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Ministry of Higher Education  
And Scientific Research  
University of Thi-Qar  
College of Science**



***DFT and TD-DFT Study of Organic Molecules:  
Nanosensor and Dye Sensitized Solar Cells  
Applications***

***A Thesis Submitted to the College of Science University of  
Thi-Qar in Partial Fulfillment of the Requirements for the  
Degree of Master of Science in Physics***

***By***

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***B. Sc. in Physics Thi-Qar 2016***

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**2018 A.D.**

**1439 H.D**

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

(( يَرْفَعُ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ  
وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ ))

صَدَقَ اللَّهُ الْعَلِيُّ الْعَظِيمُ

سورة المجادلة ( ١١ )

# ***Certificate***

*I certify that the preparation of this thesis entitled ( **DFT and TD-DFT Study of Organic Molecules: Nanosensor and Dye Sensitized Solar Cells Applications** ) was made under my supervision by **Hammood Merdas Yasir** at the department of Physics, college of science, Thi-Qar university, as a partial requirement for the degree of master of science in Physics.*

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# ***Dedication***

***To...***

***The holder of the message of AHLULBAIT .... EMAM  
HIJA (AJJALA ALLAH FARAJAH AL-SHARIF)***

***To...***

***Those whose blood was mixed with the soil of the  
homeland .... Martyrs of Iraq***

***To...***

***Whom I have missed since childhood .... my dear father***

***To...***

***Granule my heart first .... my mother compassionate***

***To...***

***Everyone who support me in this life .... my brothers and  
sisters and my friends***

***Hammood***

# ***Acknowledgement***

***All Praise is due to ALLAH lord of the world, and best prayers and peace be unto his best messenger MOHAMMED, and his pure descendants, and his noble companions.***

***Then, I would like to express my deep gratitude and appreciation to my supervisor, Prof .Dr. Falah Hasan Hanoon for suggesting the topic of the thesis to me, and for his continuous advice and his guidance throughout this work.***

***I would like to thank ,the faculty members of the Department of Physics, College of Sciences, University of Thi -Qar, for their encouragement.***

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***Finally, I would like to thank all members of my family for their help and encouragement and everyone who helped me during the preparation of this thesis.***

***Hammood***

# *List of Symbols*

| <b>Symbols</b>  | <b>Definition</b>                                                       |
|-----------------|-------------------------------------------------------------------------|
| $\eta$          | The photo conversion efficiency                                         |
| $H$             | Hamiltonian operator                                                    |
| $\Psi$          | The wave function of the physical system                                |
| $E$             | The total energy of the system                                          |
| $\hat{T}$       | The kinetic energy operator                                             |
| $\hat{V}$       | The potential energy operator                                           |
| $\hat{T}_e$     | The kinetic energy operator of the electron                             |
| $\hat{T}_n$     | The kinetic energy operator of the nucleus                              |
| $\hat{V}_{ne}$  | Component of the Coulomb attraction energy between nuclei and electrons |
| $\hat{V}_{ee}$  | Component of the Coulomb repulsion energy between the electrons         |
| $\hat{V}_{nn}$  | Component of the Coulomb repulsion energy between the nuclei            |
| $M_A$           | Mass of the nucleus A                                                   |
| $r_{iA}$        | The distance between the electron i and the nucleus A                   |
| $Z_A$           | The atomic number of the nucleus A                                      |
| $r_{ij}$        | The distance between electron i and electron j                          |
| $R_{AB}$        | The distance between the nucleus A and the nucleus B                    |
| $\nabla^2$      | Laplace operator                                                        |
| $m_e$           | Electron mass                                                           |
| $ \Psi ^2$      | The Probability                                                         |
| $\delta_{ij}$   | Delta Kronecker                                                         |
| $\Psi_{trial}$  | The speculated wave function                                            |
| $E_{trial}$     | The speculated energy                                                   |
| $E_o$           | The ground state energy                                                 |
| $E_\varphi$     | The lowest energy eigenvalue                                            |
| $\alpha, \beta$ | The spin up and spin down of electrons                                  |

Continue

| Symbols               | Definition                                                |
|-----------------------|-----------------------------------------------------------|
| $\frac{1}{\sqrt{N!}}$ | The total normalization factor                            |
| $\hat{f}_1$           | Fock operator                                             |
| $\Psi_i$              | The eigen function of the operator                        |
| $\epsilon_i$          | The eigenvalue of the energy                              |
| $V_{HF}(i)$           | Hartree-Fock potential                                    |
| $\hat{J}(j)$          | Coulomb operator                                          |
| $\hat{K}(j)$          | Exchange operator                                         |
| $C_{\mu i}$           | The molecular orbital expansion coefficients              |
| $\varphi_i$           | Basis functions                                           |
| $\varphi_j$           | The one-electron basis functions                          |
| $F_{ij}$              | Energy matrix elements                                    |
| $F$                   | Matrix consists of Fock matrix elements $C_{ji}$          |
| $C$                   | Matrix M*M of the expansion coefficients                  |
| $S$                   | Overlap matrix                                            |
| $\epsilon$            | Diagonal matrix of the orbital energies $\epsilon_i$      |
| $E_c^{HF}$            | Electron correlation energy                               |
| $E_{HF}$              | Hartree-Fock energy                                       |
| $E_{exact}$           | The exact energy                                          |
| $\Psi_e$              | The electronic wave function                              |
| $\rho(r)$             | Electron density                                          |
| $E_v$                 | The ground state energy functional                        |
| $F_{HK}[\rho]$        | The kinetic energy and all electron-electron interactions |
| $V_{ext}(r)$          | The external potential                                    |
| $K$                   | Chemical potential                                        |
| $T[\rho]$             | The kinetic energy of the system                          |
| $E_{xc}[\rho]$        | The exchange-correlation energy                           |
| $V_{eff}$             | Effective potential                                       |
| $T_{KS}$              | The kinetic energy in kohn-sham                           |
| $E[\rho]$             | The total energy of the system                            |
| $V_{xc}$              | The exchange-correlation potential                        |

Continue

| Symbols                   | Definition                                                                                                   |
|---------------------------|--------------------------------------------------------------------------------------------------------------|
| $\epsilon_i$              | Singlet electrons energies                                                                                   |
| $\lambda$                 | The scaling factor                                                                                           |
| $\varphi^\lambda$         | Wave function of the Hamiltonian operator                                                                    |
| $\bar{h}(r_1, r_2)$       | The average of the pair correlation function                                                                 |
| $\bar{\rho}_{xc}$         | The exchange-correlation average                                                                             |
| $P_2^\lambda(r_1, r_2)$   | The diagonal part of the density matrix with two particles                                                   |
| $E_x$                     | The exchange part                                                                                            |
| $\Psi_\rho$               | The exact interacting wave function                                                                          |
| $J[\rho]$                 | Nuclei coulomb repulsion                                                                                     |
| $T_s$                     | Non-interacting total energy                                                                                 |
| $Z_v$                     | The charge of the nucleus $v$                                                                                |
| $R_v$                     | The position of the nucleus $v$                                                                              |
| $N_n$                     | The total number of nuclei                                                                                   |
| $s$                       | The gradient measure variable                                                                                |
| $a_c, a_x, a_o$           | Three empirical parameters                                                                                   |
| $\epsilon_{xc}$           | The exchange correlation energy per particle                                                                 |
| $n$                       | Principle quantum number                                                                                     |
| $\xi$                     | Constant associated with effective charge of nuclei, i.e. the nuclear charge is partly shielded by electrons |
| $Y_{lm}(\theta, \varphi)$ | Spherical harmonic in which describes the angular part of the wave function                                  |
| $l$                       | Orbital quantum number                                                                                       |
| $m$                       | Magnetic quantum number                                                                                      |
| $\theta, \varphi$         | Polar angles                                                                                                 |
| $M$                       | The number of Gaussian primitive                                                                             |
| $\chi^{STO}$              | Sum of slater orbital wavefunction                                                                           |
| $\chi^{CGF}$              | Sum of gaussian orbital wavefunction                                                                         |
| $C_{lmj}$                 | Normalization constant                                                                                       |

# *List of Abbreviations*

| <b>Attribute</b>        | <b>Meaning</b>                                      |
|-------------------------|-----------------------------------------------------|
| <b>DSSC<sub>s</sub></b> | <b>Dye-Sensitized Solar Cells</b>                   |
| <b>OSC<sub>s</sub></b>  | <b>Organic Solar Cells</b>                          |
| <b>TNT</b>              | <b>Trinitrotoluene</b>                              |
| <b>NQ</b>               | <b>Nitroguanidine</b>                               |
| <b>ITO</b>              | <b>Indium Tin Oxide</b>                             |
| <b>HOMO</b>             | <b>Highest Occupied Molecular Orbital</b>           |
| <b>LUMO</b>             | <b>Lowest Unoccupied Molecular Orbital</b>          |
| <b>BO</b>               | <b>Born-Oppenheimer Approximation</b>               |
| <b>HF</b>               | <b>Hartree-Fock Approximation</b>                   |
| <b>SCF</b>              | <b>Self-Consistent Field Method</b>                 |
| <b>LCAO</b>             | <b>The Linear Combination Atomic Orbital Method</b> |
| <b>RH</b>               | <b>Roothaan-Hall Equations</b>                      |
| <b>DFT</b>              | <b>Density Functional Theory</b>                    |
| <b>HK</b>               | <b>Hohenberg-Kohn Theorems</b>                      |
| <b>KS</b>               | <b>Kohn-Sham Equations</b>                          |
| <b>KS-DFT</b>           | <b>Kohn-Sham Density Functional Theory</b>          |
| <b>TD-DFT</b>           | <b>Time-Dependent Density Functional Theory</b>     |
| <b>LDA</b>              | <b>Local Density Approximation</b>                  |
| <b>GGA</b>              | <b>Generalized Gradient Approximation</b>           |
| <b>BEF</b>              | <b>Becke Exchange Functional</b>                    |
| <b>LYP</b>              | <b>Lee-Yang-Parr Correlation</b>                    |
| <b>B3LYP</b>            | <b>Becke Three Parameters Lee Yang Parr</b>         |
| <b>LSDA</b>             | <b>Local Spin Density Approximation</b>             |
| <b>STO's</b>            | <b>Slater Type Orbitals</b>                         |
| <b>STO-nG</b>           | <b>Slater Type Orbital n Gaussian</b>               |

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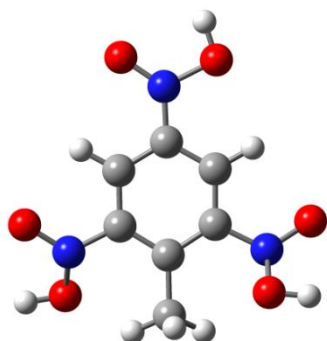
| <b>Attribute</b>                         | <b>Meaning</b>                     |
|------------------------------------------|------------------------------------|
| <b>GTO's</b>                             | <b>Gaussian Type Orbitals</b>      |
| <b>G09</b>                               | <b>Gaussian 2009 Version</b>       |
| <b>O.S</b>                               | <b>Oscillator Strength</b>         |
| <b>E<sub>g</sub></b>                     | <b>The Energy Gap</b>              |
| <b>E<sub>ad</sub></b>                    | <b>The Adsorption Energy</b>       |
| <b>E<sub>total</sub></b>                 | <b>The Total Energy</b>            |
| <b>DOS</b>                               | <b>The Density of States</b>       |
| <b>IR</b>                                | <b>Infrared Spectra</b>            |
| <b>UV</b>                                | <b>Ultraviolet</b>                 |
| <b>UV-Vis</b>                            | <b>Ultraviolet-Visible</b>         |
| <b>V<sub>oc</sub></b>                    | <b>The Open Circuit Voltage</b>    |
| <b><math>\lambda_{\text{max}}</math></b> | <b>The Maximum Wavelength</b>      |
| <b>TiO<sub>2</sub></b>                   | <b>Oxide of Titanium</b>           |
| <b>FH</b>                                | <b>Test Factor</b>                 |
| <b>MH</b>                                | <b>Dye Name</b>                    |
| <b>LT</b>                                | <b>LUMO TiO<sub>2</sub> Factor</b> |
| <b>HT</b>                                | <b>HOMO TiO<sub>2</sub> Factor</b> |

# *List of Tables*

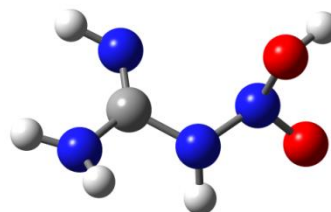
| <b>Tables</b> | <b>Subject</b>                                                                                                                                       | <b>Page</b> |
|---------------|------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 3.1           | The system name, the sensor FH, the adsorption energy ( $E_{ad}$ ), the distance, $E_g$ and the total energy ( $E_{total}$ ) of investigated sensors | 84          |
| 3.2           | Numerical results of the important electronic properties of dye MH1 before and after improvement                                                     | 88          |
| 3.3           | Numerical results of the important electronic properties of dye MH2 before and after improvement                                                     | 91          |
| 3.4           | Numerical results of the important electronic properties of dye MH3 before and after improvement                                                     | 94          |
| 3.5           | Numerical results of the important electronic properties of dye MH4 before and after improvement                                                     | 97          |
| 3.6           | Numerical results of the important electronic properties of dye MH5 before and after improvement                                                     | 100         |
| 3.7           | Numerical results of the important electronic properties of dye MH6 before and after improvement                                                     | 102         |
| 3.8           | Outcome results for all dyes under study                                                                                                             | 105         |

# *List of Chemical Structures*

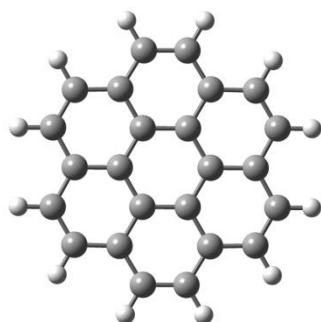
## The Chemical Structures



**TNT**



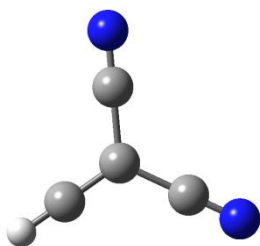
**NQ**



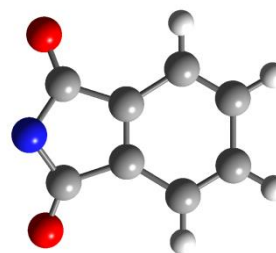
**Coronene = Addition (A)**



**Addition (B)**



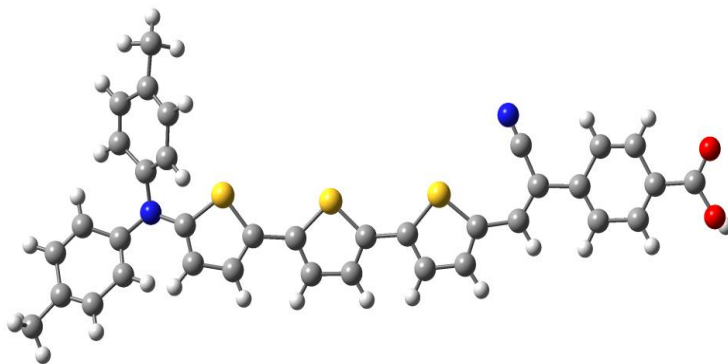
**Addition (C)**



**Addition (D)**

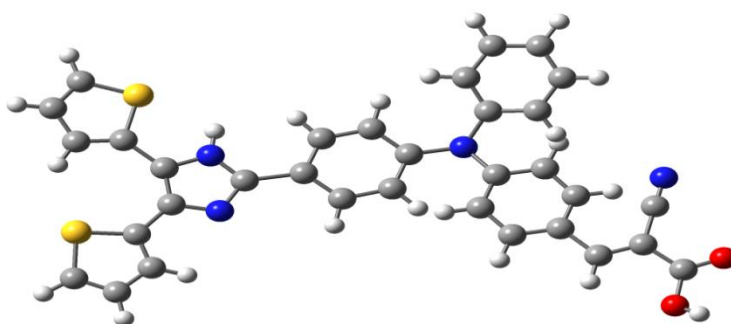
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## The Chemical Structures



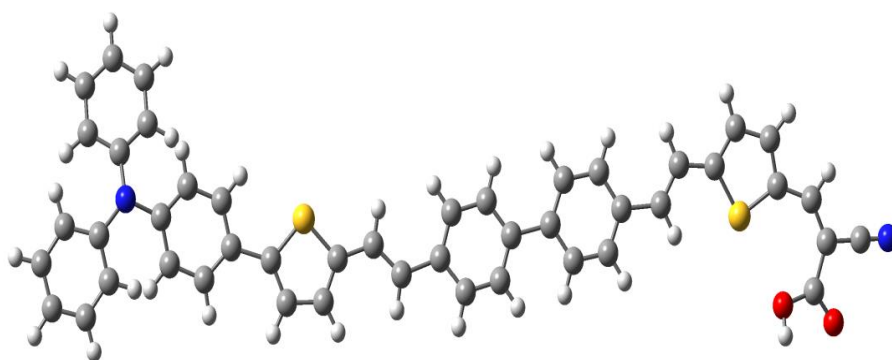
**MH1**

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**MH2**

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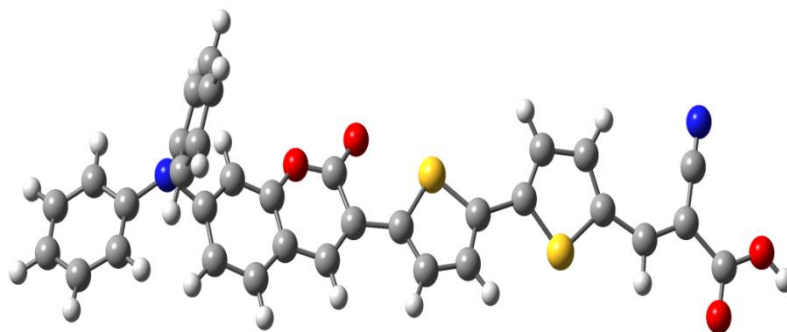


**MH3**

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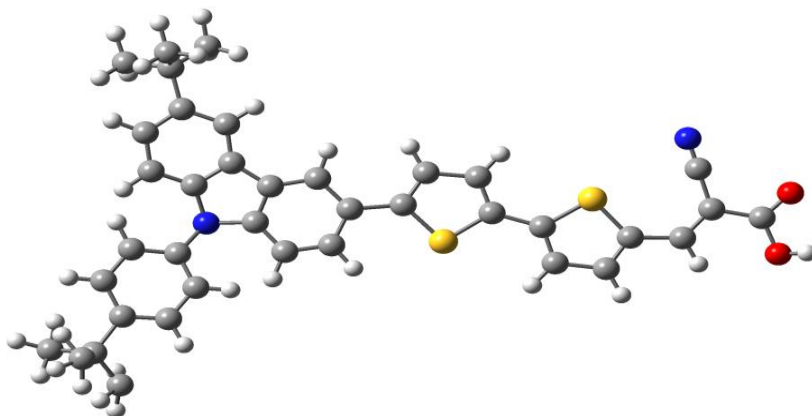
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## The Chemical Structures



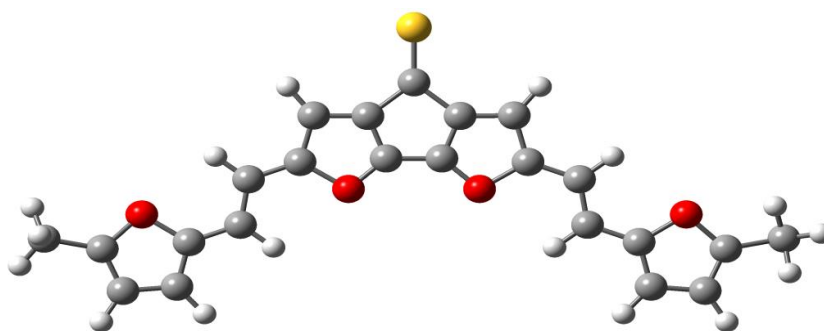
**MH4**

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**MH5**

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**MH6**

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# *List of Figures*

| <b>Figures</b> | <b>Subject</b>                                                                                                                                                          | <b>Page</b> |
|----------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 1.1            | The structure of monolayer and multilayer graphene, carbon nanotubes, and fullerene                                                                                     | 2           |
| 1.2            | Graphene diagram distribution                                                                                                                                           | 5           |
| 1.3            | Coronene, graphene structure                                                                                                                                            | 7           |
| 1.4            | Trinitrotoluene (TNT) chemical structure                                                                                                                                | 10          |
| 1.5            | Nitroguanidine (NQ) chemical structure                                                                                                                                  | 11          |
| 1.6            | Feature of any nanosensor Diagram                                                                                                                                       | 12          |
| 1.7            | Nanosensor device components                                                                                                                                            | 13          |
| 1.8            | Basic working principle of dye-sensitized solar cell                                                                                                                    | 16          |
| 1.9            | Under atmospheric sun spectrum with absorption area                                                                                                                     | 18          |
| 2.1            | The steps of solution of the density functional theory method flowchart                                                                                                 | 38          |
| 2.2            | Comparison between Slater functions and Gaussian functions                                                                                                              | 65          |
| 3.1            | (a,b) Geometrical optimization of sensor top view and side view respectively, c) HOMO distribution, d) LUMO distribution, e) DOS and f) IR spectrum                     | 72          |
| 3.2            | a) Geometrical optimization of sensor-TNT , b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum                                                       | 73          |
| 3.3            | a) Geometrical optimization of sensor-NQ , b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum                                                        | 74          |
| 3.4            | (a,b) Geometrical optimization of sensor with Al atom doping top view and side view respectively, c) HOMO distribution, d) LUMO distribution, e) DOS and f) IR spectrum | 75          |
| 3.5            | a) Geometrical optimization of sensor-TNT with Al atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum                                    | 76          |
| 3.6            | a) Geometrical optimization of sensor-NQ with Al atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum                                     | 77          |

Continue

| <b>Figures</b> | <b>Subject</b>                                                                                                                                                           | <b>Page</b> |
|----------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 3.7            | (a,b) Geometrical optimization of sensor with Cu atom doping top view and side view respectively, c) HOMO distribution, d) LUMO distribution, e) DOS and f) IR spectrum  | 78          |
| 3.8            | a) Geometrical optimization of sensor-TNT with Cu atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum                                     | 79          |
| 3.9            | a) Geometrical optimization of sensor-NQ with Cu atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum                                      | 80          |
| 3.10           | (a,b) Geometrical optimization of sensor with Ge atom doping top view and side view respectively, c) HOMO distribution, d) LUMO distribution, e) DOS and f) IR spectrum. | 81          |
| 3.11           | a) Geometrical optimization of sensor-TNT with Ge atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum                                     | 82          |
| 3.12           | a) Geometrical optimization of sensor-NQ with Ge atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum                                      | 83          |
| 3.13           | The four additions that use with dyes under study                                                                                                                        | 85          |
| 3.14           | Geometrical optimization before (left) and after (right) addition of investigated dyes.                                                                                  | 86          |
| 3.15           | HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH1                                                                                                    | 87          |
| 3.16           | The absorption of dye MH1 before (blue line) and after (red line) addition A                                                                                             | 89          |
| 3.17           | HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH2                                                                                                    | 90          |
| 3.18           | The absorption of dye MH2 before (blue line) and after (red line) addition B                                                                                             | 92          |
| 3.19           | HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH3                                                                                                    | 93          |
| 3.20           | The absorption of dye MH3 before (blue line) and after (red line) addition B                                                                                             | 95          |
| 3.21           | HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH4                                                                                                    | 96          |

Continue

| <b>Figures</b> | <b>Subject</b>                                                                                      | <b>Page</b> |
|----------------|-----------------------------------------------------------------------------------------------------|-------------|
| 3.22           | The absorption of dye MH4 before (blue line) and after (red line) addition C                        | 98          |
| 3.23           | HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH5                               | 99          |
| 3.24           | The absorption of dye MH5 before (blue line) and after (red line) addition C                        | 101         |
| 3.25           | HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH6                               | 103         |
| 3.26           | The absorption of dye MH6 before (blue line) and after (red line) addition D                        | 104         |
| 3.27           | HOMO's and LUMO's of dyes and TiO <sub>2</sub> (blue-plot before addition, red-plot after addition) | 106         |

## ***Abstract :***

The organic molecules have very important role in our life. In this study, the DFT method with B3LYP functional and 6-31G basis set was used for nanosensor candidate as a sensor for two organic molecules TNT and NQ in the Gaussian09 program package by determining two basic important parameter for each sensor. They are: distance between the organic molecules and the graphene sensor, also changing of the sensor band gap energy that will change the conductivity of the sensor device. Graphene sensor was improved by adding substitutional atoms Al, Cu and Ge, the results show the enhancement of the device performance which can see from the energy gap changing where we found that the energy gap is very affected by all organic molecules, Al atom is the better addition for TNT and NQ sensor. Some electronic properties were determined such as HOMO-LUMO distribution, adsorption energy, total energy, density of states, IR spectrum and also the optimization structure. Then using the density functional theory (DFT) and time-dependent DFT (TD-DFT) methods with B3LYP functional and 6-31G basis set to test some organic molecules by studying UV-Vis spectrum, the electronic states transition and the range of the absorption spectrum. The improvement of dyes was done by the terminal addition with organic molecules where the absorption becomes higher than that of the original dyes in the DSSC<sub>s</sub>. Some electronic properties were calculated such as HOMO-LUMO distribution, energy gap, oscillator strength and the geometrical optimization of these organic dyes.

# *Contents*

| <b>No.</b>                                 | <b>Subject</b>                                       | <b>Page</b> |
|--------------------------------------------|------------------------------------------------------|-------------|
| <b>Chapter One: Introduction</b>           |                                                      |             |
| <b>1.1</b>                                 | <b>General Introduction</b>                          | <b>1</b>    |
| <b>1.2</b>                                 | <b>Graphene</b>                                      | <b>4</b>    |
| <b>1.3</b>                                 | <b>Coronene</b>                                      | <b>7</b>    |
| <b>1.4</b>                                 | <b>Explosive Materials</b>                           | <b>8</b>    |
| <b>1.4.1</b>                               | <b>Trinitrotoluene (TNT)</b>                         | <b>9</b>    |
| <b>1.4.2</b>                               | <b>Nitroguanidine (NQ)</b>                           | <b>10</b>   |
| <b>1.5</b>                                 | <b>Nanosensor</b>                                    | <b>11</b>   |
| <b>1.6</b>                                 | <b>Organic Molecules</b>                             | <b>13</b>   |
| <b>1.7</b>                                 | <b>Organic Solar Cells</b>                           | <b>14</b>   |
| <b>1.8</b>                                 | <b>Dye-Sensitized Solar Cells (DSSC<sub>s</sub>)</b> | <b>17</b>   |
| <b>1.9</b>                                 | <b>Literature Review</b>                             | <b>19</b>   |
| <b>1.10</b>                                | <b>Thesis Outline</b>                                | <b>25</b>   |
| <b>1.11</b>                                | <b>Aim of Study</b>                                  | <b>25</b>   |
| <b>Chapter Two: Theoretical Background</b> |                                                      |             |
| <b>2.1</b>                                 | <b>Schrodinger Equation</b>                          | <b>26</b>   |
| <b>2.2</b>                                 | <b>Wave Function</b>                                 | <b>29</b>   |
| <b>2.3</b>                                 | <b>Variational Method</b>                            | <b>30</b>   |
| <b>2.4</b>                                 | <b>Born-Oppenheimer Approximation</b>                | <b>31</b>   |
| <b>2.5</b>                                 | <b>Hartree Approximation</b>                         | <b>32</b>   |
| <b>2.6</b>                                 | <b>Hartree-Fock Methods</b>                          | <b>34</b>   |
| <b>2.6.1</b>                               | <b>Hartree-Fock Approximation</b>                    | <b>34</b>   |
| <b>2.6.2</b>                               | <b>Roothaan-Hall Equations</b>                       | <b>38</b>   |
| <b>2.6.3</b>                               | <b>Post Hartree-Fock Methods</b>                     | <b>40</b>   |
| <b>2.7</b>                                 | <b>Hohenberg-Kohn Theorems</b>                       | <b>41</b>   |

Continue

| <b>No.</b>                                   | <b>Subject</b>                                           | <b>Page</b> |
|----------------------------------------------|----------------------------------------------------------|-------------|
| <b>2.8</b>                                   | <b>Kohn-Sham Equations</b>                               | <b>43</b>   |
| <b>2.9</b>                                   | <b>Exchange-Correlation Energy</b>                       | <b>48</b>   |
| <b>2.10</b>                                  | <b>Exchange-Correlation Functionals</b>                  | <b>51</b>   |
| <b>2.10.1</b>                                | <b>Local Density Approximation (LDA)</b>                 | <b>51</b>   |
| <b>2.10.2</b>                                | <b>Generalized Gradient Approximation (GGA)</b>          | <b>53</b>   |
| <b>2.10.3</b>                                | <b>Local Spin Density Approximation(LSDA)</b>            | <b>54</b>   |
| <b>2.11</b>                                  | <b>Functionals</b>                                       | <b>55</b>   |
| <b>2.11.1</b>                                | <b>Becke Exchange Functions</b>                          | <b>56</b>   |
| <b>2.11.2</b>                                | <b>Lee-Yang-Parr Correlation (LYP)</b>                   | <b>56</b>   |
| <b>2.11.3</b>                                | <b>Hybrid Functional</b>                                 | <b>57</b>   |
| <b>2.12</b>                                  | <b>Basis Sets</b>                                        | <b>58</b>   |
| <b>2.12.1</b>                                | <b>Minimal Basis Sets</b>                                | <b>59</b>   |
| <b>2.12.2</b>                                | <b>Split Valence Basis Sets</b>                          | <b>59</b>   |
| <b>2.12.3</b>                                | <b>Polarization Functions</b>                            | <b>60</b>   |
| <b>2.12.4</b>                                | <b>Diffuse Functions</b>                                 | <b>60</b>   |
| <b>2.13</b>                                  | <b>Types of Orbitals</b>                                 | <b>61</b>   |
| <b>2.13.1</b>                                | <b>Slater Type Orbitals (STO's)</b>                      | <b>61</b>   |
| <b>2.13.2</b>                                | <b>Gaussian Type Orbitals (GTO's)</b>                    | <b>62</b>   |
| <b>2.14</b>                                  | <b>Density Functional Theory (DFT)</b>                   | <b>65</b>   |
| <b>2.15</b>                                  | <b>Time-Dependent Density Functional Theory (TD-DFT)</b> | <b>68</b>   |
| <b>2.16</b>                                  | <b>Gaussian Program</b>                                  | <b>69</b>   |
| <b>2.17</b>                                  | <b>Gauss View Program</b>                                | <b>70</b>   |
| <b>Chapter Three: Results and Discussion</b> |                                                          |             |
| <b>3.1</b>                                   | <b>Nanosensors</b>                                       | <b>71</b>   |
| <b>3.1.1</b>                                 | <b>The pristine Coronene</b>                             | <b>71</b>   |
| <b>3.1.2</b>                                 | <b>Coronene + Aluminium (Al)</b>                         | <b>75</b>   |
| <b>3.1.3</b>                                 | <b>Coronene + Copper (Cu)</b>                            | <b>77</b>   |
| <b>3.1.4</b>                                 | <b>Coronene + Germanium (Ge)</b>                         | <b>80</b>   |
| <b>3.2</b>                                   | <b>Dye Sensitized Solar Cells ( DSSC<sub>s</sub> )</b>   | <b>84</b>   |
| <b>3.2.1</b>                                 | <b>Geometrical Structure Properties</b>                  | <b>85</b>   |

Continue

| <b>No.</b>                                        | <b>Subject</b>                               | <b>Page</b> |
|---------------------------------------------------|----------------------------------------------|-------------|
| <b>3.3</b>                                        | <b>Electronic Properties of Organic Dyes</b> | <b>87</b>   |
| <b>3.3.1</b>                                      | <b>Dye MH1</b>                               | <b>87</b>   |
| <b>3.3.2</b>                                      | <b>Dye MH2</b>                               | <b>89</b>   |
| <b>3.3.3</b>                                      | <b>Dye MH3</b>                               | <b>92</b>   |
| <b>3.3.4</b>                                      | <b>Dye MH4</b>                               | <b>95</b>   |
| <b>3.3.5</b>                                      | <b>Dye MH5</b>                               | <b>98</b>   |
| <b>3.3.6</b>                                      | <b>Dye MH6</b>                               | <b>101</b>  |
| <b>Chapter Four: Conclusions and Future Works</b> |                                              |             |
| <b>4.1</b>                                        | <b>Conclusions</b>                           | <b>107</b>  |
| <b>4.2</b>                                        | <b>Future Works</b>                          | <b>108</b>  |
| <b>References</b>                                 |                                              | <b>109</b>  |

# ***Chapter One***

## ***Introduction***

## Chapter One

### Introduction

#### 1.1 General Introduction

Carbon is one of the most interesting elements in periodic table [1,2]. A carbon atom has six electrons, occupying the atomic orbitals  $1s^2$ ,  $2s^2$  and  $2p^2$ . The electrons in the  $1s^2$  orbital are strongly bonded and are called core electrons. The four remaining electrons are valence electrons and are distributed to more delocalized orbitals [3]. Carbon is the material primal for life and the basis of all organic chemistry. Because of the flexibility of its bonding, carbon-based systems show an unlimited number of different structures with an equally large variety of physical properties [4].

