Density Functional Theory Adsorption of Atoms on Cytosine

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ABSTRACT The density functional theory is used to optimize the geometry of a cytosine molecule and those of several atoms including H_2 molecule, placed in the centre of the hexagon of the cytosine molecule. The adsorption of all of the first group atoms H, Li, Na, K, Cs and Fr, the second group atoms, Be, Mg, Ca, Sr, Ba , the halogens, F, Cl, Br, I and At and the rare gas atoms, He, Ne, Ar, Kr, Xe and Rn has been calculated. All these atoms are optimized and the adsorption energy has been found. The adsorption energy is found to be maximum for Ba, which is a second group element and minimum for hydrogen. In every group, as the atomic number increases, the corresponding adsorption energy increases. Apparently, in several cases, large adsorption energies are found.

(**Keywords**: Cytosine, Density-functional theory modeling, barium)

INTRODUCTION

Cytosine, $C_4H_5N_3O$ is a pyrimidine based molecule. It is one of the four constituents of the DNA which involves the pairing of adenine (A) with thymine (T) and that of guanine (G) with cytosine (C). The molecular weight of cytosine is 111.1g/mol. Apparently, the cytosine, an organic base of the pyrimidine family, was extracted from the nucleic acid of calf thymus tissue in 1894. The structure of cytosine was suggested in 1903, which was later confirmed when it was synthesized in the laboratory. The atoms adsorbed on A, T, G or C create genetic variations. Hence adsorption of atoms on these molecules is important to get rid of family peculiarities. If the extra atoms adsorbed on the DNA components are identified, chemicals can be found which can react with these extra atoms to change the genetics. The adsorption of Zn, Co and Fe on DNA components, guanine and cytosine has been reported by Alexandre et al [1]. Weightman et al [2] report that in the Au(110)/electrolyte interface the cytosine molecules form ordered structures. It is also possible to ionize the cytosine molecule by interaction with proton beams [3]. We have done extensive calculations of absorption of atoms on adenine [4], thymine [5] and heme [6].

In this paper, we report our calculation of adsorption energies of several atoms on the centre of the hexagon of the cytosine molecule. For this purpose, we simulate 24 different atoms starting from the correct number of neutrons, protons and electrons and their Coulomb interactions. We obtain the trial wave functions which minimize the energy of the quantum mechanical Schroedinger equation. The minimization gives the structural parameters, bond lengths and the bond angles. Usually, the structure calculated from the density functional theory is in reasonable agreement with the experimental values for most of the atoms. We also obtain the energies in various approximations. The local density approximation (LDA) is largely used for this purpose. It is possible to refine the calculation by using the generalized-gradient approximation (GGA) in which the atoms are connected by means of a linear gradient. The exchange interactions are fully taken into account and we calculate the energies by including the exchange interaction (GGA-X). When the problem is solved there are kinetic energy terms and there are potential energy terms. When exchange integrals are separated out, some of the integrals are left out. These integrals arise from the Coulomb interaction but can not be classified as exchange because of the restrictions on the wave functions. These integrals are called "correlations". We calculate the energy of the system with exchange as well as the correlations (GGA-XC). We are interested in making a new type of cytosine

molecule in which extra atoms are adsorbed near the hexagon of the cytosine molecule.

METHODOLOGY

The Amsterdam density functional (ADF) theory program is having all of the quantum mechanics stored in the computer including the electronic configurations of all of the atoms. Hence we can pick up any atom of our choice and construct the molecule. The equations are solved for the minimum energy and structural parameters are tabulated. The energies are also obtained for the same structure. For the static potential v(r), the energy is written as,

E=

$$\int v(r)n(r)dr + \frac{1}{2}\iint \frac{n(r)n(r')}{|r-r'|}drdr' + G[n]$$

Where n(r) is the density and G[n] is a universal function of density. The usual exchange integral is,

E_x=

$$\iint \psi_i(r_i)\psi_j(r_j)\left|\frac{e^2}{|r_i - r_j|}\right|\psi_i(r_j)\psi_j(r_i)dr_i dr_j$$

which has the i, j exchanged. When the integrals do not obey this exchange rule we call them correlations as explained by Kohm and Sham [7-10]. Starting from the first principles, we have converted the problem to numerical evaluation of energies, bond structures and the charge densities in a graphical representation.

