



Introduction

Partial atomic charges are useful for a variety of conceptual and computational applications, and there are many approaches for estimating partial charges. Here, we present a method that preserves the molecular dipole moment of a molecule determined by an electronic structural theory. Consequently, these charges can be consistently utilized with quantum mechanical (QM) calculations, including combined QM/MM and the explicit polarization (X-Pol) methods. The method is based on a model described by Thole and van Duijnen and a new feature is introduced to treat molecular polarization. The approach is called the dipole preserving and polarization consistent (DPPC) method. The DPPC method is particularly useful for large molecular systems using a semiempirical Hamiltonian that yield excellent dipoles.

Details can be found in J Comput Chem 32: 2127–2139 (2011).

Rationale

The Goal is to reproduce the dipole moment of a molecule from electronic structural calculations exactly by the use of a set of partial atomic charges.

$$\mathbf{D}_{CM} \Psi = \mathbf{D}_{CM} \mathbf{q}_k \quad (1)$$

In QM

$$\mathbf{D}_{CM} = \mathbf{D}_{MP} + \sum_{i=1}^N \mathbf{D}_{hyb}^i \quad (2)$$

We use \mathbf{D}_{MP} from Mulliken Population as the reference state, and then distribute partial charges to all atoms that reproduces the atomic hybridization dipole \mathbf{D}_{hyb}^i .

$$\mathbf{D}_{hyb}^i = \sum_k^N \Delta q_k^i \mathbf{r}_k \quad (3)$$

\mathbf{D}_{hyb}^i : hybridization dipole contribution from atom i.

Δq_k^i : distributed partial charges on atom k from \mathbf{D}_{hyb}^i .

N: number of atoms.

We obtain the dipole preserved charge (DPC) model

$$q_k^{DPC} = q_k^{MP} + \sum_i^N \Delta q_k^i \quad (4)$$

Method

Locally Distributed Dipole-Preserving Charges(DPC)

We use Lagrange multiplier to optimize a set of smallest distributed "hybridization" charges that yield the exact total and local dipole.

$$L^i = \sum_k^N \frac{(\Delta q_k^i)^2}{2w_k^j} + \left(0 - \sum_k^N \Delta q_k^i\right) \alpha^j + \left(\Delta \mathbf{D}_i - \sum_k^N \Delta q_k^i \mathbf{r}_k\right) \beta^i \quad (5)$$

Constraint on zero net charge
Constraint on preserving local dipoles

α, β : Lagrange multipliers.

w_k^j : a set of weighting functions that control the way we redistribute the charges.

$$w_k^j = \left(1 + \left| \frac{\eta_k - \eta_i}{\eta_i} \right| e^{-\lambda |r_k - r_i|} \right) \quad (6)$$

η : atomic electron negativity.

λ : a parameter with unit of Bohr², which control how diffusive the charges are distributed around atomic dipoles.

Minimization of the Lagrangian (eq. 5) by variation with respect to Δq_k^i yields the distributed charges.

Molecular Polarization Consistent Charges(DPPC)

The procedure outlined above also offers a convenient way to correct the errors in computed molecular polarization in semiempirical methods, which prevent a good description of hydrogen bonding interactions. Let α_{SE} be the molecular polarizability tensor of an approximate quantum chemical model such as AM1 or PM6, and α_{target} be the target molecular polarizability tensor from experiment or high-level QM calculation. The error in the computed induced dipole moment because of the use of a small molecular polarizability can be expressed as follows:

$$\Delta \Delta \mathbf{D}_{ind} = \alpha_{target} - \alpha_{SE} \cdot \mathbf{E}(\mathbf{R}) = \Delta \alpha \cdot \mathbf{E}(\mathbf{R}) = \Delta \alpha \cdot \alpha_{SE}^{-1} \Delta \mathbf{D}_{ind}^{SE} \quad (7)$$

We further assume that the total induced dipole moment can be decomposed into atomic contributions then we get a new atomic point dipole to be preserved by Lagrangian multiplier method:

$$\Delta \mathbf{D}^i = \mathbf{D}_{hyb}^i + \Delta \Delta \mathbf{D}_{ind}^i \quad (8)$$

Results and conclusion

Illustrative Examples

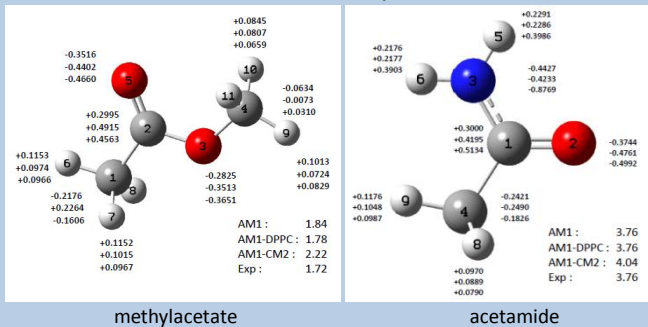


Figure 1. Computed dipole moments and partial atomic charges for methylacetate and acetamide from Mulliken population (first), the DPC method (second), and the CM2 model (third), using the AM1 models. Partial charges are determined by Mulliken population analysis given first, followed by the DPC charges and CM2 charges.

Polarization effect

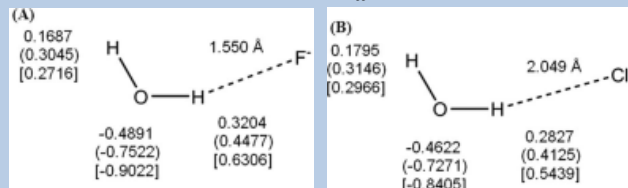


Figure 2. Computed partial atomic charges (a.u.) on the water molecule in (a) HOHCl2 and (b) HOHF2 bimolecular complexes, in which the water geometry is held as that in the gas phase from AM1 optimization. The Mulliken population charges are given first, followed by the dipole preserving charge (DPC) in parentheses and the dipole preserving and polarization consistent (DPPC) charges in square brackets.

Water dimer X-pol Potential curve

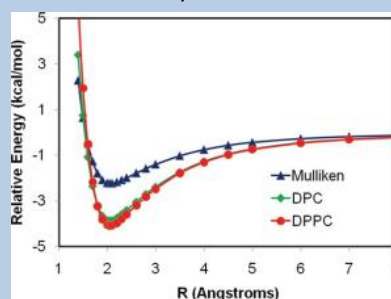


Figure 3. Interaction energy profiles for a water–dimer complex as a function of the donor hydrogen and acceptor oxygen distance. The structural arrangement of the dimer complex is depicted by the inset in the figure. The X-Pol potential with the AM1 Hamiltonian is used with each water molecule treated as a separate fragment.

Reference

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Acknowledgement

National Institutes of Health; grant number: RC1 GM091445.
National Science Foundation; grant number: CHE09-57162.