Pure carbon is found in nature in both diamond and graphite. They have very different properties, even though they only differ in the arrangement of the carbon atoms. While diamond is insulating and very hard, graphite is conducting and lubricant. In 1985 discovered the first artificial pure carbon material, which spherical shape called fullerene. Since then an intense research on other pure carbon materials begun. In 1991, carbon was produced in the form of quasi one-dimensional nanotubes. Later, in 2004, a single sheet of carbon, called graphene, has been experimentally discovered. The strictly two dimensional graphene can be seen as the basic building block for the other graphite materials, having different dimensionalities. The fullerenes can be seen as zero dimensional wrapped up graphene, the nanotubes as one dimensional rolled graphene, and graphite as three-dimensional stacked graphene, as shown in the Fig.(1.1) [3,5].

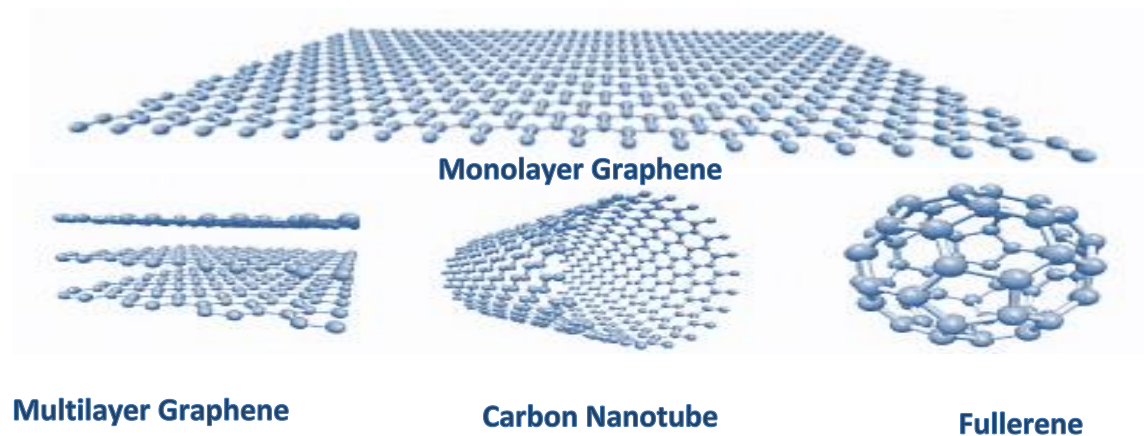


Fig.(1.1): The structure of monolayer and multilayer graphene, carbon nanotubes, and fullerene [6].

Nanomaterials are defined as materials have sizes of which in at least one dimension was in the range of 1-100 nm [7]. Therefore, nanomaterials have a much greater surface area per unit volume compared with bulk materials. surface interactions dominate nano particle behavior [8]. Nanoscale dimensions can enhance physical and chemical properties [9]. Thus diminishes the classical properties of the nano composites, surface modification has become important for nano chemists and physics [10].

Since 2004, the technology has developed rapidly as a consequence of both the realization that nanosensors instrumental for monitoring physical and chemical phenomena in regions difficult to reach, detecting biochemicals in cellular organelles, measuring nanoscopic particles in the industry, environment and Intelligent sensors are characterized as having significant data storing processing, and analyzing power. Intelligent sensors can be utilized as autonomous systems or they can be spread out in large numbers to form networks [11-13]. Explosive materials are mostly used in military battles and terrorist attacks. Sensing of these explosive molecules is one of the active areas of research for safety applications [14]. Nowadays a lot of attention is being paid to the development of methods and instrumentation for the

detection of explosives. Assuming, the methods will be found to early detect explosives by means of sensors [15].

The world energy demand is continuously, and the earth receives more solar energy in 1 hour more than the energy used in 1 year globally, considering the solar constant  $1.7 \times 10^5$  Twatt at the top of the earth's atmosphere. The solar spectrum widely ranges through 300 nm to 2500 nm with its peak at around 500-600 nm and a large fraction stems from the visible range. The dips prominently observed around 1100 nm, 1400 nm etc. due to absorption and scattering. However the solar energy incidence, around  $1\text{Kwatt/m}^2$ , is quite dilute and requires vast area of energy converters to meet the world's energy consumption. Therefore high efficiency solar energy conversion is crucial [16-18].

Solar cells convert light energy into useful electrical power. These cells are produced from light absorbing materials. The devices converting the energy of the sunlight into electricity by the photovoltaic effect discovered by the French scientist Henri Becquerel in 1839 [16]. Organic solar cells are promising since carbon is one of the most abundant elements on the earth. Finding and optimizing such materials for solar cell applications would be very helpful for the advancement of clean energy [19]. Because solar cell systems do not burn fossil fuels and do not produce the toxic air or greenhouse gas emissions associated with conventional fossil fuel fired [20]. Solar cells technology employing solar energy is regarded as the most efficient technology among all the sustainable energy technologies such as tidal power, solar thermal, hydropower, and biomass [17].

First generation solar cells, which are made from silicon, are the most efficient type of solar cells commercially available. But the drive for a cost

reduction led to new generations of solar cell technologies. They are also expensive to produce. Second generation solar cells, also known as thin film solar cells, are usually made from non-silicon materials such as copper indium gallium selenide (CIGS) and cadmium telluride (CdTe). However, due to their micrometer thickness, they are preferable to the first generation solar cells and provide some flexibility in terms of design. In addition, to production of this type of solar cell requires less materials and therefore costs less in terms of fabrication. However, the production process still involves high vacuums and temperatures. In addition, the scarcity and the toxic nature of the materials limits the mass production of this type of solar cells. The last type of solar cell is the third generation includes different types of solar cells, among which there is dye-sensitized solar cells (DSSC<sub>s</sub>), polymeric solar cells (PSC<sub>s</sub>) and small-molecule solar cells (SMSC<sub>s</sub>), collectively called organic solar cells (OSC<sub>s</sub>), are also part of the third generation of solar cells. Moreover, recent Perovskite solar cells are also considered part of the third generation of solar cells [21,22].

## 1.2 Graphene

Graphene (a two dimensional monolayer of  $sp^2$ -hybridized carbon atoms), a one-atom thick planar sheet of carbon atoms in a honeycomb lattice structure arranged into a hexagonal lattice [23-25]. Monolayer graphene could be in 2D form like a sheet. It could be cut as zigzag or armchair edge nanoribbon. Two layers graphene could be stacked into two configurations [23]. Freestanding graphene was discovered recently in 2004 by Andre Geim and Konstantin Novoselov , which earned them the Nobel Prize in Physics 2010. As it is closely related to graphite, and due to its peculiar electronic

properties, it had also been studied theoretically and computationally since 1947, as shown in the Fig.(1.2) [2,6,25].

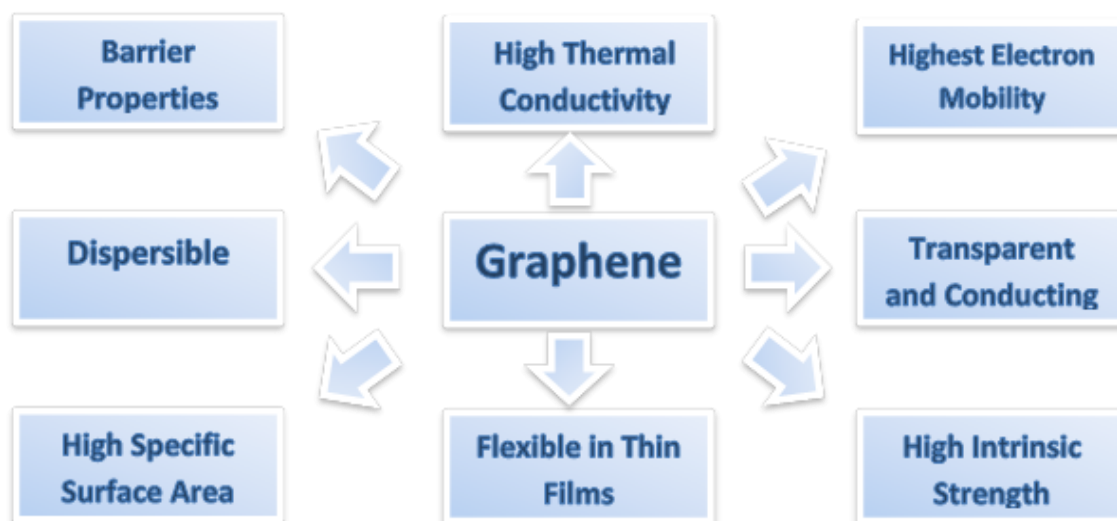


Fig.(1.2): Graphene diagram distribution.

Graphene is considered to be a promising agent for the sensing applications. A monolayer of graphene is capable of detecting individual molecules, adsorbed from gas phase or even larger molecules that would be attached to a graphene sheet from solution, indicating its applicability in sensing wide range of molecules [26]. Graphene has wide electrochemical potential window, low charge resistance, and well defined redox peaks which leads to increased sensitivity. It shows superior performance for future bio-sensing applications. It exhibits good sensitivity towards the detection of glucose. In addition,  $H_2$ , trinitrotoluene (TNT), Paracetamol, and Lectins could be sensed by Graphene [23]. It is much more widely utilized in electrochemistry due to its excellent electrical and thermal conductivity, low cost, high specific surface area, rapid heterogeneous electron transfer and simple fabrication routes. These properties makes graphene a material which could be used in the manufacture of electronic devices [27].

Despite such remarkable physical properties, the zero band gap of graphene (its valence and conduction bands overlapping each other at the Brillouin zone) is the biggest roadblock for its applications in electronic devices such as graphene field effect transistors and biochemical sensors [28]. Doping is able to open this band gap and hence improve the electronic properties and chemical reactivity of the material, therefore the Fermi level can be altered to form n-doped or p-doped material through simple physicochemical processes [2,24,29].

Because of zero mass, the electrons in graphene are governed by the Dirac equation ( the quantum mechanical description of electrons moving relativistically ) and therefore called Dirac fermions [2]. Graphene which drawn attention for its massless Dirac Fermions has an extraordinary carriers mobility 200 times higher than silicon [23]. It has extraordinary electronic excitations ( low energy ), which can be described in terms of Dirac fermions that move in a curved space. Unlike in the case of metals or common semiconductors, the electrons in graphene obey the Dirac equation rather than the Schrodinger equation [30]. The electron energy is linearly dependent on the wave vector. As a result of the linear energy-momentum dispersion relation, at the Dirac points an electron has an effective mass of zero and behaves more like a photon than a conventional massive particle whose energy-momentum dispersion is parabolic. The tight-binding calculation of the band structure of graphene is based on Schrödinger equation. At low energy levels, however, charge carrier transport can be described in a more natural way by using the Dirac equation [31-33].

Actually, it has been shown that the adsorption ability of graphene towards small organic molecules is often weak and can be significantly strengthened by doping or decorating with different heteroatoms [24]. The

electronic properties of graphene can be modified by breaking its symmetry, which can be achieved by lateral confinement, doping or functionalization and growing on a substrate [34].

### 1.3 Coronene

Coronene (Fig.(1.3)), which derives its name from its resemblance to the solar corona [35], coronene molecule has been known as polycyclic aromatic hydrocarbon (PAH) and the smallest fragment of graphene with chemical formula of  $C_{24}H_{12}$  comprising seven perifused benzene rings. It is known also as an interstellar medium as well as an inclusion in the mineral called karpatite [36-39].



Fig.(1.3): Coronene, graphene structure.

Coronene is the simplest hydrocarbon in which benzene rings completely surround a central aromatic nucleus [40]. The seven benzene rings in coronene form a planar array. The molecule is absolutely flat and resembles a layer of graphite. Therefore it is considered to be a model system for graphite [39]. Some spectroscopic studies on coronene which has molecular symmetry is called superbene [36].

Molecular structure of PAH<sub>s</sub> is characterized by two typical features: (i) Benzene rings are attached together and (ii) All peripheral carbon atoms that do not reside at ring junctions are saturated with hydrogen atoms [39]. As it is very well known that coronene is basic component of electronic materials [36]. Doping the graphene surface with heteroatoms or transition metals can improve its electronic properties and chemical reactivity [24]. The physical chemistry of this compound and its derivatives is receiving increased attention due to its charge transport and light-emitting capabilities in ordered films [41]. A number of such molecules have different optoelectronic properties and can be developed to high-performance organic electronic devices such as thin film transistors (OTFTs), light-emitting transistors (OLETs), light-emitting diodes (LEDs), Schottky barrier diode and solar cells [38,40,42]. Coronene has potential applications in solid-state lasers, field-effect transistors and pharmaceuticals [36]. Polyaromatic hydrocarbons coronene can be used as models of tiny graphene quantum dots [24].

## 1.4 Explosive Materials

Explosive events have historically been a favorite tactic of terrorists for a variety of reasons and this is likely to continue into the future, especially in our country. The principal of reacting ingredients in an explosive are fuels and oxidizers (Hydrogen, Nitrogen, Carbon and Oxygen). Other ingredients of explosives include water, gums, thickeners and cross-linking agents used in slunies , gelatinizers, densifiers, antacids, stabilizers, absorbents and flame retardants [15,43].

Explosives can be classified in various ways. Firstly one can make a distinction based on the speed of the explosion and burn rates. Low explosives

detonate relatively slowly, of the order of  $\text{cm s}^{-1}$ , and there is no associated shock wave. Black powder and propellants are examples of low explosives. High explosives detonate at speeds of the order of  $\text{km s}^{-1}$  and cause a shock wave. Examples of high explosives include trinitrotoluene (TNT), tetryl and picric acid [9,44]. Our studies focused upon the more common nitro-based explosives. They include compounds such as trinitrotoluene (TNT) and Nitroguanidine (NQ) [45].

### 1.4.1 Trinitrotoluene (TNT)

The TNT was first prepared by ( German Chemist Julius Wilbrand, 1863) and originally used as a yellow dye in its basic state; odorless, TNT will turn brown toned with prolonged exposure to sunlight [46]. TNT was introduced during 1902 in armour-piercing artillery shells by the Germans against the British Navy [45].

TNT is still widely used by the united states military, as well as construction companies around the world. The majority of TNT currently used by the US military is manufactured by Radford Army Ammunition Plant near Radford, Virginia. It was reported that the TNT is contain 2.8 mega joules per kilogram explosive energy, good chemical stability and a low sensitivity to impact and friction. For these reasons, TNT is a very commonly-used explosive [46,47].

Its potential as an explosive was not appreciated for several years mainly because it was so difficult to detonate and because it was less powerful than alternatives [46]. Interacts with alkalis (bases) to form very sensitive explosives, Not hygroscopic (i.e., having the tendency to retain water). Explosive materials are defined as materials which can, after initiation, undergo a very fast and self-propagating decomposition. TNT whose formula

is  $C_7H_5N_3O_6$  decomposes into  $N_2$ ,  $H_2$ ,  $H_2O$ ,  $CO$  and  $C$ , as shown in Fig.(1.4). This is a very rapid and highly exothermic reaction, but it has a reasonably high activation energy and it is therefore stable in an ambient environment [44].

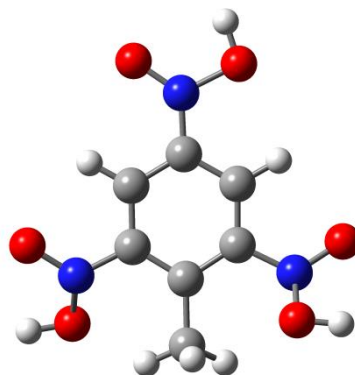


Fig.(1.4): Trinitrotoluene (TNT) chemical structure [46].

The growing production and usage of TNT has resulted in contamination of soil and water in construction sites and weapon test grounds, increasing the need for reliable sensing in aqueous environments [48-50].

### 1.4.2 Nitroguanidine (NQ)

Nitroguanidine (NQ) (Fig.(1.5)) with the formula ( $CH_4N_4O_2$ ) was first prepared by (Jousseline, 1877) and its properties investigated and described by (Vielle, 1901). During the First World War, the mixture of nitroguanidine and nitrocellulose was used as a flashless propellant. However, it was difficult to maintain the stability of such composition because nitroguanidine was reacting with nitrocellulose. It was used as a high explosive mixed with ammonium nitrate to fill mortar ammunition. Nitroguanidine was used to produce triple-base propellants. Nitroguanidine can be also used for solid rocket propellants, particularly propellants designed for the so called rocket engines, in which the steady and stable combustion takes place.

Nowadays, the studies on developing the installation for the production of bulk density, spherical and cubical nitroguanidine are conducted in the USA. Although many explosive materials are similar in that they often contain nitro groups so they can have very different properties [44,46].

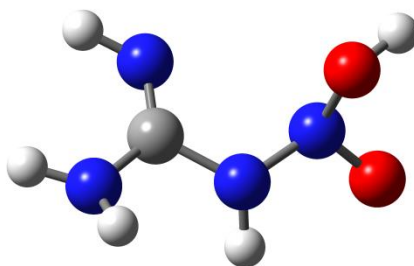


Fig.(1.5): Nitroguanidine (NQ) chemical structure [46].

## 1.5 Nanosensor

Nanosensor is Any sensor fabricated by nano technological methods. Let us agree that any sensor characterized by one of the following properties will be labeled as a nanosensor: (i) The size of the sensor is in nanoscale, (ii) Sensitivity of the sensor is in the nanoscale, or (iii) The spatial interaction distance between the sensor and the object is in nanometers [51].

Events in recent years have led to an increased need for improvements in our abilities to detect explosives. Miniature sensors with high sensitivity, fast response, high selectivity, high reliability and quick recovery, the ability to lower the deployment cost of sensors using mass production, is essential in winning the war on explosives-based terrorism [9,52]. Nanosensors have the potential to satisfy all the requirements for an effective platform for the trace detection of explosives as shown in the Fig.(1.6).

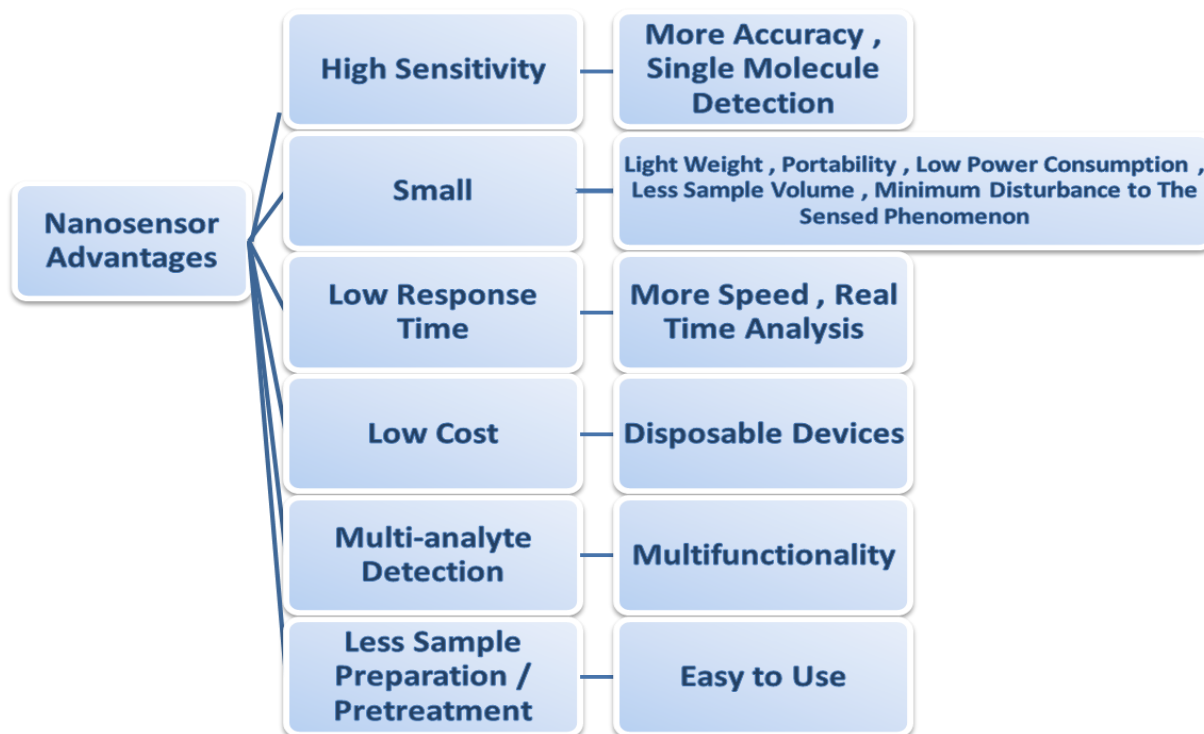


Fig.(1.6): Feature of any nanosensor Diagram [51].

Utilization of graphene in nanosensor systems was first reported in 2010. As a 2D carbon material, graphene has superior electrical properties arising from homogenous distribution of electrochemically active sites. In addition to this, extraordinary electronic band structure enables graphene to behave as a zero-band gap semiconductor and the considerable surface area allows adsorbent materials to significantly change its electrical properties by altering carrier density. Therefore, we will highlight the relevant properties of graphene in the context of chemical sensing. The high sensitivity of graphene also arises from low electrical signal noise due to its 2D crystal network structure. Although these carbon materials still have to meet crucial challenges in fabrication and optimization, continued progress in this field may lead to a sensor with superior sensitivity, as shown in the Fig.(1.7) [53,54].

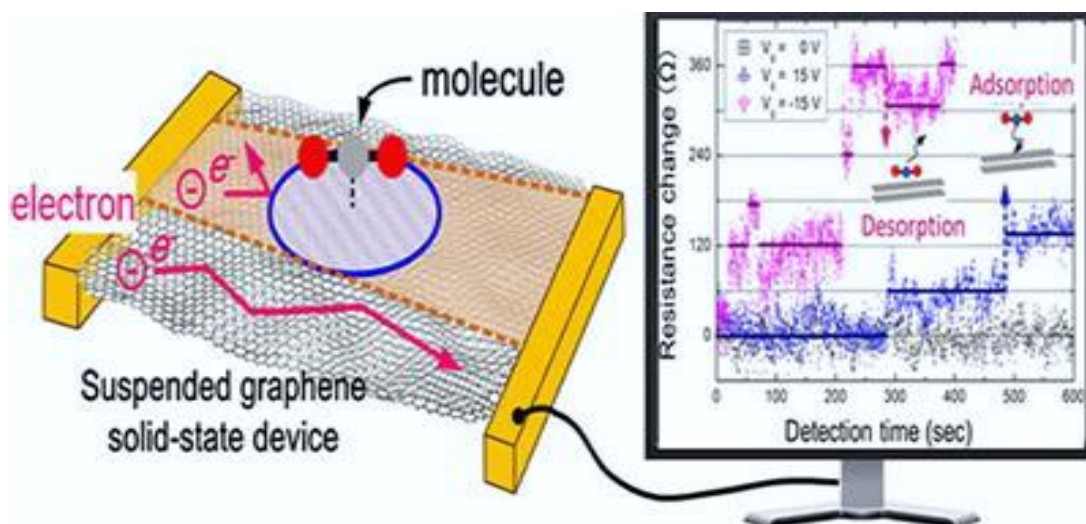


Fig.(1.7): Nanosensor device components.

Due to the strong adsorption of aromatic explosives on graphene surfaces, graphene is used for potential detection for the aromatic explosive molecules [14]. Chemically modified graphene sheets for applications in advanced sensors. Chemical modifications provide active sites for molecular adsorption, increasing its binding energy [26,54]. Trace detection of explosives typically through the sensing of the vapor emitted by the explosive material with a sensitive sensor system [9,44].

## 1.6 Organic Molecules

There is no exact scientific definition of an organic compound. As a general rule, Organic compounds are those that contain carbon. They contain one or more of the following elements: carbon (C), hydrogen (H), oxygen (O), nitrogen(N), sulfur (S), halogens (fluorine [F], chlorine [Cl], bromine [Br], iodine [I],and astatine [At]), and occasionally phosphorous (P) and metals. Because of the ability of carbon atoms to form long chains, the number of such compounds far exceeds that of other elements [51].

The field of organic electronics dates back to the mid-20th century, when organic compounds were found to conduct electricity. Ever since, a large number of organic conductors and semiconductors has been identified and synthesized. The large applications of organic molecules are electronic and optical devices, consumer electronics and screens, advanced batteries, medical applications and aids, clean energy devices, sensors and membranes, and light-harvesting antennas, among others [55].

For devices which use of the properties of single molecules it becomes important to understand from a fundamental level how molecules interact with the surface and with other molecules adsorbed on the surface. By studying single molecules adsorbed on surfaces it is possible to learn about the adsorption process itself without having to consider the effect from interactions with other molecules [56]. Upon doping from external sources, a successful organic based candidate for electronic devices should be able to transport charge carriers of both existing types, electrons and holes [55].

## **1.7 Organic Solar Cells**

Organic solar cells are alternative to inorganic solar cells like (Si) ; they can have extremely high optical absorption coefficients, They have also attracted much attention in recent years due to their advantages in low-cost manufacturing, their light weight and good mechanical flexibility. These advantages have created great interest and thus a great deal of research work is currently being devoted to increase their power conversion efficiencies and scale-up production processes. The electrical and chemical properties of organic semiconductors can be tailored by modifying the chemical structure of the compounds in endless combinations [18,30,57,58].

Organic solar cells have been widely applied in plenty of fields, such as commercial building systems or residential home systems, photovoltaic power plants, water pumping, space power supply, telecommunication, automobiles, public system power supply, other digital consumption and military uses as well [59]. Almost all organic solar cells have a planar layered structure, where the organic active layer(s) is (are) sandwiched between two different electrodes. One of them must be transparent, usually indium tin oxide (ITO). The other electrode is very often aluminium [60,61]. Subsequent to charge separation both the electron and the hole have to reach the opposite electrodes, the cathode and the anode, respectively. Thus a direct current can be delivered to an outer circuit [18].

The work of photovoltaic can be divided into four parts: (i) Absorption of light and generation of excitons, (ii) Diffusion of excitons, (iii) Dissociation of the exciton and generation of the charges, (vi) Charges transport and collection.

A charge separation process in a DSSC<sub>s</sub> consists of the following steps. (i) Photo anode absorbs incident solar energy. Upon absorption of photo energy, the electrons in the dye become excited from ground state to the excited state. (ii) Due to the difference in energy levels of the electronic states, electrons from the excited state are injected to the conduction band of the semiconductor. As a result the dye becomes oxidized. (iii) The electrolyte, which is in contact with the dye, then donates electrons to the dye restoring it to the initial state. (iv) Electrolyte then diffuses towards the catalytic electrode where the reduction reaction takes place and electrolyte restores its initial state by accepting electrons from the external circuit. (v) In addition to these forward charge transfer processes, backward charge transfer processes also occur in one complete cycle [17], as shown in the Fig.(1.8).

