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Adsorption of Atoms on Thymine: Density Functional Theory

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ABSTRACT We calculate the adsorption energy of F, Cl, Br, I, At, H, Li, Na, K, Rb, Cs, and Fr on the thymine molecule. The calculation is performed by using the quantum mechanical density functional theory. The calculation has been performed in the local density approximation (LDA), in the generalized gradient approximation with exchange (GGA-X) as well as in the generalized gradient approximation with exchange and correlations (GGA-XC). We are able to find the adsorption energy as well as its variation as a function of atomic number of the adsorbed atom.

(Thymine, Density Functional, Adsorption)

INTRODUCTION

The deoxyribonucleic acid commonly known as DNA is known to carry heredity in the arrangement of its four major constituents, adenine, thymine, guanine and cytosine. The constituents, A, T, G and C are present in equal quantities. The phosphate groups are outside the double helical arrangements of A-T and G-C and it is all covered with chromozones. It is possible to make salts of DNA which can be extracted in crystalline form. The A-T G-C should not have any extra atoms or molecules adsorbed in between otherwise, these extra atoms or molecules will be passed on from parents to children and that is known as genetic characteristics, such as a long nose or a spherical face. In physics, we are interested in calculating the adsorption energies of atoms on the components of DNA. The adsorption of adenine on graphite has been calculated by Ortmann *et al.* [1]. We have been doing this type of calculations for some time. We are able to study the adsorption of nitrogen on metal surfaces [2], the adsorption of alkali atoms on a zeolite [3], the adsorption of hydrogen molecule on the surfaces of many atoms [4]. Our calculations of vibrational frequencies in clusters of atoms are in good agreement with those measured from the Raman spectra of GeSI and GePS glasses [5, 6].

In this paper we present our calculation of adsorption of atoms on thymine by using the density functional theory. The energy of the Schroedinger equation can be calculated in several approximations. Three separate calculations are performed to obtain the adsorption energy. We calculate the adsorption energy of an atom, from the expression, $\varepsilon_1+\varepsilon_2-\Delta$ where the ε_1 is the energy of one molecule of thymine, and ε_2 is the energy of one atom and $\varepsilon_1+\varepsilon_2-\Delta$ is the energy of one molecule of adenine to which one atom has been added. In this way Δ can be obtained numerically. If ε_1 and ε_2 are both positive and the negative sign is already in the formula, positive adsorption energy shows a bound state or adsorption. Otherwise bound state must have negative energy. Hence, some times all of the energies, the energy of one atom or the energy of one molecule as well as that of the composite are all negative showing that all of these systems are bound.

THEORY

ADF is based on the Amesterdam Density Functional Theory (DFT), which has dominated quantum chemistry applications since the early 1990's. The Amesterdam Density functional package is a software for first principles electronic structure calculations. It contains many standard methods for studying energy surfaces and chemically relevant analysis. The ADF program has all the electrons for all the atoms of the periodic table memorized and it contains state of the art relativistic methods like ZORA and spin-orbit coupling to treat nuclei. ADF is especially suited for applications to transition metal compounds. The ADF includes the very latest meta-GGA and hybrid exchange – correlation functions. So we used the ADF package to solve problems of adsorption of atoms on thymine molecule. We simulated the atoms by using IBM p690, regetta which has 32×4, 1.3GHz processors. It gives the energy results in Local Density Approximation (LDA), generalized gradient with exchange (GGA-X) and generalized gradient approximation with exchange and correlations (GGA-XC). To understand the concepts of density functional theory, it is important to compare the derivation of the Hatree-Fock equations with that of the one particle density functional or Kohn-Sham equations [7]. The starting point in the derivation of Hatree-Fock (HF) theory is to express the total energy which depends on, the positions of the atoms, $\mathbf{R}_\alpha$.

HF **DFT**

$$E = E[\Psi,\mathbf{R}_\alpha] \qquad\qquad E = E[\rho,\mathbf{R}_\alpha] \tag{1}$$

$$E = \int\Psi^*[\textstyle\sum_i h_i + \sum_{i>j} 1/r_{ij}]\,\Psi\,d\tau \qquad\qquad E = T[\rho] + U[\rho] + E_{xc}[\rho] \tag{2}$$

$$\psi = \left|\psi_1(1),\psi_2,(2),\ldots..,\psi_n(n)\right| \qquad\qquad \rho(r) = \textstyle\sum_{occ}\left|\psi_i(r)\ \right|^2 \tag{3}$$

$$\frac{\partial E}{\partial \Psi} = 0 \qquad\qquad \frac{\partial E}{\partial \rho} = 0 \tag{4}$$

$$\left[-1/2\nabla^2 + V_C(r) + \mu^i{}_x(r)\right]\Psi_i = \varepsilon_i\psi_i \qquad\qquad \left[-1/2\nabla^2 + V_C(r) + \mu_{xc}(r)\right]\psi_i = \varepsilon_i\psi_i \tag{5}$$

