

Supplementary Materials: The Role of Hydrogen Bond in Designing Molecular Optical Materials

Leonardo H. R. Dos Santos and Piero Macchi

S1. Distributed Polarizabilities from QTAIM Partitioning of the Electron Density.

Here we briefly consider how distributed atomic dipole moments and polarizabilities can be computed from the QTAIM partition of the total molecular or crystal charge density distribution. For further details of the procedure, the reader is referred to Refs. [1] and [2].

QTAIM defines the expectation value of an observable over each atom in the system. Thus, the average value of the dipole moment μ over the molecule or the crystal is given as a sum of atomic contributions $\mu(\Omega)$. Each atomic moment consists of an origin-independent *polarization* term $\mu_p(\Omega)$, and an origin-dependent *charge-translation* term $\mu_c(\Omega)$,

$$\mu(\Omega) = \mu_p(\Omega) + \mu_c(\Omega) = - \int_{\Omega} [\mathbf{r} - \mathbf{R}_{\Omega}] \rho_1(\mathbf{r}) d\mathbf{r} + [\mathbf{R}_{\Omega} - \mathbf{R}_0] q(\Omega) \quad (1)$$

where $q(\Omega)$ is the net charge of the atomic basin Ω , \mathbf{R}_{Ω} is the nuclear position vector of the basin and \mathbf{R}_0 is the arbitrary origin of the molecular or crystal coordinate system. Unless $q(\Omega)$ is zero, $\mu_c(\Omega)$ is dependent on \mathbf{R}_0 . Thus, the atomic dipole moment $\mu(\Omega)$ is not generally meaningful because it is origin-dependent. However, the origin-dependent charge-translation term can be converted to an origin-independent definition:

$$\mu_c(\Omega) = [\mathbf{R}_{\Omega} - \mathbf{R}_0] q(\Omega) = \sum_{\Lambda=1}^{N_{atoms}} [\mathbf{R}_{\Omega} - \mathbf{R}_{BCP}] q(\Omega|\Lambda) \quad (2)$$

in which $q(\Omega|\Lambda)$ is called a *bond charge*, and can be interpreted as the charge induced at the basin Ω due to its interaction with the basin Λ . \mathbf{R}_{BCP} is the position vector of the bond critical point connecting the basins Ω and Λ , and the summation runs over all basins connected to Ω through a bond critical point. All quantities in Eqn. S2 are uniquely determined by the total charge density distribution partitioned according to the zero-flux surfaces of QTAIM. The bond charges can be obtained by imposing a series of constraints on the atomic and molecular charges [1,2].

As for the dipole moment, the molecular polarizability tensor can be decomposed into additive atomic contributions:

$$\alpha = \sum_{\Omega=1}^{N_{atoms}} \alpha(\Omega) = \sum_{\Omega=1}^{N_{atoms}} [\alpha_p(\Omega) + \alpha_c(\Omega)] \quad (3)$$

where $\alpha_p(\Omega)$ and $\alpha_c(\Omega)$ are the polarization and charge-translation atomic polarizability tensors that arise from the differentiation of the corresponding $\mu_p(\Omega)$ and $\mu_c(\Omega)$ atomic dipole moments with respect to the applied electric field. Given the linear response of the electron density with respect to a sufficiently small field, the derivative can be calculated numerically, using wavefunctions computed at finite electric fields. Thus, the atomic polarizability components $\alpha_{ij}(\Omega)$ are evaluated as:

$$\alpha_{ij}(\Omega) = \lim_{E_i \rightarrow 0} \frac{\mu_j^{E_i}(\Omega) - \mu_j^0(\Omega)}{E_i} \quad (4)$$

in which $\mu_j^{E_i}(\Omega)$ is the dipole moment component of the atomic basin Ω along the j direction computed with an applied electric field in direction i . Because polarizabilities have dimensions of volume, the atomic and molecular tensors can be visualized as ellipsoids in the same three-

dimensional space as the molecule, assuming $1 \text{ \AA}^3 \equiv 1 \text{ \AA}$, although a scaling factor is usually applied to reduce the size of the polarizability ellipsoids for visualization purposes.

