

Structural Studies of Partial Charges of 1,2,3 – Triazole 1,2,4 – Triazole, Imidazole, Pentazole, Pyrazole, Pyrrole, Tetrazole

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Abstract

Partial charges are created due to a symmetric distribution of electrons in chemical bonds. Partial atomic charges are used in molecular mechanics force field to compute the electrostatic interactions energy using Coulomb's law. They are also often used for qualitative understanding of the structure and reactivity of molecules. We calculated partial charges of azoles (1,2,3 – Triazole, 1,2,4 – Triazole, Imidazole, Pentazole, Pyrazole, Pyrrole, Tetrazole) are performed using DFT implemented in the Cache Software. Partial charges are created due to a symmetric distribution of electrons in chemical bonds.

Keywords: Partial charges, Cache Software, azoles, DFT.

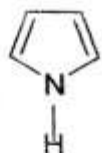
1. INTRODUCTION

Density functional theory (DFT) is widely used approach to the modeling of complex electronic systems. It first gained prominence in computational studies of condensed matter and solid-state materials, but has more recently become a standard technique in molecular physics and quantum chemistry, where it is used to obtain structure and spectroscopic information about complex molecular systems. The available empirical evidence suggests that the use of established formulations for the dependence of the exchange correlation energy on the electron density within the Kohn-Sham orbital expansion scheme yields results that are competitive in terms of accuracy with more computationally intensive ab-initio post Hartree-Fock schemes, such as second-order many bodies perturbation theory. The Hohenberg-Kohn theorems prove that an exact solution to the electronic structure problem is available given a knowledge of the universal functional relationship between the ground state energy of an interacting system and its electron density. While this is a beguiling result that provides fundamental insights into the nature of many bodies problem, the detailed form of this universal functional is unknown. Practical implementations of the Kohn-Sham scheme depend on a wide variety of approximate, parameterized functionals, leading to a model dependence that is undoubtedly the least satisfactory aspect of the scheme. Nevertheless, DFT remains the method of choice

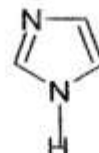
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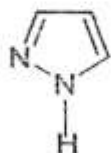
in most applications involving large number of electrons and molecular system containing large number of nuclei. These advantages are conveyed mainly by the simple independent particle structure of the Kohn-Sham equation. In order to model systems containing heavy nuclei, the methods of relativistic quantum mechanics must be adopted to capture Scalar and spin-dependent interactions that are neglected in the conventional non-relativistic formulation of quantum chemistry. The extension of DFT with in the four-component generalization of the Kohn-Sham method which we will refer to as Dirac-Kohn-Sham (DKS) Scheme was formulate by Rajagopal and Co-workers and Mardonald and Vosko. There have been many subsequent elaborations of this approach including relativistic optimized potential Schemes. These approaches avoid the use of parameterized density functional by deriving an effective exchange potential directly, by construction of the explicit functional derivative of the exact non local exchange energy with respect to the total electron density. Relativistic density functional theories have been implemented by several groups and at many levels of approximation. Density functional theory (DFT) is widely used approach to the modeling of complex electronic systems. It first gained prominence in computational studies of condensed matter and solid-state materials, but has more recently become a standard technique in molecular physics and quantum chemistry, where it is used to obtain structure and spectroscopic information about complex molecular systems. The available empirical evidence suggests that the use of established formulations for the dependence of the exchange correlation energy on the electron density with in the Kohn-Sham orbital expansion scheme yields results that are competitive in terms of accuracy with more computationally intensive ab-initio post Hartree-Fock schemes, such as second-order many bodies perturbation theory.



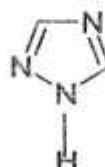
PYROLE



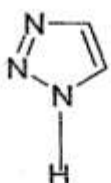
IMIDAZOLE



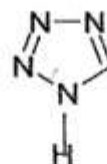
PYRAZOLE



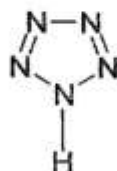
1,2,4 - TRIAZOLE



1,2,3 - TRIAZOLE



TETRAZOLE



PENTAZOLE

FIG.: AZOLES

2. METHOD OF CALCULATION

All the Calculation reported are performed using DFT implemented in the Cache Software. The detail description of the basic set optimization and about software are given below. Density functional theory is a completely different, formally rigorous, way of approaching *any* interacting problem, by mapping it *exactly*

to a much easier-to-solve non-interacting problem. In DFT the ground state energy of an atom or a molecule is written in terms of electron density $\rho(r)$, and the external potential $v(r)$ in the form,

$$E(\rho) = F(\rho) + \int dr \rho(r) v(r),$$

where $F(\rho) = T(\rho) + V_{ee}(\rho)$, $T(\rho)$ is the electronic kinetic energy functional, and $V_{ee}(\rho)$ is the electron-electron interaction energy functional. The minimization of the total energy, subject to the condition that the total number of electrons is fixed,

$$N = \int dr \rho(r)$$

lead to an Euler-Lagrange Equation of the form

$$\mu = (\partial E / \partial \rho(r))_v = v(r) + \delta F / \delta \rho(r),$$

where the Lagrange multiplier μ , is the chemical potential. The solution of this equation leads to the ground state density, from which one can determine the ground state energy. Parr et. al define the electronegativity as the negative of chemical potential,

$$\chi = -\mu = -(\partial E / \partial N)_v$$

In the Born-Oppenheimer approximation, we treat the heavy nuclei as fixed points, and we want only to solve the ground-state quantum mechanical problem for the electrons. In regular quantum mechanics, we must solve the Schrodinger equation:

$$\left\{ \frac{1}{2} \sum_{i=1,2} \nabla_i^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \sum_{i=1,2} v_{\text{ext}}(\mathbf{r}_i) \right\} \Psi(\mathbf{r}_1, \mathbf{r}_2) = E \Psi(\mathbf{r}_1, \mathbf{r}_2),$$

