internuclear distance (equilibrium has $d_{\mathrm{H-H}}=2.84a_0$), while $E_{\mathrm{exact}}(\mathrm{H,H})$ is the Coulomb energy obtained by PROMOLDEN.

$d_{\mathrm{H-H}}/a_0$	$E_{\mathrm{exact}}(\mathrm{H,H})$ (kJ mol^{-1})	$\varepsilon(\mathrm{H,H})$
2.61	397.92	<0.01
2.75	351.00	<0.01
2.85	339.87	<0.01
2.89	297.48	<0.01
3.05	250.81	<0.01
3.20	209.38	<0.01
3.36	170.13	0.01
3.69	104.45	<0.01
4.02	62.67	0.01
4.19	48.59	0.02
4.36	37.61	0.05
4.54	29.07	0.08
4.71	22.46	0.09
4.89	17.38	0.08
5.06	13.50	0.04
5.24	10.59	0.02
5.42	8.35	0.05
5.78	5.33	0.22
6.32	2.83	0.52

TABLE V. Relative error $[\varepsilon(A,B)=\Lambda_{real}^{10}(A,B)/|E_{exact}(A,B)|$ in percentage terms] in the Coulomb energy between the A and B topological atoms (as marked in Fig. 6) of the glycine molecule at its equilibrium geometry (see text), obtained by the MMS method. $d=d_{A-B}$ represents the internuclear distance for the several 1,2, 1,3, and 1,4 interactions selected, while $E=E_{exact}(A,B)$ is the Coulomb energy obtained by PROMOLDEN.

A-B	Inter.	d/a_0	E (kJ mol^{-1})	$\varepsilon(A,B)$
C1–C2	1,2	2.847	969.68	0.032
C2–O4	1,2	2.232	−3778.02	1.440
C1–N5	1,2	2.687	−1171.08	0.103
N5–H7	1,2	1.868	−586.88	2.693
C1–H9	1,2	2.060	100.92	9.807
C2–O3	1,2	2.510	−2981.62	0.332
O3–H6	1,2	1.787	−1107.36	4.360
N5–H8	1,2	1.866	−517.17	0.990
C2–N5	1,3	4.546	−1239.39	0.002
C1–O4	1,3	4.529	−599.87	0.013
C1–H7	1,3	3.956	269.98	0.068
N5–H9	1,3	3.984	−8.43	0.312
C2–H9	1,3	3.955	3.44	0.763
C2–H7	1,4	4.716	428.56	<0.001
N5–O4	1,4	5.138	918.37	0.006
O4–H9	1,4	5.788	−0.37	<0.001
H7–H9	1,4	5.368	1.10	<0.001

surface is not quite amenable to the use of sizeable β-spheres, which have to be quite finely tuned. On the other hand, the 1,3 and 1,4 results are of superb quality, showing that the MMS selection algorithm gives an optimum shifting valid for all types of interaction. The results for the interactions in N-methylacetamide included in Table VI are even

TABLE VI. Relative error $[\varepsilon(A,B)=\Lambda_{real}^{10}(A,B)/|E_{exact}(A,B)|$ in percentage terms] in the Coulomb energy between the A and B topological atoms (as marked in Fig. 6) of the N-methylacetamide molecule at its equilibrium geometry (see text), obtained by the MMS method. $d=d_{A-B}$ represents the internuclear distance for the several 1,2, 1,3, and 1,4 interactions selected, while $E=E_{exact}(A,B)$ is the Coulomb energy obtained by PROMOLDEN.