RESULTS

The cytosine molecule is shown in Fig. 1. The bond distances of each atoms are, C-C single bond length 1.54au, C=C double bond length 1.35au, C-N single bond length 1.47 au, C=N double bond length 1.46 au , N-O single bond length 1.01au and C=O double bond length 1.22au. From the experimental knowledge of the molecular structure, a molecular model is generated by using the density functional theory. Then one hydrogen atom is placed on top of the centre of the hexagon and optimizations are repeated. The position of the added hydrogen atom is shown in Fig. 2. The computed charge density of the cytosine with one H atom is shown in Fig.3. In Fig.4 we show the position of a hydrogen molecule on top of a cytosine and in Fig.5, the charge density of the same.

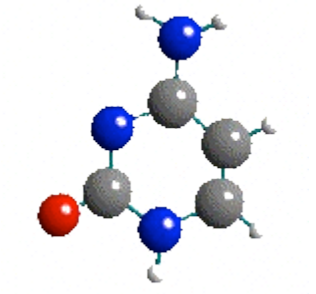

Figure 1: Cytosine in ball and stick model.

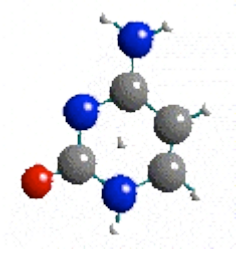

Figure 2: Adsorption of one H atom on top of the hexagonal position of the cytosine molecule.

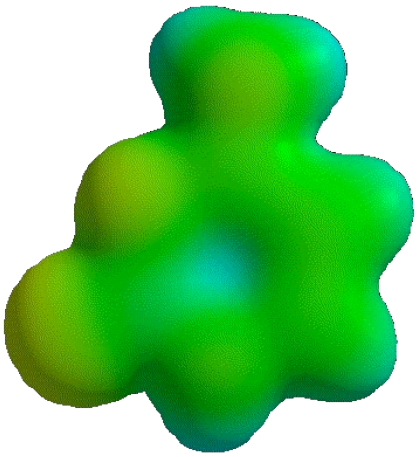

Figure 3: The charge density of H atom along with that of the cytosine molecule.

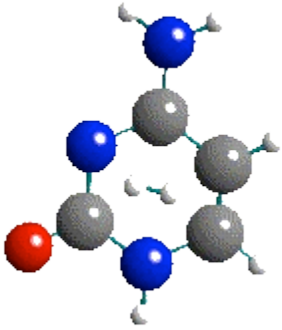

Figure 4: The position of H_2 on top of the cytosine molecule.

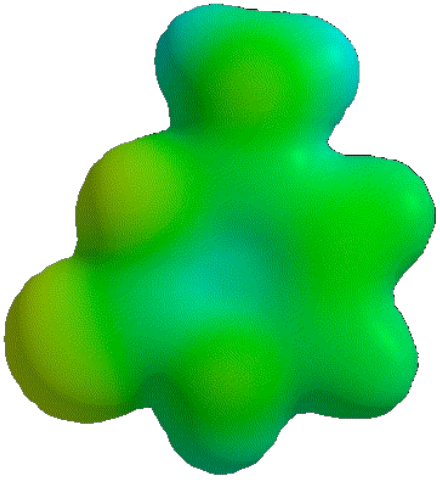

Figure 5: The charge density of cytosine with one H_2 molecule adsorbed on the hexagonal position as calculated from the first principles.

First of all the binding energy of one cytosine molecule is calculated. The energy of one atom is also calculated. Then the energy of the combination is calculated. All of these calculations are done in various approximations. The atoms are chosen according to the periodic table. The first group of atoms are selected first and computed. Similarly the calculation is repeated for the second group of atoms. It is found that Ba has the largest adsorption energy. The values of energies are obtained in LDA, GGA-X as well as GGA-XC. The same values are also obtained for the hydrogen molecule and all of these values are given in Table 1. The difference between the individual values and that of the combination is also obtained. The calculations are repeated for the hologens as well as for the rare gas atoms and included in Table1. There is a smooth variation as a function of atomic number. In Fig.6 we show the LDA adsorption energy for various groups of the periodic table. The value peaks up for the largest atomic number within a group. In Fig.7 we show the adsorption energies which are small compared with the large value for barium. In this picture the importance of chlorine as compared with that of hydrogen is very clearly exhibited.

Table 1: The static potential and various energies as calculated in various approximations. Here cyt = One molecule of cytosine.