Where the index i runs over the two electrons, and the external potential, the potential experienced by the electrons due to the nuclei, is

$$v_{\text{ext}}(\mathbf{r}) = -Z/r - Z/r - R \hat{z} / r,$$

Where Z is the charge on each nucleus, \hat{z} is a unit vector along the bond axis, and R is a chosen internuclear separation. For larger systems with N electrons, the wave function depends on all $3N$ coordinates of those electrons.

The probability density tells that the probability of finding an electron in d^3r around \mathbf{r} is $n(\mathbf{r}) d^3r$. For a system of two *non-interacting* electrons in some potential, $v_s(\mathbf{r})$, chosen somehow to mimic the true

electronic system. Because the electrons are non-interacting, their co-ordinates decouple, and their wave function is a simple product of one-electron wave functions, called *orbitals*, satisfying,

$$\left\{ -\frac{1}{2} \nabla^2 + v_S(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}),$$

where $\Phi(\mathbf{r}_1, \mathbf{r}_2) = \phi_0(\mathbf{r}_1) \phi_0(\mathbf{r}_2)$. This is a much simpler set of equations to solve, since it only has 3 co-ordinates. Even with many electrons, say N , one would still need to solve only a 3-D equation, and then occupy the first $N/2$ levels, as opposed to solving a $3N$ -coordinate Schrodinger equation. If we can get our non-interacting system to accurately 'mimic' the true system, then we will have a computationally much more tractable problem to solve.

3. RESULTS AND DISCUSSION

3.1 PARTIAL CHARGE

The calculated Partial charge of different atoms in all the azoles have been presented in table 1 by D.F.T. program. A partial charge is a charge with an absolute value of less than one elementary charge unit. Partial charges are created due to a symmetric distribution of electrons in chemical bonds. The resulting partial charges are a property only of zones within the distribution and not the assemblage as a whole for example, chemists often choose to look at a small space surrounding the nucleus of an atom when an electrically neutral atom bonds chemically to another neutral atom that is more elector-negative its electrons are partially drawn away. This leaves the region about that atoms nucleus with a partial positive charge and it creates a partial negative charge on the atom to which it is bonded.

In such a situation, the distributed charges taken as a group always carries a whole number of elementary charge units. Yet one can point to zones within the assemblage where less than a full charge resides such as the area around an atoms nucleus. This is possible in part because particles are not like mathematical points which must be either inside a zone or outside it. But are smeared out by the uncertainly principle may be both partly inside and partly outside it. Partial atomic charges are used in molecular mechanics force field to compute the electrostatic interactions energy using Coulomb's law. They are also often used for qualitative understanding of the structure and reactivity of molecules. Despite its usefulness. The concept of a partial atomic charge is somewhat arbitrary because it depends on the method used to delimit between one atom and the next. As a consequence there are many methods for estimating the partial charges.

TABLE1 : PARTIAL CHARGE

Molecule	Atom	Partial Charge
1,2,3 – Triazole	N1	-0.193
	N2	-0.106
	N3	-0.131
	C4	-0.191
	C5	-0.218
	H6	0.35
	H7	0.237
	H8	0.252
1,2,4 – Triazole	N1	-0.15
	C2	-0.142
	N3	-0.185
	C4	-0.143
	N5	-0.195
	H6	0.227
	H7	0.239
	H8	0.35
Imidazole	N1	-0.18
	C2	-0.196
	C3	-0.157
	N4	-0.254
	C5	-0.237
	H6	0.229
	H7	0.222
	H8	0.332
	H9	0.241
Pentazole	N1	-0.141
	N2	-0.05
	N3	-0.069
	N4	-0.069

	N5	-0.051
	H6	0.38
Pyrazole	N1	-0.198
	N2	-0.159
	C3	-0.215
	C4	-0.255
	C5	-0.217
	H6	0.344
	H7	0.227
	H8	0.235
	H9	0.238
Pyrrrole	N1	-0.255
	C2	-0.238
	C3	-0.246
	C4	-0.246
	C5	-0.238
	H6	0.327
	H7	0.224
	H8	0.223
	H9	0.224
	H10	0.224
Tetrazole	N1	-0.207
	N2	-0.072
	N3	-0.077
	N4	-0.13
	C5	-0.126
	H6	0.36
	H7	0.253

4. CONCLUSIONS

The concept of a partial atomic charge is somewhat arbitrary because it depends on the method used to delimit between one atom. a small space surrounding the nucleus of an atom when an electrically neutral atom bonds chemically to another neutral atom that is more elector-negative its electrons are partially drawn away. The resulting partial charges are a property only of zones with in the distribution and not the assemblage as a whole. The concept of a partial atomic charge is somewhat arbitrary because it depends on the method used to delimit between one atom. a small space surrounding the nucleus of an atom when an electrically neutral atom bonds chemically to another neutral atom that is more elector-negative its electrons are partially drawn away.

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