Charge Transfer with Constrained Density Functional Theory Imposing Restrictions on the Dipole Cartesian Components

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Density Functional Theory (DFT) is an important tool for computing physicochemical properties described by the electronic structure of the systems. Furthermore, variants of this approach have been created specifically for the study of specific properties. One of these variants is the Constrained Density Functional Theory (CDFT)[1, 2], based on the Kohn-Sham equations of DFT, in which the constraints are imposed on the charges through a specific population analysis. This procedure has proven to be a robust approach for describing charges, fluctuations in solids and electron transfer reactions in molecules.

The present work shows the development of a new methodology based on the restriction of the cartesian components of the dipole moment to study and analyze charge transfer processes in non-covalent compounds without imposing any partition in space (population analysis), using an observable to establish the charge transfer free point of reference.

This work is based on the constrained dipole moment density functional theory (CD-DFT) with restrictions on the magnitude of the dipole moment [3], extending it to the control of the Cartesian components that compose it since when using the magnitude of the dipole moment, it allows to control the charge transfer for systems with only one Cartesian component of the dipole moment different from zero. Thus, the present implementation of the theory is a complement to CD-DFT.

References

[1] Q. Wu and T. Van Voorhis, "Direct optimization method to study constrained systems within density-functional theory," *Physical Review A,* vol. 72, no. 2, p. 024502, 2005.

[2] J. Rezac and A. de la Lande, "Robust, basis-set independent method for the evaluation of charge-transfer energy in noncovalent complexes," *Journal of chemical theory and computation,* vol. 11, no. 2, pp. 528-537, 2015.

[3] J. Carmona-Espíndola, E. Núñez-Rojas, V. García-Melgarejo, J. L. Gázquez, and J. Alejandre, "Constrained dipole moment density functional theory for charge distributions in force fields for the study of molecular fluids," *The Journal of chemical physics,* vol. 152, no. 12, p. 124116, 2020.