In DFT, the derivation begins with the total energy written as a function of the total electron density for given positions of the atomic nuclei (1). In contrast to HF theory, DFT uses a physical observable, the electron density, as a fundamental quantity. In HF theory, the total energy is expressed, as an expectation value of the exact nonrelativistic Hamiltonian (2) using a Slater determinant (3) as an approximation for the total wave function. In DFT, the total energy is decomposed in a formally exact way into three terms (2), a kinetic energy term, T[ρ], an electrostatic or Coloumb energy term, U[ρ], and a many–body term, E_{xc}[ρ], which contains all exchange and correlation effects. This decomposition is constructed in such a way that [ρ] correspond to the kinetic energy of a system of non–interacting particles that yield the same density as the original electron system. The HF equations can be written in a form that resembles very closely that of the Kohn-Sham equations. In fact, the only formal difference is in the term μ(**r**). In HF theory, this term describes exchange effects and depends on the actual orbital, ψ_i , the Fock operator is acting on. In contrast, the corresponding term in DFT contains, by construction, all many–body effects and does not depend on the orbital index, i. The Hamiltonian in the DFT equations is an effective one–electron operator. It contains a one-electron kinetic energy operator, a Coloumb potential operator, Vc, which includes all electrostatic interactions (electron-electron, electron-nuclei, nuclei-nuclei), and the exchange–correlation potential operator. The DFT orbitals are the eigen functions of this operator with eigen values ε_i. The kinetic energy and the Coloumb potential operator are identical in HF theory and DFT. Approximations in DFT are introduced in the exchange correlation potential operator while, in principle, there are no conceptual approximations made in wave functions or in any other place. One could say that the Hatree-Fock equations solve the exact Hamiltonian with approximate many-body wave functions while the DFT equations solve an approximate many-body Hamiltonian with exact wave functions. Hatree-Fock based methods converge to the exact solution of the many-body Schrödinger equation through systematic improvements in the form of many-body wave functions, for example by configuration interaction expansions. DFT theory converges to the exact solution by improving the effective exchange correlation potential operator, $\mu_{xc}(\mathbf{r})$. This is equivalent to improving the description of the total exchange-correlation energy, E_{xc}, because of the relation

$$\mu_{xc}(r) = \delta E_{xc}[\rho] / d\, \rho(r) \qquad (6)$$

In other words, if the exchange-correlation functional of a system would be known, the DFT equations would provide the exact solution of the many-body problem. Currently, the most common approximation to the exchange-correlation energy is the so-called local density approximation (LDA)

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\, \varepsilon_{xc}[\rho(\mathbf{r})]\, \mathbf{dr} \qquad (7)$$

In eq. (7), $\varepsilon_{xc}[\rho]$ is the exchange-correlation energy per electron in an interacting electron system of constant density ρ. This quantity is known from many-body theory. For metallic and strongly delocalized systems with fairly constant electron density, the LDA comes very close to the exact solution whereas this approximation can be expected to be less accurate for systems with strongly varying electron densities.

It is a fundamental assumption in the LDA (7) that the length–scale associated with exchange and correlation effects is small compared with the length scale on which the electron density varies significantly. The surprisingly good results obtained for a number of solid state and molecular systems seem to indicate that it is justified to assume a rather local nature of many-body effects in solid state and molecular systems. In contrast to this approach, configuration interaction expansions use molecular orbitals, which extend spatially over entire molecule, to capture correlation effects. The slow convergence of CI expansions may actually be an indication that the length-scale implicit in molecular orbitals may not properly match the length-scale of exchange-correlation effects. In other words, perhaps the density functional picture, at least for systems with many electrons, is more "natural" for expressing exchange and correlation effects than a wave function approach. The non-local nature of the Hatree-Fock exchange term, in contrast to the local characteristics of the exchange-correlation term in the local density functional (LDF) method can also be seen from a comparison of the corresponding terms in the HF and LDF equations. To this end, the exchange term in the HF equations is written in the form of a potential energy operator.

