Density Functional Theory Investigation for Sodium Atom on Copper Clusters

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Abstract: Density functional theory has been performed for NaCu_n clusters, (n=4, 5, 6, 7). Optimization plus frequency at the ground state level, B3LYP, 3-21G basis sets has been investigated. The charges for all clusters are equal to zero (neutral charges). Molecular orbital theory has been used to find HOMO and LUMO energies. Total energy, dipole moment have been computed. Koopman's theor has been used to calculate the ionization potential and electron affinity. Also the electronegativity has been evaluated for sodium atom, pure copper clusters and NaCu_n clusters. Surfaces (HOMO and LUMO) and contours (electrostatic potential) have been carried out. All calculations have been investigated by using Gaussian 09 software package.

Keywords: DFT, B3LYP, Koopman's theor, Total Emergy, Dipole moment, Electronegativity.

1. Introduction

1.1 Density Functional Theory (DFT)

DFT is a computational quantum mechanical modeling method used in physics, chemistry and material science to investigate the electronic structure (principally the ground state) of many body systems, in particular atoms, molecules and condensed phases[1][2]. With this theory the properties of a many electron system can be determined by using functional i.e. functions of another function which in this case is the spatially dependent electron density [3]. Hence the name density functional theory comes from the use of functional of the electron density [4]. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics and computational chemistry[5]. DFT has been very popular for calculations in solid state physics since 1970s[6]. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions[7][8]. In many cases the results of DFT calculations for solid state systems agree quite satisfactorily with experimental data[9]. Computational costs relatively low when compared to traditional methods such as Hartree Fock theory and its descendants based on the complex many electron wave function despite recent improvements [10].

1.2. Basis Sets

A basis set in theoretical and computational chemistry is a set of functions called basis functions which are combined in linear combinations (generally as part of quantum chemical calculations) to create molecular orbitals[11]. For convenience these functions are typically atomic orbitals centered on atoms, but can theoretically be any function plane waves are frequently used in material calculations [12][13]. 3-21G means three Gaussian Type Orbitals for inner shell, two Gaussian Type Orbitals for inner valence and one Gaussian Type Orbital for outer valence [14]. B3LYP means Becke three parameter Lee-Yang-Parr and it has been called the hybridization method to obtain the approximations of DFT. This method was introduced by Axel Becke in 1993 to describe correlation-exchange energies[15].

1.3. Geometry Optimization

Geometry optimization is name for the procedure that attempt to find the configuration of minimum energy of the molecule[16]. The procedure calculates the wave function and the energy at starting geometry and then proceeds to search a new geometry of a lower energy. This is repeated until the lowest energy geometry is found the procedure calculates the force on each atom by evaluating the gradient (first derivative) of the energy with respect to atomic positions sophisticated algorithms are then used at each step to select a new geometry[17]. Aiming for rapid convergence to the geometry of the lowest energy. In the final minimum energy geometry the force on each atom is zero[18]. It is important to recognize that this procedure will not necessarily find the global minimum i.e. the geometry with the lowest energy[19][20].

2. Molecular Structure

Optimization plus Frequency has been carried out to optimize sodium atom and pure copper clusters. Also Optimization plus Frequency has been applied to optimize sodium on copper clusters NaCu_n. DFT has been used at 3-21G, B3LYP basis sets at the ground state with Gaussian 09 software package. Below figures of the optimized sodium atom, pure copper clusters and NaCu_n copper clusters.
3. Calculations

3.1 Total Energy

DFT partition the total energy as:
\[ E = E_T + E_V + E_J + E_{XC} \quad \ldots \ldots \ldots \ldots \ldots \ldots (1) \]

- \( E_T \): electronic kinetic energy
- \( E_V \): electron-electron repulsion
- \( E_J \): electron-electron repulsion
- \( E_{XC} \): exchange correlation term [21].

Total energy for Na atom, Cu\textsubscript{n}, NaCu\textsubscript{n} Clusters has been computed.

<table>
<thead>
<tr>
<th>System</th>
<th>Total Energy (eV)</th>
<th>Total Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>-0.043881</td>
<td>-0.043881</td>
</tr>
<tr>
<td>Cu\textsubscript{4}</td>
<td>-1.7768</td>
<td>-1.7768</td>
</tr>
<tr>
<td>Cu\textsubscript{5}</td>
<td>-2.2210</td>
<td>-2.2210</td>
</tr>
<tr>
<td>Cu\textsubscript{6}</td>
<td>-2.6653</td>
<td>-2.6653</td>
</tr>
<tr>
<td>Cu\textsubscript{7}</td>
<td>-3.1095</td>
<td>-3.1095</td>
</tr>
<tr>
<td>NaCu\textsubscript{4}</td>
<td>-1.8207</td>
<td>-1.8207</td>
</tr>
<tr>
<td>NaCu\textsubscript{5}</td>
<td>-2.2650</td>
<td>-2.2650</td>
</tr>
<tr>
<td>NaCu\textsubscript{6}</td>
<td>-2.7092</td>
<td>-2.7092</td>
</tr>
<tr>
<td>NaCu\textsubscript{7}</td>
<td>-3.1535</td>
<td>-3.1535</td>
</tr>
</tbody>
</table>

3.2 Dipole Moment

Dipole moment appears in the heteronuclear molecules. Homonuclear molecules have very small dipole moment as compared with heteronuclear, some homogenous molecules have no dipole moment [22].

