Investigation Quantum Electronic Transition of Organometallic Molecules

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Abstract. We provide a brief overview of recent calculations and predictions of electronic properties for single-molecules and discuss some principles underpinning strategies for enhancing their electronic performance. Quantum interference effects in the electronic properties of (Pyridine-2Cyclopentene Metallic) organometallic-type molecules possessing four aromatic rings were investigated theoretically. In this paper, electronic transmission properties were studied for different types of organometallic molecules. A calculation also provides a powerful tool to estimate the electrical and electronic properties. Furthermore, to probe the electronic structure of all compounds in this study we compute the UV-visible, isosurface and energies calculations. It is finding that the (HOMO and LUMO) energy changing with replace metallic atoms as well as the energy gap changes as the metal different. Therefore, this indicates the energies depend on the type of the metallic atoms in the studied molecules. All calculations were performed using density functional theory at three parameters with the Lee-Yang-Parr functional (B₃-LYP) levels with SDD basis sets.

Key Words: DFT, organometallic molecules, UV-visible calculations.

1. Introduction

Engineering and nanoscale science show advanced revolutionary potential appears in both basic science, technology. It may be an affect for our live. It can describe in size and range of the nanoscale transistor based on electronics. Mostly essential level, molecular nanoscience is the search from new phenomena and material properties, which happen at extremely small length scales, on the nanosize this is the scale use from small molecules [1-3].

The nanotechnology revolution have create an urgent request to understand the characteristics of material at the nanoscale by utilize of new concepts and theoretical methods that introduce the ideas and interpretation of the phenomenon that promotes the progress in this area. The propagation of electron waves through a single molecule could be insight in terms of the electrons transmission aspects, which include transferring of the charge carriers from one side of the molecule to the other party [4]. Nowadays, new insights in the area of molecular nanoscience have been obtained from the
application of the theoretical techniques such as density functional theory (DFT), and the molecular dynamics [4]. Advances in modeling techniques and programming resulted to an increase in the computational potential that enabled the simulation of complex systems with millions of degrees of freedom. This study includes a theoretical investigation of organometallic molecules. The density functional theory (DFT) and Time – dependent density functional theory (TD-DFT) which are implemented in Gaussian program have been used to calculate the properties of the structures under study, such as the electrons transition, the emission strength oscillator and the HOMO-LUMO gaps.

2. Theoretical method and computational details

The density functional theory application on the ground state properties for the systems, where the electron density leads to an important and open role. It predicts (the future) of the large variety of molecular characteristics, vibration frequencies, molecular compounds, ionization energies, decay energies, reaction paths, and electrical, magnetic characteristics for the molecules.

DFT gets properties for a lot of particle structure as a function of particle density. Particle density is the numbering of electrons per unit total space occupied by something for a given state. It depends only on three coordinates without any concern about the number of electrons of the system, so [5-9].

\[ N = \int \rho(\vec{x}) \, d\vec{x} \]  \hspace{1cm} (1)

Fundamental concept of DFT, Theoretical Methods for computing the ground state properties of metal, insulators and semiconductors [10], is dependent on the ground state energy; all electronic features of other ground state are note that decided by the electron density. Today, DFT is one of the most used methods in this area.

Time-dependent density functional theory (TD-DFT) spreads the important idea of the ground-state DFT which can be used to examine the excited state properties of a system in the presence of time-dependent potentials, such as electric or magnetic fields. The influence of fields on molecules could be studied with TD-DFT as an application for representative excitation energies, oscillator strength, wavelength, molecular orbital character and electronic transitions of the molecules [11-13].

The theoretical of TD-DFT based on the Runge-Gross theorem (R-G theorem). The R-G theorem explained the association between the time-dependent external potential \( V_{\text{ext}}(\vec{r}, t) \) and \( \rho(\vec{r}, t) \) of the system. R-G theorem designated that when two external efforts \( V_{\text{ext}}(\vec{r}, t) \) & \( \rho(\vec{r}, t) \) have an alteration for many time dependent functions, their own electron densities \( \rho(\vec{r}, t) \) and \( \rho'(\vec{r}, t) \) are dissimilar [14-16]. They discussed how excited states are obtain using TD-DFT. The starting point of studying time-dependent systems is the time-dependent Schrodinger equation. The TD-DFT is straight related to the Schrodinger formula \( \left[ i \hbar \frac{\partial}{\partial t} \Psi(\vec{z}, t) = \hat{H} \Psi(\vec{z}, t) \right] \) where the Hamiltonian is known to be [12, 14, 15].

\[ \hat{H} = \hat{T} + \hat{V}_{\text{elec-velec}} + \hat{V}_{\text{ext.}}(\vec{r}, t) \]  \hspace{1cm} (2)

Here, \( \hat{H} \) consists of the kinetic energy operator \( \hat{T} \) electron-electron repulsion \( \hat{V}_{\text{elec-velec}} \) (Coulomb operator) and the external effort \( \hat{V}_{\text{ext.}}(\vec{r}) \). Where \( \hat{V}_{\text{external}}(\vec{r}) \) is given of the following operators:

\[ \hat{V}_{\text{ext.}}(\vec{r}) = \sum_{i=1}^{N} \hat{V}_{\text{ext.}}(\vec{r}_i, t) \]  \hspace{1cm} (3)

