

GR/M18119 : Rigorous chemical interpretation of atomic contributions in accurate intermolecular potentials.

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1. Background – context

In this project we combined two areas that have matured independently. One is the area of accurate intermolecular potentials¹ and the other is quantum chemical topology^{2,3}, which is a rigorous method for partitioning molecules into atoms. Accurate interaction potentials need to include anisotropy and that this is best achieved by distributing the interaction over many sites in the molecule. Each site is typically but not necessarily a nuclear position and the anisotropy is compactly expressed in terms of the spherical tensor formalism. Currently our laboratory is internationally leading in the systematic study of quantum topological intermolecular potentials, an area that we believe will become increasingly important, especially in view of the advantages it offers for at short-range, ideas that are subject to a newly submitted proposal.

2. Key Advances

[1] "Atomic partitioning of Molecular Electrostatic Potentials",

D.Kosov and P.L.A. Popelier, *J.Phys.Chem.A*, **104**, 7339-7345 (2000).

First we focused on the electrostatic component of intermolecular interaction given its importance in biological systems. An understanding of the *convergence* of the electrostatic multipole expansion was vital to make solid progress. The electrostatic potential was chosen as a starting point because it is a special case of electrostatic interaction, where one of the interacting partners is just a proton. In this work we have computed for the first time the exact electrostatic potential generated by an AIM atomic fragment, called the AEP. The premise that the multipole expansion associated with bounded fragments in real space, such as AIM atoms, has poor convergence proves to be wrong. In summary, this study demonstrates that we do not need an excessively large number of multipoles to reproduce the exact *ab initio* molecular electrostatic potentials within the AIM theory. This work makes clear that the atomic population (or rank-zero multipole moment) is just one term of the expansion of a physically observable quantity, namely the electrostatic potential. Hence the AIM populations cannot be judged on their reproduction of the electrostatic potential. Instead, they must be seen in the context of a multipole expansion of the AEP. Finally we computed the exact AEP and its value obtained via multipole expansion for molecules including molecular nitrogen, water, ammonia, imidazole, alanine and valine.

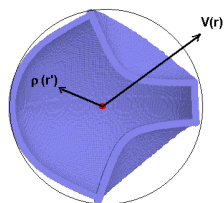


Fig.1 Since topological atoms are finite it is possible to monitor their **formal** convergence.

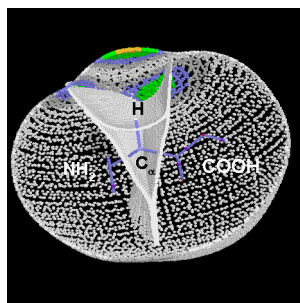


Fig.2 The deviations in the exact AEP and the AEP obtained from the multipole moments up to the octupole ($\ell=3$) for the C_c atoms in alanine. The part of the picture in front of the plotting plane is deleted in order to show the interior of the object. The largest deviations occur near the cusp-like edges of the atom and the region of closest proximity. Color code (in kJ/mol): white<0.1<grey< 0.2< blue<0.3< green < 0.4 < yellow<0.5.

[2] "Convergence of the Multipole Expansion for Electrostatic Potentials of finite Topological

Atoms", D.Kosov, P.L.A. Popelier, *J. Chem. Phys.*, **113**, 3969-3974 (2000).

We then tried to understand the cause of the excellent convergence. How can it be compatible with the admittedly highly non-spherical shape of the topological atoms? The answer lies in the exponentially decaying electron density. The convergence behaviour of the actual electron density inside an atomic basin is due to its decay rather than to the atom's shape. Indeed when the atom is filled with a uniform density the convergence worsens often by more than an order of magnitude. AIM multipole moments are adequate for the modeling of both inter- and in principle intramolecular interactions in force field (non-bonded terms). In summary we confirm that finite atomic shapes have undesirable convergence properties but that this phenomenon is in practice not relevant due to the profile of the actual electron density inside.

