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The electrostatic potential generated by topological atoms: a continuous multipole method leading to larger convergence regions

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Abstract

The electrostatic potential generated by an atom in a molecule can be conveniently expressed by traditional multipole expansions. The disadvantage of such expansions is that they introduce a divergence sphere within which the expansion diverges. Because of their finite size, atoms defined according to quantum chemical topology (QCT) yield a small divergence sphere. However the introduction of an alternative continuous multipole expansion reduces the divergence region even further. The new method allows the electrostatic potential to be evaluated accurately at short-range, which is illustrated for a pair of simple molecules.

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1. Introduction

The molecular electrostatic potential (MEP), a physical observable proposed [1] a few decades ago, has ever since been recognised as a most informative quantity [2–4], as witnessed by its wide range of applications. Just to name a few examples, molecular electrostatics operated as a tool in the interpretation of regioselectivity [5] and reactivity [6] of small molecules, served as an indicator for evolutionary conservativeness near enzyme active sites [7], featured in zeolite catalysis [8],

predicted adsorption sites on crystalline oxide surfaces [9], acted as the basis for force-field parametrisation [10] and hydration models for proteins [11] and nuclei acids [12], was used as a vehicle in host–guest complementarity in cyclodextrins [13], and was applied in structure–activity relationships of the H₂ receptor antagonists [14] and in a toxicity study of dibenzo-*p*-dioxins [15].

Such enormous range of applications warranted efficient implementation of the MEP within the LCAO-MO-SCF formalism, which was eventually achieved [16] after a momentous development of fast techniques for Gaussian integral evaluation [17]. Since the availability of such algorithms the electrostatic potential can be routinely computed by standard ab initio packages, such as GAUS-

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SIAN, on large grids in a very small fraction of the time required to solve the HF SCF equations. However, since the MEP is defined as a three-dimensional integral it has, in principle, to be recalculated at every point at which the MEP needs to be known. It is possible to avoid this recalculation by expressing the MEP as a multipole expansion. The multipole moments are then computed once and for all, which constitutes the most expensive part of the MEP evaluation. Indeed, the potential itself can be rapidly obtained at any given point from the (pre-computed) multipole moments via a polynomial expansion. The price paid for this substantial speed-up is slow convergence of the expansion or even a formal lack of convergence. One can prove that each expansion has a so-called *divergence sphere*¹ centred at its expansion center. A multipole expansion evaluated at a point within this sphere will diverge. This Letter proposes an alternative to classical multipole expansions, whether Cartesian or via spherical harmonics, that is able to converge *within* the convergence sphere.

2. Theoretical background

It is well known that a multipole expansion, centred at a *single* site, of a MEP converges poorly [18] because the convergence sphere has a large radius. The convergence behaviour improves dramatically if the expansion is distributed over multiples sites, which are conveniently chosen as the nuclear positions. There are several ways of distributing the expansion but we focus on the route offered by quantum chemical topology (QCT) [19–22]. QCT defines atoms (referred to as basins Ω) as volumes with sharp boundaries that adopt a shape dictated by the total molecular electron density. The MEP, denoted by $V(\mathbf{r})$, is then simply a sum of the atomic electrostatic potentials (AEP) of all atoms Ω_A in the molecules, or:

$$V(\mathbf{r}) = \sum_A V_A(\mathbf{r}) = \sum_A \left[\frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int_{\Omega_A} d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right], \quad (1)$$

where Z_A is the nuclear charge of atom Ω_A located at position \mathbf{R}_A , \mathbf{r}' are the three coordinates describing the molecular electron density ρ and \mathbf{r} are the three coordinates describing the MEP. Introducing $C_{lm}(\theta, \varphi)$ as (complex) renormalised spherical harmonics and using Taylor's theorem we can expand $V_A(\mathbf{r})$ as follows:

$$V_A(\mathbf{r}) = \sum_{l=0}^{\infty} r^{-l-1} C_{l0}(\theta, \varphi) Q_{l0}(\Omega_A) + \sum_{l=0}^{\infty} r^{-l-1} \sum_{m=1}^l C_{lmc}(\theta, \varphi) Q_{lmc}(\Omega_A) + \sum_{l=0}^{\infty} r^{-l-1} \sum_{m=1}^l C_{lms}(\theta, \varphi) Q_{lms}(\Omega_A), \quad (2)$$

where the index l symbolises the *rank* of the multipole expansion and $Q_{l0}(\Omega_A)$, $Q_{lmc}(\Omega_A)$ and $Q_{lms}(\Omega_A)$ represent the real QCT multipole moments [23] obtained via integration over the atomic basin Ω_A :