<table>
<thead>
<tr>
<th>System</th>
<th>Dipole Moment (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.0000</td>
</tr>
<tr>
<td>Cu\textsubscript{4}</td>
<td>0.0000</td>
</tr>
<tr>
<td>Cu\textsubscript{5}</td>
<td>0.0000</td>
</tr>
<tr>
<td>Cu\textsubscript{6}</td>
<td>0.0022</td>
</tr>
<tr>
<td>Cu\textsubscript{7}</td>
<td>0.4936</td>
</tr>
<tr>
<td>NaCu\textsubscript{4}</td>
<td>5.1930</td>
</tr>
<tr>
<td>NaCu\textsubscript{5}</td>
<td>4.5814</td>
</tr>
<tr>
<td>NaCu\textsubscript{6}</td>
<td>4.7313</td>
</tr>
<tr>
<td>NaCu\textsubscript{7}</td>
<td>4.7614</td>
</tr>
</tbody>
</table>

3.3 Electronic State

HOMO and LUMO energies represent the electronic states. HOMO : High Occupied Molecular Orbital
LUMO : Low Unoccupied Molecular Orbital [23].

<table>
<thead>
<tr>
<th>System</th>
<th>( E_{\text{HOMO}} ) (eV)</th>
<th>( E_{\text{LUMO}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>-3.4783</td>
<td>-0.5586</td>
</tr>
<tr>
<td>Cu\textsubscript{4}</td>
<td>-4.7435</td>
<td>-3.0992</td>
</tr>
<tr>
<td>Cu\textsubscript{5}</td>
<td>-4.4048</td>
<td>-2.5863</td>
</tr>
<tr>
<td>Cu\textsubscript{6}</td>
<td>-4.7854</td>
<td>-3.1349</td>
</tr>
<tr>
<td>Cu\textsubscript{7}</td>
<td>-4.1950</td>
<td>-3.0037</td>
</tr>
<tr>
<td>NaCu\textsubscript{4}</td>
<td>-3.9406</td>
<td>-2.4682</td>
</tr>
<tr>
<td>NaCu\textsubscript{5}</td>
<td>-4.3566</td>
<td>-3.0570</td>
</tr>
<tr>
<td>NaCu\textsubscript{6}</td>
<td>-3.4603</td>
<td>-2.7629</td>
</tr>
<tr>
<td>NaCu\textsubscript{7}</td>
<td>-4.7598</td>
<td>-2.8772</td>
</tr>
</tbody>
</table>

3.4 Ionization potential and electron affinity

The ionization energy of an atom or molecule describes the minimum amount of energy required to remove an electron (to infinity) from the atom or molecule in the gaseous state. Electron affinity is defined as the change in energy of a neutral atom in the gaseous phase when an electron is added to the atom to form a negative ion. In other words, the natural atom's likelihood of gaining an electron [24].

According to Koopman's theorem in which the frontier orbital energies are given as:
\[ E_{\text{HOMO}} = -I.P \quad \ldots \ldots \ldots \ldots \ldots \ldots (2) \]
\[ E_{\text{LUMO}} = -E.A \quad \ldots \ldots \ldots \ldots \ldots \ldots (3) \]
\( I.P \) : Ionization potential
3.5. Electronegativity and Chemical Potential

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons[26]. Within the framework of DFT on of the global quantities are chemical potential (\(\mu\)) which is measures the escaping tendency of an electronic cloud and the electronegativity (\(\chi\)) which is characterized the escaping tendency of electrons from the equilibrium system (e.g., atoms or molecules). Let \(E(N)\) represent a ground state electronic energy as a function of the number of electrons (N). It is well-known the derivative of \(E(N)\) with respect to (N) at a constant external potential \(V^\text{ext}\) is the chemical potential or the negative of the absolute negativity. where:

\[
\mu = \left(\frac{\partial E(N)}{\partial N}\right)^{V^\text{ext}} \approx -\chi \quad \ldots \ldots (4)
\]

The electronegativity can be done by using the method which is based on the difference between the energies of HOMO and LUMO of the neutral molecules and is known as orbital vertical.

\[
\chi = \frac{E_{\text{HOMO}} - E_{\text{LUMO}}}{2} \quad \ldots \ldots (5)
\]

Or by using the equation:

\[
\chi = \frac{I.P + E.A}{2} \quad \ldots \ldots (6)[27].
\]

4. Surfaces and Contours

Surfaces have been carried out by using molecular orbitals for HOMO and LUMO orbitals. Contours have been carried out with electrostatic potential type (ESP).
5. Results and Discussion

Table (1) represents the total energy for Na atom, Cu\textsubscript{n} clusters, NaCu\textsubscript{n} clusters. The total energy for NaCu\textsubscript{n} clusters is less than the total energy for sum of the individual Na atom plus individual Cu\textsubscript{n} clusters, and this means that the molecules have been resulted and the bonding between sodium atom and copper clusters has been found. This result agree with results of the molecular physics[28][29].