S2. Theoretical Methods for Electron Density Calculations.

In this work, molecular or aggregate electron densities were obtained by molecular-orbital wavefunction calculations at the CAM-B3LYP level of approximation [3].

Previously [4], we have tested the ability of various DFT approximations in estimating distributed polarizabilities of amino acid molecules and their hydrogen-bonded dimers. Having correlated methods (coupled-cluster, configuration interaction and second-order Møller-Plesset approximation) as benchmarking, we found that long-range corrected functionals, like CAM-B3LYP [3] or LC-BLYP [5] are able to provide quite accurate atomic dipole moments and polarizabilities at a relatively low computational cost.

Most of the calculations in this work were performed using the modest-size cc-pVDZ basis-set. Even though augmentation with diffuse functions is highly desirable to accurately estimate electric moments and polarizabilities of molecules in an infinitely diluted gas, these functions are less relevant for estimating properties in aggregates or crystals, due to the existence of a “basis-set superposition” effect that takes place among vicinal groups or molecules in aggregation [6].

Three-dimensional coordinates of *p*-nitroaniline (NANIL02) and oxalic acid hydrated (OXACDH04) were taken from measured single-crystal X-ray diffraction data. The heavier atom positions were kept at measured values and the distances to the attached H atoms were normalized to the average neutron diffraction values, as given by the International Tables for Crystallography.

All the molecular wavefunction calculations were performed using the Gaussian 09 package [7] and the corresponding charge-density distributions were partitioned in keeping with the QTAIM using the AIMAll program [8].

Crystal-orbital wavefunction calculations for *p*-nitroaniline were performed at the B3LYP/cc-pVDZ level of approximation, using the Crystal 09 package [9]. While systematic investigation of the performance of range-separated functionals to be applied under periodic boundary conditions is still incipient [10], and is outside the scope of this work, crystal-orbital calculations are unlikely to converge when diffuse functions are present in the atomic basis-sets.

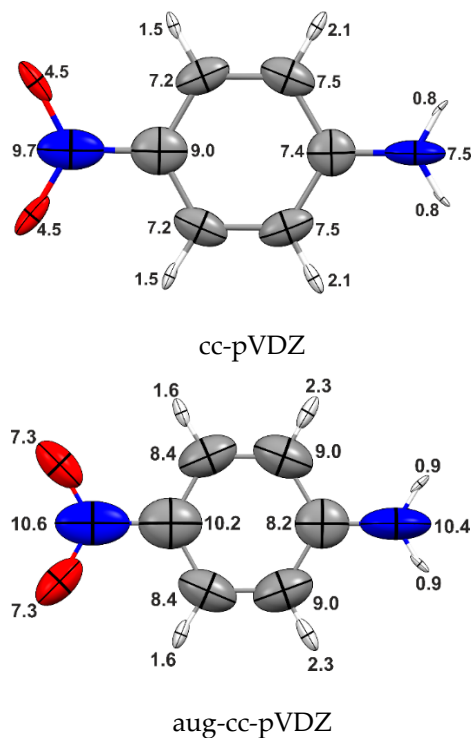


Figure S1. Cont.

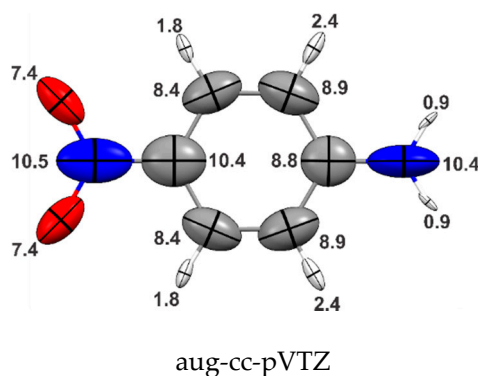


Figure S1. Effect of the basis-set on distributed polarizabilities of *p*-nitroaniline.

Distributed atomic polarizability ellipsoids after QTAIM partitioning of the molecular *p*-nitroaniline electron density, as obtained from CAM-B3LYP calculations. The isotropic polarizabilities, calculated as the arithmetical average of the main diagonal tensor components, are shown in au. The scaling factor for the ellipsoids is 0.3 \AA^2 .