ELEMENTS	POTENTIAL	LDA (ev)	GGA-X(ev)	GGA-XC(ev)
cytosine		-85.88956393	-73.53491323	-78.67256654
H	0.94377051	-0.00000371	0.00000321	-0.00000002
cyt+H	0.73930082	-82.39453030	-68.81272099	-74.53559825
#		-3.49503734	-4.72218963	-4.13696231
Li	0.34387212	0.00000188	0.00019898	-0.00000542
Cyt+Li	0.32149088	-76.41097813	-62.85833921	-68.35179713
#		-9.47858392	-10.67737504	-10.32076883
Na	0.31666686	0.00004856	0.00009497	0.00000026
Cyt+Na	0.44829161	-52.24460743	-37.55632792	-43.54911464
#		-33.64496794	-35.97829034	-35.12344564
K	0.25297544	-0.00010976	-0.00013896	0.00000634
Cyt+k	0.64292250	-26.0432325	-8.73701676	-16.05928939
#		-59.84644044	-64.79803543	-62.61326489
Rb	0.2367763	0.00002719	0.00002410	-0.00000135
Cyt+Rb	0.40741577	-8.97101732	9.37678044	1.61562659
#		-76.91851942	-82.91166957	-80.28818848

ELEMENTS	POTENTIAL	LDA	GGA-X	GGA-XC
Cs	5.34268517	-0.00001197	-0.00001156	0.00000103
Cyt+Cs	5.16573299	29.60230244	47.55035835	40.00464014
#		-115.4918783	-119.0852831	-118.6771997
Fr	4.79926533	-0.00001113	0.00000227	0.0000143
Cyt+Fr	4.59943630	53.52636118	71.93779368	64.32113962
#		-139.4159362	-145.4727046	-142.9936987
H_2	2.200779016	-6.61701237	-6.67940609	-6.66251558
Cyt+H2	1.93565051	-77.16458025	-63.23972320	-69.16063209
#		-15.34199605	-16.97459612	-16.17444403
Be	1.10194199	0.00002158	-0.00003991	0.00000088
Cyt+Be	0.96705588	-76.36352620	-61.8759724	-67.77028242
#		-9.52601615	-11.65898074	-10.90227724
Mg	0.84727517	0.00001308	0.00003425	0.00000020
Cyt+Mg	0.80208854	-52.29307065	-37.56064633	-43.52667990
#		-32.99648019	-35.97423265	-35.14588044
Ca	0.64788353	-0.00003436	-0.00004350	-0.00000020
Cyt+ca	1.20496347	-30.73410048	-13.76950602	-20.85496711
#		-55.1554978	-59.76545071	-57.81759363
Sr	0.58249508	0.00004816	0.00003759	0.00000434
Cyt+Sr	0.89410892	-6.47991878	11.63974385	3.99394719
#		-117.399666	-123.1835767	-120.6606289

ELEMENTS	POTENTIAL	LDA	GGA-X	GGA-XC
Ba	5.41549915	0.00005803	0.00005425	0.00000434
Cyt+Ba	5.2735482	55.62452873	73.92579702	66.39415489
#		-141.5140347	-147.460656	-145.0667111
F	9.2673022	-0.00016651	0.00031663	0.00001072
Cyt+F	9.32619585	-61.87445607	-46.54170674	-52.97577251
#		-24.01527437	-26.99288986	-25.69677731
Cl	5.50555246	-0.00002706	0.00011730	0.0000109
Cyt+cl	5.38460011	-27.54925361	-10.98256270	-17.99331331
#		-58.34033738	-62.55223323	-60.67924614
Br	4.68770486	0.00001265	0.00002413	0.00000038
Cyt+Br	4.48619723	-11.82277561	5.36725701	-1.81341689
#		-74.06677567	-78.90214611	-76.85914327
I	3.86933925	0.00003908	0.00003882	0.00000049
Cyt+I	3.67307764	17.43006299	35.17697476	27.83491784
#		-103.3195878	-108.7118492	-106.5674779
At	3.51202083	0.00005515	0.00004008	0.00000099
Cyt+At	3.32855966	40.62096163	58.94625171	51.47368812
#		-126.5104704	-132.4811249	-130.1462477
He	3.3658701	0.00002298	-0.00001089	-0.00000003
Cyt+He	3.30996432	-75.37827089	-61.78421266	-67.45168022
#		-10.51127006	-11.75071146	-11.22088035