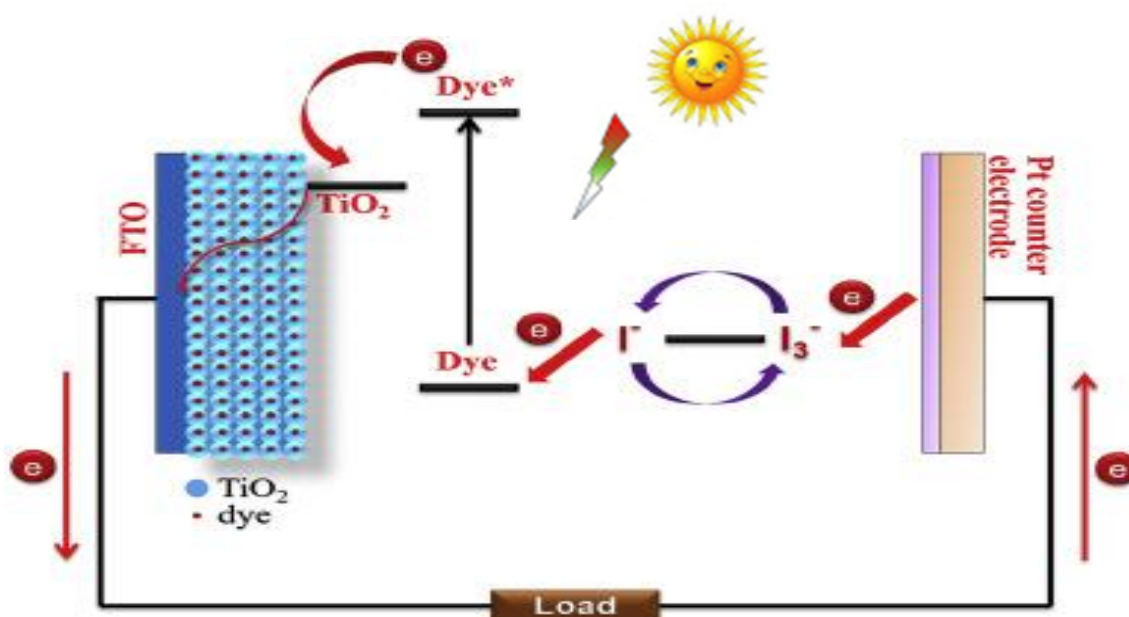


Fig.(1.8): Basic working principle of dye-sensitized solar cell [62].

The photophysics of this system is based on highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the donor and acceptor materials which, in terms of light absorption, are conceptually similar to the conduction and valence band in an inorganic semiconductor. In organic materials the LUMO and HOMO levels do not interact strongly enough to form a conduction band and a valence band like in inorganic semiconductors [63].

Also some reflection losses should be present, anti-reflection coatings and structured surface of the device can be used. Due to multiple reflections, the effective optical path for absorption is much larger than the actual film thickness [8,60].

The fill factor (FF) is an important parameter for solar cell/module; it represents the area of the largest rectangle, which fits in the I-V curve. The importance of FF is linked with the magnitude of the output power[64]:

$$FF = \frac{I_{MP} * V_{MP}}{I_{SC} * V_{oc}} \quad \dots(1.1)$$

$I_{MP}$ : The maximum-power current.

$V_{MP}$ : The maximum-power voltage.

$I_{SC}$ : The short-circuit current.

$V_{oc}$ : The open-circuit voltage.

The ratio of the output power divided by the input power is the photo conversion efficiency  $\eta$ , also called Power Conversion Efficiency (PCE) [22]:

$$\eta = FF \frac{I_{SC} \cdot V_{oc}}{P_{IN}} \quad \dots(1.2)$$

$P_{IN}$ : The light power incident on the device.

This technology is still not ready for commercialization, organic solar cells still attract a lot of interest. The company Heliatek, producing small-molecule organic solar cells, has been awarded in 2015 as Technology Pioneer by World Economic Forum. Organic solar get their name from the nature of the light absorbing material, which is based on carbon [22].

## 1.8 Dye-Sensitized Solar Cells (DSSCs)

Dye-sensitized solar cells (DSSCs) have received considerable attention as the most promising candidates for renewable energy systems in recent years, due to their cost-effectiveness, ease of fabrication, environmentally friendly and have a relatively high solar-to-electric energy conversion efficiency. [65-69].

DSSCs are fabricated of abundant and cheap materials using inexpensive processes (e.g. doctor blade) and are likely to be a significant contributor to the future commercial photovoltaic technology. The role of the dye is similar to the role of chlorophyll in plants; it harvests solar light and transfers the energy via electron transfer to a suitable material to produce electricity as opposed to chemical energy in plants. Dye sensitized solar cells were invented by Michael Gratzel et al. Also called dye solar cell or Grätzel cell, named after its inventor, who developed it in 1991 together with Brian O'Regan, new solar cell working on the principle of plant photosynthesis, it has generated a lot of interest leading to an exponential growth in research relating to DSSCs [17,69,70].

The physical insight provided by computational modeling may help engineer new dyes and assess their performance. Many electronic structure calculations have been done for various dye molecules, typically employing density functional theory (DFT) for the ground state properties and time-dependent DFT (TD-DFT) for the absorption spectrum [71]. The effected spectra of this type of solar cell have the range from 400 nm to 1300 nm which covers visible and infrared spectrum as shown in Fig.(1.9).

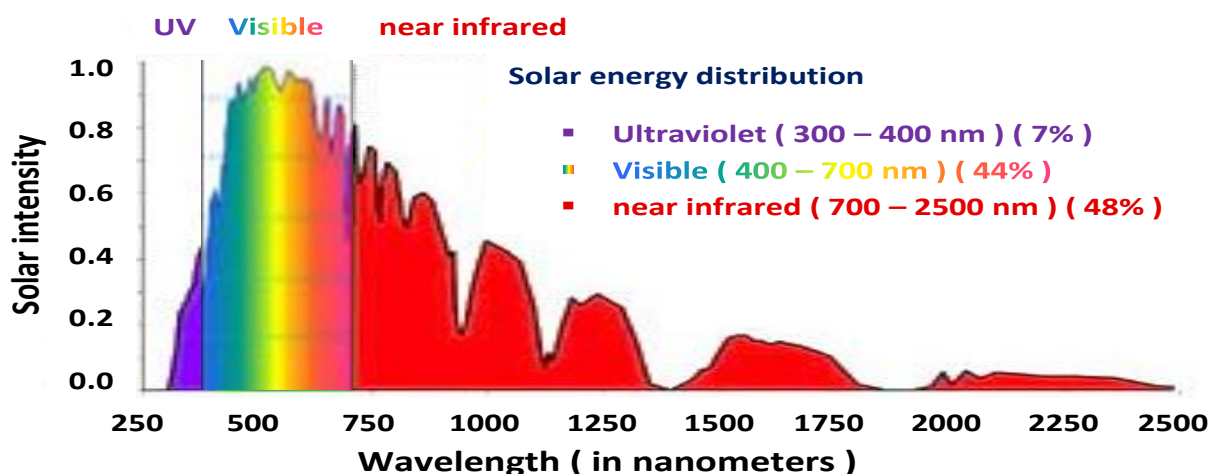


Fig.(1.9): Under atmospheric sun spectrum with absorption area [72].

## 1.9 Literature Review

Ravi Mosurkal et al in 2004 carried out a study on a number of organic dyes to identify photosensitizers for dye-sensitized solar cell applications with well-matched redox potentials and good absorption characteristics. Redox potentials, absorption and solar cell properties of these dyes are presented. Two possible ways of electron transfer, namely direct charge transfer via formation of strong charge transfer complexes and the conventional excited state electron injection through the HOMO-LUMO energy level matching are discussed in these dyes. Though solar cell efficiency is found to be low in these organic dyes for fabricating practical devices, this study suggests a promising alternative approach to dye selection from commercial sources for dye-sensitized solar cells and for further investigation to identify more organic systems with improved efficiency [73].

Matt Law et al in 2005 excitonic solar cells including organic, hybrid organic and dye-sensitized cells (DSCs) are promising devices for inexpensive, large-scale solar energy conversion. As an ordered topology that increases the rate of electron transport, a nanowire electrode may provide a means to improve the quantum efficiency of DSCs. Important differences in transport, internal electric field distribution and light scattering should make comparative studies of wire and particle devices fruitful. Raising the efficiency of the nanowire cell to a competitive level depends on achieving higher dye loadings through an increase in surface area. The advantages of the nanowire geometry are even more compelling for other types of excitonic photocells, such as inorganic–polymer hybrid devices [74].

Nagatoshi Koumura et al in 2006 succeeded in increasing the electron lifetime in DSSCs using organic dyes by the addition of long alkyl groups at

the oligothiophene linkage and have demonstrated the highly efficient performance of the DSSCs using the dyes. Our molecular design of alkyl-functionalized dyes strongly suggests the promising performance of molecular solar cells based on organic dyes. To achieve similar solar cell performance of DSSCs based on Ru dyes, we are now synthesizing new organic dyes with further molecular designs [75].

Ruikui Chen et al in 2007 described the relationship between the dye structure, photophysical and photoelectrochemical properties, and performance of DSSCs. Small changes to the structural of dyes result in significant changes in redox energies and adsorption manner of the dyes, affecting dramatically the performance of DSSCs based on these dyes [76].

Zhijun Ning et al in 2008 studied the synthesis and photophysical / electrochemical properties of a series of novel starburst triarylamine-based organic dyes as well as their application in dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells (DSSCs). For the four designed dyes, the starburst triarylamine group and the cyanoacetic acid take the role of electron donor and electron acceptor, respectively. This work suggests that the dyes based on starburst triphenylamine donor are promising candidates for improvement of the performance of the DSSCs [77].

Renzhi Li et al in 2009 six organic dyes with different conjugated linkers such as furan, bifuran, thiophene, bithiophene, selenophene, and biselenophene have been prepared in combination with the dihexyloxy-substituted triphenylamine donor and the cyanoacrylic acid acceptor. For the first time proved that furan and selenophene can be employed as stable units in dye-sensitized solar cells, enlarging the selection range of building blocks for further dye design [78].

Nailiang Yang et al in 2010 introduce graphene as 2D bridges into the nanocrystalline electrodes of dye-sensitized solar cells, which brought a faster electron transport and a lower recombination, together with a higher light scattering. The short-circuit current density was increased by 45%, and the conversion efficiency was increased by 39%. The incorporation of 2D nanomaterial with 0D nanoparticles can also be extended to other electronic devices, especially using graphene as an electron acceptor and charge transfer medium [79].

R. Chowdhury et al in 2011 studied the effect of organic molecule adsorption on the transport of single-layer graphene nanoribbons in a two probe configuration. These molecules could be useful to simulate the effects on the electronic transport of zigzag graphene nanoribbons for the development of graphene-based sensor devices [80].

William J. Potscavage in 2011, the first modern solid-state solar cell based on organic materials with an efficiency close to or higher than 1% was developed by C. W. Tang during his time at Eastman Kodak [57].

Yinghui Liu in 2012, the Plextronics, US, used P3HT and derivatives of C60, achieved the 5.4% PCE in 2007 and 7.0% PCE in 2010. Both of the Heliatek, Germany, and the Konarka Technologies, US, successfully produced the organic solar cells with the 8.3% PCE in 2010. But the best record which has been admitted by now is the 9.26% PCE which was declared by the Mitsubishi Chemical, Japan, in March of 2011 [59].

Perry T. Yin et al in 2013 concluded that graphene nanoparticle hybrid structures can act synergistically to offer a number of unique physicochemical properties that are desirable and advantageous for sensing applications. These graphene nanoparticle hybrid structures are particularly interesting because

not only do they display the individual properties of the nanoparticles and of graphene, but they can also exhibit additional synergistic properties thereby enhancing the achievable sensitivity and selectivity using a variety of sensing mechanisms. In particular, focus on the preparation of graphene nanoparticle hybrid structures as well as their application in electronic, electrochemical, and optical sensors [81].

Abha Misra in 2014 studied, the chemical sensing behavior of the carbon nanotube and graphene based sensors for detecting various chemical analytics . A focus on detection mechanisms has been provided to assess their relative potential under different environmental conditions. The performance of these two carbon allotropes is compared based on their sensitivity towards various types of electron donating and accepting molecules. Although these carbon materials still have to meet crucial challenges in fabrication and optimization, continued progress in this field may lead to a sensor with superior sensitivity for a wide range of applications [54].

Mehrdad Mahkam et al in 2015 performed a computational study density functional theory (DFT) on the adsorption of explosive materials on single-walled carbon nanotubes in gas phase. The main purpose of this study is to gain fundamental insights of explosive materials on the electronic properties of the side-wall carbon nanotube, and how these effects could be used to design more sensitive molecules sensing devices [46].

Irina V. Zaporotskova et al in 2016, the main regularities of the structure, energy parameters and sensor properties of modified semiconducting systems on the basis of carbon nanotubes have been studied by analyzing the mechanisms of nanotube interaction with functional groups

(including carboxyl and amino groups), metallic nanoparticles and polymers leading to the formation of chemically active sensors [7].

Rowshan Rahmanian in 2017, organic solar cells have reached confirmed power conversion efficiencies of over  $11.2 \pm 0.3\%$ , which is on a par with the latest dye-sensitized solar cells ( $11.9 \pm 0.4\%$ ) [82].

S. Bashiri et al in 2017 studied interaction (AA) drug with the pristine, B, Al, Ga, Si, and Ge-doped C60 using (DFT) calculations. The pristine C60 fullerene shows a good sensitivity to (AA) drug based on the work function calculations. show that replacing a C atom of C60 with the impurity atoms, especially Si and Ge, significantly improves both the reactivity and sensitivity to the (AA) drug. The work function of these sensors largely decreases by the (AA) adsorption which increases the electron emission from its surface. Thus, an electronic noise can be detected in the presence of the (AA) drug which leads to its recognition [83].

Weixia Hu et al in 2017, a series of triphenylamine-based dye sensitizers were designed by modifying the auxiliary acceptors and their positions for the potential use in dye-sensitized solar cells (DSSCs). The geometrical structures, photo induced charge transfer character together with optical properties for these dyes adsorbed on  $(\text{TiO}_2)_6$ . The results illustrate that the dyes with auxiliary acceptors close to the cyanoacrylic acid show very narrow band gap (HOMO-LUMO), leading to an obvious red shifted absorption band in contrast to the dyes with additional acceptors next to the donor part. Further analyses of the dye- $(\text{TiO}_2)_6$  systems manifest that there has strong electronic coupling between the dyes and the  $(\text{TiO}_2)_6$  surface [84].

Diego Cortes Arriagada et al in 2018 studied the adsorption of pollutant gases ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{H}_2\text{S}$ ) onto Fe-doped graphene nanosheets (FeG) on

the basis of density functional theory calculations. The most stable adsorption configurations, binding characteristics, electronic properties and stability at room temperature of the FeG-Gas interactions is fully analyzed. The electron acceptor/donor character of (CO, CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>S) molecules when adsorbed onto (FeG) causes charge transfer processes that are responsible for the change in conductance of (FeG) ; thus, the response of the HOMO LUMO gap of (FeG) under gas adsorption could be useful for sensing applications [85].

Zahra Khodadadi in 2018, the theoretical studies have shown that pristine graphene weakly absorbs (H<sub>2</sub>S) molecule. The adsorption of (H<sub>2</sub>S) molecule on pristine, transition metal (Ni, Cu and Zn)- doped graphene and metal-decorated graphene nanosheets have been investigated via first principles approach based on Density Functional Theory (DFT). He adsorption of (H<sub>2</sub>S) gas on several kinds of graphene nanosheets was studied by three different models. The calculations show that the adsorption energy of (H<sub>2</sub>S) on Cu-doped graphene nanosheet is the highest among all the other metal-doped graphene nanosheet systems [86].

W. Taouali et al in 2018, search of novel high-performance materials for use in organic solar cells, they used density-functional theory and time-dependent density functional theory to design a series of organic small molecules derived from the recently synthesized BT(-2T-DCV-Hex)<sub>2</sub> donor molecule. In this work, they replaced the BT unit by different acceptors in order to improve their electronic properties, optical absorption and performance in organic solar cell applications. They found that the hybrid functional B3PW91 with the 6-31G(d) basis set gave highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the BT(-2T DCVHex)<sub>2</sub> in better agreement with the

experimental oxidation and reduction potentials. However, the range-separated hybrid functional WB97XD was the most appropriate functional for describing the maximum absorption wavelength [87].

### **1.10 Thesis outline**

The thesis is divided into four chapter, in the Chapter 1 of it, we show the introduction and literature review of nanosensor and dye sensitized solar cells systems, as well as the aim of the study. Chapter 2 reviews the theoretical background, to understand the theoretical basis of the methods used. In Chapter 3 review the improvement of nanosensor devices used to detect organic molecules explosive material (TNT and NQ). Also study the optical and electronic properties of some dyes used in dye-sensitive solar cells and ways to improve these dyes. Finally, chapter 4 describes our conclusions, and suggests issues for future research.

### **1.11 Aim of Study**

1. Improvement nanosensor device by some suitable atoms for enhancing the detection of organic molecules explosive material ( TNT and NQ ).
2. Studying the optical and electronical properties of some dyes that use in dye sensitized solar cell.
3. Improvement these dyes by adding terminal organic molecules.

# ***Chapter Two***

## ***Theoretical Background***

## Chapter Two

### Theoretical Background

#### 2.1 Schrodinger Equation

Schrodinger equation is the fundamental equation to describe the motions of atomic, subatomic systems, electrons, nucleus, and even macroscopic systems [88]. The solution of the Schrodinger equation can be found by usual procedure known from quantum mechanics textbooks [89]. It deals with all problems which associated with the electronic structure of the materials. Schrodinger equation is given by [90-92]:

$$H \Psi = E \Psi \quad \dots (2.1)$$

$H$ : Hamiltonian operator.

$\Psi$ : The wave function of the physical system i.e. the eigen function of the Hamiltonian operator.

$E$ : The total energy of the system.

Where the total energy  $E$  is obtainable when the differential equation solved. The Hamiltonian operator of a molecular system with nuclei  $M$  and number of electrons  $N$  can be expressed by the equation [93]:

$$H = \hat{T} + \hat{V} \quad \dots (2.2)$$

$\hat{T}$ : The kinetic energy operator.

$\hat{V}$ : The potential energy operator.

or by the equation [93,94]:

$$H = \widehat{T}_e + \widehat{T}_n + \widehat{V}_{ne} + \widehat{V}_{ee} + \widehat{V}_{nn} \quad \dots (2.3)$$

$\widehat{T}_e$ : The kinetic energy operator of the electron.

$\widehat{T}_n$ : The kinetic energy operator of the nucleus.

$\widehat{V}_{ne}$ : Component of the Coulomb attraction energy between nuclei and electrons.

$\widehat{V}_{ee}$ : Component of the Coulomb repulsion energy between the electrons.

$\widehat{V}_{nn}$ : Component of the Coulomb repulsion energy between the nuclei.

The terms in Eq.(2.3) can be written as follows [95]:

$$\widehat{T}_e = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad \dots (2.4)$$

$$\widehat{T}_n = -\frac{1}{2} \sum_{A=1}^M \frac{\nabla_A^2}{M_A} \quad \dots (2.5)$$

$$\widehat{V}_{ne} = - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \quad \dots (2.6)$$

$$\widehat{V}_{ee} = \sum_{i=1}^M \sum_{i>1}^N \frac{1}{r_{ij}} \quad \dots (2.7)$$

$$\widehat{V}_{nn} = \sum_{A=1} \sum_{B>A} \frac{Z_A Z_B}{R_{AB}} \quad \dots (2.8)$$

$M_A$ : Mass of the nucleus A .

$r_{iA}$ : The distance between the electron i and the nucleus A .

$Z_A$ : The atomic number of the nucleus A .

$r_{ij}$ : The distance between electron i and electron j . Where  $\vec{r}_{ij} = |\vec{r}_i - \vec{r}_j|$

$R_{AB}$ : The distance between the nucleus A and the nucleus B .

$Z_B$ : The atomic number of the nucleus B .

$\nabla^2$ : Laplace operator.

For the rest of this thesis all equations will be written in atomic units :

$$e = m_e = \hbar = 4\pi\epsilon_0 = 1$$

Hence, Hamiltonian operator can be written in atomic units by the equation [93]:

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{\nabla_A^2}{M_A} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^M \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad \dots (2.9)$$

In Cartesian coordinates Laplace operator is given by [93,94]:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \dots (2.10)$$

Quantization of energy of the particle is a remarkable feature of the quantum mechanics i.e. a particle cannot have any energy or continuous energy, but can have only that permitted energy described by Schrodinger equation [96].

## 2.2 Wave Function ( $\Psi$ )

In classical physics, a particle's position is specified by a definite location. In quantum mechanics, systems are described by wave functions. It is a mathematical formula describes the motion of the electron. The value of wave function which accompanies moved particle at a point in the space and time involves with the probability to find that particle in that space and time. The probability density per unit volume described by the wave function ( $\Psi$ ) at a point in space and time proportional to value of  $|\Psi|^2$  at the space and time [96]. This interpretation to value of  $|\Psi|^2$  has been introduced at first time by Max Born in 1927. The wave function of the system may be normalized or orthogonal, so that one can write [97]:

$$\int \Psi_i \Psi_j d\tau = \delta_{ij} \quad \dots (2.11)$$

$$\delta_{ij} = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases} \quad \dots (2.12)$$

$\delta_{ij}$ : Kronecker Delta.

In physics, the wave function is not an observable quantity but  $|\Psi|^2$  can be interpreted as a probability density and when it is multiplied by the volume of the area give the probability [91].

In 1924, Louis de-Broglie suggested that every moving particle has a wave associated with it, which is also known as matter wave. Further, Erwin Schrodinger in continuation to DE Broglie's hypothesis introduced a differential wave equation of second order to explain the wave nature of matter and particle associated with wave. This equation is analogous to the

equation for waves in optics, which assumes that the particle behaves as wave and yields solution in terms of a function called the wave function [96].

### 2.3 Variational Method

The variational principle is a very useful analytical tool for the study of the ground state energy of any dynamical system. Since most problems in physics and chemistry cannot be solved exactly, for that reason approximated method are used. The basic idea of the variational method lies in the choice of a trial wave function for the problem at hand; which consists of some adjustable parameters usually called the variational parameters. These variational parameters are usually adjusted until the energy of the trial wave function is minimized. Once this is done, the resulting trial wave function and its corresponding eigen values are variationally approximated to the exact wave function and the ground state energy of a system without solving the Schrodinger equations. The success of the variational method depends on the initial “guess” what the ground-state wave function looks like [98].

Variational principle states that the expectation value of the Hamiltonian for trial wavefunction ( $\psi_{ij}$ ) must be greater than or equal to the actual ground state energy. Mathematically , one can have [98,99]:

$$[\langle \Psi_{trial} | H | \Psi_{trial} \rangle \approx E_{trial}] \geq E_o \quad \dots (2.13)$$

$\Psi_{trial}$ : The speculated wave function.

$E_{trial}$ : The speculated energy.

$E_o$ : The ground state energy.

## 2.4 Born-Oppenheimer Approximation

The Born-Oppenheimer (BO) approximation is one of the basic approximations in molecular science. It allows us to separate the fast electronic motion from the usually much slower motion of the nuclei and to visualize the molecule as a set of nuclei moving on the potential energy surface provided by the electrons in a specific electronic state [100]. The BO approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the BO approximation is the fact that the mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000 times). Because of this difference, the nuclei move much more slowly than the electrons. The Born-Oppenheimer separates of nuclear and electronic wavefunctions. Although this factoring, the total wavefunction is in general an excellent approximation [101]:

$$\Psi_{total} = \Psi_{electronic} \Psi_{nuclear} \quad \dots(2.14)$$

The electronic wave function depends only on locations of the forces, but the nuclear wave function depends on the electronic configuration [102]. All properties of matter are in principle described by the well-known Schrodinger equation (in the time-independent approximation) in Eq.(2.1). Any observable can be extracted from the many-body wavefunction  $\Psi$ , and  $E$  is the total energy of the system. The Hamiltonian operator  $H$  in general depends on both electronic and nuclear degrees of freedoms. The BO approximation allows to decouple the electronic and nuclear dynamics due to the large difference in mass between electrons and nuclei, ( $m_e / M_n \sim 10^{-3} - 10^{-5}$ ). The electron problem can thus be reduced to  $N$  electron Hamiltonian in which the nuclei are assumed to be fixed at some given positions [103].

The ultimate goal of most quantum chemical approaches is the approximate solution of the time-independent, non-relativistic Schrodinger equation. This is the famous Born-Oppenheimer or clamped-nuclei approximation. Of course, if the nuclei are fixed in space and do not move, their kinetic energy is zero ( $T=0$ ) and the potential energy due to nucleus-nucleus repulsion is merely a constant ( $V=\text{cons.}$ ). Thus, the complete Hamiltonian given in Eq.(2.9) reduces to the so-called electronic Hamiltonian [94]:

$$H_e = -\frac{1}{2}\sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^M \sum_{j>i}^N \frac{1}{r_{ij}} = \widehat{T}_e + \widehat{V}_{ne} + \widehat{V}_{ee} \dots (2.15)$$

The Born-Oppenheimer or adiabatic approximation is widely used to simplify the very complex many-body problem of electrons in solids and molecules, assuming that electrons equilibrate much faster than the atomic motion of the ionic cores. Without this approximation, most molecular and solid state problems become difficult or impossible to solve analytically. Although the BO approximation is valid in most materials and molecular systems, there are a few situations in which it does not hold, including some low atomic weight compounds, intercalated graphite, and graphene Clean [104].

## 2.5 Hartree Approximation

Since one cannot solve the exact Hamiltonian of the atom ( “exact” within some model; the ultimate Hamiltonian is not known and perhaps does not even exist ) one starts with an approximate, separated ( Hartree, Hartree-Fock ) Hamiltonian [105]. The electrons are assumed to be non-interacting,

and so the N-electron wavefunction is just the product of the one-electron wavefunctions [106]:

$$\Psi_i = \Psi_1(r_1) \Psi_2(r_2) \dots \Psi_N(r_N) \quad \dots(2.16)$$

Each electron is treated as moving in a mean field potential,  $V(r)$ . This potential models the effects of all the other particles in the system, as well as any external potential acting on the system. The equation of one-electron is of the form [107]:

$$-\frac{1}{2} \nabla^2 \Psi_i(r) + V(r) \Psi_i(r) = E_i \Psi_i(r) \quad \dots(2.17)$$

Where  $V(r)$  includes both the nuclear-electron interaction :

$$V_{nucleus}(r) = -Ze^2 \sum_R \frac{1}{|r-R|} \quad \dots(2.18)$$

and the mean field arising from the N-1 other electrons. We smear the other electrons out into a smooth negative charge density  $\rho(r')$  leading to a potential of the form :

$$V_{electron}(r) = -e \int dr' \rho(r') \left( \frac{1}{|r-r'|} \right) \quad \dots(2.19)$$

where

$$\rho(r) = \sum_i^{occupied} |\Psi(r)|^2 \quad \dots(2.20)$$

The sum runs over all occupied states. These equations are known as the Hartree equations [108].

## 2.6 Hartree-Fock Methods

### 2.6.1 Hartree-Fock Approximation

Hartree-Fock (HF) approximation is developed to solve time independent Schrodinger equation, and in order to solving Schrodinger equation for all electrons in the system requires to solve it for about  $10^{23}$  atoms, i.e. differential equations [94], and this is very difficult so that Hartree-Fock in 1928 suggests an iterative self-consistent field method (SCF) [109,110].

In a uniform system these wave functions would take the form of simple plane waves. According to the variation principle [94,111], if a given system is described by a set of unknown parameters, the set of parameter values which correctly describes the ground state of the system is just that set of values which minimizes the total energy, this can be expressed as [88,94,111]:

$$E_{\varphi} = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} \geq E_o \quad \dots(2.21)$$

Where  $E_{\varphi}$  is the lowest energy eigenvalue of the trial function  $\varphi$  and  $E_o$  is the ground state energy. Using this theorem, the exact ground-state wave function is approximated by the trial function that gives the lowest energy. Hartree found the Hamiltonian equation of the many-electron system and it was possible to treat each electron separately as a single-particle [112].

The wave function of HF approach can be written in a compact way as a Slater determinant. The determinant considers the spin of all the electrons and the Pauli exclusion principle. Eq.(2.22) below is an example of a slater determinant for a system of N-electrons [107,113]:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(1) \alpha(1) \Psi_1(1) \beta(1) & \Psi_2(1) \alpha(1) \Psi_2(1) \beta(1) & \dots & \Psi_N(1) \alpha(1) \Psi_N(1) \beta(1) \\ \Psi_1(2) \alpha(2) \Psi_1(2) \beta(2) & \Psi_2(2) \alpha(2) \Psi_2(2) \beta(2) & \dots & \Psi_N(2) \alpha(2) \Psi_N(2) \beta(2) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_1(N) \alpha(N) \Psi_1(N) \beta(N) & \Psi_2(N) \alpha(N) \Psi_2(N) \beta(N) & \dots & \Psi_N(N) \alpha(N) \Psi_N(N) \beta(N) \end{vmatrix} \quad \dots(2.22)$$

Where  $\psi$  is the electronic wave function,  $\alpha$  and  $\beta$  are the spin up and spin down of electrons, respectively, and  $(1/\sqrt{N!})$  is a normalization factor.

The initial approximation (i) : is the central field approximation, i.e. electron-electron coulomb repulsion forces must take into account, and this gives an average of the repulsion effect, but it is not the explicit repulsion interaction variational accounts [102].

The another approximation (ii) : results from fact that the wave function must be described by a mathematical function which is exactly known for one electron system. This method reduces problems of many particles into sets of eigenvalue problems of one particle, and it is called Hartree-Fock equations [113].

$$\hat{f}_1 \Psi_i = \varepsilon_i \Psi_i \quad \dots(2.23)$$

$\Psi_i$ : The eigen function of the operator  $\hat{f}$ .