$$Q_{l0} = \int_{\Omega_A} d\mathbf{r}' \rho_{\text{tot}}(\mathbf{r}') r'^l C_{l0}(\theta', \varphi'),$$

$$Q_{lmc} = \int_{\Omega_A} d\mathbf{r}' \rho_{\text{tot}}(\mathbf{r}') r'^l C_{lmc}(\theta', \varphi'), \quad (3)$$

$$Q_{lms} = \int_{\Omega_A} d\mathbf{r}' \rho_{\text{tot}}(\mathbf{r}') r'^l C_{lms}(\theta', \varphi'),$$

where $\rho_{\text{tot}}(\mathbf{r}') = \sum_A Z_A \delta(\mathbf{r}' - \mathbf{R}_A) - \rho(\mathbf{r}')$. The Taylor expansion is invoked to separate (or factorise) $1/|\mathbf{r} - \mathbf{r}'|$ into quantities in \mathbf{r}' space (i.e., the multipole moment integrands) and quantities in \mathbf{r} space (the distance dependence r^{-l-1} and the angular dependence expressed as $C_{lm}(\theta, \varphi)$).

We proved before [24] that, for a variety of atoms, a QCT multipole expansion converges to within 0.1 kJ/mol from the exact atomic electrostatic potential at rank four (i.e., $l = 4$, hexadecapole moment). Triggered by previously made incorrect statements [25–27] we explained the reason for this favourable convergence in a subsequent contribution [28]. This formal convergence

¹ In line with the complementary interpretation of a pessimist and an optimist of a half-filled glass this sphere is sometimes also called the convergence sphere.

was guaranteed because the potential was always evaluated outside the divergence sphere. Topological atoms benefit from being finite, which renders the radius of their divergence sphere also finite. Alternative pictures of atoms propose an infinite extension of the atom, and hence introduces an infinite radius of convergence. This means that for such non-topological atoms the electrostatic potential they generate can never be expressed by a formally convergent Taylor expansion.

Monitoring [29] the convergence behaviour of atom–atom Coulomb interaction in supermolecules is vital to make progress in designing a topological force field. Even by just relying on high-rank electrostatic interactions we can say that QCT atoms perform well in predicting geometries and energies of small van der Waals complexes [30], DNA base pairs [31] and water clusters [32]. However, if needed, convergence can be accelerated [33] by introducing extra non-nuclear sites without altering the topological partitioning of the electron density and hence the numerical values of the multipole moments.

The existence of a divergent region of the Taylor multipole expansion is ultimately due to the convergence condition $|x| < 1$ in the well-known expansion of $1/(1-x) = 1 + x + x^2 + x^3 + \dots$. This fundamental convergence issue can be circumvented by abandoning the Taylor expansion in favour of an integral representation, inspired by the Casimir–Polder [34] identity, given in the following equation:

$$\frac{1}{A+B} = \frac{2}{\pi} \int_0^\infty dv \frac{AB}{(A^2 + v^2)(B^2 + v^2)}, \quad A, B > 0, \quad (4)$$

where v is a frequency. This identity is used in a different context to ours, namely in order to write dispersion coefficients as a function of independently evaluated polarisabilities of system A and B at imaginary frequencies. However, the main feature of interest of Eq. (4) is the fact that this integral representation of $1/(A+B)$ factorises A and B . For our purpose we have to factorise a different expression, i.e., $1/|\mathbf{r} - \mathbf{r}'| = [r^2 + r'^2 - 2rr' \cos \gamma]^{-1/2}$. This leads to the integral representation in Eq. (5),

after calling upon a known Laplace transform [35] and some adept algebra:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \int_0^\infty dt e^{-rt} \exp(r't \cos \gamma) J_0(r't \sin \gamma) \quad \text{if } r > r' \cos \gamma, \quad (5)$$

where t is a mere parameter, $J_0(z)$ is the Bessel function of the first kind of (integer) order zero, and γ is again the angle between \mathbf{r} and \mathbf{r}' . Substitution of Eq. (5) into Eq. (1) yields

$$\begin{aligned} V(\mathbf{r}, \Omega_A)_{\text{elec}} &= \int_0^T dt \exp(-rt) \int_{\Omega_A} dr' \rho(r') \\ &\quad \times \exp(r't \cos \gamma) J_0(r't \sin \gamma) \\ &= \int_0^T dt e^{-rt} Q(t) \end{aligned} \quad (6)$$

for the electronic part of the electrostatic potential generated by atom Ω_A . Note that the convergence condition, $r > r' \cos \gamma$, reduces to the stricter condition, $r > r'$, in the worse possible scenario of $\cos \gamma$ being unity. We also note that the infinite boundary in Eq. (5) has been replaced by a finite parameter T in Eq. (6), thereby enabling the integral over \mathbf{r} to be evaluated via numerical quadrature, with typically Gauss–Legendre weights w_i

$$V(\mathbf{r}, \Omega_A)_{\text{elec}} = \sum_{i=1}^{n_{\text{quad}}} w_i \exp(-rt_i) Q(t_i). \quad (7)$$

We call the quantities $Q(t)$ *Bessel moments*. In principle $Q(t)$ is a continuous function but since the integral over the variable t is carried out via a quadrature the Bessel moments are represented by a string of n_{quad} components. Unfortunately this set of components is different for every given position vector \mathbf{r} . However they remain invariant for all points lying on a line marked by this position vector \mathbf{r} .