$$\mu'_x(r) = -\sum_j \delta(\sigma_i, \sigma_j) \left\lfloor \int \psi_i^*(r) \psi_j^*(r') 1/|r - r'| \psi_j(r) \psi_i(r') dr' \right\rfloor / \left\lfloor \psi_i^*(r) \psi_i(r) \right\rfloor \qquad (8)$$

This HF exchange operator, which includes only interactions between electron with the same spin, depends on the orbital, ψ_i, and contains information of all wave functions from the entire system. Thus, the operator is highly non-local. The HF exchange operator (8) does not contain any Columb screening which causes a well-known qualitative breakdown of HF theory in the limit of the homogeneous electron gas.

In LDF theory, the corresponding term can be written in the form

$$\mu_{xc} = \varepsilon_{xc}[\rho(\mathbf{r})] + \rho(\mathbf{r}) \{\delta\varepsilon_{xc}[\rho(\mathbf{r})] / \delta\rho(\mathbf{r})\} \qquad (9)$$

This exchange-correlation operator contains information of just the electron density at point **r** and the exchange correlation energy, ε_{xc}, associated with that density. The essence of the LDA is the assumption that the exchange-correlation energy arising from a volume element, dr, in an inhomogeneous system is the same as if that volume element would be embedded in a homogeneous electron gas of that density. Further more, it is assumed that the total exchange-correlation energy of a system can be obtained by integrating the local contributions over all space. For computational purposes it is convenient to represent the results for ε_{xc} and μ_{xc} at various densities in analytic form. It is found that such representation can be written as,

$$\mu_{xc}(\mathbf{r}) = \alpha\, \rho(\mathbf{r})^{1/3} + \ldots \qquad (10)$$

in which the leading term has the form which was originally proposed by Slater in the Xα method. Thus, the Xα method can be seen as an approximation to the LDA. It should be noted again, though, that the LDA does not contain any empirically adjustable parameters, but is based on a rigorous first-principles many-body approach. The generalized gradient approximations (GGA's) for the exchange-correlation energy improve upon the local spin density (LSD) description of atoms, molecules and solids. Kohn-Sham density functional theory is widely used for self-consistent-field electronic structure calculations of the ground-state properties of atoms, molecules and solids. In this theory, the sum of the exchange and correlation energy is,

$$E_{xc} = Ex + Ec \qquad (11)$$

as a functional of the electron spin densities, $\eta_\uparrow(\mathbf{r})$ and $\eta_\downarrow(\mathbf{r})$ must be approximated. The most popular functionals have a form appropriate for slowly varying densities: the local spin density (LSD) approximation

$$E^{(LSD)}{}_{xc}[\eta_\uparrow,\eta_\downarrow] = \int d^3r\,\eta\,\varepsilon^{unif}{}_{xc}(\eta_\uparrow,\eta_\downarrow) \quad (12)$$

Where $\eta = \eta_\uparrow + \eta_\downarrow$, and the generalized gradient approximation (GGA)

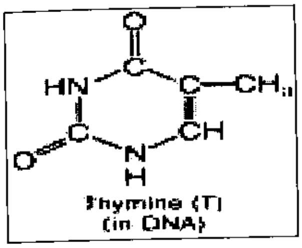
$$E_{xc}[\eta_\uparrow,\eta_\downarrow] = \int d^3r f(\eta_\uparrow,\eta_\downarrow,\nabla\eta_\uparrow,\nabla\eta_\downarrow) \quad (13)$$