$\hat{f}_1$ : Fock operator.

$\varepsilon_i$ : The eigenvalue of the energy.

Fock operator for each electron can be defined as [114]:

$$\hat{f}_1 = -\frac{1}{2} \nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} + V_{HF}(i) \quad \dots(2.24)$$

Hartree-Fock potential  $V_{HF}(i)$  describes the average repulsion potential by each electron which results from another  $(n - 1)$  electrons, and it has two components, coulomb operator  $\hat{J}_1(j)$  and exchange operator  $\hat{K}_1(j)$ , Hence :

$$V_{HF}(i) = \sum_j^N \hat{J}_1(j) - \hat{K}_1(j) \quad \dots (2.25)$$

Coulomb operator describes coulomb repulsion average between electrons, but the exchange operator stands for the non-classical self-repulsion. These operators can be defined as [111,115]:

$$\hat{J}_1 \Psi_i(2) = \int \frac{\Psi_i^*(1) \Psi_i(1)}{|\vec{r} - \vec{r}'|} dV' \Psi_j(2) \quad \dots (2.26)$$

$$\hat{K}_1 \Psi_l(2) = \int \frac{\Psi_l^*(1) \Psi_l(1)}{|\vec{r} - \vec{r}'|} dV' \Psi_k(2) \quad \dots (2.27)$$

A further restriction involves expanding the molecular orbitals in terms of basis functions  $\varphi_i$  linear combinations of one-electron functions according to the linear combination atomic orbital (LCAO) method [113,116].

Thus an individual molecular orbital is defined as :

$$\Psi_i = \sum_{j=1}^N C_{ji} \varphi_j \quad \dots (2.28)$$

$C_{ji}$  represents the molecular orbital expansion coefficients. The basis functions  $\varphi_j$ .

For orbital expansion an appropriate set of basis functions has to be selected, with that the coefficients  $C_{ji}$  may then be adjusted to minimize the total electronic energy calculated from the many-electron wave function. The resulting value of the energy will then be as close as possible to the exact

energy  $E_o$  of the ground state of the system within the selected limitations [117].

$$E ( \varphi_1 , \varphi_2 , \dots , \varphi_N ) \geq E_o \quad \dots(2.29)$$

The equality sign shall be applied only in case  $\psi_i$  is the exact ground state function. The new Hartree-Fock equations have eigenvalues that turn out to differ by 10–20 percent from those obtained using Hartree equations supplemented by the condition arising from the exclusion principle [118].

The idea is to solve the Schrodinger equation for an electron moving in the potential of the nucleus and all the other electrons. We start with a guess for the trial electron charge density, solve  $Z/2$  one-particle Schrodinger equations (initially identical) to obtain  $Z$  electron wavefunctions. Then we construct the potential for each wavefunction from that of the nucleus and that of all the other electrons, symmetrize it, and solve the  $Z/2$  Schrodinger equations again. Fock improved on Hartree's method by using the properly antisymmetrized of wavefunction ( Slater determinant ) instead of simple one-electron wavefunctions. Without this, the exchange interaction is missing. This method is ideal for a computer, because it is easily written as an algorithm [119], as in the Fig.(2.1).

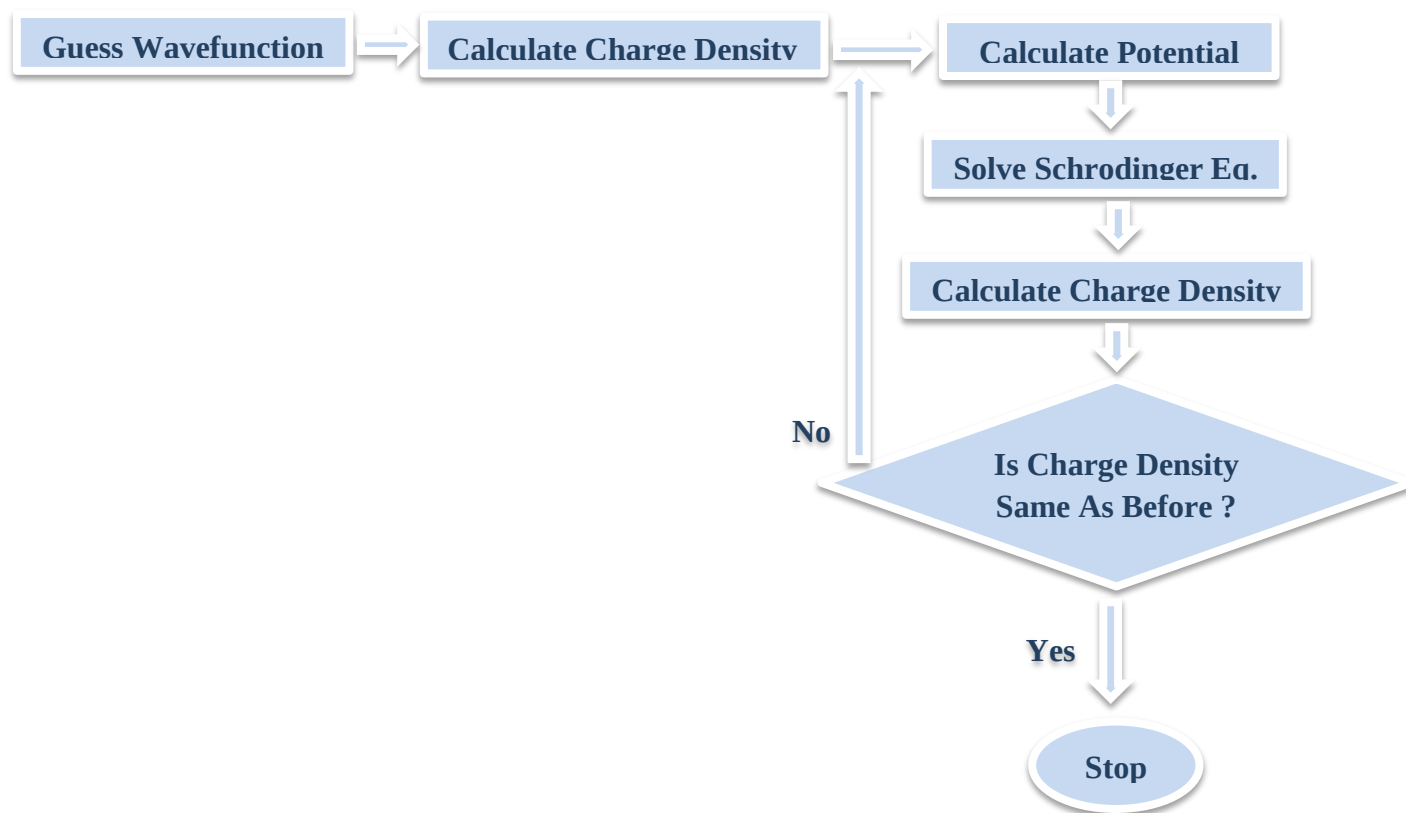


Fig.(2.1): The steps of solution of the density functional theory method flowchart.

### 2.6.2 Roothaan-Hall Equations

Transform the Hartree-Fock equations into the Roothaan equations by introducing a basis set [120-122]. The premise for the Roothaan-Hall (RH) equations is that the molecular orbitals can be expanded as a linear combination of known K one-electron functions:

$$\Psi_i(r) = \sum_j^k C_{ji} \varphi_j(r) \quad \dots(2.30)$$

For each spin orbital i . Hence [123,124]:

$$\hat{f}(r) \sum_j C_{ji} \varphi_j(r) = \epsilon_i \sum_j C_{ji} \varphi_j(r) \quad \dots(2.31)$$

Multiplying Eq.(2.31) by  $\varphi_i^*$  from left and integrating both sides, obtained :

$$\sum_j C_{ji} \int dr \varphi_i^* \hat{f}(r) \varphi_j = \epsilon_i \sum_j C_{ji} \int dr \varphi_i^* \varphi_j \quad \dots(2.32)$$

Where

$$F_{ij} = \int dr \varphi_i^* \hat{f}(r) \varphi_j \quad \dots(3.33)$$

$$S_{ij} = \int dr \varphi_i^* \varphi_j \quad \dots(3.34)$$

The one-electron basis functions  $\varphi_j$  are not necessarily orthogonal and therefore the matrix elements  $S_{ij}$  describe the overlap between two functions, i and j, and form the  $K \times K$  overlap matrix  $S$ . The Fock matrix  $F$ , also  $K \times K$ , is formed from the matrix elements  $F_{ij}$ . Both matrices are Hermitian, for real orbitals, they are real and symmetric [124]. The Hartree Fock-roothaan equation can be written in simple form as matrices:

$$F C = C S \epsilon \quad \dots (2.35)$$

$F$ : Matrix consists of Fock matrix elements  $C_{ji}$ .

$C$ : Matrix  $M \times M$  of the expansion coefficients.

$S$ : Overlap matrix.

$\epsilon$ : Diagonal matrix of the orbital energies  $\epsilon_i$ .

The orbitals  $\Psi_i$  can be found by solving the eigen value equation with corresponding Hartree-Fock operator  $\hat{f}_1$ . This deems the RH equations nonlinear and in order to solve a nonlinear system an iterative approach is used: the SCF procedure since each orbital depends on all the other orbitals [102].

### 2.6.3 Post Hartree-Fock Methods

The HF method was of limited accuracy, especially because it was not able to properly reproduce the correlation between the electrons. Indeed, as mentioned above, the exchange term in the Fock equations vanishes in the case of electrons of different spin [125].

The basic problem that result from HF method solution was that the evaluated energy of the system is larger than the exact value, this result from fact that HF theory has no adequate treatment of electron correlation because it considers that each electron experiences an average field of the other electrons, hence the electrons in Hartree-Fock also over estimated with closed average, so that electron-electron interaction can be predicted. To calculate Correlation Energy ( $E_c$ ) we need to use what are known as post-Hartree Fock methods [126].

These methods can be applied to evaluate not only the electron correlation energy at various post-Hartree-Fock levels, but also the total energy at Hartree-Fock and density functional theory (DFT) levels [127]. Electron correlation energy ( $E_c^{HF}$ ) can be defined as the energy difference between the exact energy ( $E_{exact}$ ) and Hartree-Fock energy ( $E_{HF}$ ) [97,128]:

$$E_c^{HF} = E_{exact} - E_{HF} \quad \dots (2.36)$$

In addition to dynamics of correlation instantaneous electron-electron repulsion, N dynamic or static correlation participates in ( $E_c^{HF}$ ).

Most current post Hartree-Fock methods take Hartree-Fock wave function as a starting point and try to eliminate Hartree-Fock deficiency of correcting the correlation, there are many kinds of post Hartree-Fock methods such as Moller Plesset (MP), Configuration Interaction(CI), Complete Active

Space Self Consistent Field (MCSCF) and correlation-consistent (CC). Usually most post-Hartree Fock calculation are performed for only the valance electrons, when valance electrons are most important [115].

## 2.7 Hohenberg-Kohn Theorems

Density functional theory (DFT) has become a basic tool for the study of electronic structure of matter, and the most widely used many-body approach for electronic structure calculations and has significantly impacted on modern science and engineering, in which the Hohenberg-Kohn (HK) theorem in 1964 plays a fundamental role in the development of DFT [129,130]. The HK theorems constitute a fundamental advance in quantum mechanics. As a consequence, they have furthered our understanding of the electronic structure of matter: atoms, molecules, solids, clusters, surfaces, and lower dimensional electronic systems such as quantum dots and graphene [131]. It has been proved that the ground state of many electron system can be determined by the ground state of electron density  $\rho(r)$  [111,132].

The two theorems of Hohenberg and Kohn are [117]:

Theorem (i) : the ground state energy of many electron system is a unique universal functional of ground state electron density  $\rho(r)$ .

Theorem (ii) : the functional of ground state energy is minimized by the ground state electron density  $\rho(r)$  for a many electron system.

The electron density is the number of electrons  $N$  per unit volume for a given state. A functional is just a function that depends on a function. This is a statement of a variational principle, which referred to the variational theorem

[119]. According to these theories the properties of the ground state of many electron system can be expressed as the electron density of the ground state  $\rho(r)$ . The ground state energy  $E_V$  can be described by the relation [117,122]:

$$E_V[\rho] = \int \rho(r) V_{ext}(\vec{r}) d\vec{r} + F_{HK}[\rho] \quad \dots (2.37)$$

$$\text{or } F_{HK}[\rho] = E_V[\rho] - \int \rho(r) V_{ext}(\vec{r}) d\vec{r} \quad \dots (2.38)$$

$F_{HK}[\rho]$ : A function of  $\rho(r)$  which include the kinetic energy and all electron-electron interactions.

$V_{ext}(\vec{r})$ : The external potential.

The variation in the ground state energy satisfied with the principle [133]:

$$\delta \left\{ E_V[\rho] - K \left[ \int \rho(\vec{r}) d\vec{r} - N \right] \right\} = 0 \quad \dots (2.39)$$

And this gives :

$$K = \frac{\delta E_V[\rho]}{\delta \rho(\vec{r})} = V_{ext}(\vec{r}) + \frac{\delta F_{HK}[\rho]}{\delta \rho(r)} \quad \dots (2.40)$$

K: chemical potential.

One can observe ( $F_{HK}[\rho]$ ) is the universal function independent on ( $V_{ext}(r)$ ). Properties of the ground state of many electron system exactly can be found from the Eqs.(2.39) and (2.40) [122]. Hohenberg theorem has been proposed to deal with the polarized electron state with no spin. Later it has been expanded to imply polarized electron state with spin, finite temperature, and relatively conditions. Hohenberg and Kohn give no concrete expression of the energy functional ( $F_{HK}[\rho]$ ) in which the kinetic energy functional and exchange functional were unknown [94,134].

Hohenberg-Kohn theorems proposed a basic idea that the ground state electron density constructs all the ground state physics for many-electron system. However, these theorems did not give the concrete expression of energy functional ( $F_{HK}[\rho]$ ) in which kinetic functional and exchange-correlation functional were not known. At the same time, one had no idea how to construct the ground state electron density  $\rho(r)$  of many-electron system [88,111].

In 1965, Kohn and Sham derived the Kohn Sham (KS) orbital equations, a set of equations for finding the density in a self-consistent fashion [122].

## 2.8 Kohn-Sham Equations

Kohn-Sham density functional theory (KS-DFT) has become a standard technique for solving electronic structure problems. KS-DFT provides a reasonable compromise between accuracy and efficiency thus enabling the simulation of systems of several hundreds of atoms [135,136]. The modern formulation of DFT originated in the work of Hohenberg and Kohn, on which based the other classic work in this field by Kohn and Sham [129].

According to Hohenberg and Kohn, the energy function ( $F_{HK}[\rho]$ ) for interacting many electron systems can be written as [115,137]:

$$F_{HK}[\rho] = T[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[\rho] \quad \dots (2.41)$$

In which  $T[\rho]$  the kinetic energy of the system, the second term represents the classical Coulomb energy, ( $E_{xc}[\rho]$ ) stands for the exchange-

correlation energy in which describe the non-classical interactions of the electrons, which include all many body effects. The first principle calculations cannot be achieved because expressions of the functionals ( $E_{xc}[\rho]$ ) and ( $T[\rho]$ ) are not concrete. The model is very flexible and widely applicable because the exchange-correlation term can be well adapted to a great variety of problems. This is one of the reasons why the approach was very successful in the last 40 years, and Walter Kohn was awarded the Nobel prize in 1998 for this idea [137].

Kohn and Sham presented an implementation of DFT. The idea is to replace the physical system of interacting electrons with a fictitious system (the KS system) of non-interacting electrons. These two systems have the same ground state electron density. In the KS system, an electron is supposed to move in an effective potential ( $V_{eff}$ ), consists of three terms: (i) The external potential which is usually generated by the attraction between the electron and the nucleus, (ii) The Hartree potential which describes the repulsion between electron and electron, and (iii) The exchange-correlation potential which is caused by certain non-classical Coulomb interactions [138-140]. The basic idea, for non-interact system ( $\rho(\vec{r})$ ) can be expressed as sets of auxiliary additional orthogonal functions  $\Psi_i(\vec{r})$ . One can write [116,141]:

$$\rho(\vec{r}) = \sum_i \Psi_i^*(\vec{r}) \Psi_i(\vec{r}) \quad \dots (2.42)$$

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij} \quad \dots (2.43)$$

The kinetic energy in Kohn-Sham method is given by the equation :

$$T_{ks}[\rho] = -\frac{\hbar^2}{2m} \int \sum_{i=1}^N \Psi_i^*(\vec{r}) \nabla^2 \Psi_i(\vec{r}) d\vec{r} \quad \dots (2.44)$$

With consideration of the interaction between the many bodies, the real kinetic energy ( $T[\rho]$ ) in Eq.(2.41) is not equal to ( $T_{ks}[\rho]$ ), the difference between ( $T[\rho]$ ) and ( $T_{ks}[\rho]$ ) can be gathered with exchange-correlation ( $E_{XC}[\rho]$ ) as follows [142]:

$$E_{XC}[\rho] = E[\rho] - T_{ks}[\rho] \quad \dots (2.45)$$

And the ground state energy functional can be written as [116]:

$$E_V[\rho] = T_{ks}[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{XC}[\rho] + \int d\vec{r} \rho(\vec{r}) V_{ext}(\vec{r}) \quad \dots (2.46)$$

For systems with more electrons, the potential is expanded in a set of functions and the expansion parameters varied such that the potential yields the true density [139]. By applying variation principle to the Eq.(2.46) one can get:

$$\frac{\delta}{\delta \Psi_i^*(\vec{r})} \left\{ E[\rho] - \int d\vec{r} \sum_i \varepsilon_i \Psi_i^*(\vec{r}) \Psi_i(\vec{r}) \right\} = 0 \quad \dots (2.47)$$

$E[\rho]$  : The total energy of the system.

Finally one can get Kohn-Sham equations:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{XC}[\rho] + V_{ext}(\vec{r}) \right\} \Psi_i(\vec{r}) = \varepsilon_i \Psi_i(\vec{r}) \quad \dots (2.48)$$

The exchange potential is defined as the partial derivative of the exchange energy functional with respect to the charge density.

where:

$$V_{xc}[\rho] = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \quad \dots (2.49)$$

( $V_{xc}[\rho]$ ) stands for the exchange-correlation potential, in which it has been modified to contain all the difference between the interacting and non-interacting kinetic energy in Eq.(2.45). One should note that KS equations calculate self-consistently with regard the wave function  $\Psi_i(\vec{r})$  influences by the electron density ( $\rho(\vec{r})$ ) in which includes in the Hamiltonian operator. By solving set of KS Eq.(2.47) of the self-consistently one can get the total energy of the system [133,143]:

$$E = \sum_i^N f_i \varepsilon_i - \frac{1}{2} \iint \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[\rho] - \int d\vec{r} \rho(\vec{r}) V_{ext}(\vec{r}) \quad \dots (2.50)$$

Obviously, the total energy was not equal to sets of singlet electron energies ( $\varepsilon_i$ ). The excitation energy from i state to j state is not ( $\varepsilon_i - \varepsilon_j$ ), thus physics of Kohn-Sham equations is not equal to that of Schrodinger equation. Significance of Kohn-Sham equations is that reduce an interacting many-body system problem into a set of independent equations which describe the state of single electron state in effective potential of other electrons [88]. The major problem in DFT is to find the exchange-correlation energy ( $E_{xc}$ ), which is used as a mathematical term. If the exact exchange-correlation function is known, the system is solved exactly [116]. As previously seen this function results from the Hamiltonian difference between an interacting many electron systems and non-interacting single electron system. This term consists of all effects of exchange and correlation interactions as well as Pauli's exclusion principle between the electrons with the same spin orientation and instantaneous reaction of the electrons with opposite spins [94].

So far, the most successful way to implement DFT is the method proposed by Kohn and Sham. In fact, this method is so widely used that many researchers simply say DFT when they really mean KS-DFT. In 1964, Pierre Hohenberg and Walter Kohn proved that the energy and electronic properties of atoms and molecules are uniquely determined by the electron density  $\rho(\mathbf{r}) \equiv \rho(x; y; z)$ . The work of Hohenberg and Kohn has become the beginning of what is now called density functional theory (DFT), one of the most successful and widely used methods of electronic structure calculations [144].

Machine learning holds the promise of learning the energy functional via examples, bypassing the need to solve the KS equations. This should yield substantial savings in computer time, allowing larger systems. The majority of these applications involve predicting properties of molecules or materials from large databases of KS-DFT calculations. Fewer still have focused on finding the functionals of DFT as a method of performing KS electronic structure calculations without solving the KS equations. The KS-DFT computational electronic structure method determines the properties of many-body systems using functionals of the electron density. While its computational bottleneck is the solution of the KS equations that describe the non-interacting particles [136].

The standard approach for optimizing Hartree Fock and Kohn Sham one-electron density matrices is essentially a two-step iterative procedure. In the first step of each iteration, a new density matrix is generated by a Roothaan Hall diagonalization of the Fock/KS matrix. In the second step, this new density matrix is linearly combined with the previous density matrices to yield an optimal, averaged density matrix for the subsequent iteration [145].

## 2.9 Exchange-Correlation Energy

Exchange-Correlation Energy ( $E_{XC}[\rho]$ ) is defined as the difference between the exact energy and other contributions. The crucial simplification in the density functional is the relationship between the interacting system, whose energy and density we seek, and the fictitious, non-interacting system for which we solve equations. Kohn-Sham exchange functional and correlations functional is given by the equation [146]:

$$E_{XC}[\rho] = T[\rho] + T_s[\rho] + V_{ee}[\rho] - J[\rho] \quad \dots (2.51)$$

Hamiltonian operator is multiplied by the scaling factor ( $\lambda$ ), for ( $\lambda=1$ ) the system of fully interacting electrons can be found, while at ( $\lambda=0$ ) the non-interacting electron system can be found. For Hohenberg-Kohn theory of non-interacting electron system one can have:

$$F_{\lambda=1}[\rho] = F[\rho] = T[\rho] + V_{ee}[\rho] \quad \dots (2.52)$$

$$F_{\lambda=0}[\rho] = T_s[\rho] \quad \dots (2.53)$$

$J[\rho]$ : Nuclei coulomb repulsion.

$F[\rho]$ : The total energy.

$T_s[\rho]$ : Non-interacting total energy.

Hence one can write the Eq.(2.51) with the form:

$$E_{XC}[\rho] = F_{\lambda=1}[\rho] + F_{\lambda=0}[\rho] - J[\rho] \quad \dots (2.54)$$

Then:

$$E_{XC}[\rho] = \int_0^1 d\lambda \frac{\partial F_\lambda[\rho]}{\partial \lambda} - J[\rho] \quad \dots (2.55)$$

By using Hellmann-Feynman Theory [147]:

$$\frac{\partial F_\lambda[\rho]}{\partial \lambda} = \langle \varphi^\lambda | V_{ee} | \varphi^\lambda \rangle \quad \dots (2.56)$$

$\varphi^\lambda$ : Wave function of the Hamiltonian operator.

The Eq.(2.55) can be written as:

$$E_{XC}[\rho] = \int_0^1 d\lambda \langle \varphi^\lambda | V_{ee} | \varphi^\lambda \rangle - J[\rho] \quad \dots (2.57)$$

$$= \frac{1}{2} \iint \frac{1}{r_{12}} \rho(r_1) \bar{\rho}_{XC}(r_1, r_2) dr_1 dr_2 \quad \dots (2.58)$$

The exchange-correlation average ( $\bar{\rho}_{XC}$ ) is defined as the equation [102,146]:

$$\bar{\rho}_{XC}(r_1, r_2) = \rho(r_2) \bar{h}(r_1, r_2) \quad \dots (2.59)$$

$\bar{h}(r_1, r_2)$ : The average of the pair correlation function.

$$\int_0^1 d\lambda P_2^\lambda(r_1, r_2) = \frac{1}{2} \rho(r_1) \rho(r_2) [1 + \bar{h}(r_1, r_2)] \quad \dots (2.60)$$

$P_2^\lambda(r_1, r_2)$ : The diagonal part of the density matrix with two particles.

The exchange-correlation energy only depends on the spherical average ( $\bar{\rho}_{XC}(r_1, r_2)$ ). So the approximations that can give an exact value, even if the description of the non-spherical parts is quite inaccurate [146]:

$$E_{XC}[\rho] = \frac{1}{2} \int dr \rho(r) \int_0^\infty 4\pi s ds \rho_{XC}^{SA}(r, s) \quad \dots (2.61)$$

where:

$$\rho_{XC}^{SA}(r, s) = \frac{1}{4\pi} \int_{\Omega} \rho_{XC}(r, \hat{r}) d\vec{r} \quad \dots(2.62)$$

In the 1930s it was already realized that the HF method it was limited accuracy, especially because it was not able to properly reproduce the correlation between the electrons. The exchange term in the Fock equations vanishes in the case of electrons of different spin [125]. The origin of the name comes from the fact that the HF approximation misses part of the (electron correlation). From KS-DFT, the exchange-correlation functional divides ( $E_{XC}$ ) into the exchange part ( $E_X^{ks}$ ) and the correlation part ( $E_C^{ks}$ ) [148,149]:

$$E_{XC}[\rho] = E_X^{ks}[\rho] + E_C^{ks}[\rho] \quad \dots (2.63)$$

$E_C^{ks}[\rho]$ : Hartree-Fock exchange energy which is calculated from Kohn-Sham determinant  $\varphi_{\rho}$ :

$$E_X^{ks}[\rho] = \langle \varphi_{\rho} | V_{ee} | \varphi_{\rho} \rangle - J[\rho] \quad \dots (2.64)$$

$$E_C^{ks}[\rho] = \langle \Psi_{\rho} | \widehat{V}_{ee} | \Psi_{\rho} \rangle - \langle \varphi_{\rho} | \widehat{V}_{ee} | \varphi_{\rho} \rangle \quad \dots (2.65)$$

$\Psi_{\rho}$ : The exact interacting wave function.

The correlation energy is defined as the difference between the total exact energy and the sum of kinetic and exchange energies. Correlations are a result of the collective behavior of electrons to screen and decrease the Coulomb interaction. The quality of a DFT calculation is determined by how close the approximate exchange and correlation comes to the exact value [119].

## 2.10 Exchange-Correlation Functionals

### 2.10.1 Local Density Approximation (LDA)

The exchange-correlation functional is the key object in the understanding and application of density functional theory (DFT). The simple local density approximation provided the basis for much of the work on the electronic structure of solids in the 1950's and early 1960's. The calculation of electronic band structures and related quantities is, one of the success stories of modern condensed matter physics. The experience obtained in solving Schrodinger-like equations with local effective potentials and the improvement in numerical methods and computers have been decisive in carrying out density functional calculations in recent years [146].

LDA approximation includes functionals derived by analytical theory of a homogeneous electron gas, and applied to non-homogeneous densities. The approximation takes the formula [150,151]:

$$E_{XC}[\rho] = \int \rho(r) \varepsilon_{XC}[\rho(r)] dr \quad \dots (2.66)$$

Where  $\varepsilon_{XC}$  is the known exchange-correlation energy per electron in homogeneous electron gas with the density  $\rho$ . Exact dependence of  $E_{XC}[\rho]$  on  $(\rho)$  is a functional dependence. This means that in general the energy per particle in a point does not depend only on the value of the density in that point. Instead, it depends on the value of the density in all points (i.e. it is non-local). The LDA eliminates this problem with a very simple assumption that makes also the calculation cheaper. In fact, to calculate the energy one needs to know the density only in a given point and not all over space [152].

The potential  $V_{xc}(r)$  is defined as the exchange potential for the spatially uniform electron gas with the same density, can be written as follows [150,153]:

$$V_{xc}(r) = \varepsilon_{xc}(r) + \rho(r) \frac{\delta \varepsilon_{xc}[\rho]}{\delta \rho(r)} \quad \dots (2.67)$$

LDA has energy density with local density value of the homogeneous electron gas at each point in the space and this very successful to obtain ground state properties of many systems [154]. The exchange-correlation energy density ( $\varepsilon_{xc}$ ) can be written as [155]:

$$\varepsilon_{xc}(r) = \varepsilon_x(r) + \varepsilon_c(r) \quad \dots (2.68)$$

Hartree-Fock exchange of homogeneous electron gas is [146,151]:

$$\varepsilon_{xc}[\rho] = -\frac{4}{3} \left( \frac{3}{\pi} \rho \right)^{\frac{1}{3}} \quad \dots (2.69)$$

The exchange energy of homogeneous electron gas is:

$$\varepsilon_c = \frac{\gamma_c}{1 + \beta_1 + \sqrt{r_s} + \beta_2 r_s} \quad r_s > 1 \quad \dots (2.70)$$

$$\varepsilon_c = A \ln r_s + B + C r_s \ln r_s + D r_s \quad r_s < 1 \quad \dots (2.71)$$

The constants  $\gamma_c$ ,  $\beta_1$ ,  $\beta_2$ ,  $A$ ,  $B$ ,  $C$  and  $D$  have known values.

$$r_s = \left[ \frac{3}{4\pi\rho} \right]^{\frac{1}{3}} \quad \dots (2.72)$$

In LDA, the exchange correlation energy has the formula [156]:

$$\rho_{xc}^{LDA}(r_1, r_2) = (\rho(r_1) \bar{h}_0(|r_1 - r_2|), r_1) \quad \dots (2.73)$$

$(\bar{h}_0(|r_1 - r_2|), \rho(r_1))$ : the average pair correlation function of homogeneous electron gas.

The LDA exchange-correlation density is:

$$\varepsilon_{xc}(\rho(r_1)) = \frac{1}{2} \int \frac{1}{r_{12}} \rho_{xc}^{LDA}(r_1, r_2) dr_2 \quad \dots (2.74)$$

For getting approved clear results it can use an empirical function of type:

$$E_{xc} = \int F_{xc} [\rho, \nabla \rho] dr \quad \dots (2.75)$$

The potential ( $V_{xc}(r)$ ) is given by:

$$V_{xc}(r) = \frac{\partial F_{xc}}{\partial \rho(r)} = \sum_{\alpha=1}^3 \frac{\partial}{\partial r_x} \left[ \frac{\partial F_x}{\partial (\nabla \alpha_\rho)} \right] \quad \dots (2.76)$$

LDA is less suitable for prediction of the properties of atoms and molecules, since the density is not slowly varying in case of atoms and molecules [153].

