THEORETICAL STUDY OF ELECTRONIC PROPERTIES OF AZOLES

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ABSTRACT:- We Calculated atomic orbital electron population and orbital energies of azoles(1,2,3 – Triazole 1,2,4 – Triazole, Imidazole, Pentazole, Pyrazole, Pyrrole, Tetrazole). All the Calculation reported are performed using DFT implemented in the Cache Software. The predicted the charged distribution are generally similar to those given by ab-initio SCF 4-31G calculation. In the present calculation both the molecular orbital HOMO and LUMO or not having the same symmetry. An electron from HOMO to LUMO. The LOMO became more and more degenerate with the HOMO.

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 is 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 body perturbation theory.

The Hohenbery-Kohn theorems prove that an exact solution to the electronic structure problem is available given a knowledge of the universe functional relationship between the rotation energy of an interacting system and its electron density. While this is a beguiling results that provides fundamental insights into the nature of many body 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 functional, leading to a model dependence that is

undoubtedly the least satisfactory aspect of the scheme. Never the less, DFT remains the methods of choice 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 elaboration 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 level of approximation.
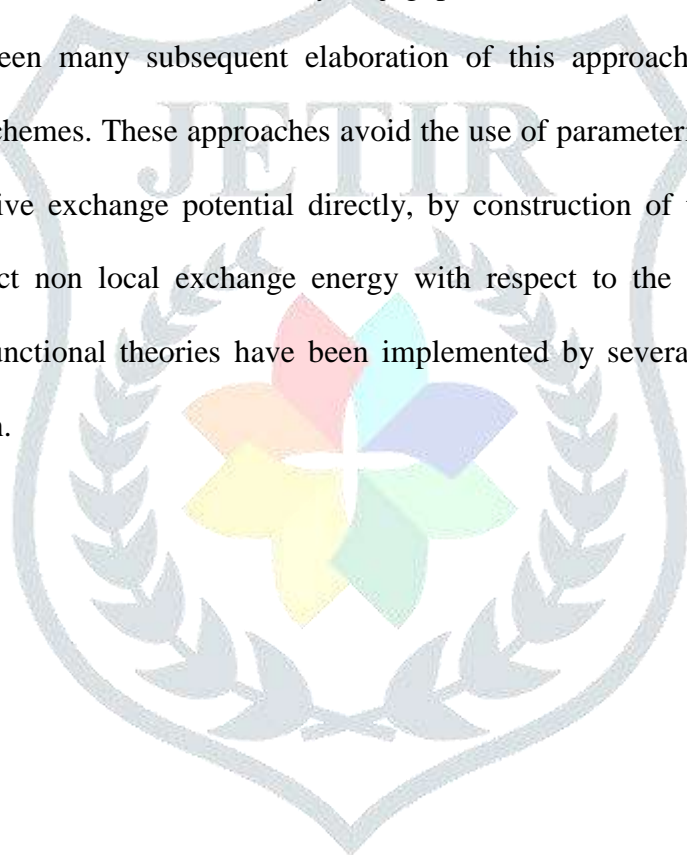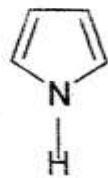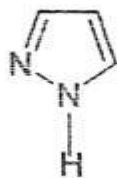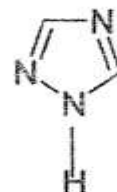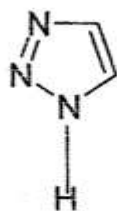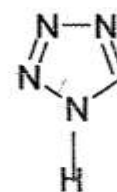
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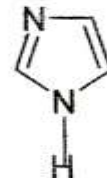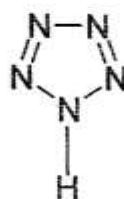
IMIDAZOLE

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. Semi empirical quantum chemistry methods are based on the Hartree Fock formalism, but make many approximations and obtains some parameters from empirical data. They are very important in computational chemistry for treating large molecules where the full Hartree-fock method. The use of empirical parameter appears to allow some inclusion of electron correlation effects into the method. Semi empirical calculations have been most successful in the description of organic chemistry where only a two elements are used extensively and molecules are moderate size. Parameterized model numbers 3 developed by J.J.P. Stewart   and first published in 1989. The PM3 method uses the same formalism and equations as the AM1 method. The only difference are (1) PM3 uses two Gaussian functions for the core Repulsion function instead of the variable number used by AM1 (2) The numerical values of the parameters are different. Density functional theory is a quantum mechanical modelling method used in physics and chemistry to investigate the electronic structure of many body systems in particular atoms molecules and the condensed phase with this theory. The properties of a many electron system can be determined by using functional, so as functions of :- another function which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functional of the electron density. DFT is among the most popular & versatile methods available in condensed matter physics computational physics and chemistry.