[3] "Atom-atom Partitioning of molecular Coulomb Energy", P.L.A. Popelier and D.S. Kosov,

J. Chem. Phys., **114**, 6539-6547 (2001).

Then we focused on the Coulomb energy between atoms in *supermolecules*. We proposed an atom-atom partitioning of the Coulomb interaction, denoted by E_{AB}^{coul} , based on the topology of the electron density. Our atom-atom Coulomb interaction energy should *not* be confused with the electrostatic component of the intermolecular interaction defined within the perturbation approach. Instead we introduce an atom-atom Coulomb

interaction energy that uses the total molecular or supermolecular electron density as its input. Atom-atom contributions to the molecular intra- and intermolecular Coulomb energy are computed exactly, i.e. via a double integration over atomic basins, and by means of the spherical tensor multipole expansion, up to rank $L = \ell_A + \ell_B + 1 = 5$. The convergence of the multipole expansion is able to reproduce the exact interaction energy with an accuracy of 0.1–2.3 kJ/mol at $L=5$ for atom pairs, each atom belonging to a different molecule constituting a van der Waals complex, and for non-bonded atom-atom interactions in single molecules. The atom-atom contributions do not show a significant basis set dependence (3%) provided electron correlation and polarisation basis functions are included. The proposed atom-atom Coulomb interaction energy can be used both with post-Hartree-Fock wave functions, without recourse to the Hilbert space of basis functions, and experimental charge densities in principle. We provide computational details of this method and apply it to $(C_2H_2)_2$; $(HF)_2$; $(H_2O)_2$; butane; 1,3,5-hexatriene; acrolein and uracanic acid, thereby covering a cross section of hydrogen bonds, and covalent bonds with and without charge transfer. The Coulomb interaction energy between two molecules in a van der Waals complex can be computed by summing the additive atom-atom contributions between the molecules. Our method is able to extract from the supermolecule wavefunction an estimate of the molecular interaction energy in a complex, without invoking the reference state of free non-interacting molecules. Provided quadrupole-quadrupole interactions are included the convergence is adequate between atoms belonging to different interacting molecules. Within a single molecule the convergence is reasonable except for bonded neighbours.

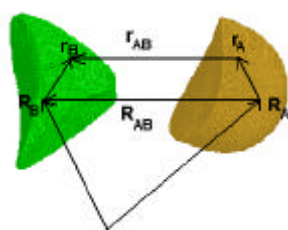


Fig.3 Coordinate system used in the description of the Coulomb interaction between two atomic basins Ω_A and Ω_B .

[4] "A Fast Algorithm to compute Atomic Charges using the Topology of the Electron Density",
P.L.A. Popelier, *Theor. Chem. Acts*, **105**, 393-399 (2001).

A new algorithm is proposed that calculates AIM atomic charges using surface integrals only. The divergence theorem expresses the atomic charge as the flux of the total molecular electric field through the boundary of the atomic basin. Since the molecular electric field can be calculated analytically by very fast algorithms and since the surface integration requires one to two orders of magnitude less quadrature points, an atomic charge can now be obtained within several minutes rather than hours on a typical PC or workstation for reasonably sized systems. This approach also contributes to the robustness and accuracy of atomic integration because it does not suffer from the cusp problem or the multiple intersection problem. Beside a reduction in the number of quadrature points the new algorithm should provide a more straightforward route to obtain atomic charges.

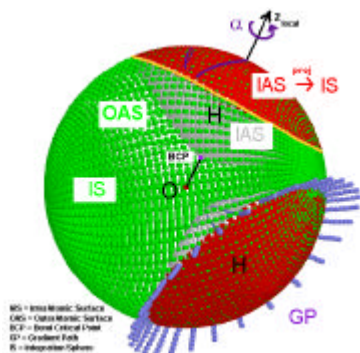


Fig.4 The atomic charge of oxygen in water via surface integrals. The oxygen atom is bounded by two Interatomic Surfaces (IAS, grey) and the Outeratomic Surface (OAS, pure green). The Integration Sphere (IS, green and green/red) has a radius of 5.4 a.u. determined by a $\rho=10^{-7}$ a.u. cut-off. Each IAS is projected onto the IS (red). The flux through this part of the IS is subtracted from the flux through the whole IS. The boundary of one IAS is shown in amber. It consists of the intersection of the IAS with the IS, and is also the boundary of the IS-projected IAS patch (red). The z -axis of the local axes system describing this patch is shown, together with its independent surface parameters α (angle) and ℓ (path length on IS).