3. Results and discussion

In Fig. 1 we compare the exact electrostatic potential generated by a nitrogen atom in N_2 and the potential obtained by a multipole expansion of varying rank l . The point on the molecular axis at which the potential is evaluated is 2 a.u. away from

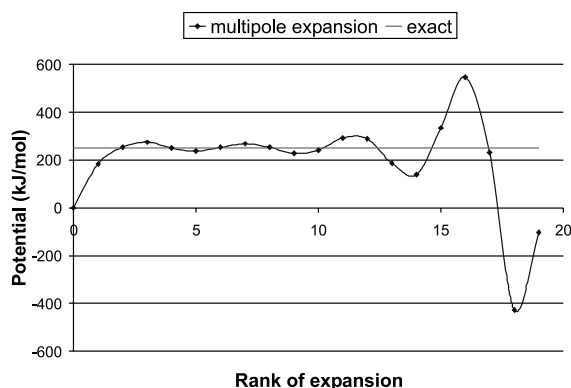


Fig. 1. Comparison of the exact electrostatic potential generated by a nitrogen atom in N_2 and the potential obtained by a multipole expansion of variable rank.

the midpoint (i.e., origin) of N_2 , at the other side of the potential-generating atom. Although a plateau of pseudo-convergence is reached between rank 3 and 11, severe convergence problems arise beyond rank 15. Oscillations already present in the pseudo-convergence plateau amplify to such an extent that any truncation of the multipole expansion leads to useless results. However, we should point out that at the scale of Fig. 1 the 'minor' oscillations in the plateau also give unacceptably large errors.

Next we illustrate the dramatic improvement in convergence that the newly developed Bessel moment representation offers. Fig. 2 shows this improvement along the whole of the molecular axis rather than in one point. The nitrogen atom generating the potential is bounded by an interatomic surface at the molecular origin ($z = 0$ a.u.) on the left-hand side, and by the $\rho = 5 \times 10^{-6}$ a.u. contour surface (at $z = 6.5$ a.u.) at the right-hand side. Convergence behaviour has been investigated for three values of the parameter T , fixing the number of quadrature points, n_{quad} , to 100. This high value of n_{quad} eliminates effects due to insufficient quadrature density. We return to this issue in Fig. 3. It is clear from Fig. 2 that inside atomic basin the potential diverges very quickly, while outside the atomic basin superb convergence can be obtained, even with a moderately low T value of 5. When $T = 50$ minimal deviations of 10^{-5} kJ/mol can be achieved right up to the boundary of the atom. The most important

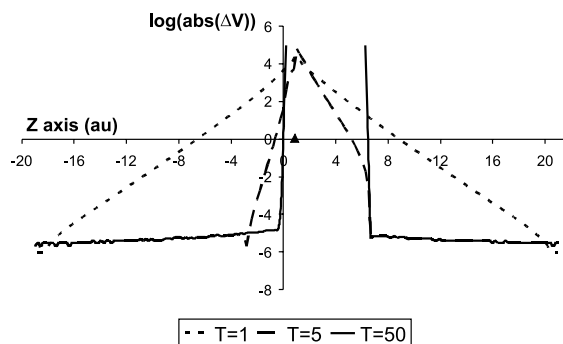


Fig. 2. The absolute difference (in kJ/mol but on a log scale) between the exact electrostatic potential generated by a nitrogen atom in N_2 and that obtained by a Bessel moment representation along the molecular axis. The parameter T is set to 1, 5 or 50. The nuclear position of the nitrogen atom (generating the potential) is marked by a small triangle at $z = 1.0$ a.u. The $T = 50$ curve is arbitrarily truncated at 10^5 kJ/mol.