### 2.10.2 Generalized Gradient Approximation (GGA)

The Local Density Approximation (LDA) is only a functional of the interacting charge densities. The Generalized Gradient Approximations (GGA) are functionals of the interacting charge densities and the gradient of the charge densities [157]. The electron density of real molecule frequently changes from position to another. To getting more accurate approximation of exchange correlation energy, the functionals include not only electron density but also contain gradient electron density [151,153].

Hence, one can have:

$$E_{XC}^{GGA}[\rho_\alpha, \rho_\beta] = \int f(\rho_\alpha, \rho_\beta, \nabla \rho_\alpha, \nabla \rho_\beta) \overrightarrow{dr} \quad \dots (2.77)$$

$\alpha$  : up spin.

$\beta$  : down spin.

In general, these functionals show improvement over Local Spin Density Approximation (LSDA) because it takes the density variation with positions into account. For simplifying the problem,  $(E_{XC})$  often can be written as a sum of exchange term  $(E_X)$  and correlation term  $(E_C)$  as follows [111]:

$$E_{XC} = E_X + E_C \quad \dots (2.78)$$

The exchange energy functional can be found from Hartree-Fock exchange term with Kohn-Sham orbitals instead of Hartree-Fock orbitals, and an approximated solution for  $(E_C)$  can be sought. The various exchange correlation functionals have been developed independently and can be combined in different ways. One of the popular GGA functionals is BLYP in which Becke in 1988 pair between exchange energy functional and Lee-Yang-Parr functional [88].

### 2.10.3 Local Spin Density Approximation (LSDA)

LDA is the simplest approximation of  $(E_{XC}[\rho])$ , in which supposes the system is a homogeneous electron gas, and  $(E_{XC}[\rho])$  depends on the local value of the electron density. Therefore,  $E_{XC}[\rho]$  can be written as the formula [112,158]:

$$E_{XC}^{LDA}[\rho] = \int \rho(r) \varepsilon_{XC}[\rho] d\vec{r} \quad \dots (2.79)$$

As compared with LDA, LSDA gives a definition to exchange correlation potential in terms of the density of up spin ( $\alpha$ ) and down spin ( $\beta$ ) to improve calculations of open-shell system properties. Hence some can have [115,149]:

$$E_{XC}^{LSDA}[\rho_\alpha, \rho_\beta] = \int \rho(\vec{r}) \varepsilon_{XC}[\rho_\alpha, \rho_\beta] d\vec{r} \quad \dots (2.80)$$

$\varepsilon_{XC}$ : the exchange correlation energy per particle.

Local spin density approximation supplied with better results than Hartree-Fock, for certain properties such as the equilibrium structure, vibrational frequencies and dipole moments. However it cannot calculate the values of energy with high accuracy as desired many computational chemists. Generally, Local Spin Density Approximation (LSDA) supplies with real informations for those systems in which is closely resemble a homogeneous electron gas. In which the density changes slowly with position. However, actually the atomic and molecular systems have no homogeneous electron densities, and this requires models more sophisticated [88,132], but LSDA remains the most popular way to do electronic-structure calculations in solid state physics [149].

## 2.11 Functionals

The exchange correlation part of energy function remains unknown and must be approximated. This term treaded with an approximated method. Despite there are many different available functionals, nearly all are derived

from electron density of homogeneous electron gas. It can be calculated by statistical thermodynamic. There are many approximations such as local density approximation (LDA), generalized gradient approximation (GGA), Becke exchange functional (BEF), Lee-Yang-Parr correlation (LYP) and the hybrid functional (B3LYP) [159].

### 2.11.1 Becke Exchange Functions (BEF<sub>s</sub>)

Becke exchange functions are given by [160]:

$$E_{xc} = E_x^{LDA}[\rho] - \int F_x[s] \rho^{\frac{4}{3}} dr \quad \dots (2.81)$$

$$s = \frac{|\nabla\rho|}{\rho^{\frac{4}{3}}} \quad \dots (2.82)$$

s: The gradient measure variable.

$$F_x[s] = 2^{-\frac{1}{3}} \beta \frac{s^2}{1 + 6\beta \sinh^{-1}(s)} \quad \dots (2.83)$$

Using Hartree-Fock exchange energy for noble gas atom one can get optimization of  $\beta$ .

### 2.11.2 Lee-Yang-Parr Correlation (LYP)

The basic postulate for Lee-Yang-Parr is established on approximation formula for correlation energy of Helium atom [161]:

$$\rho(r_1, r_2) = C \rho_2^{HF}(r_1, r_2) \quad \dots (2.84)$$

When replacing  $(\rho_2^{HF})$  by  $(\rho_1)$  and using the integration one can have:

$$E_C^{LYP} = \int \rho \left[ \frac{-a}{1+dX} (1 + bC_F e^{-CX}) \right] + \int ab |\nabla \rho|^2 X^5 \frac{e^{-CX}}{1+dX} \frac{1}{24} \left[ 1 + \frac{7}{3} \left( CX + \frac{dX}{1+dX} \right) \right] dr \quad \dots (2.85)$$

$$X = \rho^{-\frac{1}{3}} \quad \dots (2.86)$$

All constants are known.

### 2.11.3 Hybrid Functional

It is a kind of approximations of the exchange-correlation energy functionals in DFT theory, which incorporates a part of exact exchange from Hartree-Fock theory with exchange-correlation from other sources (ab-initio and semi-empirical). The exact exchange energy functionals can be expressed in terms of Kohn-Sham orbitals more than the density so, it is termed an implicit density functional. The hybrid exchange-correlation functional is generally constructed as a linear combination of the exact exchange functionals of Hartree-Fock ( $E_X^{HF}$ ) and a number of the explicit density functionals of exchange-correlation. The parameters, which determine the weight of each individual functional, are naturally specified by fitting the functionals predictions to experimental or accurately calculate thermochemical data. For example, the famous popular exchange-correlation functional (B3LYP) [145]:

$$E_{XC}^{B3LYP} = E_{XC}^{LDA} + a_0(E_X^{HF} - E_X^{LDA}) + a_X(E_X^{GGA} - E_X^{LDA}) + a_C(E_C^{GGA} - E_C^{LDA}) \quad \dots (2.87)$$

$a_C, a_X$  and  $a_0$  are three empirical parameters and the best values of these parameters are  $a_C = 0.81$ ,  $a_X = 0.72$ ,  $a_0 = 0.20$ . This way was introduced by Axel Becke in 1993 to describe correlation exchange energies. This way is called hybrid because of using corrections for both gradient and correlations-exchanges [162].

## 2.12 Basis Sets

Theoretically, the basis set may be comprised of an infinite number of functions. In practice, due to the limited capacity of computer systems, the basis sets of atomic or molecular systems must be truncated, having finite sizes. Conversely, very large basis sets are not always more appropriate for molecular calculations and sometimes balanced small sets could be more appropriated for this task [163].

In general the basis set is a collection of vectors which spans a space in which a problem is solved. The basis set in theoretical and computational chemistry is a set of functions which called basis functions. It is functionals in which used to describe the shape of orbitals in atoms [112]. In quantum chemistry the basis set usually refers to the sets of non-orthogonal one particle functions which is used to build molecular orbitals, in which the molecular orbitals result from linear combination of atomic orbitals [102]. These functions are typically atomic orbitals centered on atoms. The atomic orbital has one electron function. Choosing a model of a chemical system, almost always involves a trade-off between accuracy and computational cost. More accurate methods and larger basis sets make jobs run longer. Larger basis sets give a better approximation to the atomic orbitals as they place fewer restrictions on the wavefunction. Larger basis sets attract a higher

computational cost. Standard basis sets are carefully designed to give the best description for the lowest cost [148]. The choice must take accuracy of results and CPU time into account. Molecular orbitals and entire wave functions are created by linear combination of the basis functions and angular functions. Most semi-empirical methods use predefined basis sets. The widespread availability of programs for electronic structure and the advances in the technology of computers have improved the theoretical calculations which support the experimental research. Ab-initio electronic structure methods are used to explain molecular properties. But ab-initio and DFT calculations require specified basis sets, i.e. in ab-initio and DFT methods the basis set should specify. Most calculations are done by using the existing basis sets [148,164].

### **2.12.1 Minimal Basis Sets**

It is a small number of basis functions which need to describe the ground state of the component atoms (represent all the electrons of each atom). In the molecule the common name of the minimal basis sets Slater Type Orbital n Gaussian (STO-nG), in which ( $n=2,\dots,6$ ) which represent number of Gaussian primitive functions which include compos of single basis functions [112]. The following some examples of minimal basis sets: Slater Type Orbital Two Gaussian (STO-2G), Slater Type Orbital Three Gaussian STO-3G, Slater Type Orbital Six Gaussian STO-6G [142].

### **2.12.2 Split Valence Basis Sets**

One way to increase the size of the basis set is to take more basis functions per atom. In this basis sets the atomic orbitals of the inner shell are represented by one basis function, valence orbitals are represented by two or

more basis sets (Pople basis sets), which is one of the simple ways of extended basis sets to increase the number of basis functions which are used per orbital. Split basis sets employ more than one basis function for each valence orbital and only one basis function for each core orbital [112]. For example, valence double Zeta (VDZ) which employs two basis functions for valence orbital, second example valence triple Zeta (VTZ) which uses three. Another example, 3-21G means three Gaussian type orbitals for inner shell, two Gaussian type orbitals for inner valence and one Gaussian Type Orbital (GTO) for outer valence. Hence, split valence basis sets supply with better description of the molecular orbitals [162].

### 2.12.3 Polarization Functions

Split valence basis sets could be improved by adding orbitals with different shapes. The polarization functions is denoted by asterisk (\*) and two asterisk (\*\*) which add to light atoms (Hydrogen and Helium). The polarization is also denoted by the symbols (p, d, f). The symbol p means p-function can be added to the basis set with p-type orbital, The symbol d means d-function can be added to the basis set with d-type orbital. These basis sets have been developed by Pople [94].

### 2.12.4 Diffuse Functions

It is denoted in Pople-type sets by a plus sign (+) and two plus sign (++) which are also added to the light atoms (Hydrogen and Helium). These are very shallow Gaussian basis functions which is more accurate representation for the tail portion of the atomic orbitals, which are distant from atomic nuclei. These additional basis functions may be also important in other soft molecular

systems. Basis sets with diffuse functions are important for systems where electrons may be far from the nucleus [162].

## 2.13 Types of Orbitals

### 2.13.1 Slater Type Orbitals (STO's)

The first intuition in the choice of a mathematical function for performing an atomic calculation is to use similar functions to those of a hydrogen atomic orbital. This is the reason Zener and Slater proposed in 1930 [165]. Slater-type orbitals are defined in spherical coordinates as [111,166]:

$$\chi^{\text{STO}} = N r^{n-1} e^{-\xi r} Y_{lm}(\theta, \varphi) \quad \dots (2.88)$$

where :

$\chi^{\text{STO}}$ : Total wavefunction.

N : Normalization constant.

n: Principle quantum number.

$\xi$ : Constant associated with effective charge of nuclei, i.e. the nuclear charge is partly shielded by electrons.

$Y_{lm}(\theta, \varphi)$ : Spherical harmonic in which describes the angular part of the wave function.

$Y_{lm}(\theta, \varphi)$  can be given by the equation [102]:

$$Y_{lm}(\theta, \varphi) = \sqrt{\frac{2l+1}{4\pi}} (\sin \theta)^m e^{im\varphi} \sum_{j=0}^{l-m} C_{lmj} (\cos \theta)^{l-m-2j} \quad \dots (2.89)$$

l: Orbital quantum number.

m: Magnetic quantum number.

$$C_{lmj} = \frac{\sqrt{2l+1}}{(l-m)!} \frac{(2(l-j))! (-1)^j}{(l-m)! 2^j j! (l-m-2j)!} \quad \dots (2.90)$$

$C_{lmj}$ : Normalization constant.

In general, these functions are named Slater type orbitals (STO) or Slater type functions (STF). It is well-known the excellent behavior shown by the STO functions in the near and far regions of the atomic nucleus. This fact allows the STO basis sets to reproduce correctly the regions near the nucleus without increasing the angular quantum numbers. On the other hand, they decay properly in the long  $r$  distances, in a similar way to that of the atomic orbitals in the regions far away from the nucleus [166].

### 2.13.2 Gaussian Type Orbitals (GTO's)

Unfortunately such functions (STF<sub>s</sub>) are not suitable for fast calculations of multicenter integrals, so Gaussian-type functions (GTFs) were introduced to remedy the difficulties Transforming from a local polar coordinate system to a Cartesian one [165]. Gaussian type orbitals can be written in terms of Cartesian coordinates [166]:

$$\chi^{GTO} = N x^{lx} y^{ly} z^{lz} e^{-\xi r^2} \quad \dots (2.91)$$

N: Normalization factor in which ensures that  $\langle \chi_\mu | \chi_\mu \rangle = 1$ .

$\xi$ : The exponent orbital shows how compacts (large  $\xi$ ) or diffuses (small  $\xi$ ) for the resulting function.

Sum of  $l_x, l_y, l_z$  determine the type of orbital, for example  $l_x + l_y + l_z = 1$  is a p-orbital. The sum of exponents of Cartesian coordinates ( $L = l + m + n$ ) is used analogously to the angular momentum quantum number for atoms to mark Gaussian primitives as s-type ( $L=0$ ), p-type ( $L=1$ ), d-type ( $L=2$ ), f-type ( $L=3$ ) etc. [167]

$r^2$  dependence in the exponential is deficiency of GTO's with respect to STO's orbitals. GTOs have two main problems. First an improper behavior nears the nuclei at  $r \rightarrow 0$ , second problem is that GTO falls off too rapidly far from the nuclei compared with the STO. Therefore, the tail of the wave function in GTO's stands for poorly [112]. One should estimate three times in GTO's to get the same accuracy of STO's. One of disadvantages of STO's is many-center integrals, such as Coulomb and Hartree-Fock-exchange is difficult in STO's calculations. Also it does not play advantage role in modern wave function which is established on codes of quantum chemistry [102].

Cartesian GTOs are used in molecular calculations because the multicenter integrals are easily evaluated due to the Gaussian theorem that allows to express the product of two Gaussian functions centered in two different points of the space as another Gaussian function centered in a third point located on the line that joins the two initial points. For Coulomb and Hartree-Fock exchange terms, the analytical solution is available for Gaussian functions. Hence, GTO's basis functions in Hartree-Fock and the related methods are popular because of the high efficiency of the algorithms of analytical calculations of many-center integrals. The combination of DFT methods with GTO is very popular in calculations of molecular systems. There are also several periodic DFT programs described in the literature that employ GTO basis sets [168].

Naturally one should use contracted GTO basis functions, in which several primitive Gaussian functions are mixed to give a contract Gaussian functions (CGF), hence one can have [162]:

$$\chi_l^{\text{CGF}} = \sum_i^M C_{ij} \chi_a^{\text{GTO}} \quad \dots (2.92)$$

$\chi_l^{\text{CGF}}$ : Sum of Gaussian orbital wavefunction.

M: The number of Gaussian primitive functions which is used in linear combination.

The coefficients  $C_{ij}$  are varied in order to minimize the energy and are known as molecular orbital expansion coefficients. It is generally assumed by chemists that molecules can be viewed as a collection of slightly distorted atoms. That is, the energy required to completely ionize a molecule is only slightly different from the energy required to completely ionize the constituent atoms, and the molecular charge density only differs little from the sum of the atomic densities. Hence it is natural to require that the primitive basis set provide an accurate description of the atoms [166]. The following figure shows the difference between Slater and Gaussian functions.

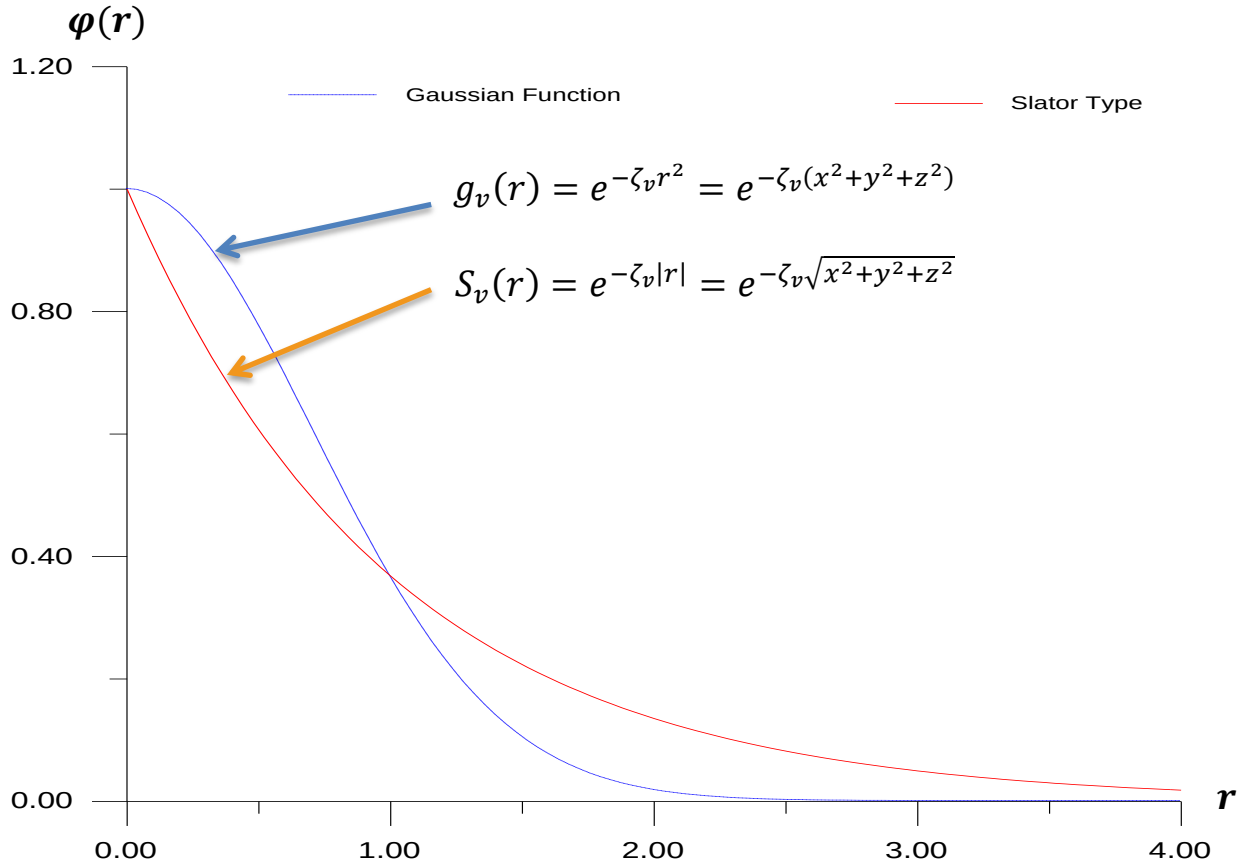


Fig.(2.2): Comparison between Slater functions and Gaussian functions [162].

## 2.14 Density Functional Theory (DFT)

DFT is a quantum mechanical theory used in Solid-State Physics, Chemistry, Biochemistry, Geology and Astrophysics to investigate the electronic structure more than 25 years. This has led to its enormous popularity and widespread success, in describing structural and electronic properties in a vast class of materials, ranging from atoms and molecules to simple crystals to complex extended systems (including glasses and liquids) [136].

This method differs from the HF method and its decedents by replacing the many-body electronic wave function, which depends on  $4N$  coordinates ( $3N$  spatial coordinates and the  $1N$  spin coordinate), with the electronic density, which depends only on the three Cartesian coordinates  $x$ ,  $y$ , and  $z$ , (For  $N$  electrons in a solid, which obey the Pauli principle and repulse each other via the Coulomb potential) assuming fixed nuclear positions. For any system has  $N$  electrons, the wave function approximation becomes more complicated when the number of electrons in the system increases. With DFT the properties of many electron system can be expressed by using functionals, i.e. functions of another function which in this case is the spatially dependent electron density [156].

DFT is a ground-state theory in which the emphasis is on the charge density as the relevant physical quantity. Excited states can be predicted, but these predictions are not on the same footing as predictions for ground-state energies [119]. It is intractable to solve the Schrodinger equation directly even using the modern advanced supercomputers except for few systems. Instead of using wavefunctions in high dimensions, DFT applies the particle density in three dimensions to model the system. The Kohn-Sham approach introduces orbitals back into DFT in order to calculate exactly the non-interacting kinetic energy. Minimizing the energy produces a set of equations known as the Kohn-Sham equations, We understand that the theoretical basis of DFT is the Hohenberg-Kohn theorem [130].

The theory is simple and the implementations efficient compared with other methods. A useful balance between accuracy and computational cost. This allowed much larger systems to be treated than by traditional ab-initio methods, while retaining much of their accuracy [169]. Thomas and Fermi in 1927 develop approximation based on statistical distribution of the electrons

in molecular systems. The energy has been assumed as a function of electron, and it is given by the kinetic energy of a homogeneous electron gas [170]. DFT has been introduced in two seminal papers in the 1960's by Hohenberg-Kohn in 1964, and Kohn-Sham in 1965 [171].

Despite the recent improvements in density functional theory Control Processing Unit (CPU) time is drastically reduced, the reason is that DFT scales with the same order as HF theory. The multiple determinant calculations require very large basis sets, whereas DFT can produce accurate results with relatively small basis sets. This is due to the poor convergence of the correlation energy when the inter-electronic distance becomes very small. Recently DFT methods is carried out in most commercial ab-initio program package. In most cases, the results of DFT for solid state systems agree quite satisfactorily with experimental data [170].

The electron density that minimizes the energy of the above functional is the true electron density corresponding to the full solution to the Schrodinger equation. Guess the functional form and vary the electron density iteratively until the energy is minimized [119]. So DFT has conquered the rational minds of the quantum chemists and computational chemists, but has it also won their hearts? To many, the success of DFT appeared somewhat miraculous, and maybe even unjust and unjustified. Unjust in view of the easy achievement of accuracy that was so hard to come by in the wave function based methods. And unjustified it appeared to those who doubted the soundness of the theoretical foundations [165].

## 2.15 Time-Dependent Density Functional Theory (TD-DFT)

The (non-relativistic) time-dependent Schrodinger equation for the many-electron wavefunction  $\Psi(t)$  [172]:

$$H(t) \Psi(t) = i \frac{\partial \Psi(t)}{\partial t} \quad \dots(2.93)$$

$$H(t) = \hat{T} + \widehat{V}_{ee} + \widehat{V}_{ext}(t) \quad \dots(2.94)$$

For a given initial wavefunction  $\Psi(0)$ . Here, the kinetic energy and electron-electron repulsion, are, respectively :

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2, \text{ and } \widehat{V}_{ee} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|r_i - r_j|} \quad \dots(2.95)$$

and the “external potential” represents the potential that electrons experience due to the nuclear attraction and due to any field applied to the system :

$$\widehat{V}_{ext}(t) = \sum_{i=1}^N V_{ext}(r_i, t) \quad \dots(2.96)$$

$V_{ext}(r_i, t)$  can represent the Coulomb interaction of the electrons with a set of nuclei, possibly moving along some classical path,

$$V_{ext}(t) = -\sum_{v=1}^{N_n} \frac{Z_v}{|r - R_v(t)|} \quad \dots(2.97)$$

Where  $Z_v$  and  $R_v(t)$  denote the charge and position of the nucleus  $v$ , and  $N_n$  stands for the total number of nuclei in the system. This may be useful to study, e.g., scattering experiments, chemical reactions, etc.

What has made TD-DFT so incredibly successful is the Kohn–Sham (KS) system: the density of the interacting many-electron system is obtained as the density of an auxiliary system of non-interacting fermions, living in a one-body potential [173].

As early as 1933, Bloch proposed a time-dependent Thomas-Fermi model. Ando, Peuckert, Zangwill and Soven ran the first time-dependent KS calculations, assuming a TD-KS theorem exists. They treated the linear density response to a time-dependent external potential as the response of non-interacting electrons to an effective time-dependent potential. Ando calculated resonance energy and absorption line shapes for inter subband transitions on the surface of silicon, while Peuckert, Zangwill, and Soven studied rare-gas atoms [174]. In analogy to ground-state KS theory, this effective potential was assumed to contain an exchange-correlation part,  $V_{xc}(r, t)$ , in addition to the time-dependent external and Hartree terms. Peuckert suggested an iterative scheme for the calculation of  $V_{xc}$  [175].

TD-DFT is being used today in an ever-increasing range of applications to widely-varying systems in chemistry, biology, solid-state physics, and materials science. The vast majority of TD-DFT calculations today lie in spectroscopy, yielding response and excitations of atoms, molecules, and solids [176].

## 2.16 Gaussian Program

Gaussian program is used in quantum chemistry, quantum physics and solid state physics. Commercially available through (Gaussian Inc.). The program runs by assuming form all computational procedures in Microsoft windows, adding to enter through the web. Gaussian is the more effective program which is available to the learners and students researchers through North Carolina institute for computational chemistry services. Gaussian09 can be indicated by the symbol G09, in which refers to the year 2009. Gaussian carries out many calculations of ab-initio, semi-empirical and DFT methods.

Also Gaussian implement many calculations with complicated ways such as  $MP_x$ , in which x denotes to the way level. For example,  $MP_2$  and  $MP_4$ . The name Gaussian came from using Gaussian type orbitals. Originally John Pople has used an attempt to overcome the computational difficulties which emerges from using Slater orbitals [177].

All quantities used in calculations inside Gaussian are in atomic units to simplify mathematical equations by setting many fundamental constants equal to 1. A Hartree is a unit of energy used in computational chemistry, and is easily converted to other, more familiar units (Hartree a.u. = 27.211 eV) [147].

## 2.17 Gauss View Program

Gauss view program has been designed to import the input files from Gaussian program. Also it is used to show output files from Gaussian program with image dimensions. Gauss view does not employ in calculations but it simplifies the work in Gaussian program and supplies the users with three essential benefits: The first, it makes the user to draw the molecules, also it enables to rotation, transformation and change the size through the mouse. The second, it allows to investigate many Gaussian calculations, it deals with the complication in input setting for routine work by a progressive ways. The third, it permits to inspect of Gaussian calculations results by using different geometrical technique and this bind with equilibrium of molecular model, molecular orbital and electronic density surface [132].

# *Chapter Three*

*Results*

*and*

*Discussion*

## Chapter Three

### Results and Discussion

#### 3.1 Nanosensors

In this part of discussion we focus on the important properties of the organic molecule sensors that limit the efficiency of this device as sensors for explosive material (TNT and NQ).

##### 3.1.1 The Pristine Coronene

The pristine Coronene is shown in Fig.(3.1) with two side view, HOMO, LUMO, the density of states (DOS) and IR spectrum. The DFT (with B3LYP method /6-31G basis set) gives the energy gap (  $E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$  ) and the total energy ( $E_{\text{total}}$ ), these parameters is the reference to get the pivotal factor (FH) that we created as the indicator for successful of the new sensor and the stability of improved sensor. When the Coronene improve by suitable substitution atom where :

$$FH = \{ E_g (\text{sensor}) - E_g (\text{sensor/molecule}) \} / E_g (\text{sensor}) \quad \dots(3.1)$$

So when it is increases this indicate to the better improved sensor. Total energy ( $E_{\text{total}}$ ) values calculated of coronene-doped are much higher compared to those of pristine coronene. When the total energy increase, this parameter would be of great importance of estimation of stability the structures. Fig.(3.1 c,d) shows the HOMO and LUMO respectively without any molecules adsorption as well as e and d shows the DOS and IR spectrum respectively the distance between green and red lines gives the  $E_g$  , the peaks in IR spectrum reveals the C—C , C=C and C—H (bonds).

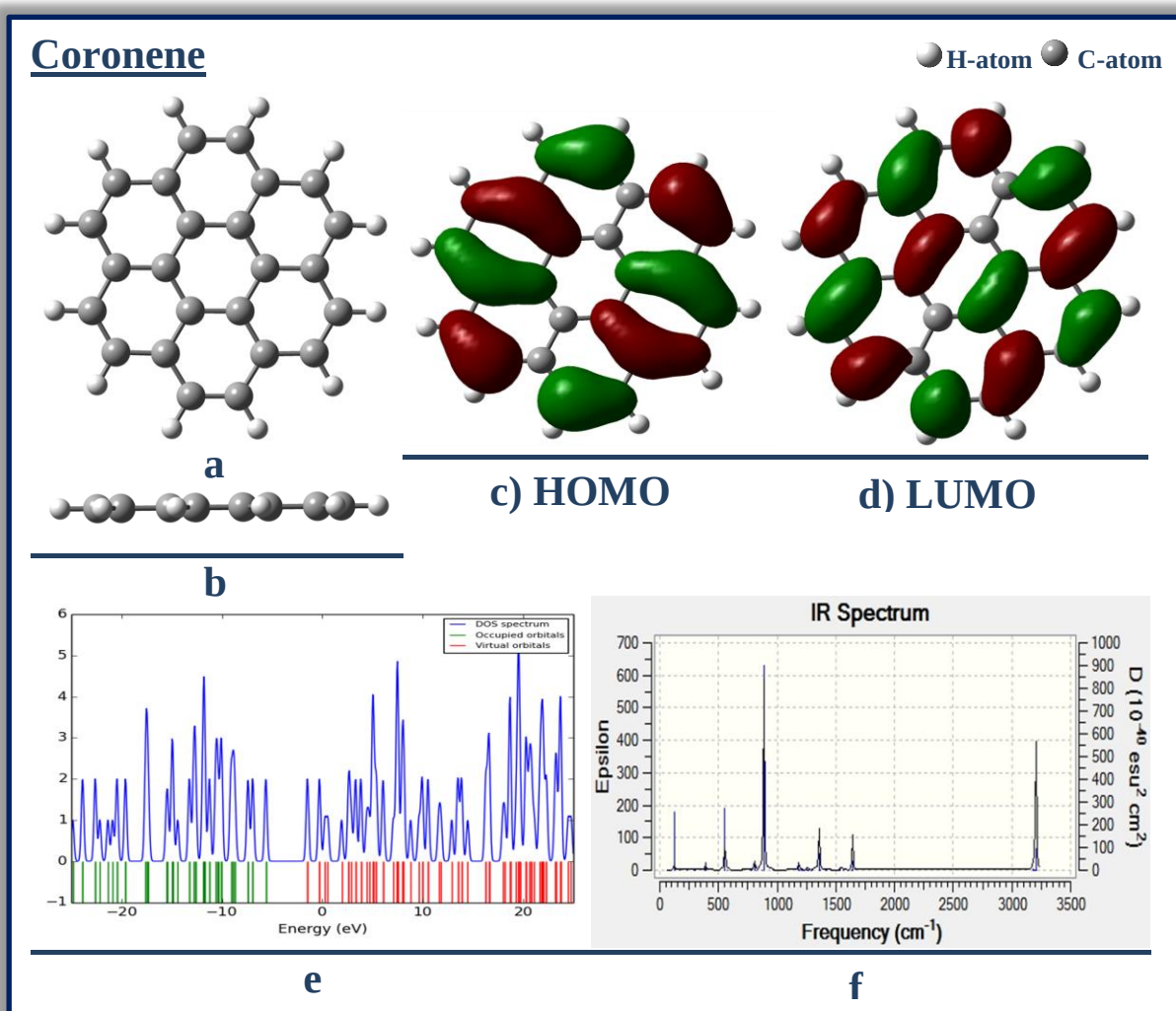


Fig.(3.1): (a,b) Geometrical optimization of sensor top view and side view respectively, c) HOMO distribution, d) LUMO distribution, e) DOS and f) IR spectrum.