In comparison with LSD, GGA's tend to improve total energies, atomization energies, energy barriers and structural energy differences. GGA's expand and soften bands an effect that sometimes corrects and sometimes overcorrects the LSD prediction. Typically, GGA's favor density inhomogeneity more than LSD does. Semiempirical GGA's can be remarkably successful for small molecules and not for delocalized electrons in a uniform gas or a simple metal. The density functional one-particle equations (5) have to be solved in an iterative self-consistent-field (SCF) procedure similar to that used in Hatree-Fock theory. The procedure begins with a starting density corresponding to a certain geometric arrangement of the nuclei. Usually, the starting density is constructed from a superposition of atomic densities. The Coloumb operator of the DFT equations can be evaluated either explicitly by solving Poisson's equation or by calculating Coloumb integrals for a given basis set using a fitted density. The former procedure is most commonly used in solid state calculations where the calculations of the Coloumb potential involve summations over the entire lattice. It is also employed in Dmol program in which numerical basis functions are used. In the case of Gaussian-type basis functions, it is more convenient to follow the latter procedure. The calculation of the exchange-correlation potential is typically done on numerical grid in real space and the results are then fitted or expressed in a convenient analytic form. In the standard procedure, the DFT equations are solved by expanding the one-particle wave functions (molecular orbitals) variationally into a basis set. Once the Hamiltonian and overlap matrix elements are calculated, the eigen values and eigen vectors are found from the diagonalization of the matrix. Following an Aufbau principle, the orbitals are occupied and a new density is formed. This completes one cycle in the SCF procedure. At this point, convergence acceleration schemes are used to create a new input density from the previous input and output densities. After self-consistency is achieved, the total energy for this geometry with the corresponding molecular properties can be calculated. If the goal is a geometry optimization, the energy gradients are evaluated and used in the choice of a new geometry. A new SCF cycle is then started with the new geometry. At this point, the SCF cycle can be started with the SCF density from the previous geometry, provided that the geometry has not changed too much. In general, DFT SCF procedures seem to converge somewhat slower than corresponding Hatree-Fock calculations. Typical closed-shell organic molecules do not pose any serious challenges for the SCF convergences. In the present work, we use only the DFT for which the computer program is available.

DFT ADSORPTION OF ATOMS ON THYMINE

In this study we have examined the adsorption of alkaline and halogen atoms on thymine (2-oxy-4-oxy-5 methylpyrimidine). Alkaline group carries the atoms like H, Li, Na, K, Rb, Cs and Fr. For the halogen group Cl, F, Br, I and At, the geometry optimizations were carried out by Density Functional Theory (DFT). The adsorption of alkaline and halogen atoms including H_2 molecule has been calculated keeping in the centre of pyrimidine group. It is found that adsorption energy for Fr is high and for H is low in alkaline group. Similarly, adsorption energy is high for At and low for F in the halogen group. In both groups adsorption energy increases with increasing atomic number. Thymine ($C_5H_6N_2O_2$) is one of the bases of the nuclic acid found in DNA (Deoxyribo Nuclic Acid). Its molecular weight is 126.12 Daltons. It can form base pair with adenine (A-T). In RNA (Ribo Nuclic Acid) thymine is replaced with

Uracil. The molecular structure of thymine is given in Figure 1.1 and the charge density is given in Figure 1.2.



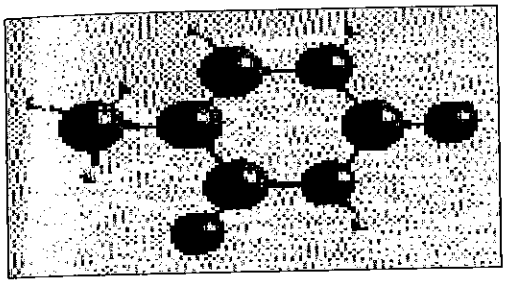


Figure 1.1. The stick and ball model of thymine

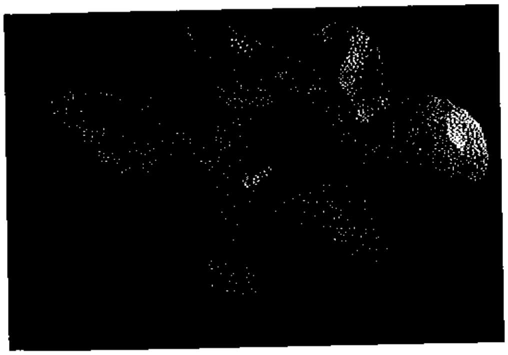


Figure 1.2. The molecular structure, bond picture and the charge density of thymine calculated by us

We report our results of adsorption of alkaline, halogen and H_2 molecule on thymine by using ADF. The Schrodinger equations can be solved for a cluster of large number of atoms and the bond energy is calculated. Along with the energy, the geometry of the cluster of atoms is also optimized and bond distances are determined. The program gives the values in LDA, GGA-X, and GGA-XC. The bond distances of each atoms in thymine are found to be, C – C bond length 1.54A, C = C double bond length 1.36A, C – N bond length 1.47A, C – H bond length 1.08A, N–H bond length 1.01A and C = O bond length 1.22A. First the binding energy of thymine molecule energy values (E_1) has been calculated and the energy values (E_2) are separately calculated for each of the atoms. After that we adsorbed the atom on pyrimidine, then optimized and found the energy values (E_3). The differences in energy values are found using