A-B	Inter.	d/a_0	E (kJ mol^{-1})	$\varepsilon(A,B)$
C1–C2	1,2	2.861	269.53	0.302
C2–O3	1,2	2.260	−3586.80	1.243
C2–N4	1,2	2.552	−3043.09	0.297
N4–C5	1,2	2.737	−1257.22	0.152
N4–H6	1,2	1.871	−610.77	1.982
C1–H10	1,2	2.048	84.59	9.714
C1–H11	1,2	2.048	98.38	8.727
C5–H7	1,2	2.046	96.43	7.542
C5–H8	1,2	2.048	115.10	6.227
C1–O3	1,3	4.478	−127.55	0.062
C1–N4	1,3	4.596	−119.80	0.022
O3–N4	1,3	4.219	1361.30	0.008
C2–C5	1,3	4.615	819.68	0.003
C2–H6	1,3	3.834	550.04	<0.001
C5–H6	1,3	3.997	233.51	0.112
C1–H6	1,4	4.821	28.96	0.091
O3–H6	1,4	5.867	−278.64	<0.001
C1–C5	1,4	7.177	34.42	0.076
O3–C5	1,4	5.209	−482.07	<0.001
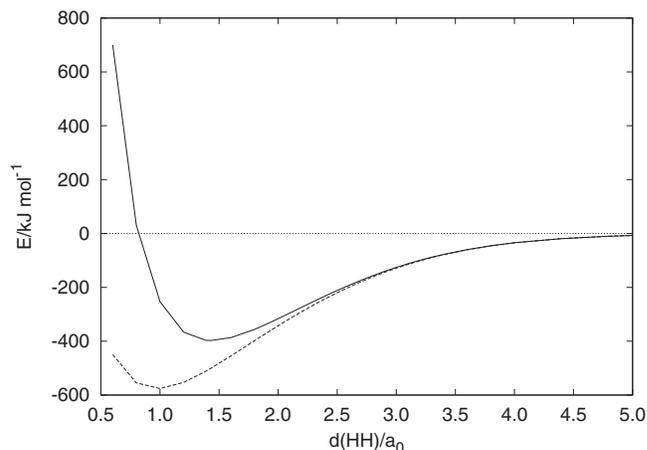
FIG. 7. Binding energy of H_2 as a function of internuclear distance with (full line) and without (dashed line) the interatomic total Coulombic interaction. Notice how the last curve preserves a Morse-like shape.

better for the 1,2 interactions (again with the exception of C–H interactions), and equally superb for the 1,3 and 1,4 interactions. Overall, the MMS selection algorithm shows its usefulness across the whole interaction range: it can give optimum results for 1,3 and 1,4 interactions, and the best results one could obtain in 1,2 interactions.

Returning to the original purpose of this work, as described in the Introduction, an interesting question arises. A robust and potentially future proof force field needs to describe well defined interaction terms. The Coulomb interaction between topological atoms is an important example of such a well defined term. This is why we aim to siphon off the Coulomb term from the total energy. The question is now how this action affects a typical Morse potential that expresses the total interaction between two atoms. Molecular hydrogen serves as a useful prototype system to investigate this. Figure 7 shows the total interaction energy as a function of internuclear distance as well as this energy minus the Coulomb interaction energy. Remarkably, the latter curve preserves the overall Morse shape but has its minimum shifted toward a shorter distance as a result of the repulsive character of the total Coulomb energy. Hence, a Hooke type law will still be valid in describing the remaining energy very near the minimum. If this result is universal then the force field formulae that describe the remaining non-Couloumb interactions barely need to change.

V. CONCLUSIONS

Popelier *et al.*[17] have shown that the atomic partition based on the QTAIM allows for the recovery of intermolecular electrostatic interactions accurately, contrary to the opinion expressed until then in the existing literature. To do this, they used the spherical tensor multipole atomic moments and the Multipole Expansion (ME), achieving convergent expressions for the electrostatic interaction between topological atoms belonging to different molecules. However, the ME prevented the extension of this procedure to topological atoms directly bonded or separated by two or three bonds without additional modifications. The Multipole Shifting (MS) method[14,15] achieved good results for 1,3 and 1,4 interac-

tions, but its previous implementation failed for 1,2 interactions. Therefore, it was necessary to overcome these limitations to obtain force fields based on topological atoms.

We have implemented a new algorithm for the MS method in the RHOLM code. This algorithm displays very good relative and absolute (0.03–0.3 kJ/mol) errors for 1,3 and 1,4 interactions, but only reasonable ones for 1,2 interactions, overcoming the ME problems even in the most difficult 1,2 electrostatic interactions between topological atoms, such as the strong, shortest-range covalent interaction of the H_2 molecule. Thus, the new algorithm overcomes the limitation of the original one.