The detail description of the basic set optimization and about software are given below. All the calculation are performed with the help of cache software. we have used cache software for calculating the following properties for azoles and its derivatives. Density functional theory (DFT) as long been the mainstay of electronic structure calculations in solid-state physics, and has recently become popular in quantum chemistry. This is because present-day approximate

functional provide a useful balance between accuracy and computational cost, allowing much larger system to be treated than traditional *ab initio* method, while retaining much of their accuracy. Nowadays, traditional wave function method, either variational or perturbative, can be applied to find highly accurate results on smaller systems, providing benchmarks for developing density functional, which can then be applied to much larger systems.

But DFT is not just another way of solving the Schrodinger equation. Nor is it a method of aromatizing empirical results. 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 $V_{cc}(\rho)$ 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 for

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

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 a Kohn-Sham calculation, the basic steps are very much the same, but the logic is entirely different. Imagine a pair of non-interacting electrons which have precisely the same density $n(r)$ as the physical system. This is the Kohn-Sham system, and using density functional method, one can derive its potential $v_s(r)$ if one knows how the total energy E depends on the density. A single simple approximation for the unknown dependence of the energy on the density can be applied to all electronic system, and predicts both the energy and self-consistent potential

for the fictitious non-interacting electrons. In this view, the Kohn-Sham wave function of orbital is not considered an approximation to the exact wave function. Cache computer aided chemistry enables to apply mathematical models from classical and quantum mechanics to calculate experimental results. Cache enables create a chemical sample model and perform calculations to discover molecular properties and energy values using computational applications which apply equations from classical mechanics and quantum mechanics. If we have run an experiment that employed a quantum mechanical procedure previously, this information is already present in the sample file and we do not to re-compute it unless we have changed the geometry of the molecule.

3 -   RESULTS AND DISCUSSION :-

 3.1.   ATOMIC ORBITAL ELECTORN POPULATION : The atomic orbital electron population of azoles have been presented in the table1. Some of interesting features regarding these charges are discussed below.

1-   The neglect of inner most 1S orbital of all the non-hydrogenic atoms, (Carbon, and nitrogen) in the present PM3 calculation is justitied because of the fact that the ab-initio populations (Singh and Yadav, 1985) on these orbital of inner most 1S orbital is not significantly involved in the chemical bonds.

2-   The sp^2 hybridization on a carbon atom requires an orbital charge description of the type $2S^{'}$, $2P^{'}_x$, $2P^{'}_y$, $2P^{'}_z$. This expected behavior followed closely in our computed results.

The 2S orbital of all the carbon in 1,2,3-triazole shows a population of approximately 1.22e (C4-1.219, C5-1.227) so that there is a deficit of about 0.78e from sp^2 configuration. This deficit represents promotion from 2S to 2P orbital is explained as being energ gain in molecular formation from sp2 hybridized orbital. However this deficit is slightly small (approximately 0.75e) in 1,2,4-triazole. Similar results have been found in earlier ab-initio calculations.

3-   A close inspection of charges at various orbital of azoles reveals the following results.

(i) In 1,2,3-triazole, a charge in seen to migrate from the $2P_y$ orbital of C4 to 2S orbital of N2.

(ii) In 1,2,4-triazole, the migration of charge taken place from $2P_y$ orbital of C4 to 2S orbital of N1.

(iii) In imidazole, a charge migrate from $2P_y$ orbital of C3 to 2S orbital of N1.

(iv) In pentazole, the migration of charge is seen from $2P_y$ of N2 to the 2S orbital of N2.

(v) In pyrazole, a charge is seen to migrate from $2P_x$ orbital of C3 to 2S orbital of N2.

(vi) In pyrrole, the migration of charge taken place from $2P_y$ orbital of N1 of the 2S orbital C3.

(vii) In tetrazole, a charge is seen to migrate from $2P_y$ orbital of C5 to the 2S orbital of N2.

The above result shows that the migration of charges taken place from $2P_y$ orbital to 2S orbital. The 1S and $2P_z$ orbital of all the molecules do not taken part in such migrations. This result prepares a basis to assume SP^2 hybridization among σ orbital 2S, $2P_x$ and $2P_y$ for applying similarity transformation to evaluate the board orders and bond lengths of the atoms.