[5] "Distributed Polarisability of the Water Dimer : Charge Transfer along the Hydrogen Bond"
M. in het Panhuis, P.Popelier, R.W. Munn and J.G.Angyán, *J Chem.Phys.*, **114**, 7951-7961(2001).

The topological partitioning of electronic properties (TPEP) approach at Hartree-Fock level is used to investigate charge transfer response in a water dimer. Distributed polarisability components are employed to calculate the change in electron density under external fields. It was found that charge flow between the water monomers is most significant along the direction of the hydrogen bond. The molecular polarisability of the molecules in the dimer is reduced owing to formation of the hydrogen bond. Calculation of distributed polarisability is desirable for practical applications. For example, Karlström has calculated distributed polarisabilities using the uncoupled Hartree-Fock method and used them to devise the polarisable water potential NEMO. Calculation of distributed polarisability is also desirable for conceptual understanding of how the electron

distribution responds to the external influence of electric fields, affording insights that go beyond those available from analysis of the ground-state electron distribution. The calculation of the atomic and molecular polarisability of the dimer (and by implication of other sets of molecules) also proves to be a powerful tool for providing insight into the effect of interaction on the electron density and its response to electric fields. In particular, the separate molecular polarisabilities in the dimer can be calculated from the distributed components of the molecular polarisability of the dimer, which is not possible using standard *ab initio* packages. Various extensions of the present work can be envisaged. We have already calculated non-linear response in the form of distributed hyperpolarisabilities for urea, which prove to have a significant effect on the calculated non-linear response of the crystal. In this respect there is a need to extend the method to frequency-dependent response.

[6] [“The Convergence of the Electrostatic Interaction based on topological Atoms”](#)

[P.L.A. Popelier, L. Joubert and D.S.Kosov, *J.Phys.Chem.A.*, **105**, 8254-8261 \(2001\).](#)

Here we focus on a topological intermolecular potential without the perturbation approach. We are interested in a *careful* test of this proposal in the context of the successful Buckingham-Fowler model, using improved algorithms. Particular attention was paid to the convergence of both the energy and the geometry of a set of van der Waals complexes, with respect to the rank L of the multipole expansion. For the first time this convergence behaviour has been contrasted with exact values, obtained without multipole expansion, via 6D integration over two atomic basins. We find that, although the AIM results converge more slowly than the DMA results, excellent agreement is obtained between the two methods at high rank ($L=6$), both for geometry as well as intermolecular electrostatic interaction energy. This is the first time that a direct, complete and explicit comparison between AIM and Distributed Multipole Analysis (DMA) has been made. Contrary to views expressed before in the literature this work opens an avenue to introduce the topological approach in the construction of an accurate intermolecular force field. It is here that the high degree of transferability of the functional groups defined by AIM will be extremely useful.

[7] [“Distributed Response Analysis of Conductive Behaviour in Single Molecules”, M.in het Panhuis,](#)

[R.W.Munn, P.L.A. Popelier, J.N.Coleman, B.Foley and W.J.Blau, *Proceedings of the National Academy of Sciences \(USA\)*, **99**, 6514-6517 \(2002\).](#)