$$E_1+E_2-\Delta=E_3 \qquad (14)$$

In this way we calculated bond energy values of alkali atoms, halogens as well as hydrogen on a molecule of thymine. The calculated adsorption energy is highest for Frantium (Z = 87) and smallest for Hydrogen (Z = 1) in first group atoms. The binding energy values and atomic number (Z) of H, Li, Na, Rb, Cs, and Fr are given in Table 1, and the charge density is given in various parts of Figures. 2.1 to 2.14. The adsorption energy is highest for atenine (Z = 85) and smallest for fluorine (Z = 9) in halogen group atoms. The binding energy values and atomic numbers (Z) of F, Cl, Br, I, At are given in Table 2 and corresponding pictures are given in various parts of Figures 3.1 to 3.12. It has been noted that as the atomic number (Z) increases, the energy uniformly increases. After completion of adsorption of atoms on thymine molecule, we observed that the energies in various approximations LDA, GGA-X, and GGA-XC slightly differ. Similarly, the H_2 molecule is absorbed in the same way and the energy values and adsorption pictures are given in Table 3, and the charge densities are given in Figures 3.2, 3.4, 3.8, 3.10 and 3.12.

Table 1. The optimized energy values for alkaline group atoms on thymine

Sl No.	MOLECULES & ATOMS	ATOMIC No. (Z)	LDA (eV)	GGA-X (eV)	GGA-XC(eV)
	H (E_1)		-0.00000371	0.00000321	0.00000002
1	**Thymine(E_2)**	1	**-91.87729541**	**-77.15888719**	**-83.26017197**
	Thy + H(E_3)		-87.38328479	-71.59884744	-78.24905145
	Δ		-4.49401433	-5.56003654	-5.0192205
	Li		0.00000188	0.00019898	-0.00000542
2	Thy + Li	3	-82.29963713	-66.51018324	-72.91595781
	Δ		-9.5776564	-10.64850497	-10.34421958
	Na		-0.00004856	0.00009497	0.00000026
3	Thy + Na	11	-59.51742128	-42.54089680	-49.48247760
	Δ		-32.35982557	-34.61789554	-33.35982557
	K		-0.00010976	-0.00013890	0.00000634
4	Thy + K	19	-34.55356208	-15.01474872	-23.29118997
	Δ		-57.32384309	-62.14427737	-59.96897566
	Rb		0.00010976	0.00002410	-0.00000135
5	Thy + Rb	37	-15.77081596	4.91030009	-3.82106773
	Δ		-76.10645226	-82.06916318	-79.43910559
	Cs		-0.0001197	-0.00001156	0.00000103
6	Thy + Cs	55	23.68426058	43.84957588	35.29636832
	Δ		-115.561568	-121.0084746	-118.5565393
	Fr		-0.00001113	0.00000227	0.00000143
7	Thy + Fr	87	47.59192933	68.31774771	59.66617096
	Δ		-139.4692359	-145.4766326	-142.9263415