4- The electronic charges on 1s orbital of the hydrogen atoms which is attached to the ring carbon are small in comparison to the charge on 1S orbital of hydrogen which found in all azoles.

5- If the compare the charges on 2S orbital of Nitrogen and carbon in all azoles than we final that the charges on 2S orbital of nitrogen is greater than that of carbon.

6- The charge distribution of that nitrogen atom from which hydrogen is attached, are found in following orders :

$$2P_z > 2S > 2P_y > 2P_x$$

The similar trend is also found in all azoles.

Thus the predicted the charged distribution are generally similar to those given by ab-initio SCF 4-31G calculation.

3.2 ORBITAL ENERGIES : The energies of molecules orbital of azoles have been presented in table-2

The silent feature of these results are following.

1. The energies of highest occupied molecular orbital have negative energies while the energies of lowest unoccupied molecules orbital have positive energies. This results is similar to the ab-initio results.

2. In 1,2,3-triazole the first LUMO has negative energy (-10.290). This indicates that the molecular orbital partially occupied.

3. The negative values of calculated highest occupied molecular orbital (HOMO) energies provide and estimate for the molecular ionization potential in accordance with KOOPMAN'S theorem.

4. Similarly the electron Affinities can be estimated from the calculated lowest unoccupied molecular orbital (LUMO) energies.

5. The validities of KOOPMAN theorem has been discussed by several authors.

6. From a study of several aromatic hydro-carbon, it is concluded that thin theorem over estimate the experimental ionization potential by 2 to 4 ev.

In the present calculation both the molecular orbital HOMO and LUMO or not having the same symmetry therefore it is not possible to speak on excited configuration of molecules on excited. An electron from HOMO to LUMO. The LOMO became more and more degenerate with the HOMO. A closes examination of the P orbital showed that it was not the lowest eigen function of local potential. Since the orbital had several, indicating that many lower energy orbital must exist.

TABLE 1 : ATOMIC ORBITAL ELECTRON POPULATION

Molecules	Atoms	Orbitals				
		1 S	2 S	2 Px	2 Py	2 Pz
1,2, 3-Triazole	N1	-	1.287	0.945	0.999	1.492
	N2	-	1.718	1.299	0.938	1.214
	N3	-	1.662	0.993	1.287	1.105
	C4	-	1.219	0.969	0.927	1.070
	C5	-	1.227	0.946	0.992	1.117
	H6	0.898	-	-	-	-
	H7	0.845	-	-	-	-
	H8	0.840	-	-	-	-
1,2,4-Triazole	N1	-	1.706	1.224	1.521	1.288
	C2	-	1.243	0.950	0.909	0.973
	N3	-	1.656	1.006	1.303	1.197
	C4	-	1.257	0.998	0.911	1.056
	N5	-	1.275	0.958	0.978	1.483
	H6	0.837	-	-	-	-
	H7	0.829	-	-	-	-
	H8	0.900	-	-	-	-
Imidazole	N1	-	1.646	1.048	1.259	1.163
	C2	-	1.207	0.947	0.934	1.044
	C3	-	1.252	0.980	0.922	1.101
	N4	-	1.250	0.956	0.963	1.518
	C5		1.225	0.952	0.978	1.772
	H6	0.858	-	-	-	-
	H7	0.837	-	-	-	-
	H8	0.930	-	-	-	-
	H9	0.847	-	-	-	-
Pentazole	N1	-	1.326	0.953	1.025	1.449
	N2	-	1.720	1.309	0.952	1.167
	N3	-	1.699	0.966	1.273	1.107
	N4	-	1.699	1.177	1.062	1.107
	N5	-	1.720	1.142	1.119	1.167
	H6	0.851	-	-	-	-

Pyrazole	N1	-	1.258	0.944	0.972	1.477
	N2	-	1.702	1.236	1.041	1.277
	C3	-	1.212	0.930	0.946	1.014
	C4	-	1.190	0.957	0.958	1.108
	C5	-	1.226	0.966	0.964	1.121
	H6	0.914	-	-	-	-
	H7	0.860	-	-	-	-
	H8	0.865	-	-	-	-
	H9	0.851	-	-	-	-
Pyrrole	N1	-	1.231	0.950	0.945	1.509
	C2	-	1.221	0.954	0.969	1.165
	C3	-	1.182	0.953	0.946	1.079
	C4	-	1.182	0.944	0.955	1.079
	C5	-	1.221	0.966	0.957	1.165
	H6	0.944	-	-	-	-
	H7	0.857	-	-	-	-
	H8	0.877	-	-	-	-
	H9	0.877	-	-	-	-
	H10	0.857	-	-	-	-
Tetrazole	N1	-	1.298	0.959	1.009	1.487
	N2	-	1.725	1.231	1.010	1.223
	N3	-	1.684	1.058	1.183	1.070
	N4	-	1.682	1.061	1.211	1.177
	C5	-	1.264	0.977	0.942	1.041
	H6	0.883	-	-	-	-
	H7	0.816	-	-	-	-