The *ab initio* computational approach of distributed response analysis is used to quantify how electrons move across conjugated molecules in an electric field, in analogy to conduction. The method promises to be valuable for characterizing the conductive behaviour of single molecules in electronic devices. We have shown that the *ab initio* computational technique of distributed response analysis can, in principle, be used to quantify the conduction behaviour of a single molecule acting as a switching region in a nanoscale field effect transistor design. In an analogy to conduction, it is shown that once an electron is introduced on one side of the molecule, it has the ability to move across the molecule. The calculations demonstrate in detail how charge flow occurs in *para*-nitroaniline(pNA), *meta*-nitroaniline(mNA) and fluorobenzene(FB). On the basis of our calculations, we predict that pNA has a more efficient conductive behaviour than mNA and FB. We established the empirical result that 1 unit of molecular total conduction number(CN) is approximately equal to 1/6 a.u. of (static) molecular polarisability. This result has been used to estimate the conductive behaviour of similar conjugated molecules by using the average molecular polarisability. It was predicted that 4,4'-biphenyldithiol has a CN of 25.6 and therefore should have the most effective conduction behaviour of the molecules investigated. We are currently investigating how accurately our CN predicts the results of experiments on molecular conductance such as those reported by Schön⁴. We envisage that distributed response analysis could then be used to identify superior molecular switches from molecular CN before the molecules are experimentally investigated.

[8] [“The Elusive Atomic Rationale for DNA Base Pair Stability”, P.L.A.Popelier and L.Joubert,](#)

[J.Am.Chem.Soc., **124**, 8725-8729 \(2002\).](#)

In the area of molecular recognition and supramolecular chemistry researchers are in need of rules that predict the stability of a complex, beyond counting the number of hydrogen bonds. Jorgensen provided such a rule in 1990⁵, known as the secondary interaction hypothesis. This rule focuses on “cross-contacts” between frontier atoms and penalises “donor-donor” or “acceptor-acceptor” interactions on the basis of simple electrostatic point charges. We investigated if this secondary interaction hypothesis could be supported by AIM. After a careful and systematic analysis of 27 natural base pairs the answer proved to be negative.

We questioned the existence of subsets of atoms in two different bases forming a complex whose interaction energy parallels the *total* interaction energy. After a series of calculations designed to find support for the secondary interaction hypothesis we fail to find a physical basis for it in quantum chemistry when applied across molecular aggregates consisting of a very different number and type of atoms. Only in comparisons between highly similar chemical environments could the secondary interaction be invoked for the right reason⁶. However, in general simple rules to rationalise the pattern of energetic stability across naturally occurring base pairs in terms of subsets of atoms remains elusive. This work cautions against unjustified use of secondary interactions, which may lead to the same quandary that the hydrogen bond once introduced by its over-generalised use.

[9] [“Improved Convergence of the Atoms in Molecules multipole expansion of electrostatic interaction.”](#) L.Joubert and P.L.A.Popelier, *Molec.Phys.*, in press (2002).

In this paper we continue our study of the convergence properties of multipolar expansions of topological atoms. To assess the quality and the speed of this convergence we made systematic comparisons with an accurate and well-known anisotropic electrostatic model called DMA. A set of small van der Waals systems was investigated as well as a set of much larger DNA base pairs. Based on a clearly made distinction between partitioning and distribution it is shown for the first time how topological multipole moments can be distributed to off-nuclear sites. The introduction of extra sites improves the convergence of AIM without detracting from the way it partitions molecular information among atoms. In the AIM context the addition of extra sites is more beneficial to the convergence of the electrostatic interaction energy of *small* systems. However for large systems excellent convergence is found with AIM *without* the introduction of extra sites. This advantage further encourages the development of a topological intermolecular force field.

[10] [“DNA base pairing : towards a topological intermolecular force field for biological systems”](#) L.Joubert and P.L.A.Popelier, *PhysChemChemPhys*, **4**, 4353-4359 (2002).