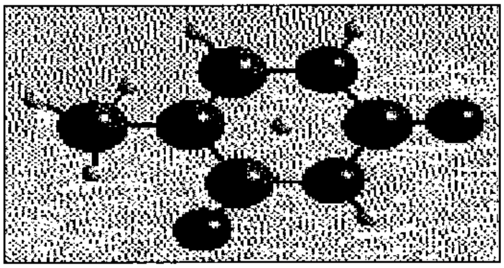


Figure 2.1. One hydrogen atom in the center of hexagon of thymine molecule

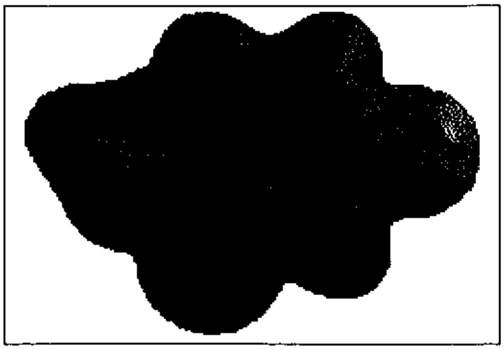


Figure 2.2. The charge density map of thymine molecule with H atom

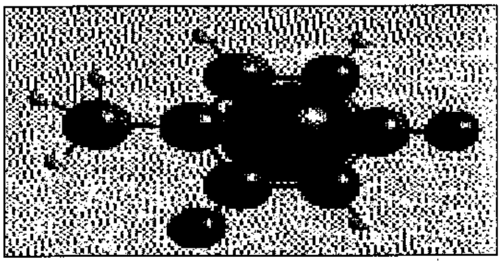


Figure 2.3. The adsorption of one Li atom on thymine

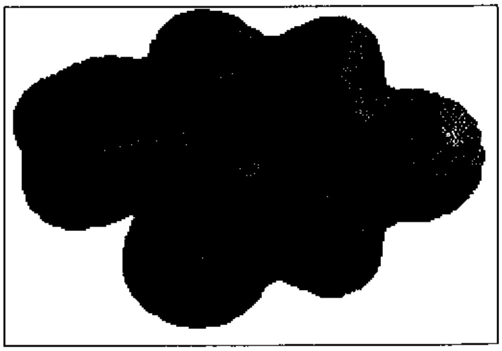


Figure 2.4. The charge density map of thymine with one Li

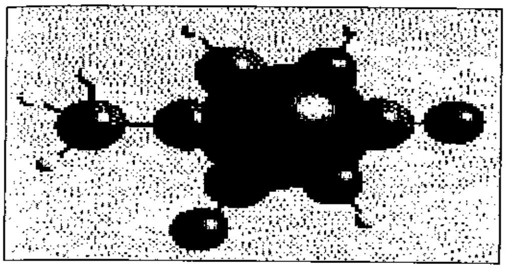


Figure 2.5. The adsorption of one atom of Na on thymine

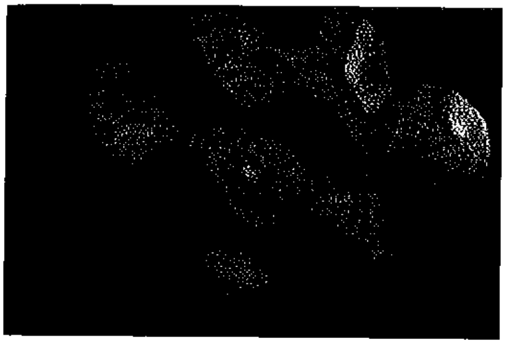


Figure 2.6. The charge density map of thymine with atom of Na

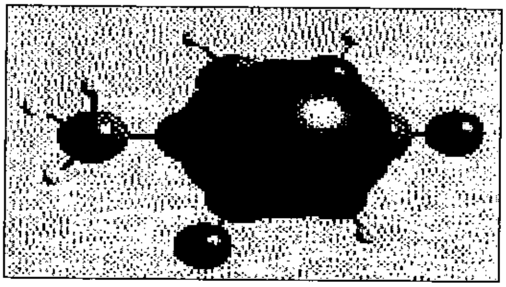


Figure 2.7. The adsorption of one atom of K on thymine

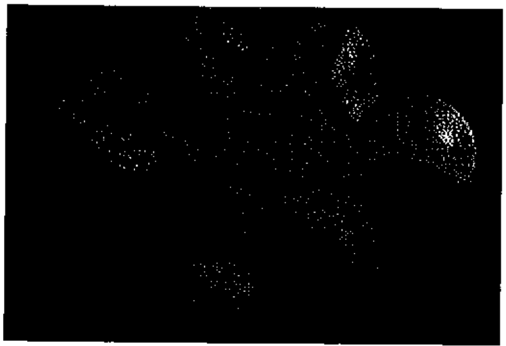


Figure 2.8. The charge density of thymine with one atom of K

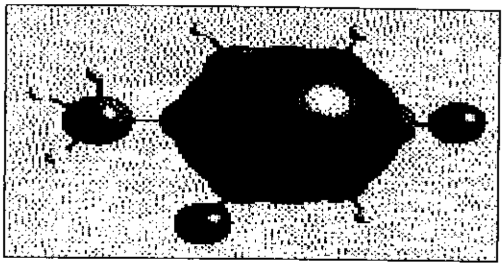


Figure 2.9. The one atom of Rb with thymine

Figure 2.10. The charge density of thymine with one atom of Rb

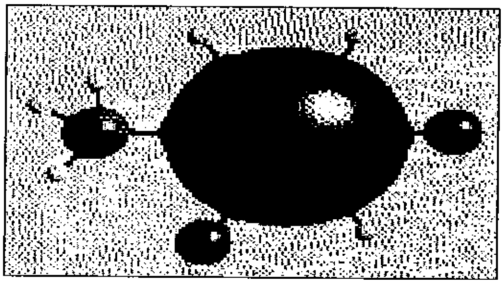


Figure 2.11. One atom of Cs along with one molecule of thymine