The densities of the system rise from a fixed first state \( \Psi(t_0) = \Psi(0) \). The first state, \( \Psi(0) \) is arbitrary, it must not be the ground condition or some Eigen state of the first effort \( \hat{V}_{\text{ext.}}(\vec{r}, t_0) = \hat{V}_0(\vec{r}) \). The R-G theorem indicates that there exists a one-to-other contrast between the time-dependent external effort \( \hat{V}_{\text{ext.}}(\vec{r}, t) \), and the time-dependent electron density \( \rho(\vec{r}, t) \), for system developing from a constant first many-body state. Translation to it, density can specify the external potential and next helps get the time-dependent many-particle wave functions [12, 16].
3. Electronic Properties

The computation of molecular electronic properties in this study implemented by Koopmans theorem (KT). Description of the calculated properties is shown as below.

3.1 HOMO-LUMO Gap

HOMO and LUMO are two of the important of molecular orbitals, where the HOMO refers to highest occupied molecular orbital and LUMO refers the low unoccupied molecular orbital. The two most important molecular orbitals MOs are called the frontier orbitals as they lies at the outmost boundaries of the electrons of the structure. The HOMO, which is the highest energy orbital containing electrons, is the orbital acting as an electron donor. Inversely, the LUMO, is the lowest energy orbital having area to accept electrons. The band gap $E_{\text{gap}}$ represented the different of the energies between the HOMO and LUMO levels as \[ E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \] (4). HOMO, LUMO and their resultant band gap did not only regards the path of the structures interacts with other species, but their band gap managed label the chemical reaction and kinetic constancy of the molecule. A molecule with a small boundary orbital gap is more polarizable and is related with a high chemical reaction, lowest kinetic stability and it is termed as a little hardness molecule \[17, 18\]. When an electron is transfer to a high energy level, where it fills unoccupied molecular orbitals, the resulting state called the raised state \[19\].

4. Electronic Transitions

The absorption of UV or visible rays correspond to the excitation of outer electrons. There are three modes of electronic transfers, which can considered as first, are the transitions including p, s, and n electrons, the second are the transitions involving charge-transfer electrons and the third are the transitions including d and f electrons. When an atom or molecule absorption energy, electrons are transferred from their ground level to a higher-level state. In a molecule, the atoms can vibrate and rotate with regard to each other. These rotations and vibrations also have separate energy states, which can considered as existence pack on top of each electronic level \[20, 21\]. Absorption of ultraviolet and visible rays in organic molecules is limited to some functional groups (chromospheres) that include valence electrons of low excitation energy. The spectrum of a molecule including these chromospheres is compound \[22, 23\]. Possible electronic transitions p, s, and n electrons shown as in figure (1).

![Figure 1. The electronic transitions of p, s, and n electrons [23].](image-url)
5. Results and Discussion

Figure 2. Shows relax structures of the structures under study. They are labeled (1-4), with same anchor group (anchor atom) but only the deferent in metal atoms at the center molecules.

To explain and understand the behavior of the absorption spectra of the structures under studying, it is necessary to find out the electronic structures for the studied compounds. Table (1) shows the compute boundary orbital energies and (LUMO-HOMO) energy gap (Egap) of the each compound. Accounts in Table (1) noticed that all the studied structure display delocalization of the LUMO and localization of HOMO. Results showed the HOMO and LUMO are a big different and this suggests that different metal in the structures play important roles on electronic properties and refinement the electron
accepting ability and the impact of symmetry and distribution of aromatic rings on the value energies of HOMO and LUMO, which can’t be neglect. The ranking of LUMO energy is, \(2 < 4 < 3 < 1\). The results illustrated the found of the electron attracting to the different metal in the structure go to different value for LUMO and therefore reducing the band gap. As well, the presence of double C-C bonds leads to a decrease of the LUMO and decreasing the band gap due to delocalization for both HOMO and LUMO energies because adding atoms (different metal atoms) in the center molecules leads to a reduction in the band gap.

The band gap (Egap) for the studied compounds has been get from the separation LUMO-HOMO energy by using the (B3LYP/SDD-DFT) mathematical calculations. The calculated band gaps were decrease of the studied compounds (the energy gap for the molecules study is decreasing with changing metal atom to the original molecule in the center molecules). As noticed, compounds (1 to 4) observe a lower energy gap in range semiconductor material due to added to a double C = C bonds between the organic molecules and metal adding. Figure (3) shows energy gaps of the studied compounds.

### Table 1. HOMO, LUMO energies and Energy gap.

| Molecules | HOMO(eV) | LUMO(eV) | Egap(eV) |
|-----------|----------|----------|----------|
| A1Fe      | -5.729   | -2.478   | 3.251    |
| A1Co      | -8.985   | -6.429   | 2.556    |
| A1Ru      | -5.721   | -2.486   | 3.235    |
| A1Pt      | -5.344   | -3.085   | 2.259    |

As seen in table (1), all above energy states and energy gap were different with the difference in the metal used in the structure. Therefore, the energy gap is approximately dependent on the subgroup of atoms added to the reference molecule.