Fig.(3.2) shows the distance between Coronene and the nearest neighbor atom ( $3.301 \text{ \AA}$ ) of the TNT molecules. The LUMO reveals that the TNT represent as acceptor and this is clear from the spatial charge distribution, the FH factor equal to (0.320) with the adsorption energy ( $E_{ad} = -0.370 \text{ eV}$ ) indicates the good response, where :

$$E_{ad} = E_{total} (molecule/sensor) - E_{total} (sensor) - E_{total} (molecule) \quad \dots(3.2)$$

Fig.(3.2 d) shows the decrease of the  $E_g$  when comparison with Fig.(3.1 e), on the other hand the new peaks that appear in Fig.(3.2 e) gives the N—O ,

N—C and O—H (bonds). This interpretation of IR spectrum and DOS applies on the all structures under study. All bond resonances have very good agreement with the experimental data of the chemical library of IR spectrum tables. The height of the density of states in both HOMO and LUMO are the same approximately and so this refers to the possibility of the electronic transition between them. So one expect that the electronic transition may occurs between many states in HOMO and LUMO but with different probability as we can see in the next discussion.

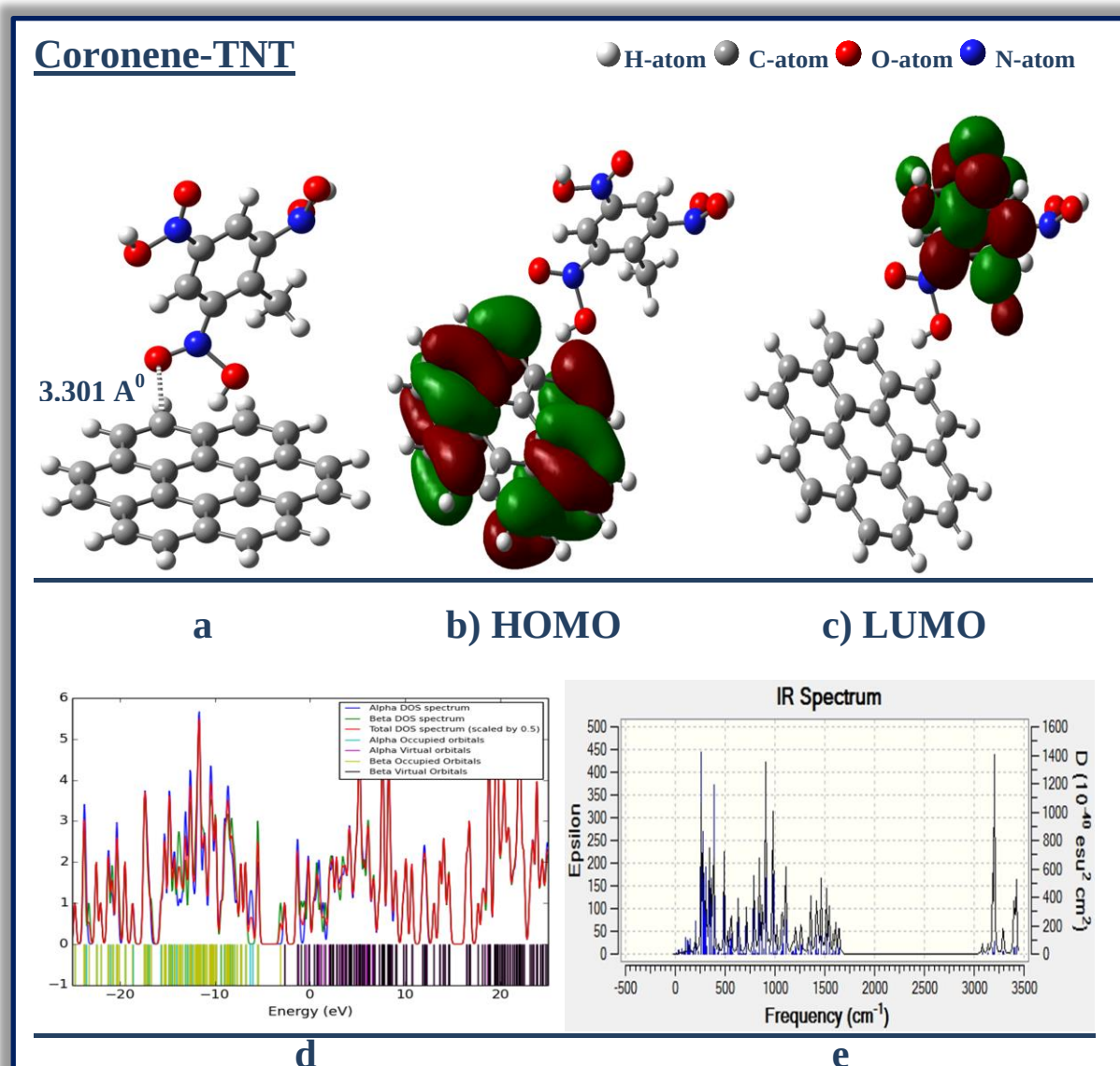


Fig.(3.2): a) Geometrical optimization of sonser-TNT , b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum.

The results indicate that the pristine Coronene is a good (sensor - TNT) contrary to the pristine Coronene has non-substantial impact for sensing NQ that is to say, due to the magnitude of the FH = 0.039 with ( $E_{ad} = -1.370$  eV), this small FH as a reason to the small NQ molecules that stay  $E_g$  with no change and the NQ in this situation does not represent an acceptor as the LUMO distribution shows. The distance between the nearest neighbor atom of the NQ molecules and the sensor is ( $3.166 \text{ \AA}$ ).

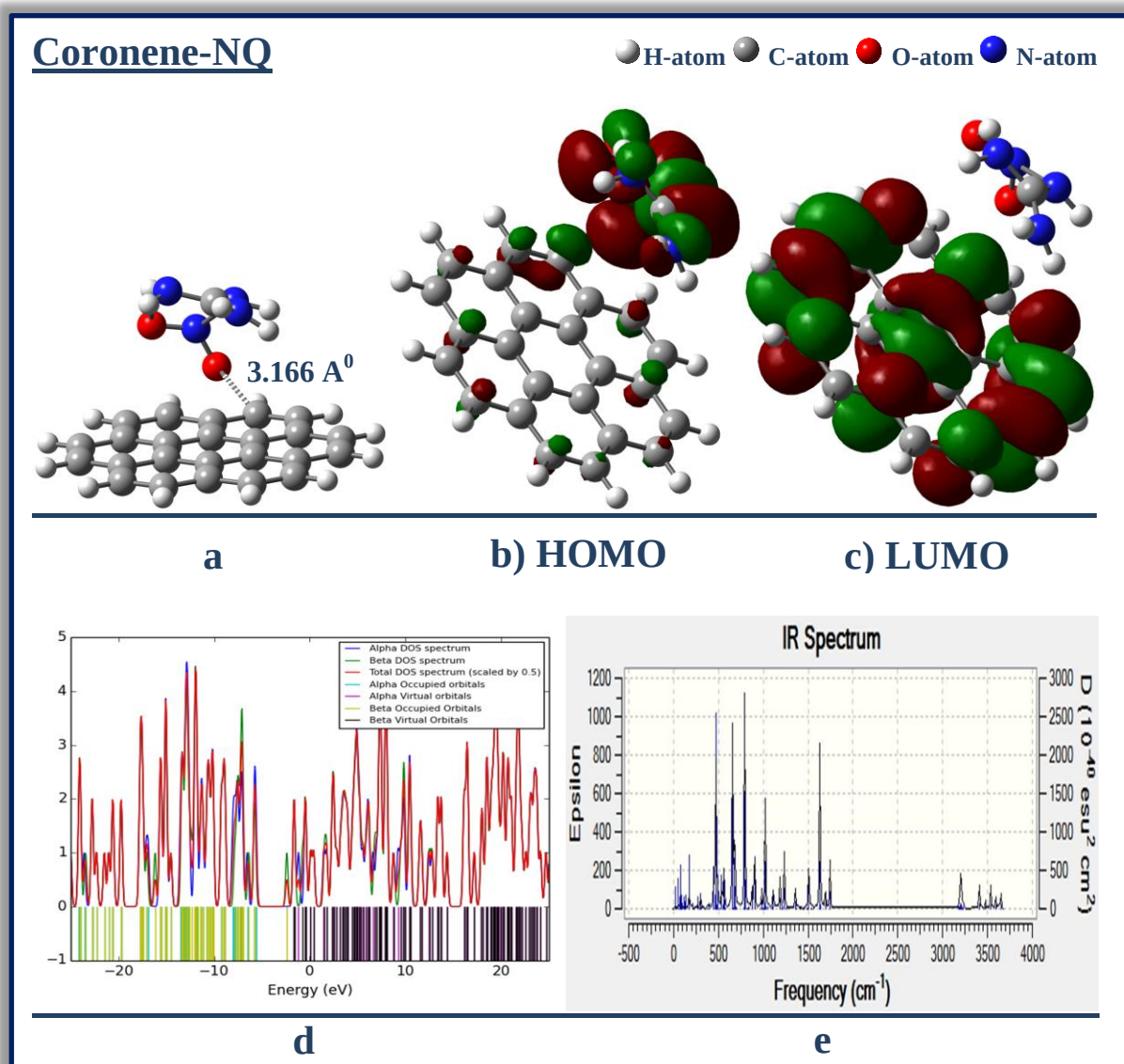


Fig.(3.3): a) Geometrical optimization of sensor-NQ , b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum.

### 3.1.2 Coronene + Aluminium (Al)

From Fig.(3.4 a,b) one can show the transformation from 2D to 3D in nanoscale when the Coronene has one Al atom as the substitution atom. Fig.(3.4 c,d,e,f) give the same previous electronic properties, when this structure is used as a sensor for TNT .

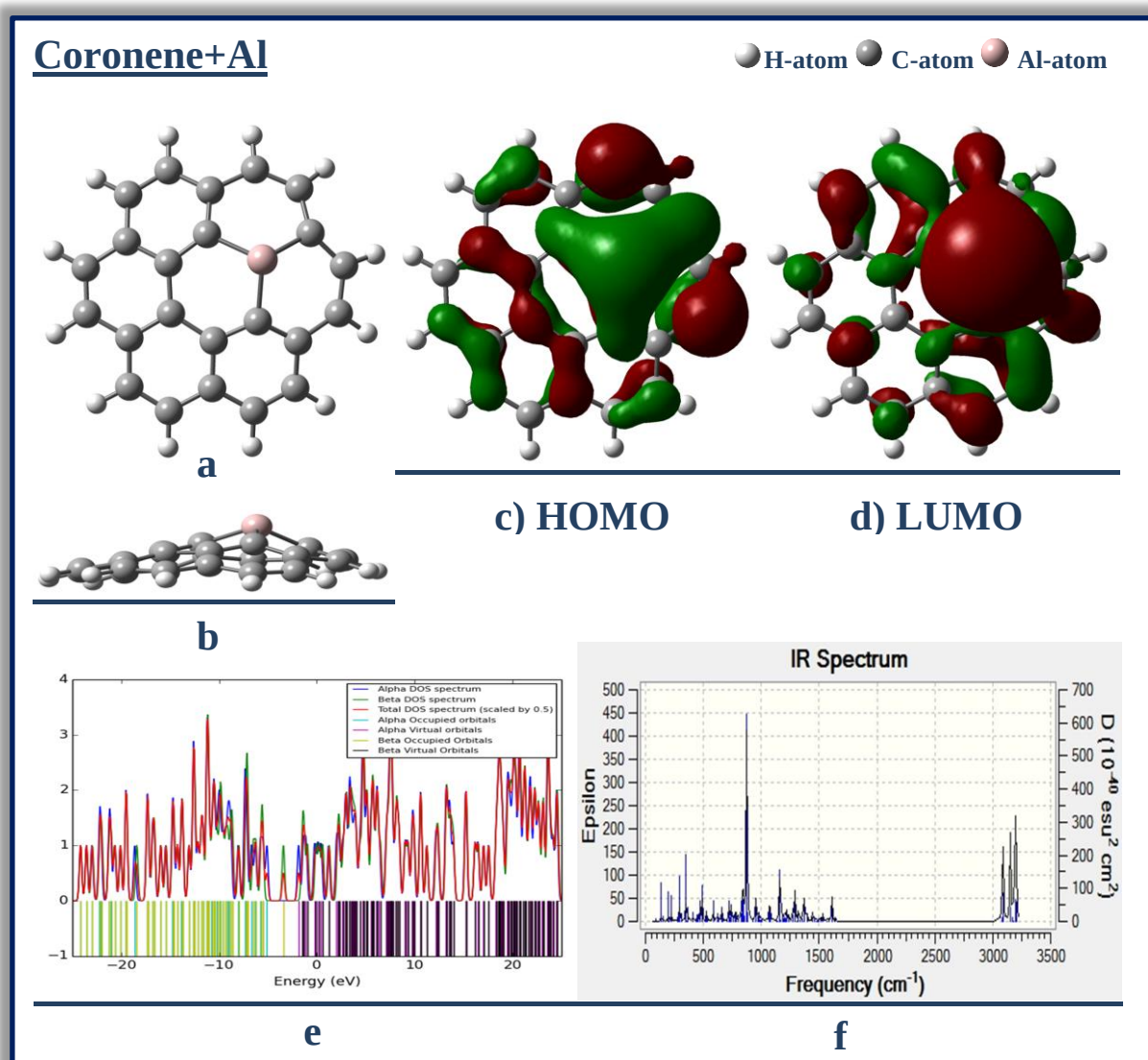


Fig.(3.4): (a,b) Geometrical optimization of sensor with Al atom doping top view and side view respectively, c) HOMO distribution, d) LUMO distribution, e) DOS and f) IR spectrum.

The outcome results of FH gives the maximum sensing since FH = 0.822 with ( $E_{ad} = -2.182$  eV) contrary with pristine Coronene, the sensor spatial the acceptance behavior. The distance between the nearest neighbor atom of the TNT molecules and the sensor is ( $1.844 \text{ \AA}$ ).

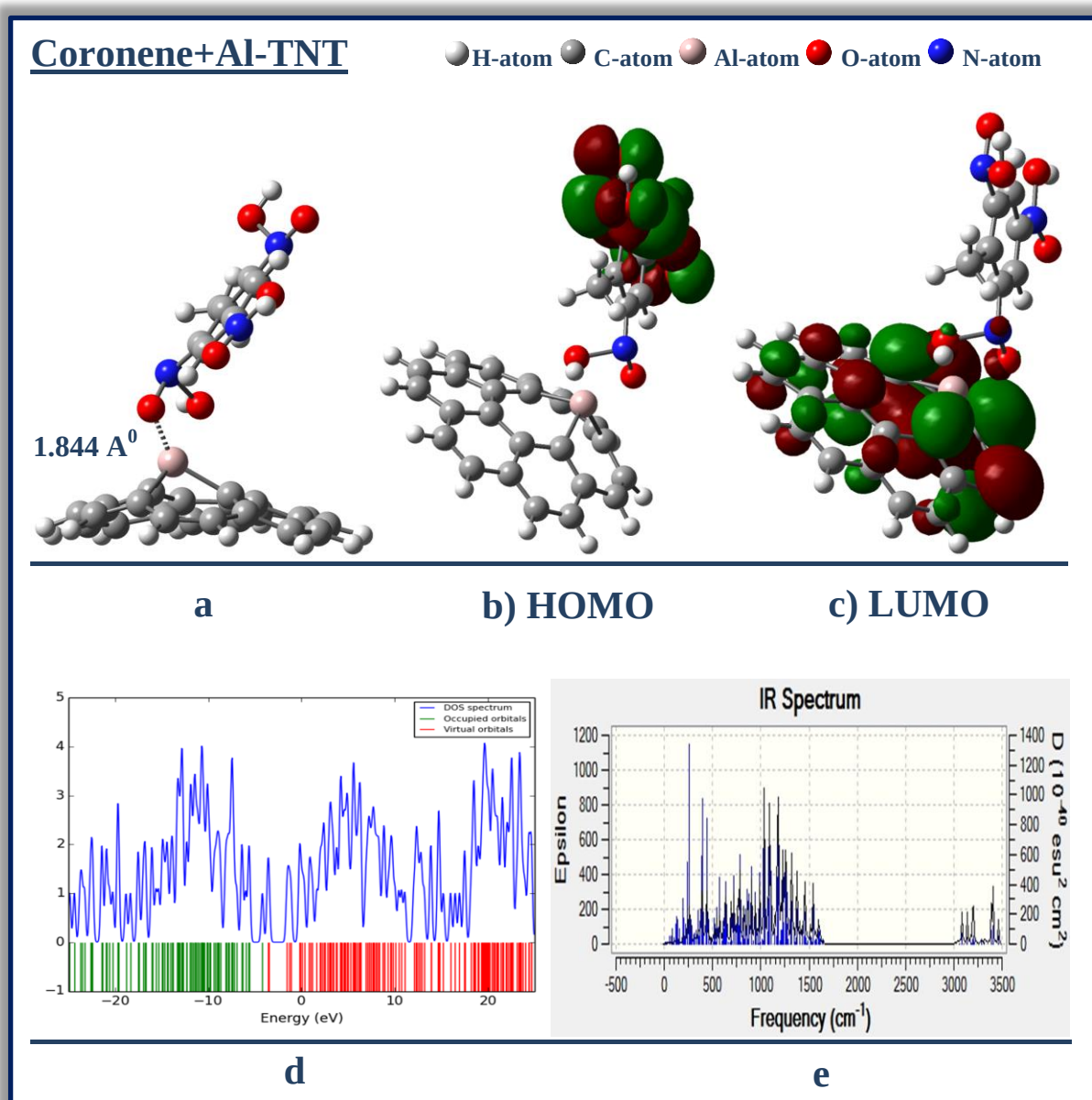


Fig.(3.5): a) Geometrical optimization of sensor-TNT with Al atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum.

The Al atom makes the Coronene a good sensor for NQ molecules as in Fig.(3.6 a) with ( $1.841 \text{ \AA}$ ) separation distance with NQ molecules whereas  $FH = 0.236$  with ( $E_{ad} = -4.679 \text{ eV}$ ), LUMO of the sensor behave as acceptor again.

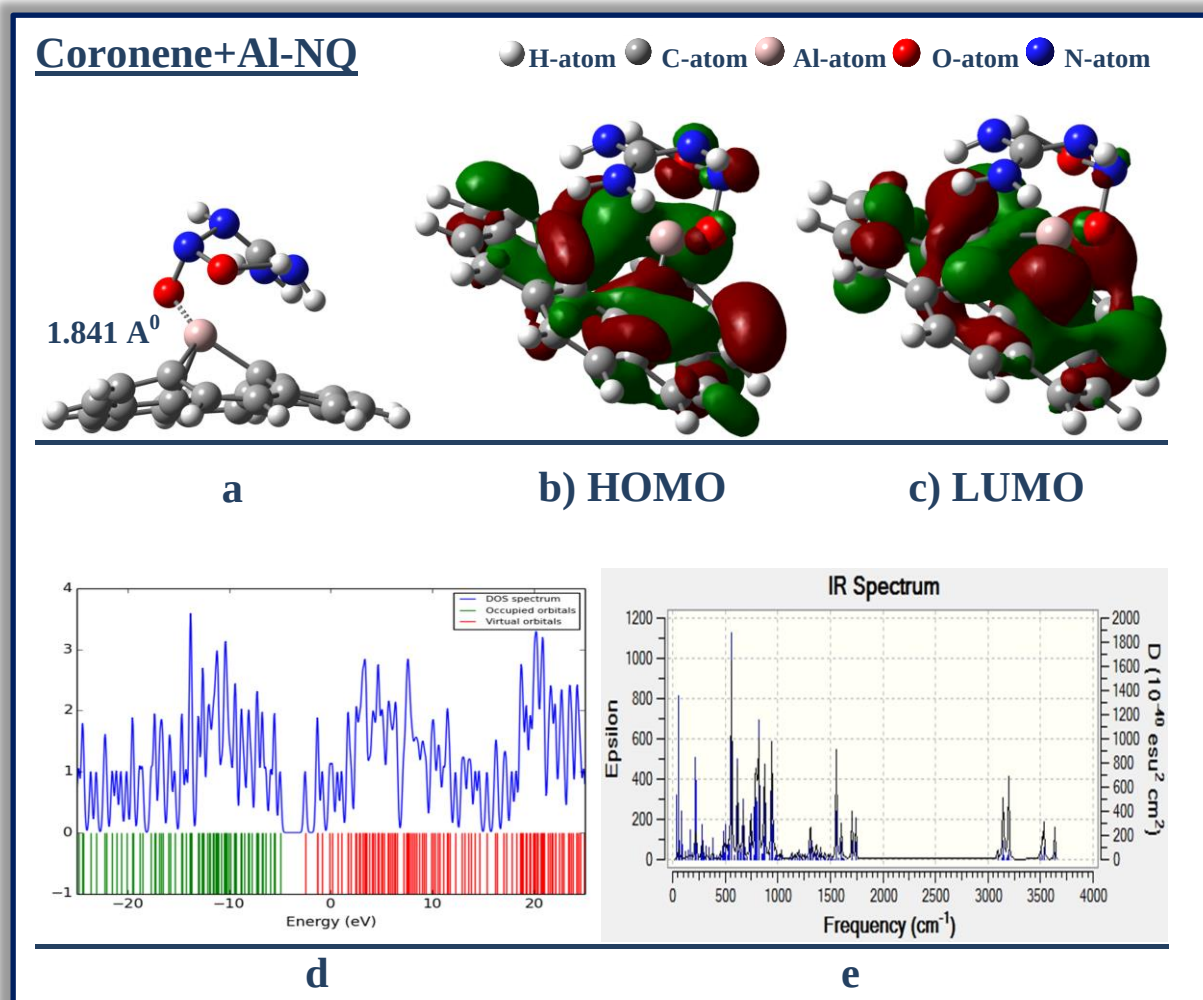


Fig.(3.6): a) Geometrical optimization of sensor-NQ with Al atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum.

### 3.1.3 Coronene + Copper (Cu)

Fig.(3.7) shows another metal atom substitution it is Cu atom. The 2D-3D transformation in nanoscale is clear with  $FH = 0.680$ , ( $E_{ad} = -1.184 \text{ eV}$ )

and separation distance of  $1.897 \text{ \AA}$  the TNT molecule represents acceptor parts as shown in Fig.(3.8 b,c), whereas HOMO and LUMO localized in TNT molecules, on the contrary from Fig.(3.9) illustrates NQ sensing with separation distance of  $1.839 \text{ \AA}$  with  $FH = 0.112$ , ( $E_{ad} = -2.693 \text{ eV}$ ). The HOMO and LUMO localized on the sensor.

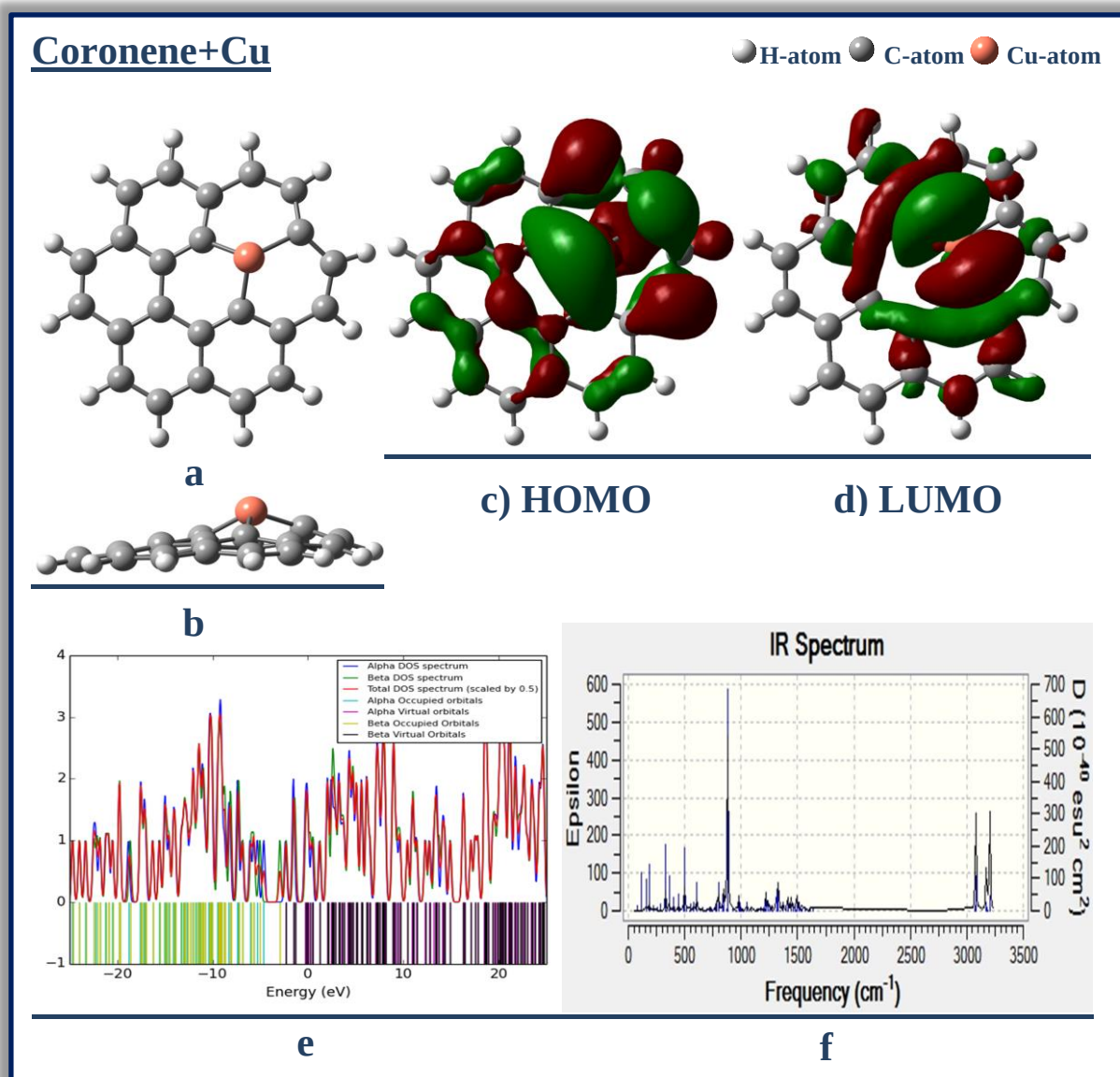


Fig.(3.7): (a,b) Geometrical optimization of sensor with Cu atom doping top view and side view respectively, c) HOMO distribution, d) LUMO distribution, e) DOS and f) IR spectrum.