Following the success of the topological electrostatic model on van der Waals complexes we assessed its performance on the important biological problem of DNA base-pairing. Geometries and intermolecular interaction energies predicted by AIM supplemented with a hard-sphere or the Lennard-Jones potential have been compared with other methods in two stages. First with supermolecular HF, MP2 and B3LYP calculations at 6-31G(d,p) level and then with other potentials such as MK, NPA and DMA at 6-311+G(2d,p) level. The geometries for all 27 base pairs predicted by AIM and B3LYP differ by 0.08\AA and 3.5° for 55 selected intermolecular geometrical parameters, while the energies show an average discrepancy of 6 kJ/mol. The B3LYP functional proves to be a reliable alternative to MP2 since their energies are in excellent agreement (~ 1 kJ/mol). Globally the AIM interaction energy curve follows the same pattern as that of MK, NPA and DMA. The MK model systematically underestimates the interaction energy and NPA shows undesirable fluctuations. Surprisingly the convergence of the AIM multipole expansion is somewhat better than that of DMA, but both have similar basis set dependence. A test of AIM on a DNA tetrad suggests that it is able to predict geometries of more complex nucleic acid oligomers than base pairs.

Our work clearly demonstrates that the electrostatic description dominates DNA base pair patterns but more work is needed to predict the three most stable base pairs better. A current inadequacy of our AIM potential is that it is combined with empirical potentials, and hence not completely derived from *ab initio* calculations. Ultimately the AIM potential should draw all its information from *ab initio* calculations on monomers. Given the success of topological distributed polarisabilities induction energies could be included next, while work on the modeling of exchange-repulsion is warranted.

[11] [“A Quantum Topological Potential for the Water Solvation of Serine and Tyrosine”](#) P.L.A.Popelier and M.Devereux, submitted.

Building on the success of the topological electrostatic model in connection with small van der Waals complexes and DNA base pairs we now focused on “peptide hydration”. First we worked on pure water clusters (up to the nonamer) and compared our results with B3LYP/6-311+G(2d,p) supermolecular calculations and the popular TIP4P and TIP5P potentials. We report the following selection of intermediate results: (i) the interaction ranks $L=3,5$ perform better than $L=4,6$, possibly due to asymmetry of interaction description in the latter (i.e. $L=4$ contains dipole-quadrupole and quadrupole-dipole, not quadrupole-quadrupole. So although it includes dipoles and quadrupoles of both interaction partners, it never includes them together.). (ii) Lower rank representations are more successful in geometry prediction for the larger water clusters. (iii) the amino acids perturb the structure of the water clusters very little, compared to the pure water clusters (see Fig.5). (iv) TIP4P good for interatomic distances, often better than $L=6$ for geometries but $L=5$ better overall.

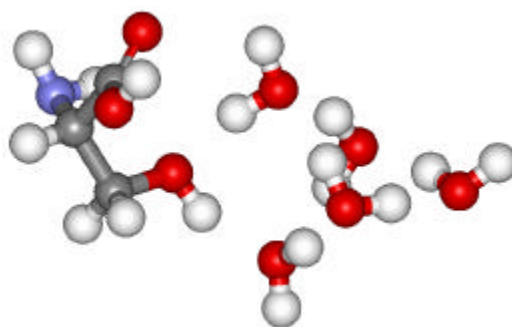
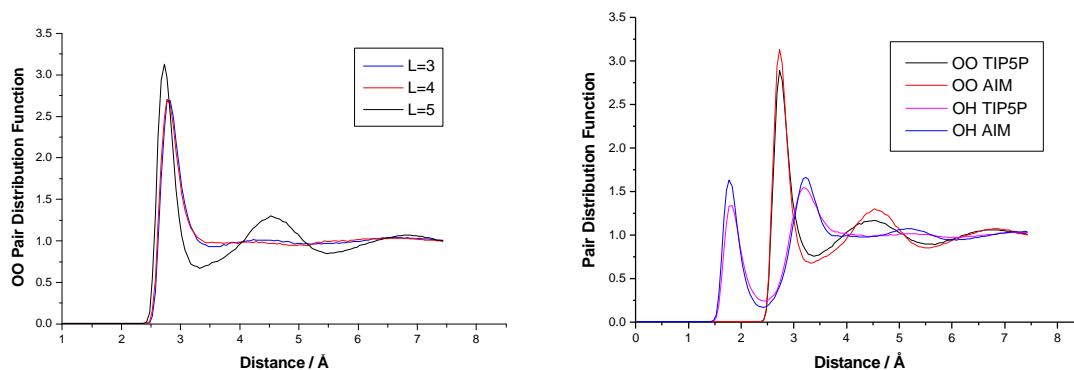


Fig.5 A ball-and-stick representation of a low-energy minimum of serine with five water molecules.