TABLE 2 : ORBITAL ENERGIES

Molecules	Atoms	Orbitals				
		1 S	2 S	2 Px	2 Py	2 Pz
1,2, 3-Triazole	N1	-	-38.071	-27.735	-27.441	-21.409
	N2	-	-19.861	-18.942	-15.749	-15.266
	N3	-	-15.132	-12.254	-10.912	-10.665
	C4	-	-10.290	0.013	0.964	1.034
	C5	-	2.678	3.229	3.835	4.108
	H6	4.862	-	-	-	-
	H7	5.127	-	-	-	-
	H8	6.866	-	-	-	-
1,2,4-Triazole	N1	-	-37.800	-27.994	-26.821	-21.003
	C2	-	-20.552	-18.680	-16.035	-15.028
	N3	-	-14.965	-11.815	-10.707	-10.700
	C4	-	-10.394	0.105	0.988	1.178
	N5	-	2.532	3.238	3.766	4.533
	H6	5.114	-	-	-	-
	H7	5.240	-	-	-	-
	H8	6.596	-	-	-	-
Imidazole	N1	-	-38.205	-27.552	-26.906	-20.319
	C2	-	-19.831	-18.796	-15.206	-14.938
	C3	-	-14.259	-14.197	-10.203	-10.083
	N4	-	-9.467	0.696	1.324	1.697
	C5	-	3.041	3.274	3.993	4.238
	H6	4.613	-	-	-	-
	H7	5.644	-	-	-	-

	H8	5.810	-	-	-	-
	H9	6.757	-	-	-	-
Pentazole	N1	-	-38.134	-28.775	-28.188	-22.532
	N2	-	-22.153	-19.748	-17.014	-14.703
	N3	-	-12.958	-12.722	-12.331	-12.252
	N4	-	-12.007	-1.256	-0.229	0.016
	N5	-	2.881	3.021	3.701	3.793
	H6	6.314	-	-	-	-
Pyrazole	N1	-	-38.281	-27.819	-26.800	-20.468
	N2	-	-20.264	-18.299	-15.282	-14.460
	C3	-	-14.303	-14.127	-11.081	-9.889
	C4	-	-9.684	0.536	1.496	1.540
	C5	-	3.010	3.556	4.113	4.315
	H6	4.483	-	-	-	-
	H7	5.546	-	-	-	-
	H8	5.748	-	-	-	-
	H9	6.575	-	-	-	-
Pyrrole	N1	-	-38.688	-27.444	-26.962	-19.685
	C2	-	-19.388	-18.989	-14.645	-14.415
	C3	-	-13.536	-13.453	-13.373	-9.206
	C4	-	-8.926	-1.113	1.815	2.070
	C5	-	3.523	3.584	4.340	4.530
	H6	4.778	-	-	-	-
	H7	4.837	-	-	-	-
	H8	6.218	-	-	-	-
	H9	6.251	-	-	-	-

	H10	6.400	-	-	-	-
Tetrazole	N1	-	-37.963	-28.303	-27.448	-21.997
	N2	-	-20.735	-19.145	-16.850	-15.948
	N3	-	-13.207	-11.665	-11.591	-11.381
	N4	-	11.091	-0.524	0.338	0.496
	C5	-	2.212	3.319	3.680	4.177
	H6	4.577	-	-	-	-
	H7	6.741	-	-	-	-

CONCLUSIONS:- Theoretical study of electronic properties (orbital electron population and orbital energies) of azoles. The migration of charges taken place from $2P_y$ orbital to 2S orbital. The 1S and $2P_z$ orbital of all the molecules do not taken part in such migrations. This result prepares a basis to assume SP^2 hybridization among σ orbital 2S, $2P_x$ and $2P_y$ for applying similarity transformation to evaluate the board orders and bond lengths of the atoms. a study of several aromatic hydro-carbon, it is concluded that thin theorem over estimate the experimental ionization potential by 2 to 4 ev. The energies of highest occupied molecular orbital have negative energies while the energies of lowest unoccupied molecules orbital have positive energies.

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