Figure 2.12. The charge density of one atom of Cs with one molecule of thymine

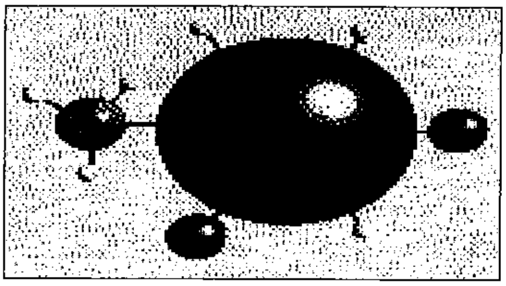


Figure 2.13. One atom of Fr along with one molecule of thymine

Figure 2.14. The charge density of one atom of Fr along with one molecule of thymine

Table 2. The optimized energy values for Halogen atoms on thymine

Sl No.	MOLECULES & ATOMS	ATOMIC No. (Z)	LDA (eV)	GGA-X (eV)	GGA-XC (eV)
	F		-0.00016651	0.00031663	0.00001072
1	Thy + F	9	-69.46483714	-51.95666048	-59.29501008
	Δ		-22.41262478	-25.20191008	-23.96515117
	Cl		-0.00002706	0.00011730	0.00000109
2	Thy + Cl	17	-33.53393291	-14.48459830	-22.59916245
	Δ		-59.33338956	-62.67417159	-60.66854631
	Br		0.00001265	0.00002413	0.00000038
3	Thy + Br	35	-18.15132817	1.43512384	-6.85526376
	Δ		-73.72595459	-78.5939869	-76.40490776
	I		0.00003908	0.00003882	0.00000049
4	Thy + I	53	11.85260842	31.89856532	23.52969835
	Δ		-103.7298648	-109.0574137	-106.7898698
	At		0.00005515	0.00004008	0.00000099
5	Thy + At	85	35.11149933	55.57916810	47.17705839
	Δ		-126.9887396	-132.7380152	-130.4372293