If one decides to employ this MMS algorithm to improve ME convergence, two tasks must be performed in the near future: (a) adjust the new algorithm for specific cases, and (b) verify the transferability of the shifts between transferable topological atoms. Finally, we would like to suggest that, although devised for the QTAIM multipole moments discussed here, the MMS algorithm within the MS method is in principle capable of improving the convergence of more general ME cases, and hence its usefulness exceeds the present scope.

ACKNOWLEDGMENTS

APPENDIX: THE MULTIPOLAR EXPANSION, REFERENCE FRAMES, COMPLEX AND REAL TERMS

Traditionally, the ME has been defined as

$$
r_{12}^{-1} = |\vec{r}_B - \vec{r}_A + \vec{R}|^{-1}
$$
$$
= \sum_{l_A m_A} \sum_{l_B m_B} \mathcal{R}_{l_A m_A}(\vec{r}_A) \mathcal{T}_{l_A m_A l_B m_B}^G(\vec{R}) \mathcal{R}_{l_B m_B}(\vec{r}_B), \quad (A1)
$$

where $m_A = -l_A, \ldots, l_A$ ($m_B = -l_B, \ldots, l_B$) and $l_A = 0, \ldots, \infty$ ($l_B = 0, \ldots, \infty$), and the *regular spherical harmonics* are defined as

$$
\mathcal{R}_{lm}(\vec{r}) = N_l r^l Y_{lm}(\theta, \phi), \quad (A2)
$$

where $Y_{lm}(\theta, \phi)$ are the (complex) *spherical harmonics* and

$$
N_l = \sqrt{\frac{4\pi}{2l+1}}. \quad (A3)
$$

$\mathcal{T}_{l_A m_A l_B m_B}^G(\vec{R})$ represents an *interaction tensor*, where the superscript G means that the global coordinate system defined in Fig. 1 is used. Introducing the ME in Eq. (1) gives

$$
E_{\text{elec}}(A,B) = \sum_{l_A m_A} \sum_{l_B m_B} \mathcal{Q}_{l_A m_A}^G(\Omega_A) \mathcal{T}_{l_A m_A l_B m_B}^G(\vec{R}) \mathcal{Q}_{l_B m_B}^G(\Omega_B), \quad (A4)
$$

where

$$
\mathcal{Q}_{l_A m_A}^G(\Omega_A) = Z_{\Omega_A} \delta_{l_A,0} - \int_{\Omega_A} \rho(\vec{r}_A + \vec{R}_A) \mathcal{R}_{l_A m_A}(\vec{r}_A) d\vec{r}_A, \quad (A5)
$$

$$
\mathcal{Q}_{l_B m_B}^G(\Omega_B) = Z_{\Omega_B} \delta_{l_B,0} - \int_{\Omega_B} \rho(\vec{r}_B + \vec{R}_B) \mathcal{R}_{l_B m_B}(\vec{r}_B) d\vec{r}_B, \quad (A6)
$$

are the QTAIM total (and complex) *multipole moments*, including the nuclear charge.

The QTAIM multipole moments are generally obtained in local reference systems centered on the topological atoms which are going to be translated and rotated. They have an arbitrary orientation with respect to the global coordinate system. The QTAIM multipole moments in the global system are related to the multipole moments obtained in the local system through:

$$
\mathcal{Q}_{lm}^G(\Omega) = \sum_{m'=-l}^{l} [D_{mm'}^l(\alpha, \beta, \gamma)]^* \mathcal{Q}_{lm'}^L(\Omega), \quad (A7)
$$

where (α, β, γ) are the Euler angles of the rotation that takes the global axes to the local axes and $D_{mm'}^l(\alpha, \beta, \gamma)$ are the elements of the Wigner rotation matrix. Using this relationship, Eq. (A4) becomes

$$
E_{\text{elec}}(A,B) = \sum_{l_A m_A} \sum_{l_B m_B} \mathcal{Q}_{l_A m_A}^L(\Omega_A) \mathcal{T}_{l_A m_A l_B m_B}^L(\vec{R}) \mathcal{Q}_{l_B m_B}^L(\Omega_B), \quad (A8)
$$

where $\mathcal{T}_{l_A m_A l_B m_B}^L(\vec{R})$ is an interaction tensor that takes into account the relative orientation between the global and the two atomic local reference systems. Moreover, it can be obtained from stable recurrence relations.[16]