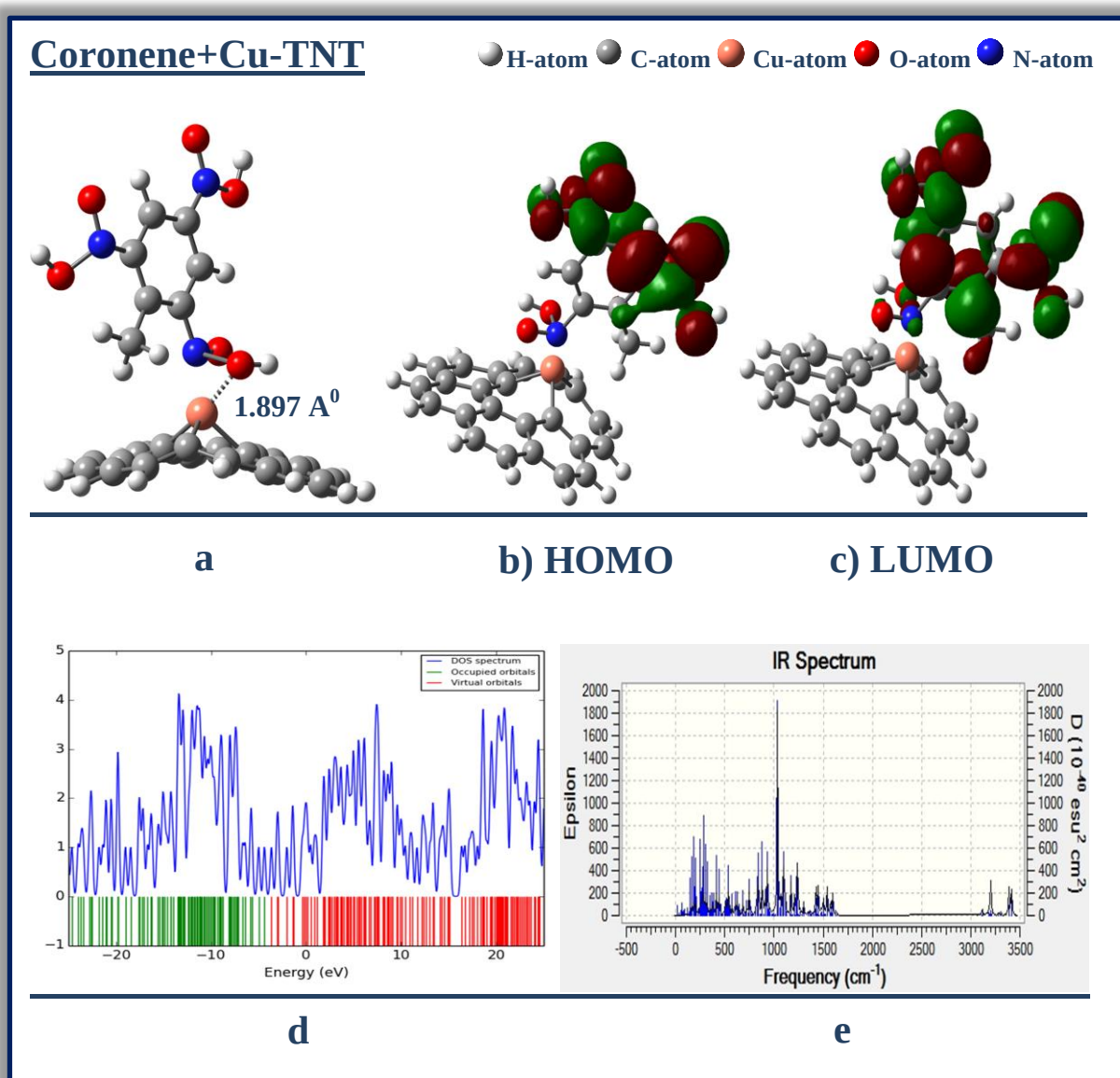


Fig.(3.8): a) Geometrical optimization of sensor-TNT with Cu atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum.

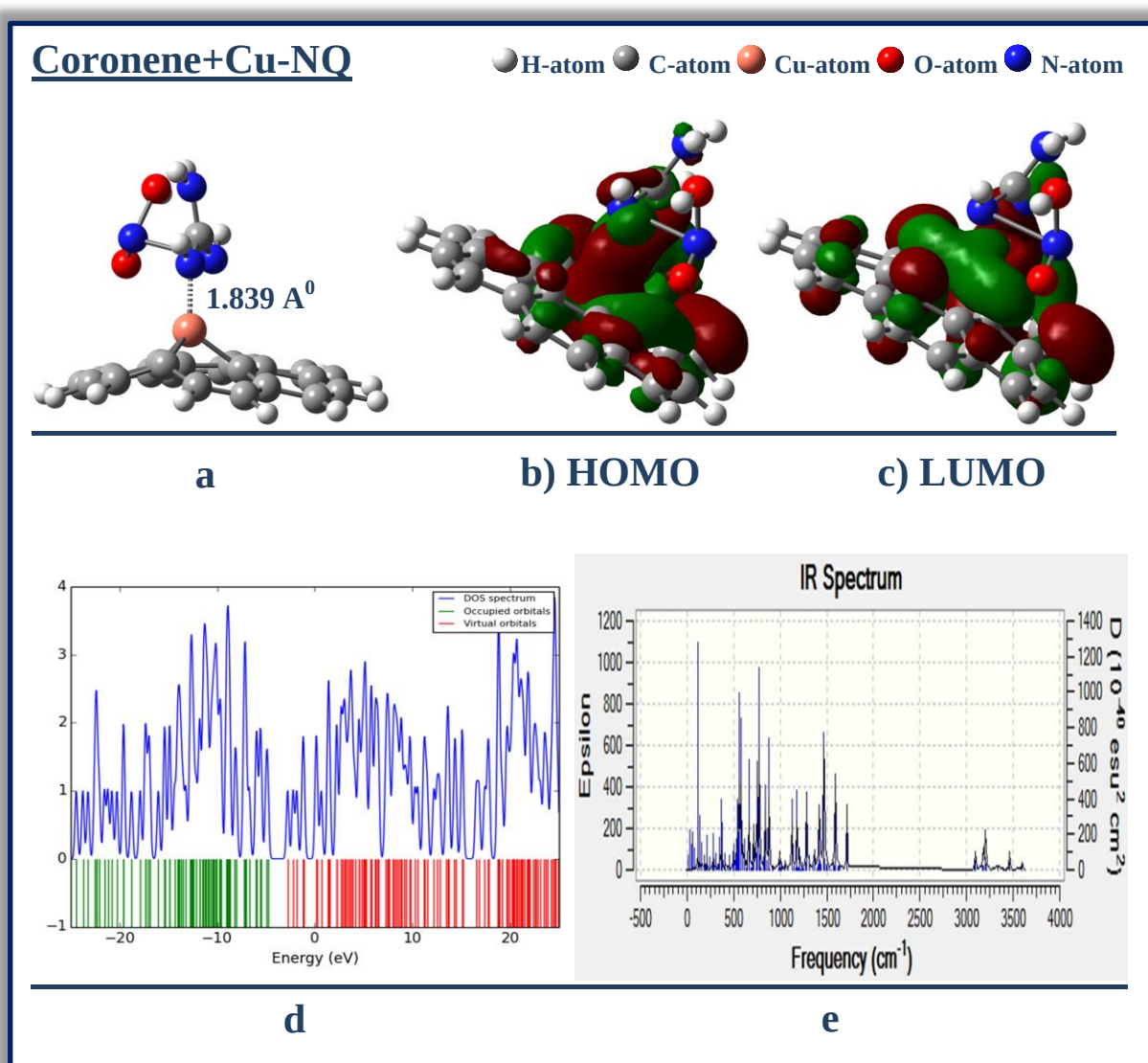


Fig.(3.9): a) Geometrical optimization of sensor-NQ with Cu atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum.

### 3.1.4 Coronene + Germanium (Ge)

The new substitution atom that used to improve Coronene sensor is Ge . Ge atom has non-substantial impact on the 2D-3D transformation since it has the same bond strength of the C . It can be easily shown from Fig.(3.10 a) and Fig.(3.11) the separation distance of (1.820 Å) and the charge distribution as acceptor of the sensor. The 2D-3D transformation in nanoscale begins when TNT approach to the sensor and with FH = 0.518 and ( $E_{ad} = -3.169$  eV).

From Fig.(3.12) the HOMO and LUMO lies in the NQ sensor with FH = 0.041 , ( $E_{ad} = -3.801$  eV) and separation distance of  $1.911 \text{ \AA}$  .

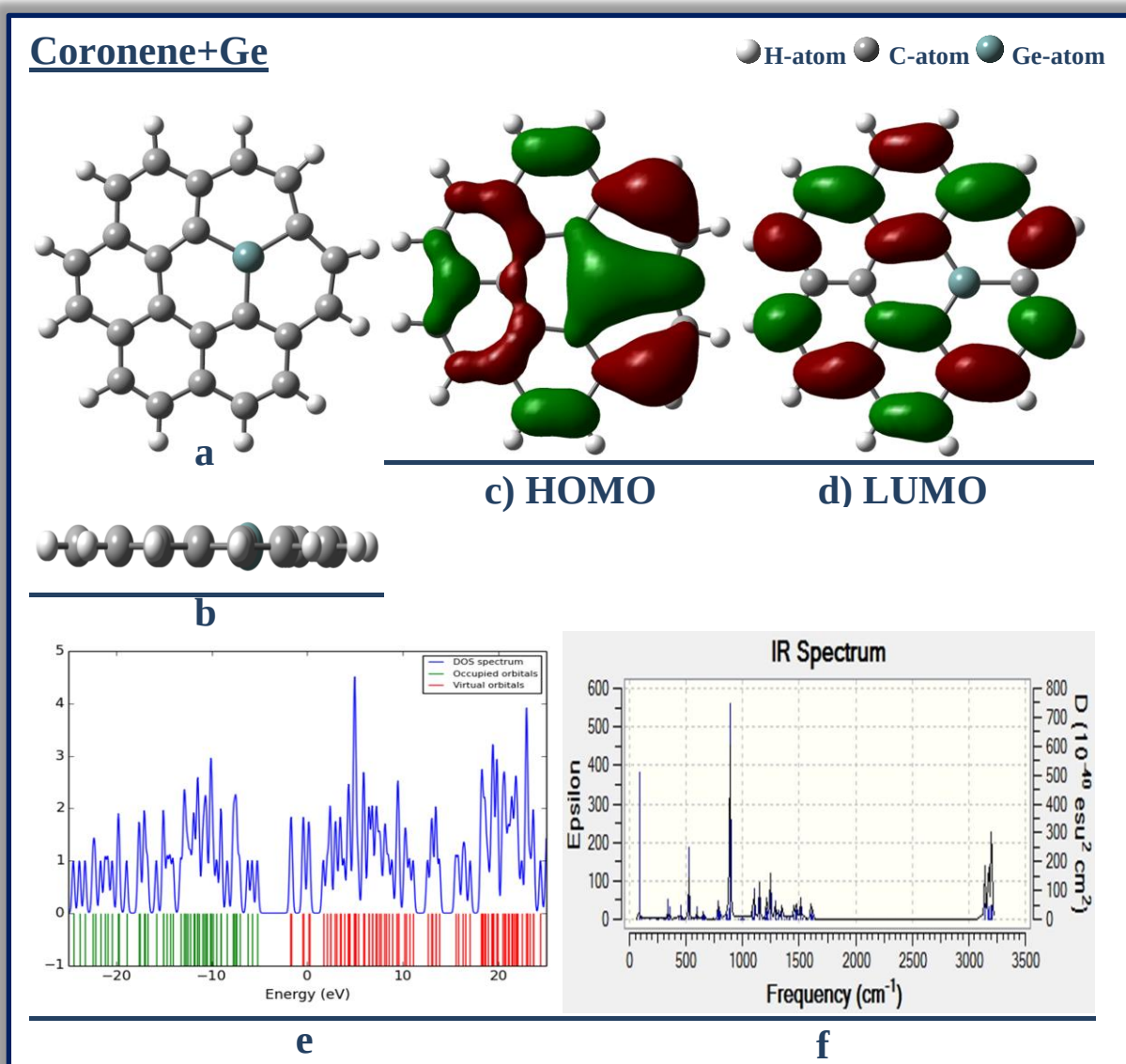


Fig.(3.10): (a,b) Geometrical optimization of sensor with Ge atom doping top view and side view respectively, c) HOMO distribution, d) LUMO distribution, e) DOS and f) IR spectrum.

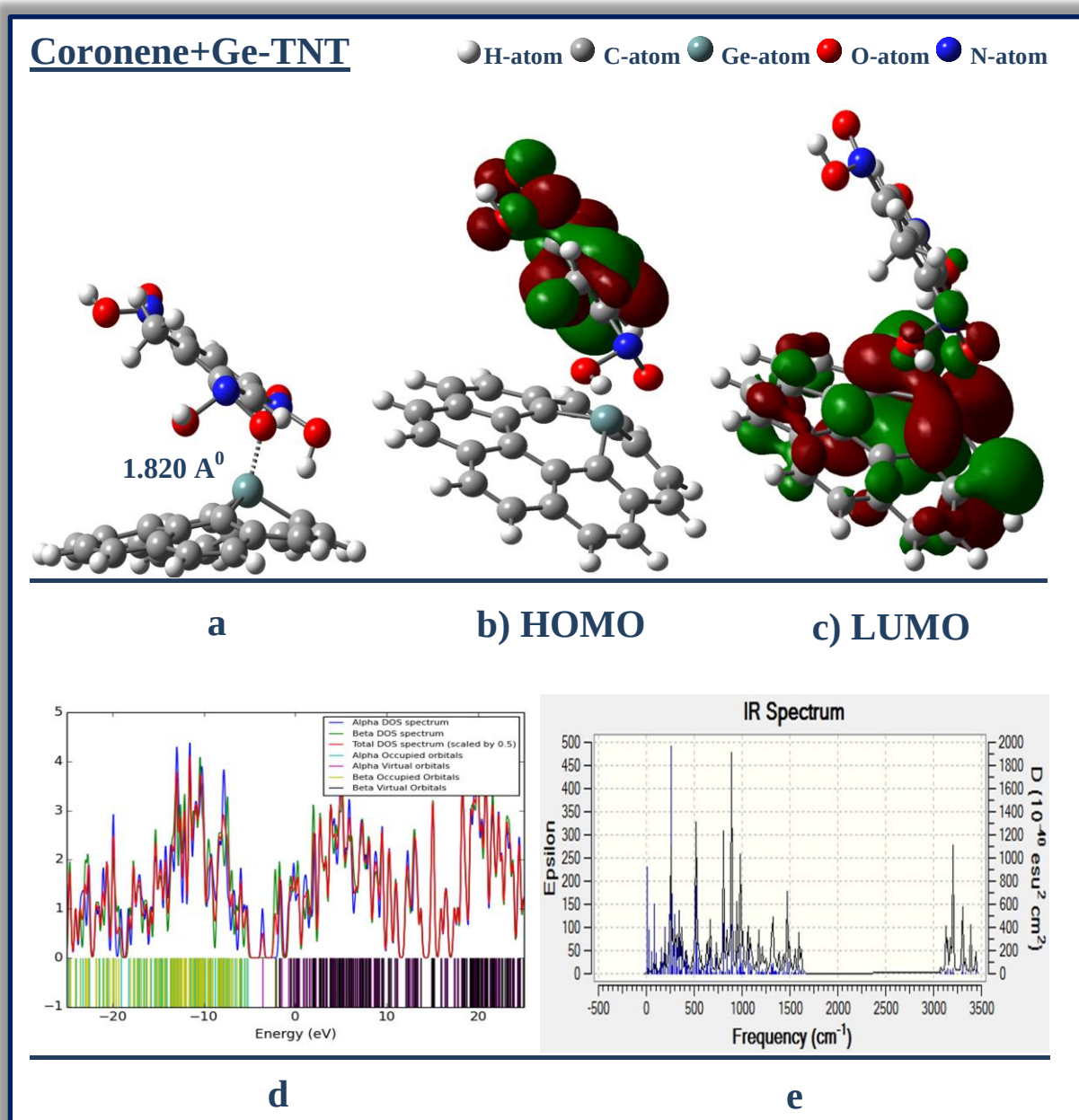


Fig.(3.11): a) Geometrical optimization of sensor-TNT with Ge atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum.

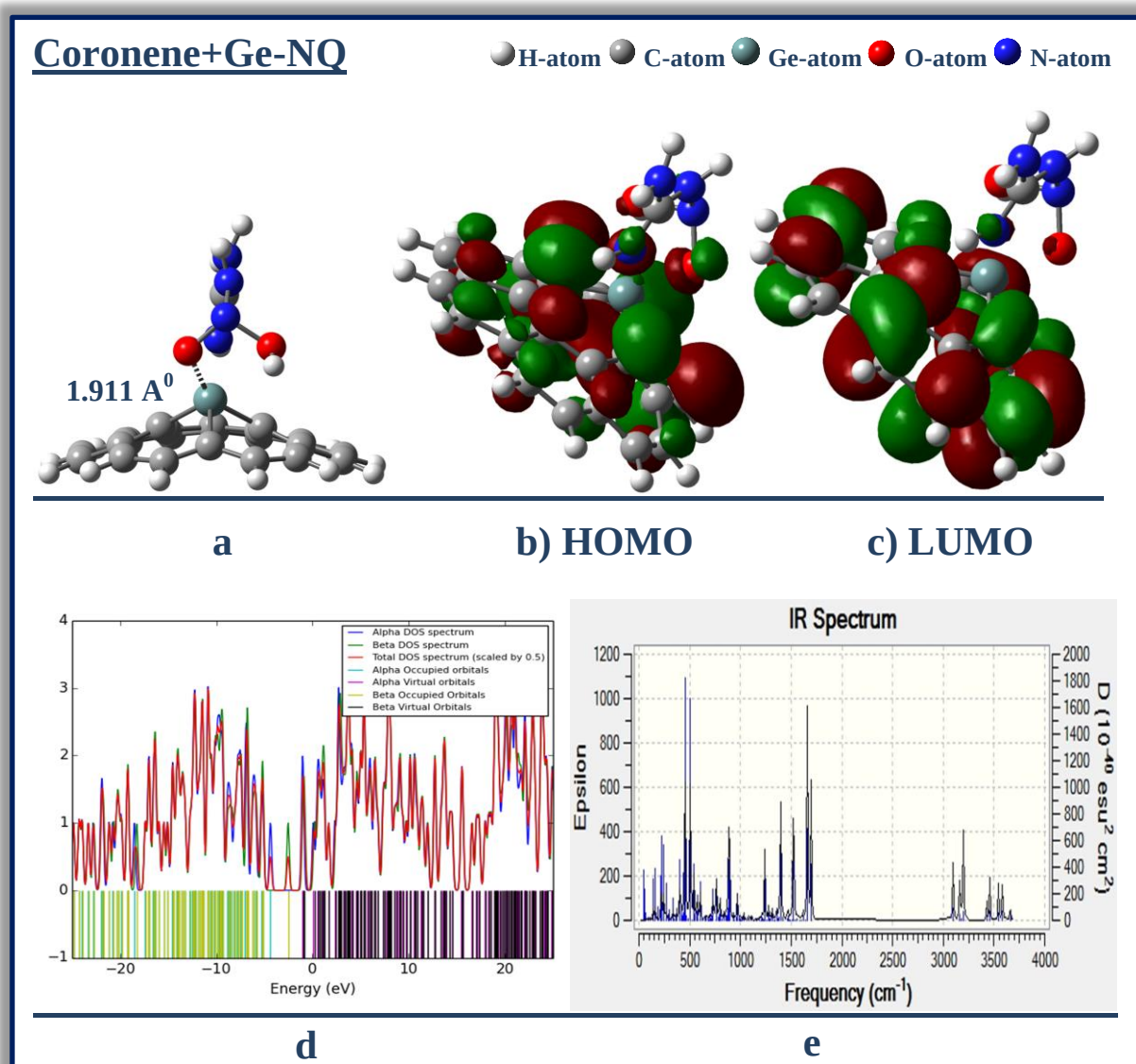


Fig.(3.12): a) Geometrical optimization of sensor-NQ with Ge atom doping, b) HOMO distribution, c) LUMO distribution, d) DOS and e) IR spectrum.

Generally the FH's are in the sequence: Coronene-TNT < Coronene+Ge-TNT < Coronene+Cu -TNT < Coronene+Al-TNT . As well as the sequence of FH's for NQ are: Coronene-NQ < Coronene+Ge-NQ < Coronene+Cu-NQ < Coronene+Al-NQ . It is evident that the Coronene has a good sensing performance for TNT and NQ .

Outcome results can be listed in the Table (3.1).

Table (3.1): The system name, the sensor FH, the adsorption energy ( $E_{ad}$ ), the distance,  $E_g$  and the total energy ( $E_{total}$ ) of investigated sensors.

| structure       | FH    | $E_{ad}$<br>( eV ) | Distance<br>( $\text{\AA}^0$ ) | $E_g$<br>(eV) | $E_{total}$<br>(eV) |
|-----------------|-------|--------------------|--------------------------------|---------------|---------------------|
| TNT             | ...   | ...                | ...                            | ...           | -23995.78           |
| NQ              | ...   | ...                | ...                            | ...           | -11104.62           |
| Coronene        | ...   | ...                | ...                            | 4.132         | -24946.31           |
| Coronene+Ge     | ...   | ...                | ...                            | 3.483         | -80155.80           |
| Coronene+Cu     | ...   | ...                | ...                            | 2.285         | -68334.68           |
| Coronene+Al     | ...   | ...                | ...                            | 3.229         | -30471.54           |
| Coronene-TNT    | 0.320 | -0.370             | 3.301                          | 2.807         | -48942.46           |
| Coronene+Ge-TNT | 0.518 | -3.169             | 1.820                          | 1.676         | -104154.76          |
| Coronene+Cu-TNT | 0.680 | -1.184             | 1.897                          | 0.728         | -92331.65           |
| Coronene+Al-TNT | 0.822 | -2.182             | 1.844                          | 0.574         | -54469.50           |
| Coronene-NQ     | 0.039 | -1.370             | 3.166                          | 3.969         | -36052.30           |
| Coronene+Ge-NQ  | 0.041 | -3.801             | 1.911                          | 3.338         | -91264.23           |
| Coronene+Cu-NQ  | 0.112 | -2.693             | 1.839                          | 2.029         | -79442.00           |
| Coronene+Al-NQ  | 0.236 | -4.679             | 1.841                          | 2.463         | -41580.84           |

### 3.2 Dye Sensitized Solar Cells ( DSSC<sub>s</sub> )

The second part of the results deals with the important properties that control on the DSSC performance such as HOMO, LUMO,  $E_g$ ,  $E_{total}$ , LT ( $LT = E_{LUMO}^{Dye} - E_{LUMO}^{TiO_2}$ ), HT ( $HT = E_{LUMO}^{TiO_2} - E_{HOMO}^{Dye}$ ), the open-circuit Photovoltage ( $V_{OC} = E_{LUMO}^{Dye} - E_{LUMO}^{TiO_2}$ ), the maximum wavelength ( $\lambda_{max}$ ), oscillator strength (OS), Electronic transition beside the orbital spatial of the electronic transition and the UV-Vis spectra. All the above properties established before and after the suitable addition of organic molecules

(A, B, C and D) as shown in Fig.(3.13) in the suitable position. Increase total energy for investigated dyes of virtual name (MH1A, MH2B, MH3B, MH4C, MH5C and MH6D) Compared to the original dyes (MH1, MH2, MH3, MH4, MH5 and MH6) gives more stable and lower reactive for system.

Generally LT and HT have positive signal for ensuring the electronic injection from LUMO of dye to (TiO<sub>2</sub>) and HOMO of dye still lower than (TiO<sub>2</sub> = -4.0 eV) energy. Also Eg after addition became small for dye MH1A , MH2B, MH4C and MH5C . Whereas Eg after addition became bigger for dye MH3B and MH6D , as shown in the following tables for each dye.

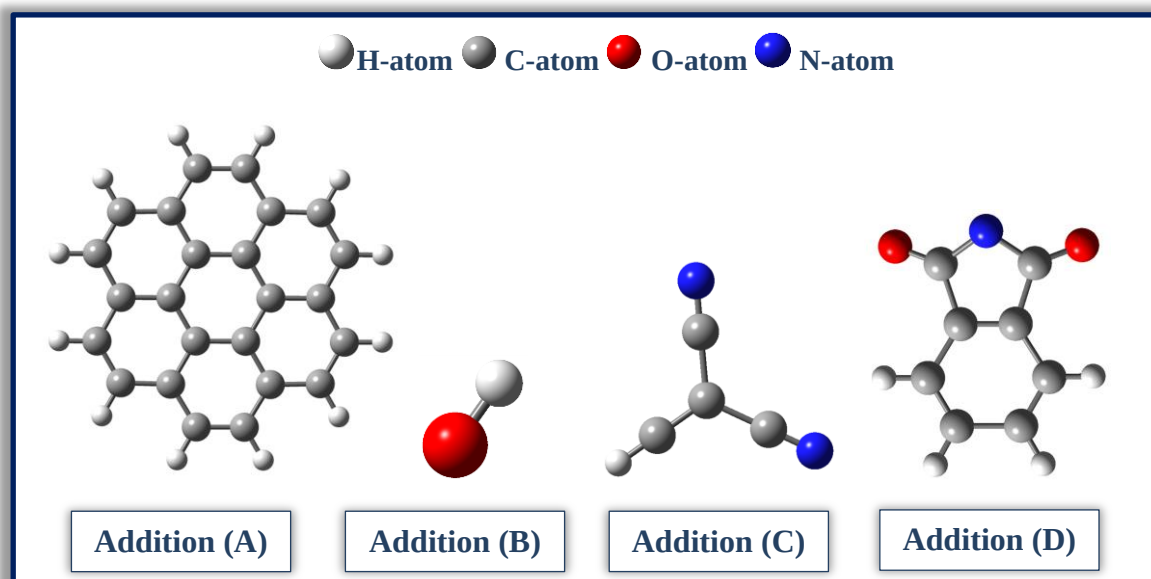


Fig.(3.13): The four additions that use with dyes under study.

### 3.2.1 Geometrical Structure Properties

The geometrical structures of investigated dyes, which are a candidates to get high performance, are shown in Fig.(3.14). The optimization of this geometrical structure was obtained using (DFT with B3LYP method / 6-31G basis set) approach.

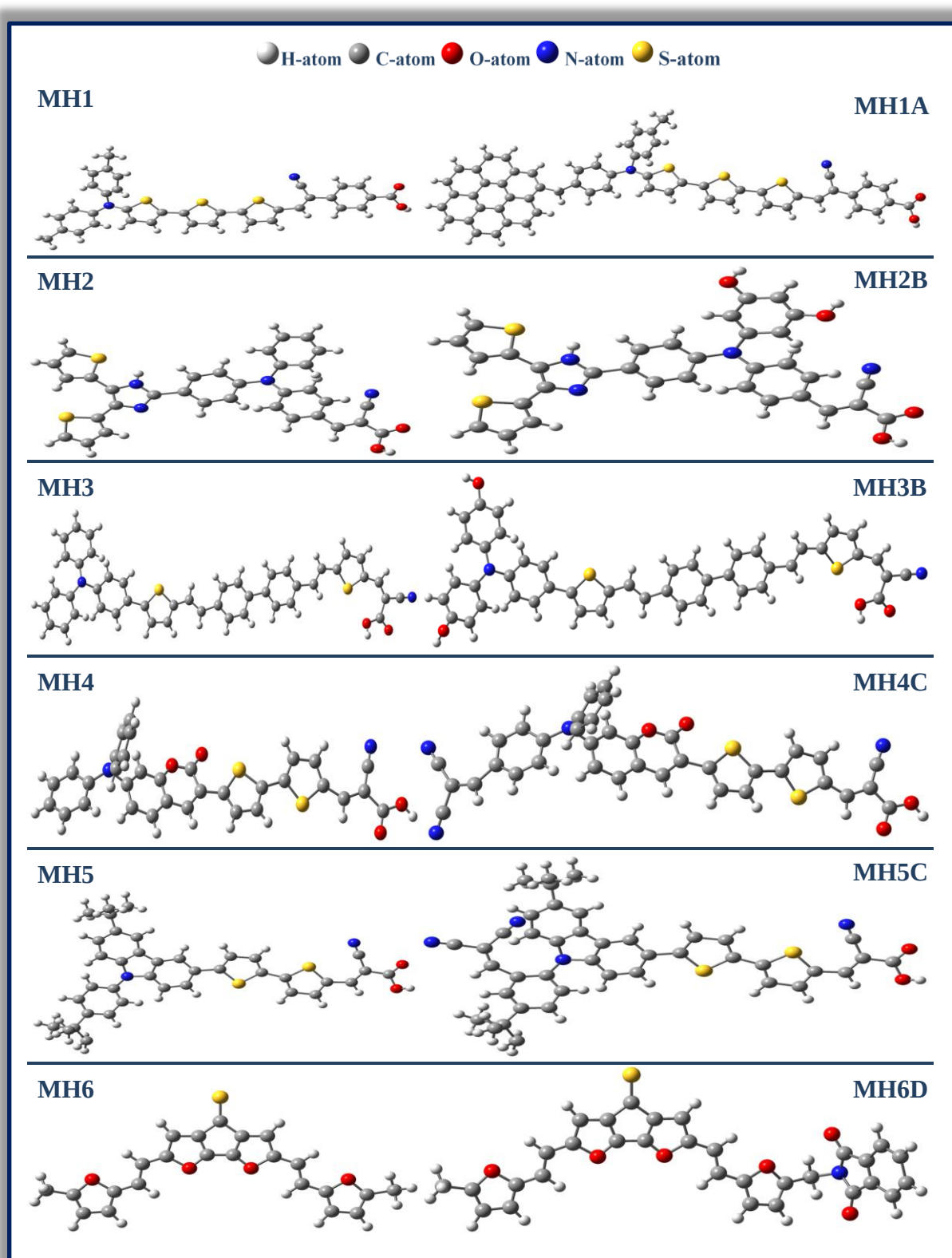


Fig.(3.14): Geometrical optimization before (left) and after (right) addition of investigated dyes.

### 3.3 Electronic Properties of Organic Dyes

#### 3.3.1 Dye MH1

Using TD-DFT with B3LYP method / 6-31G basis set, the dye MH1 improved by adding Coronene (A) in the left side. The HOMO part before and after adding has no substantial impact in the orbitals spatially whereas the electronic transition was changed to  $\text{LUMO}_{+2}$ .