**Figure 3.** (a) \(E_{HOMO}\) and \(E_{LUMO}\) of all structures; (b) HOMO-LUMO gap (eV) of all structures.

Total Energy is the total energy \(E_T\) in a.u. for the studied compounds was calculated and listed in Table (2). As seen from mentioned table, the \(E_T\) is approximately independent on the position of the same subgroups in the compounds but depends only on the number of electrons in the compounds, this a sign to that the total energy is a reflection of the binding energy for each compound. \(E_T\) is inversely proportional with the number of electrons; it decreased with increasing the number of electrons in the compound. Figure (4) shows the \(E_T\) for the studied compounds. On the other hand, the corresponding calculated values of virial ratio \((-V/T)\) for the studied compounds in Table (2) showed they lie in the same range for such compounds, in which the experimental value for hydrogen atom (-
V/T=2.0032)\cite{15}. Above results indicate to good relax was found without any imaginary frequency for each one of the studied compounds by employing the DFT method.

Table 2. The total energy $E_T$ and (-V/T) for the compounds.

| Compound | $E_T$ a.u. | - V/T |
|----------|------------|-------|
| A1Fe     | -1234.708  | 2.0498|
| A1Co     | -1256.410  | 2.0536|
| A1Ru     | -1274.674  | 2.0600|
| A1Pt     | -1296.118  | 2.0747|

Figure 4. Total energy of the compounds.

Density of states of the studied compounds were illustrate in figure 5. As shown, in all compounds the degeneracy of occupied molecular orbitals are greater than that the virtual molecular orbitals, in which refers to localization of HOMO and delocalization of LUMO and an indication to that the DOS was distributed in the (occupied orbital). Conduction band greater than in the (virtual orbital) Valance band. The electron in compounds 2(A1Co) can easily transform from the valence to conduction band in comparison with other compounds, this for the reason that the DOS in the conduction band are more than DOS in the valence band. This property is made from these compounds to behave appropriate electronic applications when interacts with other molecules or species.
UV-Vis Spectra From the founded relax molecular structures with the B3LYP/SDD-DFT method, the Ultraviolet-Visible UV-Vis spectra of the compounds under study were studied and analyzed using the time dependent-self-consistent field Time Depending-SCF method with the same SDD-DFT and basis sets. Figure 6 illustrates that structures have direct and indirect transition (transition the charge or electron from one to another) from the occupied orbital band to virtual orbital band with absorption wavelengths (690.82, 576.08, 471.31 and 449.03) nm, respectively. Table 3 shows the obtained values of absorption energy $E_{abs}$ (eV), absorption wavelength $\lambda_{max}$ (nm), oscillator strength O.S, molecular orbital character MOC % and transition states.
Compound 1 (AlFe-TD)

Compound 2 (AlCo-TD)
Figure 6. UV-Visible spectra of the compounds ($\varepsilon \equiv$ intensity of A.U.)
Table 3. The absorption spectra calculations of the compounds.

| Molecules | $E_{abs}$ (eV) | $\lambda_{max}$ (nm) | O.S | MO Character % |
|-----------|----------------|----------------------|-----|----------------|
| A1Fe      | 1.7948         | 690.82               | 0.0139 | “H-2->L+3 (13%), H-1->L+4 (27%), HOMO->LUMO (18%), HOMO->L+3 (21%) H-2->LUMO (9%), H-2->L+7 (3%), HOMO->L+7 (6%)” |
| A1Co      | 2.1522         | 576.08               | 0.1051 | “H-11->L+1 (22%), H-10->LUMO (38%), H-1->LUMO (28%) H-10->L+2 (5%), H-9->L+1 (2%)” |
| A1Ru      | 2.6306         | 471.31               | 0.1203 | “H-2->LUMO (24%), HOMO->LUMO (50%) H-3->LUMO (4%), H-3->L+2 (3%), H-2->L+2 (5%), H-1->L+3 (3%), HOMO->L+2 (6%)” |
| A1Pt      | 2.7611         | 449.03               | 0.4899 | HOMO->LUMO (12%), HOMO->L+1 (76%), H-7->LUMO (4%), H-1->LUMO (3%), H-1->L+1 (2%)” |

6. Conclusions

The compounds in this paper have direct and indirect electron transitions from the HOMO to LUMO molecular orbitals and at wavelengths within the visible spectrum to (A1Fe, A1Co, A1Ru and A1Pt). In all these single molecules, we find that the wavelength decreases with the increase in the atomic number of the metals used (by increasing the number of electrons of these metals). As it can be observed, we find that the compounds, A1Fe has a wavelength of (690 nm), the compound A1Co has a wavelength of (576 nm), the compound A1Ru has wavelength (471 nm) and the compound A1Pt has wavelength (449 nm). We note from table (3) that the atomic or molecular transfers in molecules (1, 3, and 4) are direct and indirect transitions according to the percentage shown in the table (3) for each transition, but in the second molecule only indirect transfers.

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