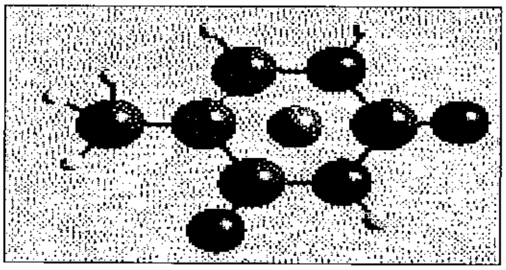


Figure 3.1. Adsorption of F on thymine

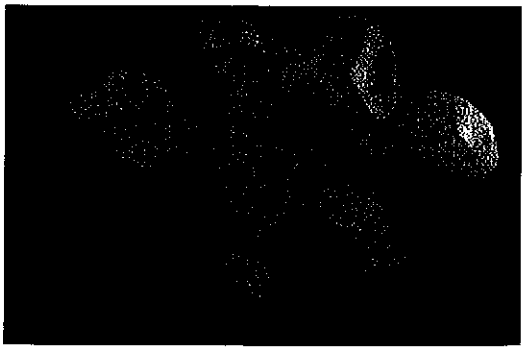


Figure 3.2. The charge density map of thymine with F

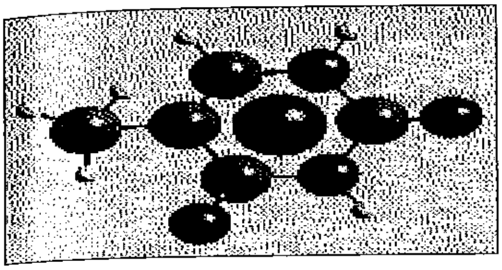


Figure 3.3. Adsorption of Cl on thymine

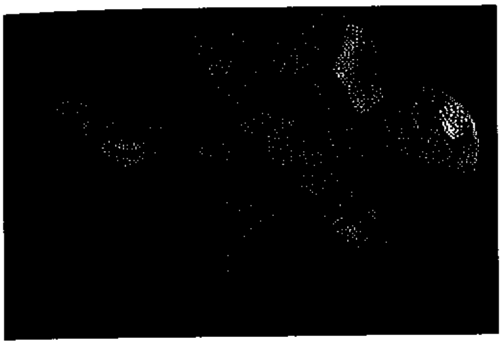


Figure 3.4. The charge density map of thymine with one Cl atom

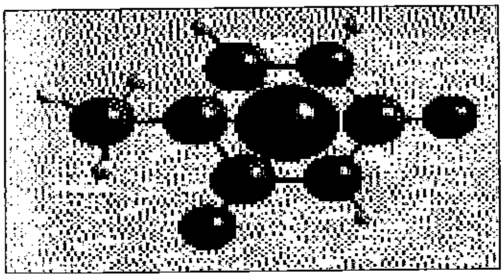


Figure 3.5. Adsorption of one atom of Br on thymine

Figure 3.6. The charge density map of thymine with one atom of Br

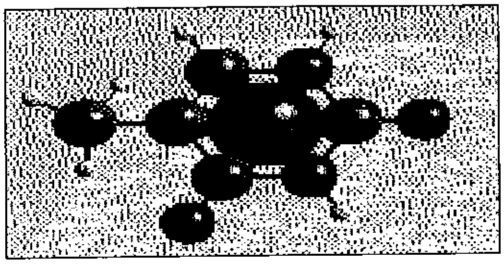


Figure 3.7. Adsorption of one atom of I on thymine

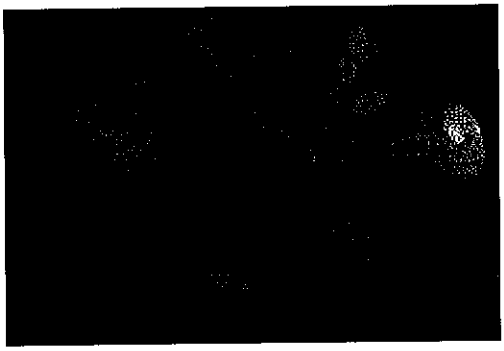


Figure 3.8. The charge density map of thymine with one atom of I

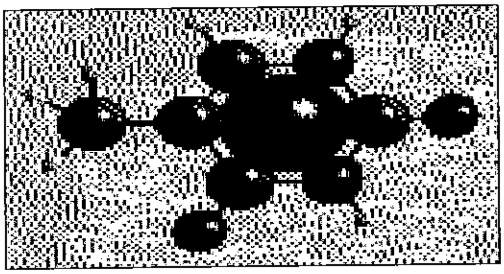


Figure 3.9. Adsorption of one atom of At on thymine

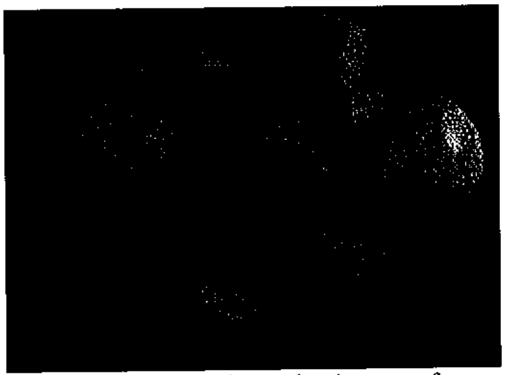


Figure 3.10. The charge density map of thymine with one atom of At

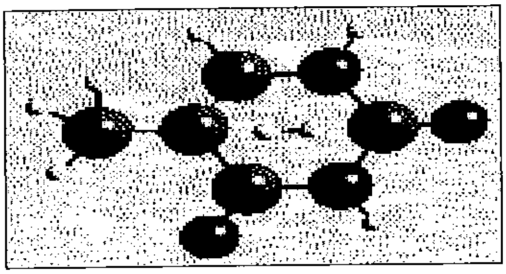


Figure 3.11. Adsorption of one molecule of H_2 on thymine

Figure 3.12. The charge density map of thymine with one molecule of H_2

Table 3. The optimized energy values for H_2 molecule on thymine

Sl No.	MOLECULES & ATOMS	ATOMIC No. (Z)	LDA (eV)	GGA-X (eV)	GGA-XC (eV)
	H_2		-6.61701237	-6.67940609	-6.66251558
1	Thy + H_2		-84.50589714	-68.41571458	-75.22075123
	Δ		-13.98841064	-15.4225787	-14.70193632

CONCLUSIONS

We have obtained the adsorption of several atoms and hydrogen molecule on one atom of thymine by using the quantum mechanical density functional theory. We have solved the Schroedinger equation in several approximations. It shows that there are bound states of atoms on thymine. Although we have considered the center of hexagon only for the calculation of adsorption, it is possible to select some other positions also, such as on oxygen which is connected by a double bond. The site selectivity is known in the case of thymine [8] as well as in the case of nitrogen on surfaces [2].

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