For the sake of simplicity, it is more convenient to work with real QTAIM multipole moments (which are represented by italics Q); these are related to their complex analogs (represented by calligraphic $\mathcal{Q}$) through the unitary transformation

$$
Q_{lm}(\Omega) = \sum_{m'=-l}^{l} C_{mm'} \mathcal{Q}_{lm'}(\Omega), \quad (A9)
$$

where the $C_{mm'}$ are determined by the rules

(1) $C_{mm'} = 0$ if $|m| \neq |m'|$,
(2) $C_{00} = 1$,
(3) $C_{mm} = (-1)^m / \sqrt{2}$,
(4) $C_{m\bar{m}} = 1/\sqrt{2}$,
(5) $C_{\bar{m}m} = -i(-1)^m / \sqrt{2}$,
(6) $C_{\bar{m}\bar{m}} = i/\sqrt{2}$.

Note that in the last four rules, it is assumed that $m > 0$. Additionally, the last three rules use $\bar{m} = -m$ to simplify the

notation. Moreover, analogous expressions allow to define the real regular harmonics $R_{lm}(\vec{r})$ in terms of the complex ones $\mathcal{R}_{lm}(\vec{r})$. These definitions have been used in the final expression for the Coulomb energy between topological atoms, Eq. (4), where we have simplified $T_{l_A m_A l_B m_B}(\vec{R})$ instead of $T^L_{l_A m_A l_B m_B}(\vec{R})$, which is a real (notice again the change from $\mathcal{T}$ to T) local frame interaction tensor that can also be obtained from stable recurrence relations.[16]

Another important point to be noticed is the original definition of the shifts in terms of complex harmonics and their translation into real harmonics. Shifting again by $\vec{c}$ the origin of the local coordinate system associated with a topological atom, the (complex) shifted multipole moments $\mathcal{Q}^{\vec{c}}_{lm}(\Omega)$ can be obtained from

$$\mathcal{Q}^{\vec{c}}_{lm}(\Omega) = \sum_{l'm'} \mathcal{Q}^{\vec{0}}_{l'm'}(\Omega) \sqrt{\binom{l+m}{l'+m'}\binom{l-m}{l'-m'}} \mathcal{R}_{l-l'm-m'}(\vec{c}),$$

(A10)

where $\mathcal{Q}^{\vec{0}}_{lm}(\Omega)$ are the original multipole moments, $l' = 0, \ldots, l$, $m' \leq |l'|$, and $\mathcal{R}_{lm}(\vec{c})$ are the (complex) regular spherical harmonics defined by Eq. (A2). This is analogous to the process described in Eq. (7), and hence the real MS matrix can be computed as

$$W_{l'm',lm}(\vec{c}) = \sum_{m_1=-l}^{l} \sum_{m_2=-l'}^{l'} \sum_{m_3=l'-l}^{l-l'} C_{mm_1} C^*_{m'm_2} C^*_{m_3(m_1-m_2)}$$
$$\times \sqrt{\binom{l+m_1}{l'+m_2}\binom{l-m_1}{l'-m_2}} R_{l-l'm_3}(\vec{c}) \quad \text{(A11)}$$

so that $R_{lm}(\vec{c})$ are the real regular spherical harmonics. Notice that, although it appears to involve a triple sum, the properties of the $C_{mm'}$ coefficients are such that, at most, two terms survive among those with $m_1 = \pm m$, $m_2 = \pm m'$, and $m_3 = \pm(m+m')$, $\pm(m-m')$, and they are always real.

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