Table S1. Effect of the basis-set on the molecular polarizability of *p*-nitroaniline.

| Basis Set | α_1 | α_2 | α_3 | α_{ISO} | $\Delta\alpha$ |
|-------------|------------|------------|------------|----------------|----------------|
| cc-pVDZ | 31.3 | 82.8 | 126.4 | 80.2 | 82.5 |
| aug-cc-pVDZ | 53.2 | 93.1 | 147.9 | 98.1 | 82.4 |
| aug-cc-pVTZ | 53.6 | 93.4 | 148.3 | 98.4 | 82.4 |

Table S2. Distributed polarizability of oxalic acid. Diagonal polarizability tensor (au) for the carboxylic groups in oxalic acid, calculated in isolation and in some hydrogen-bonded aggregates at the CAM-B3LYP/cc-pVDZ level of theory. ^a

| $\text{C}_2\text{H}_2\text{O}_4 \cdot x \text{ H}_2\text{O}$ | α_1 | α_2 | α_3 | α_{ISO} | $\Delta\alpha$ |
|--|------------|------------|------------|----------------|----------------|
| 0 | 7.9 | 18.2 | 19.6 | 15.2 | 11.1 |
| 2 (mHB) ^b | 7.8 | 18.5 | 22.4 | 16.2 | 13.1 |
| 2 (sHB) ^b | 7.8 | 17.9 | 20.6 | 15.5 | 11.7 |
| 4 | 7.6 | 18.5 | 22.6 | 16.3 | 13.4 |

Notes: ^a For $\text{C}_2\text{H}_2\text{O}_4 \cdot 2 \text{ H}_2\text{O}$, two aggregates were considered, mHB include only the water molecules forming the two longer hydrogen bonds in Figure 3 ($\text{C}_2\text{H}_2\text{O}_4$ is the hydrogen-bond acceptor), while sHB include only those forming the shorter bonds ($\text{C}_2\text{H}_2\text{O}_4$ is the donor).

References

1. Krawczuk, A.; Pérez, D.; Macchi, P. PolaBer: A program to calculate and visualize distributed atomic polarizabilities based on electron density partitioning. *J. Appl. Cryst.* **2014**, *47*, 1452–1458.
2. Keith, T.A. *The Quantum Theory of Atoms in Molecules*; Matta, C.F.; Boyd, R.J.; Wiley-VCH: Weinheim, Germany, 2007, pp 61–94.
3. Yanai, T.; Tew, D.P.; Handy, N.C. A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.
4. Dos Santos, L.H.R.; Krawczuk, A.; Macchi, P. Distributed Atomic Polarizabilities of Amino Acids and their Hydrogen-Bonded Aggregates. *J. Phys. Chem. A*, **2015**, *119*, 3285–3298.
5. Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. Long-Range Correction Scheme for Generalized-Gradient-Approximation Exchange Functionals. *J. Chem. Phys.* **2001**, *115*, 3540–3544.
6. Hammond, J.R.; Govind, N.; Kowalski, K.; Autschbach, J.; Xantheas, S.S. Accurate dipole polarizabilities for water clusters $n = 2$ –12 at the coupled-cluster level of theory and benchmarking of various density functionals. *J. Chem. Phys.* **2009**, *131*, 214103.

7. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A., Jr.; Vreven, T.; Kudin, K.N.; Burant, J.C. *et al.* *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, USA, 2009.
8. Keith, T.A. *AIMAll*, Version 14.04.17; TK Gristmill Software: Overland Park, KS, USA, 2014.
9. Dovesi, R.; Saunders, V.R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C.M.; Pascale, F.; Civalleri, B.; Doll, K.; Harrison, N.M.; Bush, I.J.; D'Arco, P.; Llunell, M. *CRYSTAL09 User's Manual*. University of Torino: Torino, Italy 2009.
10. Sansone, G.; Civalleri, B.; Usvyat, D.; Toulouse, J.; Sharkas, K.; Maschio, L. Range-separated double-hybrid density-functional theory applied to periodic systems. *J. Chem. Phys.* **2015**, *143*, 102811.



© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons by Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).