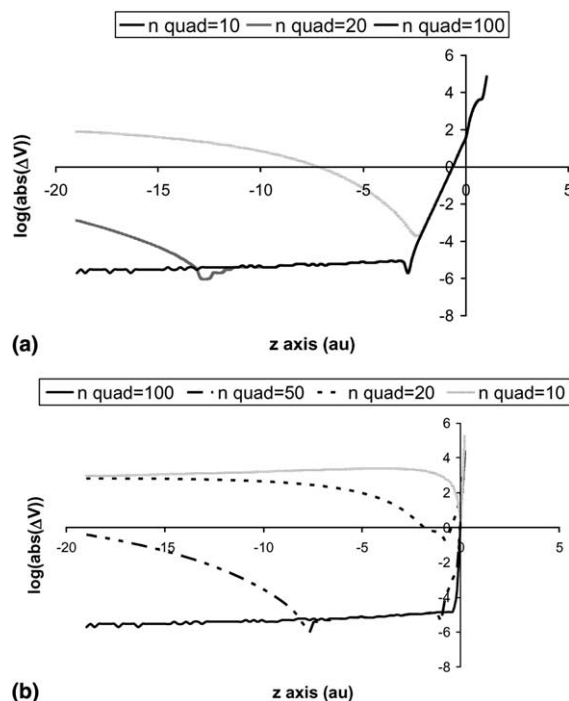


Fig. 3. The difference between the exact electrostatic potential generated by a nitrogen atom in N_2 and one obtained by a Bessel moment representation along the molecular axis as a function of the number of quadrature points n_{quad} for (a) $T = 5$ and (b) $T = 50$.

conclusion is that the potential can be evaluated with great precision in inside the divergence sphere. This will be vividly illustrated later (Figs. 4 and 5).

Fig. 3 focuses on the question on how many quadrature points are required for a given T value. If $T = 5$ (Fig. 3a) then 20 quadrature points suffice to obtain virtually perfect agreement with the exact electrostatic potential. If T is set to 50 (Fig. 3b) then 20 points is not sufficient, but about 70 (not shown) would guarantee negligible errors up about 15 a.u. away from the interatomic surface. In summary we state that ensuring short-range convergence is achieved by increasing the parameter T , but at the cost of increasing the number of quadrature points. The latter is necessary to make certain that the Bessel moment representation remains trustworthy at long-range as well.

In Fig. 4 we take up again the point made before concerning the convergence of the Bessel moment representation *within* the divergence sphere. Fig. 4 shows the difference between the exact atomic potential and the one by Bessel moment representation ($n_{\text{quad}} = 20$, $T = 5$) in a plane containing the molecular axis of N_2 . We deliberately set T to a moderate value in order to study the convergence behaviour with a small number of Bessel moments. Also, we know that if T were set to 50 the convergence would be excellent to right

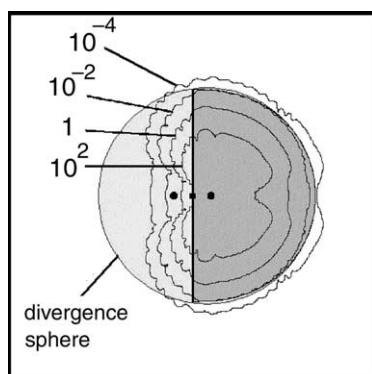


Fig. 4. A contour plot (kJ/mol) of the difference between the exact potential generated by the nitrogen atom on the right (solid circle in dark shaded region) in N_2 and the potential obtained by Bessel moments in a plane containing the molecular axis. The divergence sphere is marked by a light shaded disk, partially overlapping with a dark shaded region representing the atomic basin of the nitrogen atom.

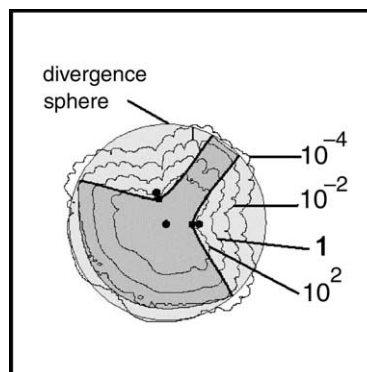


Fig. 5. A contour plot (kJ/mol) of the difference between exact potential generated by oxygen in water and the potential obtained by Bessel moments in the molecular plane. Shading code is the same as in Fig. 4.

up to the atom's boundary. It is clear that reasonable to excellent convergence can be obtained well within the confines of the divergence sphere. Fig. 5 confirms the success of the Bessel representation, now in oxygen in water.

Further research is currently carried out to ensure convergent expansions, at short-range, between the charge distributions of two interacting topological atoms.

4. Conclusion

The replacement of the classical multipole expansion by a Bessel moment representation involving Bessel functions enables the virtually exact computation of the atomic electrostatic potential at short-range. With a reasonable number of pre-computed 'continuous moments' it is now possible to predict the electrostatic potential far within the divergence sphere, right up to the boundary of the topological atom. The newly proposed procedure guarantees formal convergence of an expanded potential generated by a finite rigorously defined atom.

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