Table (2) represents the dipole moment for Na atom, Cu\textsubscript{n} clusters, NaCu\textsubscript{n} clusters. The dipole moment for Cu\textsubscript{4}, Cu\textsubscript{5} clusters equal to zero, so this molecules have no dipole moment. The dipole moment for Cu\textsubscript{6} equal to (0.0002 Debye), so this molecule has very small dipole moment. The dipole moment for Cu\textsubscript{7} equal to (0.4936 Debye), so this molecule has small dipole moment. In general the dipole moment for Cu\textsubscript{n} clusters is much smaller than the dipole moment for NaCu\textsubscript{n} clusters, as shown in table (2). For example, the dipole moment for NaCu\textsubscript{4} cluster equal to (5.1930 Debye), the dipole moment for NaCu\textsubscript{5} cluster equal to (5.1930 Debye), the dipole moment for NaCu\textsubscript{6} cluster equal to (4.5814 Debye). Cu\textsubscript{n} clusters are homonuclear, thus these molecules have no interact with the electromagnetic rays and don’t give rotational spectrum, so these molecules don’t have dipole moment changes during the rotation. But NaCu\textsubscript{n} clusters have dipole moment varies during the rotation and this dipole moment generates because these molecules heteronuclear, so these molecules have a rotation and during process of absorption the molecule to the radiation the dipole moment interact with the electric field of the electromagnetic rays, so the rotation has been generated with the dipole moment.

This results are in general agreement with the basics of the spectroscopy science[30][31].

Table (3) stands for HOMO and LUMO energies for Na atom, Cu\textsubscript{n} clusters, NaCu\textsubscript{n} clusters. HOMO energies for copper clusters is higher than the HOMO energies for sodium atom, so the electrons will release to the unoccupied orbitals, therefore, copper represents the accepto, sodium represents the donor, and this results are in a good agreement with that obtained from reference [32].

Table (4) stands for the ionization potential and electron affinity for Na atom, Cu\textsubscript{n} clusters, NaCu\textsubscript{n} clusters. The ionization potential is close to work function for the solid Cu[33]. The work function for the transition metals decrease dramatically when the alkali-metal adds to transition metal, also adding alkali-metal to transition metals tend to...
adsorption the alkali metal on the transition metal, and this procedure causes reduction of the work function of the transition metals. The correlation obtained only between the covalent electrons i.e. between 3s in Na and 4s in Cu. The size of cluster affect on the work function and this is very clearly in table(4), note that the work function of NaCuₙ closes to the work function of Cuₙ and, this means when we increase the number of Cu atoms in NaCuₙ clusters, the work function of NaCuₙ back to similar the work function of the pure copper clusters. So the values of the work function of Cuₙ clusters decreases when we add sodium atom to Cuₙ clusters except NaCu₂ and this is because of increasing number of copper atoms with respect to sodium. Many experimental and theoretical works have been devoted to investigating Cu clusters.[34][35][36]. The experimental data for copper approximately (4.59eV)[37].

Table(5) represents the electronegativity for Na atom, Cuₙ clusters, NaCuₙ clusters. Note that the electronegativity for Cuₙ clusters is greater than the electronegativity of Na atom so sodium atom will adsorb on copper clusters. Although copper and sodium are metals and they have a low electronegativity because all metals have low electronegativity but the atomic size of Na is greater than the atomic size for Cu, thus sodium will adsorb on copper clusters because the electronegativity decrease as the atomic size increase.

This result agree with basics of physical chemistry [38].

6. Conclusions

When we use density functional theory at ground state level with B3LYP, 3-21G basis sets for Na atom, Cuₙ clusters, NaCuₙ clusters, we conclude that the sodium atom adsorbs on copper clusters, we know this through the values HOMO energies because the molecule which has high HOMO energy release the electrons to the unoccupied orbitals, also we conclude the work function decrease when we add alkali-metal to transition metal except NaCu₂ cluster, the work function for NaCuₙ closes to Cuₙ cluster, another quantity prove that sodium atom adsorbs on copper clusters is the electronegativity, all copper clusters have electronegativity greater than Na atom, and this means sodium adsorbs on copper.

7. Acknowledgements

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