ELEMENTS	POTENTIAL	LDA	GGA-X	GGA-XC
At	3.51202083	0.00005515	0.00004008	0.00000099
Cyt+At	3.32855966	40.62096163	58.94625171	51.47368812
#		-126.5104704	-132.4811249	-130.1462477
He	3.3658701	0.00002298	-0.00001089	-0.00000003
Cyt+He	3.30996432	-75.37827089	-61.78421266	-67.45168022
#		-10.51127006	-11.75071146	-11.22088035
Ne	11.81095361	-0.00000882	-0.00017386	0.00000477
Cyt+Ne	11.72560389	-54.26402651	-39.14073761	-45.42858508
#		-31.62554624	-34.39434948	-33.24397068
Ar	6.91271004	0.00005684	-0.00014059	0.00000403
Cyt+Ar	6.68269113	-14.28230017	2.30586663	-4.6874587
#		-71.60720692	-75.84092045	-73.98509781
Kr	5.75114495	-0.00000937	-0.00002974	-0.00000002
Cyt+Ar	5.47456065	2.48726113	19.64487177	12.42770545
#		-88.37683443	-83.17981474	-91.10026601
Xe	4.67263566	-0.00000543	-0.00000295	-0.00000001
Cyt+Xe	4.36041998	30.48509377	48.20169909	40.80432364
#		-116.3746631	-121.7366153	-119.4770842

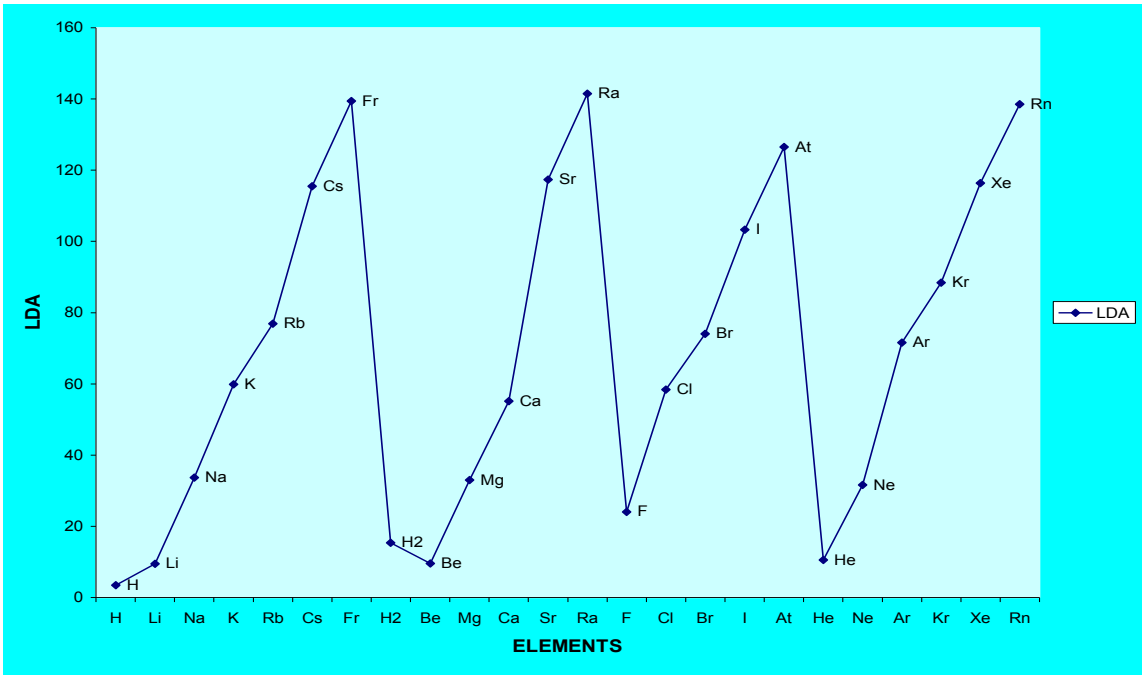

Figure 6: The adsorption energies of all of the atoms of the first group, the second group, the halogens and the rare gas atoms on cytosine, showing the maximum for Ba.