[12] “Molecular Dynamics Simulation of Water with a Quantum Topological Potential including high rank multipole interactions.” S.Liem, M.Leslie and P.L.A.Popelier, submitted.

Molecular Dynamics (MD) simulations of liquid H₂O and HF were carried out with the electrostatic interaction represented up to L=5, and repulsion and dispersion via a LJ potential. The purpose of this extra study is to explore how very high multipole moments perform in simulations. The Ewald summation technique, developed for multipoles beyond dipoles by Leslie, accounted for the long-range nature of the multipole interactions. After preliminary calculations monitoring stability it was decided to perform the “NPT ensemble” simulations with 216 molecules at 278, 288, 300, 308 and 318K and pressure of 1 atm. The equations of motion was integrated using a time step size of 0.5 fs with total simulation times up to 150 ps (300,000 steps). All simulations were carried out using a new modified version of DL_POLY⁷. Our results reveal the importance of including higher multipoles (L=5) in the liquid simulation. For L<5, the pair distribution function does not show a second peak in the region between 4 and 5 Å. In addition, the valley between the 1st and 2nd peak is too shallow. For L=5, the OO, OH and HH pair distribution function are almost identical to those generated using the TIP5P potential⁸. With only two adjustable parameters, σ (3.140 Å) and ϵ (0.753 kJmol⁻¹) in the Lennard-Jones potential function, the density of the equilibrated system is 0.999 gcm⁻³, which is comparable to experimental results.

We have also carried out MD simulations for liquid HF using the same ensemble but with only 125 molecules and at a temperature of 273 K and a pressure of 1.0 atm. Again with only 2 adjustable parameters ($\sigma = 2.85$ Å and $\epsilon = 0.60$ kJmol⁻¹), the equilibrated system density is close to the experimental value. The various pair distribution functions are comparable to other simulation results⁹.



3. Further Research

The next important topic to investigate by means of the topological approach is the short-range interaction. As research progressed it became increasingly clear that one should take advantage of a unique feature that the quantum topological approach offers, namely that atoms and hence molecules never overlap. Instead, molecules are perceived as malleable units that respond to each other's presence by distorting their own atoms. This *ansatz*, which is a radical departure from classical thinking in the field of intermolecular interaction, will eliminate the need for damping functions and penetration energies. Furthermore we have a way of extracting the exchange-repulsion interaction from *ab initio* calculations via the topological method. This will do away with the use of the empirical modelling of repulsion via hard-sphere or Lennard-Jones potentials. Furthermore, since the concept of a free molecule – extrapolated to short-range – disappears, polarisation and dispersion ceases to exist. These contributions are only well-defined in the long-range polarisation expansion (Hirshfelder). The topological approach enables a proper definition of a molecule at any range. These ideas have been worked out in a detailed proposal containing 20 eqs, which is submitted to EPSRC for funding.

4. Dissemination

Other than the extensive write-up of our work, all in peer-reviewed international journals, this work has been aired in three UK and one French seminar (S) and three international conferences (C) :

- [S1] “The Topological Partitioning of Molecules : Golden Scissors ?”, Dept. of Chemistry, Nov 2000, Univ. of Birmingham, Birmingham, GB.
- [S2] “Topological Atoms”, Dept. of Chemistry, Nov 2001, Cambridge Univ., GB.
- [S3] “Quantum Topological Atoms”, Dept. of Chemistry, Jan 2002, Univ. of Manchester, GB.
- [S4] “Quantum Topological Atoms : Electrostatic Potential, Coulomb and Electrostatic Interactions”, Ecole Nationale Supérieure de Chimie de Paris, Paris, France, July 2002.
- [C1] Symposium on Molecular Informatics and Combinatorial Quantum Chemistry, Institute for Advanced Study, Collegium Budapest, Hungary, Feb 2001.
- [C2] Gordon Research Conference on Electron Distribution and Chemical Bonding, South Hadley, Massachusetts, USA, July 2001.
- [C3] Fourth Congress of the International Society for Theoretical Chemical Physics, ICTCP-IV, Marly-le-Roi (Paris), France, July 2002.