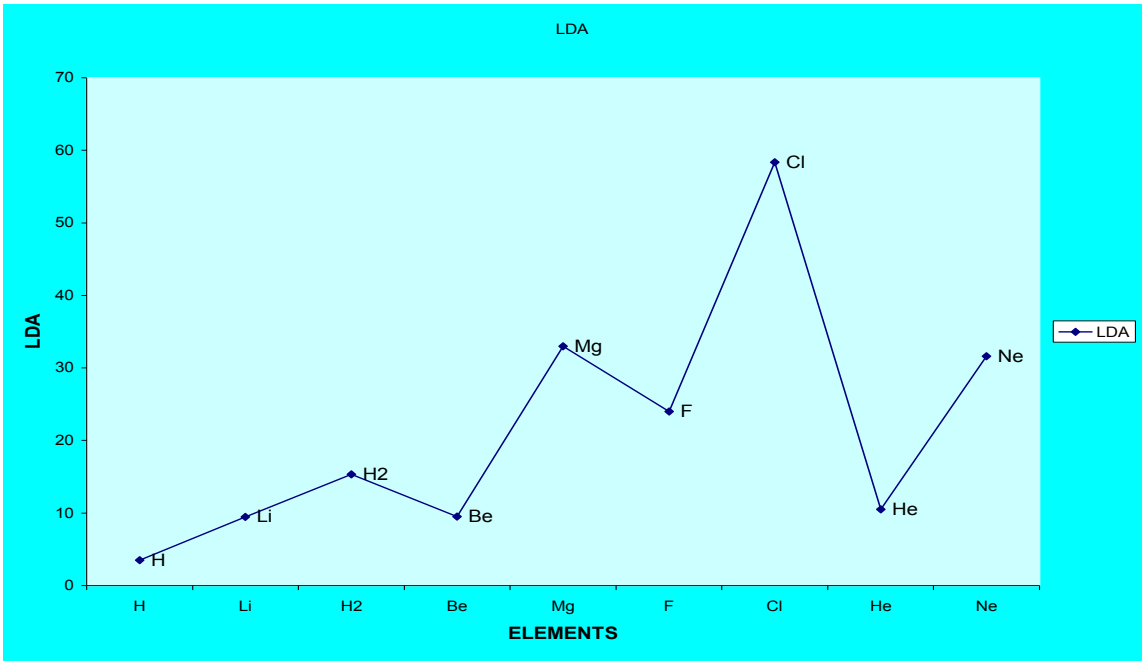

Figure 7: A selection of atoms with low energies shows the importance of chlorine atoms as compared with hydrogen.

CONCLUSIONS

We have calculated the energies of four different columns of the periodic table and that of a molecule of cytosine and one molecule of hydrogen. We also make pairs of cytosine with various atoms, one at a time and find the adsorption energy. From this study we find that various atoms get adsorbed on cytosine and from the atoms studied Ba has a strong effect on cytosine. Usually there are a lot of water molecules in the real system which often contains Ba as an impurity. We find that Ba strongly adsorbs in DNA. In another paper we have reported that NaCl is adsorbed on chlorophyll [11].

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REFERENCES

1. Alexandre S. S., Hervieux P. A., Charpentier and Ruiz-Lopez, F. (2008), Geometry and electronic structure of M-DNA(M=Zn^{2+}, Co^{2+} and Fe^{2+})Phys. Rev. A 78: 042702-1-5.

2. Weightman P., Dolan G. J., Smith C. I., Cuquerella, Almod N. J., Farrell T, Fernig D.G., Edwards C. and Martin D. S. (2006), Orientation of ordered structures of cytosine and cytidine 5'-monophosphate at Au(110)/liquid interfaces, Phys. Rev. Lett. 96: 086102-1-4.

3. Dal Cappello C., Hervieux, Charpentier I. and Ruiz-Lopez F. (2008), Ionization of the cytosine molecule by protons: Ab initio calculation of differential and total cross sections, Phys. Rev. A 78:042702-1-4.

4. Kassim, H. A., Yusof N, Devi V. R. and Shrivastava K. N. (2008), The quantum mathematical modeling of adsorption of Atoms on adenine, AIP Conf. Proc. 971: 29-33.

5. Zabidi N. A., Rosli A. N, Kassim H A, Shrivastava K. N., Venkateswar Rao P. And Radhika Devi V. (2007), Adsorption of atoms on thymine: Density functional theory, Mal. J. Sci. 26: 99-109.

6. Kassim H A, Yusof N., Devi V. R. and Shrivastava K. N. (2008), The quantum mathematical modeling of adsorption of atoms on heme, AIP Conf. Proc. 971:34-38.

7. Kohn W. and Sham L. J. (1965), Quantum density oscillations in an inhomogeneous electron gas, Phys. Rev. 137: A 1697-A1705.

8. Kohn W. and Sham L. J. (1965), Self-consistent equations including exchange and correlation effects, Phys. Rev. 140: A1133- A 1137.

9. Sham L. J. and Kohn W. (1966), One-particle properties of an inhomogeneous interacting electron gas, Phys. Rev. 145:561-567.

10. Kohn W.(1998), Electronic structure of matter, wave functions and density functionals, Rev. Mod. Phys. 71: 1253-1265.

11. Rosli A. N, Zabidi N. A., Kassim H. A., Mohd Arof A. K. and Shrivastava K. N. (2009), Mal. J. Sci. 28: 99-104.