5. Project Summary

We have focused on a new representation of long-range intermolecular interactions by combining the spherical tensor formalism with the quantum topological approach. Our work has proven that this approach offers a perfectly viable and reliable route in predicting energies and geometries of van der Waals complexes including those of biological relevance. As a result the commonly held view in the literature that the quantum topological approach is not suitable for this purpose needs to be revised. For example in ref.1, p.111 we read that "... *Though neither [AIM&Voronoi polyhedra] is suitable for application of intermolecular forces because they have poor convergence properties.*" This statement is clearly wrong in the light of our findings.

We have extensively compared our topological method with the popular Distributed Multipole Analysis (DMA) method and with supermolecular calculations. We must conclude that the topological method is equivalent to DMA, and that both are able to predict accurately geometries of complexes many orders of magnitude faster than supermolecular calculations. Whereas DMA ad hoc technique to model electrostatics accurately the topological approach has a much wider context and allows interpretation as well as prediction.

We achieved the following milestones :

- The calculation of the exact electrostatic potential of a topological atom and a demonstration of the satisfactory convergence of its multipole expansion.
- An understanding of why the convergence properties are much better than hitherto assumed in the literature in spite of the highly non-spherical shape of the atoms.
- The computation of the exact Coulomb interaction between two atoms and a rigorous study of the convergence behaviour of the corresponding multipolar series expansion.
- A fast and novel algorithm to compute a topological atom's charge, using surface integrals only.
- A study of distributed polarisability of the water dimer concluding that field-induced charge flow occurs predominantly along the direction of the hydrogen bond and that the dimer's polarisability is reduced due to hydrogen bond formation.
- A careful comparison of energies and geometries of small van der Waals complexes generated by AIM, Distributed Multipole Analysis (DMA) (both with Hard-Sphere repulsion) and supermolecular calculations. AIM and DMA interaction energies differ by 1.3 kJ/mol and angles by 1.3° on average.
- The prediction that *para*-nitroaniline has a more efficient conductive behaviour than *meta*-nitroaniline and fluorobenzene on the basis of an *ab initio* computational technique of topologically distributed response analysis, and the observation that 1 unit of molecular total conduction number is approximately equal to 1/6 a.u. of (static) molecular polarisability.
- A thorough analysis of the atom-atom breakdown of the electrostatic interaction in 27 natural nucleic acid base pairs and the concomitant invalidation of Jorgensen's "secondary interaction hypothesis".
- A proof of convergence speed-up via shifting of topological multipole moments to non-nuclear sites and the favourable convergence properties of larger complexes (such as DNA base pairs) compared to DMA.
- The accurate prediction of the geometries for 27 base pairs with topological multipole moments and the broad recovery of their ranking according to interaction energy. Successful prediction of geometrical features of one of the important and topical quadruplex base pairs called TATA(WC).
- A systematic comparison between the topological model's results for water clusters (up to nine monomers) and hydrated serine and tyrosine and those of TIP4P/5P potentials and supermolecular calculations.
- The first MD simulation with a topological electrostatic potential supplemented with Lennard-Jones parameters with high-order Ewald summation, applied to liquid water and HF.

In summary, our meticulous work has laid the groundwork for a full topological intermolecular potential drawn from *ab initio* supermolecular information. A topological potential is valid irrespective of computational scheme (plane wave, Slater, Gaussian, basis set stability), properly rooted in quantum mechanics and part of a much wider context than previous ad hoc methods. Moreover it enables a rigorous extraction of chemical insight from wave function. We believe that, now that convergence issues are properly understood, we are in a good position to reap the advantages of a quantum topological potential, especially for short-range interactions.

6. References

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