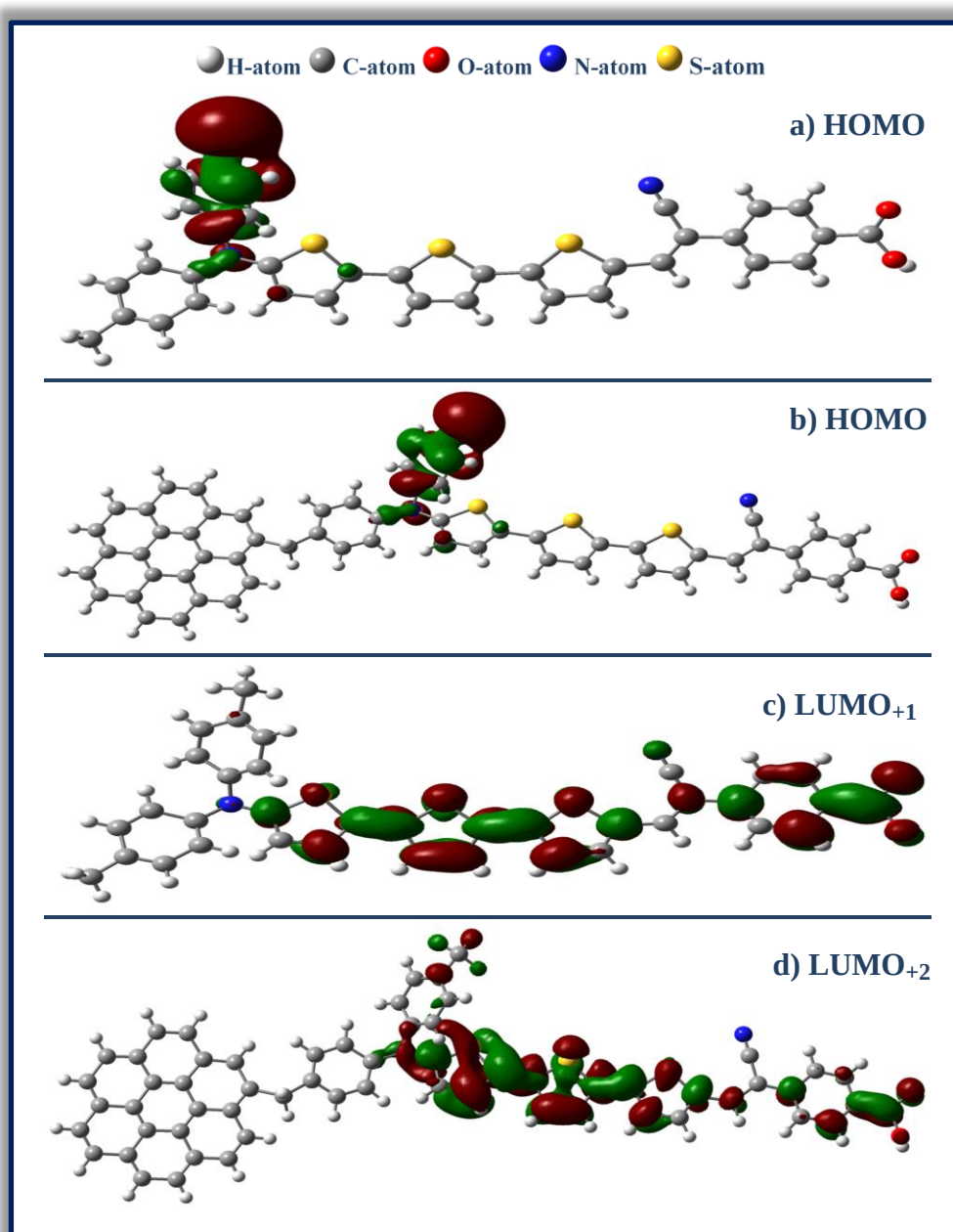


Fig.(3.15): HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH1 .

The important electronic properties are listed in Table (3.2). The results indicate that the energy gap becomes smaller because of decreasing of the LUMO and increasing HOMO. The addition of Coronene gives the original dye some states of energy as can be shown in Fig.(3.15 d) since it has high charge mobility. LT, HT positive signal for ensuring the electronic injection from dye to the (TiO<sub>2</sub>) semiconductor for all investigated dyes.

Table (3.2): Numerical results of the important electronic properties of dye MH1 before and after improvement.

| Property (unit)                 | Before Addition           | After Addition            |
|---------------------------------|---------------------------|---------------------------|
| <b>H-n<sup>*</sup> ( eV )</b>   | <b>-4.53</b>              | <b>-4.45</b>              |
| <b>L+n<sup>*</sup> ( eV )</b>   | <b>-1.80</b>              | <b>-1.93</b>              |
| <b>E<sub>g</sub> ( eV )</b>     | <b>2.73</b>               | <b>2.52</b>               |
| <b>Electronic Transition</b>    | <b>HOMO-&gt;L+1 (92%)</b> | <b>HOMO-&gt;L+2 (80%)</b> |
| <b>LT ( eV )</b>                | <b>2.20</b>               | <b>2.07</b>               |
| <b>HT ( eV )</b>                | <b>0.53</b>               | <b>0.45</b>               |
| <b>V<sub>oc</sub> ( eV )</b>    | <b>2.20</b>               | <b>2.07</b>               |
| <b>E<sub>total</sub> ( eV )</b> | <b>-76903.99</b>          | <b>-101808.25</b>         |
| <b>λ<sub>max</sub> ( nm )</b>   | <b>498</b>                | <b>573</b>                |
| <b>OS ( eV )</b>                | <b>0.0257</b>             | <b>0.0303</b>             |

\* H-n (n = 0,1,2,...)

L+n (n = 0,1,2,...)

n = 0 , refers to basic HOMO and LUMO.

From Fig.(3.16) it is easy to observe that the spectra range from 380 to 1400 (nm) approximately and has a red-shifted with possessing absorption from 1050 to 1350 and  $\lambda_{\max}$  shift 75nm with OS from 0.0257 to 0.0303 (eV). This reveals the high light harvesting efficiency.

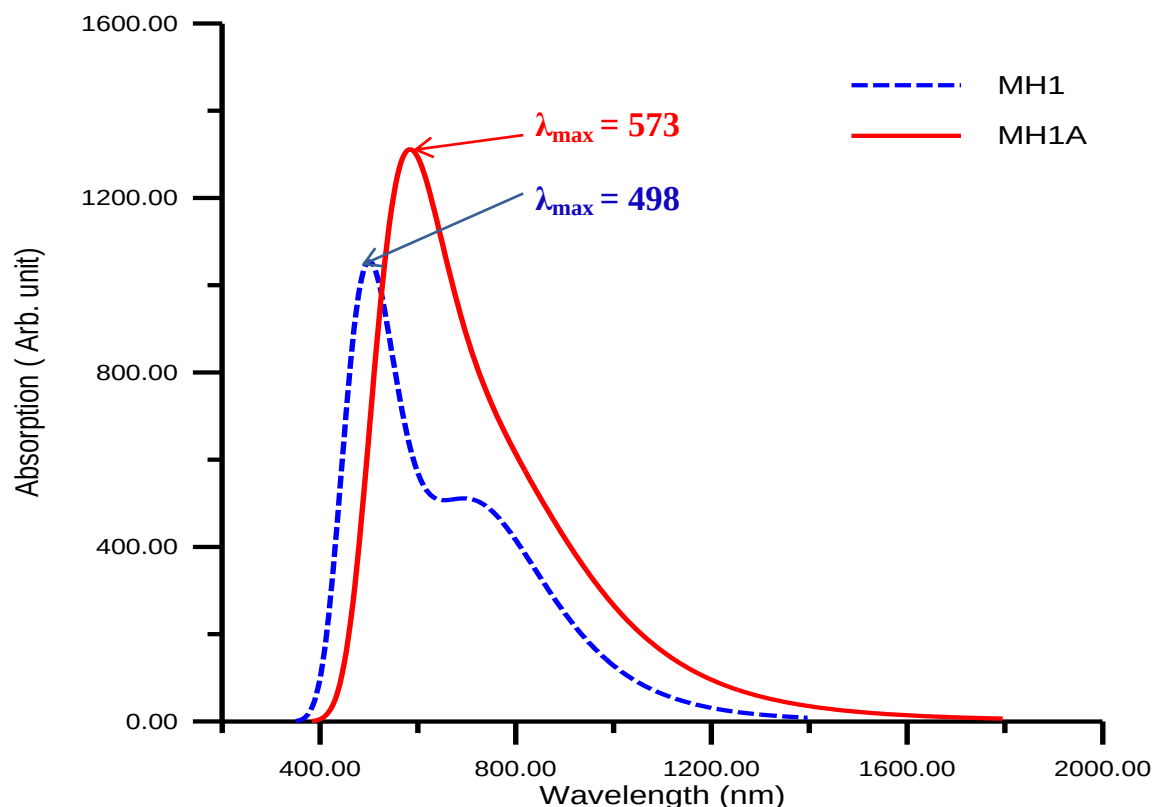


Fig.(3.16): The absorption of dye MH1 before (blue line) and after (red line) addition A .

### 3.3.2 Dye MH2

Based on the related references some dyes (dye MH2) have improved by adding two Hydroxyl molecules (two-B). From Fig.(3.17) one can see the difference between original HOMO<sub>2</sub> and HOMO<sub>1</sub> after addition whereas the electron still transfer from LUMO dye to LUMO (TiO<sub>2</sub>) semiconductor.

The original HOMO<sub>2</sub> distribution transfer from S atoms to OH molecules because OH have high electronegativity.

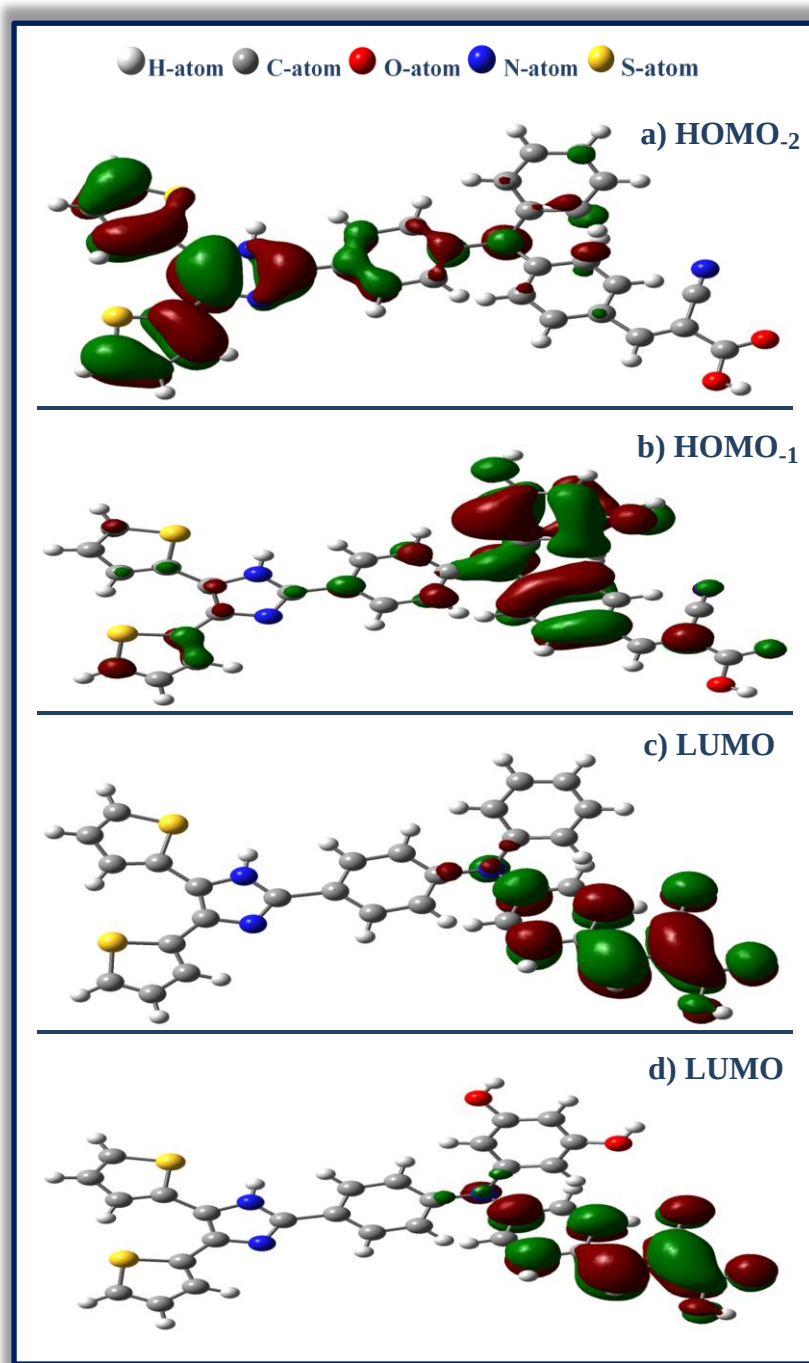


Fig.(3.17): HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH2 .

The numerical data listed in the Table (3.3).

Table (3.3): Numerical results of the important electronic properties of dye MH2 before and after improvement.

| <b>Property (unit)</b>                          | <b>Before Addition</b>    | <b>After Addition</b>     |
|-------------------------------------------------|---------------------------|---------------------------|
| <b>H-n ( eV )</b>                               | <b>-6.41</b>              | <b>-5.98</b>              |
| <b>L+n ( eV )</b>                               | <b>-2.54</b>              | <b>-2.36</b>              |
| <b>Eg ( eV )</b>                                | <b>3.87</b>               | <b>3.62</b>               |
| <b>Electronic Transition</b>                    | <b>H-2-&gt;LUMO (74%)</b> | <b>H-1-&gt;LUMO (90%)</b> |
| <b>LT ( eV )</b>                                | <b>1.46</b>               | <b>1.64</b>               |
| <b>HT ( eV )</b>                                | <b>2.41</b>               | <b>1.98</b>               |
| <b>V<sub>oc</sub> ( eV )</b>                    | <b>1.46</b>               | <b>1.64</b>               |
| <b>E<sub>total</sub> ( eV )</b>                 | <b>-65923.91</b>          | <b>-69999.06</b>          |
| <b><math>\lambda_{\text{max}}</math> ( nm )</b> | <b>367</b>                | <b>382</b>                |
| <b>OS ( eV )</b>                                | <b>0.2765</b>             | <b>0.3717</b>             |

Fig.(3.18) illustrate the small  $\lambda_{\max}$  shifted 15nm a few shift in the spectrum, see the edges. Whereas the absorption from 12000 to 15000 as well as OS from 0.27 to 0.37 .

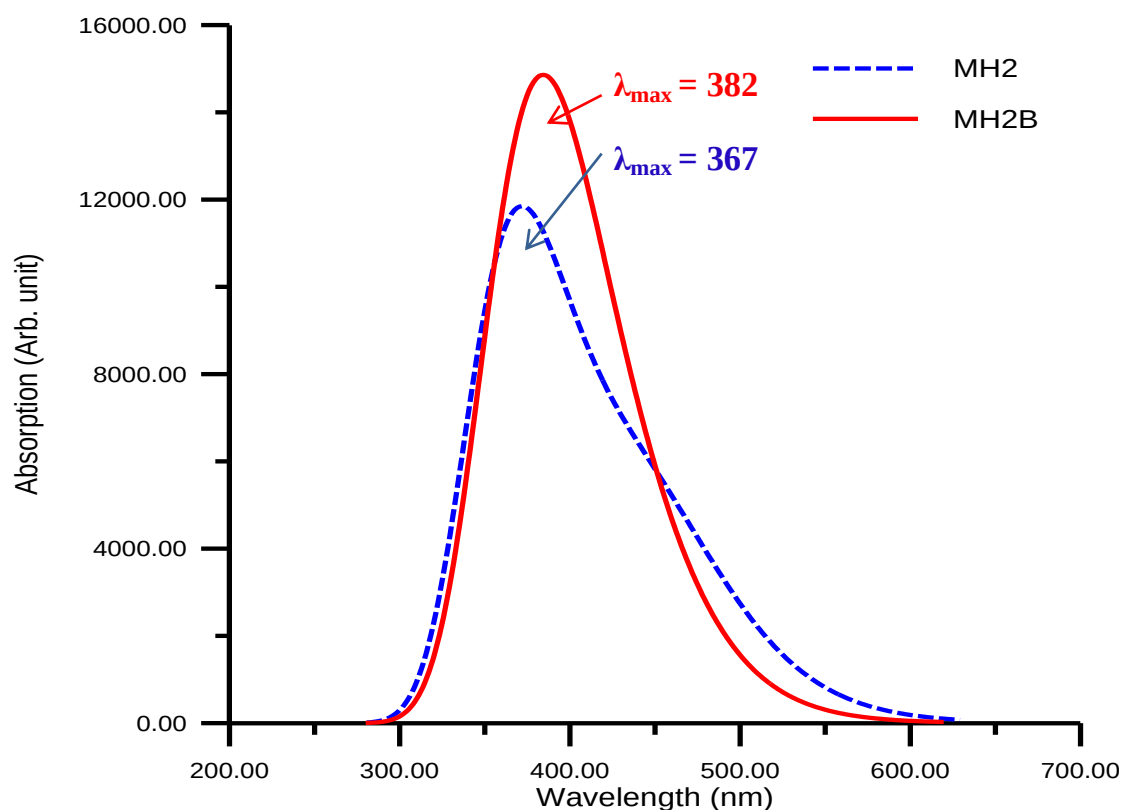


Fig.(3.18): The absorption of dye MH2 before (blue line) and after (red line) addition B .

### 3.3.3 Dye MH3

The B addition is also suitable for the dye MH3 and it has no effect on the electron transition i.e. electron still transfer from HOMO<sub>2</sub> to LUMO in both with or without addition as observed from Fig.(3.19) .

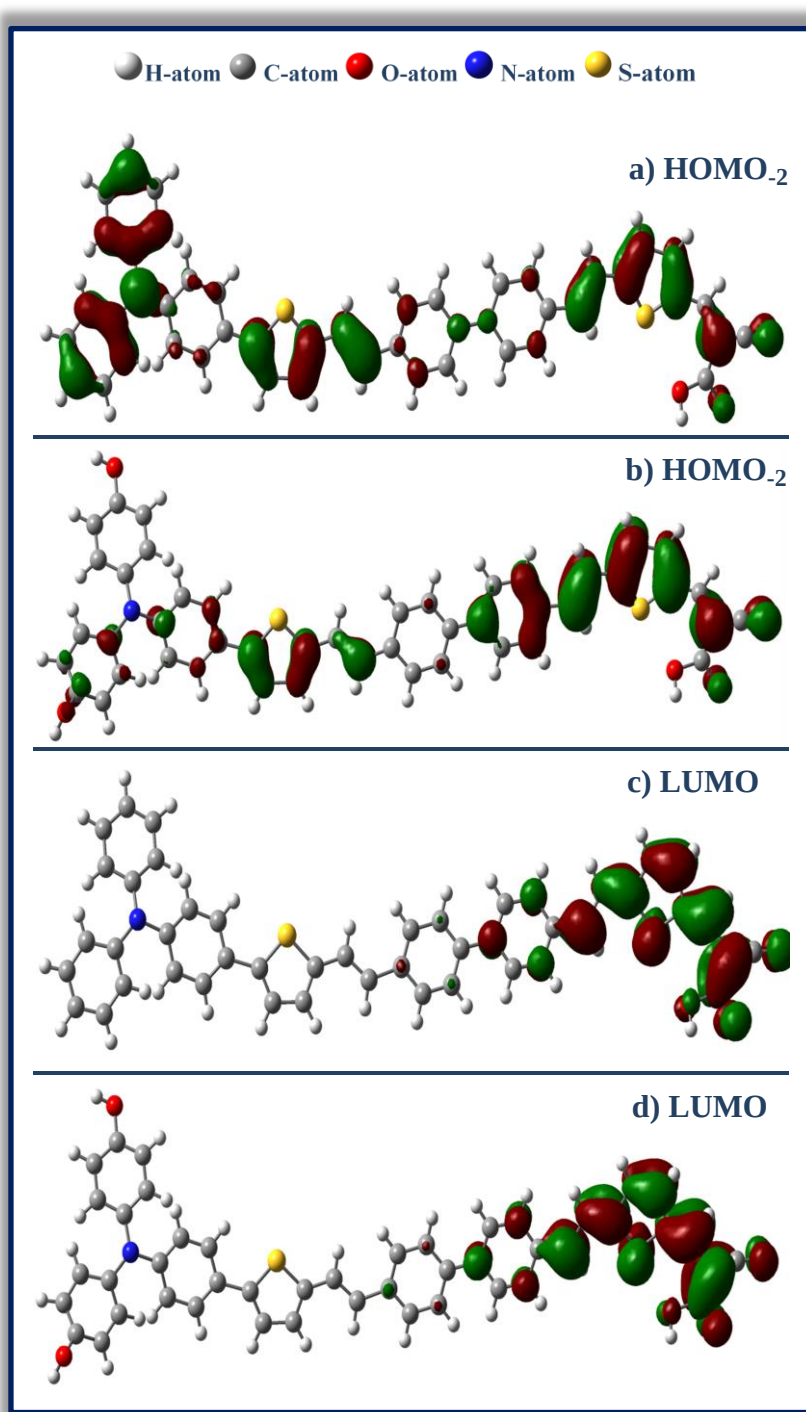


Fig.(3.19): HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH3 .

The numerical data listed in the Table (3.4).

Table (3.4): Numerical results of the important electronic properties of dye MH3 before and after improvement.

| Property (unit)               | Before Addition | After Addition  |
|-------------------------------|-----------------|-----------------|
| H-n ( eV )                    | -6.09           | -5.98           |
| L+n ( eV )                    | -3.07           | -2.93           |
| Eg ( eV )                     | 3.02            | 3.05            |
| Electronic Transition         | H-2->LUMO (91%) | H-2->LUMO (84%) |
| LT ( eV )                     | 0.93            | 1.07            |
| HT ( eV )                     | 2.09            | 1.98            |
| V <sub>oc</sub> ( eV )        | 0.93            | 1.07            |
| E <sub>total</sub> ( eV )     | -76532.84       | -80603.20       |
| $\lambda_{\text{max}}$ ( nm ) | 424             | 424             |
| OS ( eV )                     | 0.9140          | 1.6607          |

From Fig.(3.20) the absorption peak has increased from 73000 to 82000 with OS shift from 0.9140 to 1.6607 (eV) and exactly in the same range spectrum and same  $\lambda_{\max}$ .

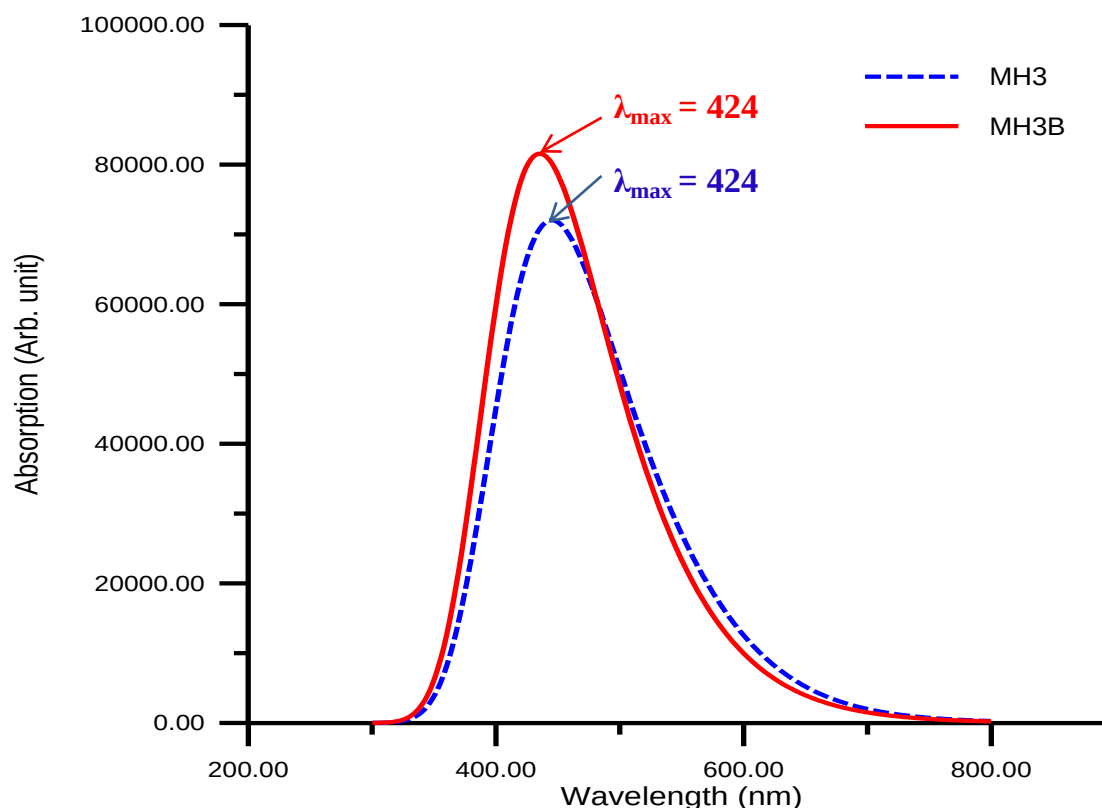


Fig.(3.20): The absorption of dye MH3 before (blue line) and after (red line) addition B .

### 3.3.4 Dye MH4

Another addition is the famous organic molecules C was added, apparently from Fig.(3.21) the electron transferring was changed from (HOMO - LUMO) to (HOMO - LUMO<sub>+1</sub>) since the Nitrogen has electronegativity less than S and O .

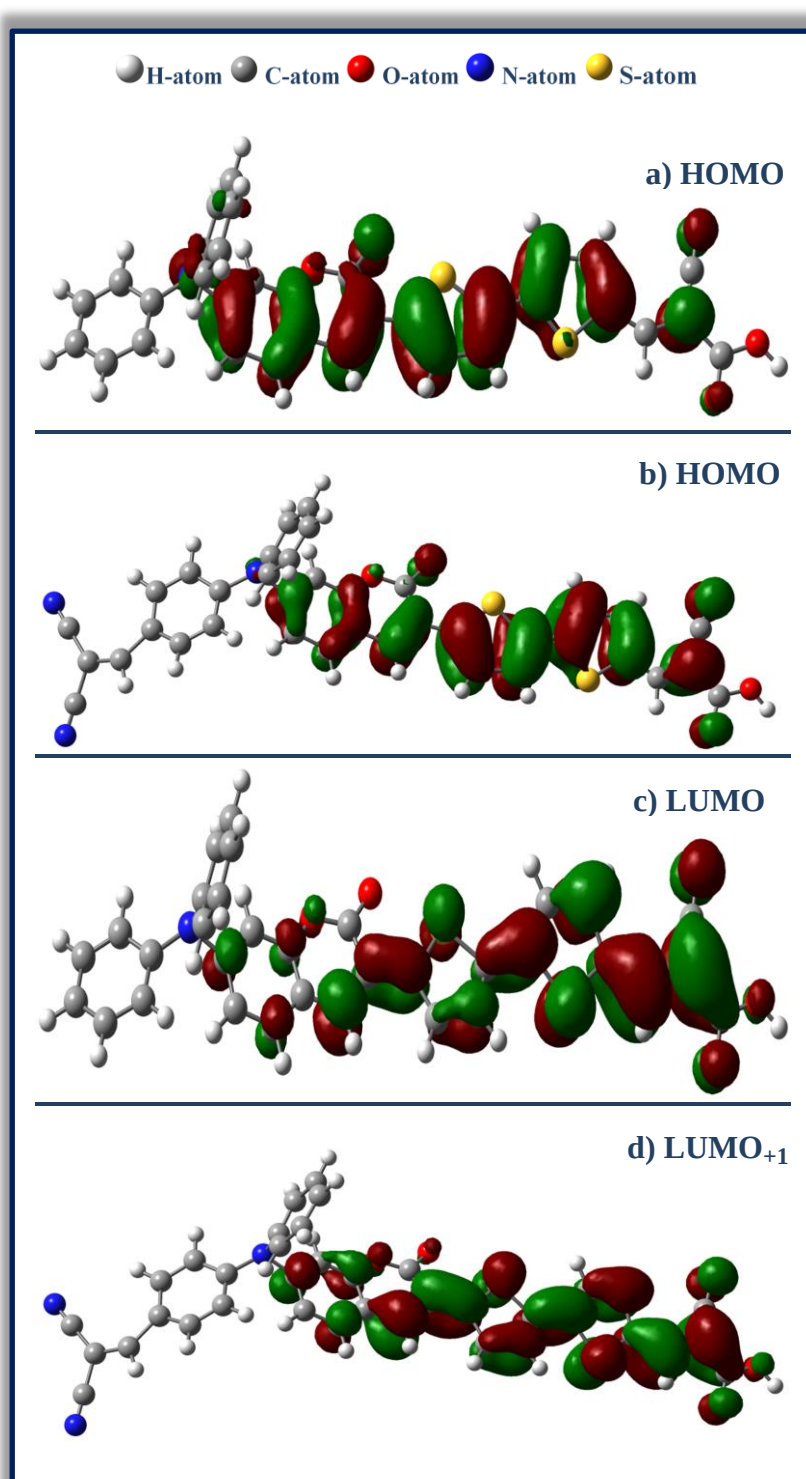


Fig.(3.21): HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH4 .

The numerical data listed in Table (3.5).

Table (3.5): Numerical results of the important electronic properties of dye MH4 before and after improvement.

| <b>Property (unit)</b>                          | <b>Before Addition</b>     | <b>After Addition</b>     |
|-------------------------------------------------|----------------------------|---------------------------|
| <b>H-n ( eV )</b>                               | <b>-5.76</b>               | <b>-5.85</b>              |
| <b>L+n ( eV )</b>                               | <b>-2.88</b>               | <b>-3.04</b>              |
| <b>Eg ( eV )</b>                                | <b>2.88</b>                | <b>2.81</b>               |
| <b>Electronic Transition</b>                    | <b>HOMO-&gt;LUMO (99%)</b> | <b>HOMO-&gt;L+1 (98%)</b> |
| <b>LT ( eV )</b>                                | <b>1.12</b>                | <b>0.96</b>               |
| <b>HT ( eV )</b>                                | <b>1.76</b>                | <b>1.85</b>               |
| <b>V<sub>oc</sub> ( eV )</b>                    | <b>1.12</b>                | <b>0.96</b>               |
| <b>E<sub>total</sub> ( eV )</b>                 | <b>-67014.13</b>           | <b>-74099.68</b>          |
| <b><math>\lambda_{\text{max}}</math> ( nm )</b> | <b>473</b>                 | <b>476</b>                |
| <b>OS ( eV )</b>                                | <b>1.2225</b>              | <b>1.7194</b>             |

Fig.(3.22) illustrates the increasing of the absorption from 54000 to 70000 approximately with some red-shifted. As we can see the  $\lambda_{\max}$  has very small shifted from 473 to 476 (nm) with OS from 1.2 to 1.7 (eV) .

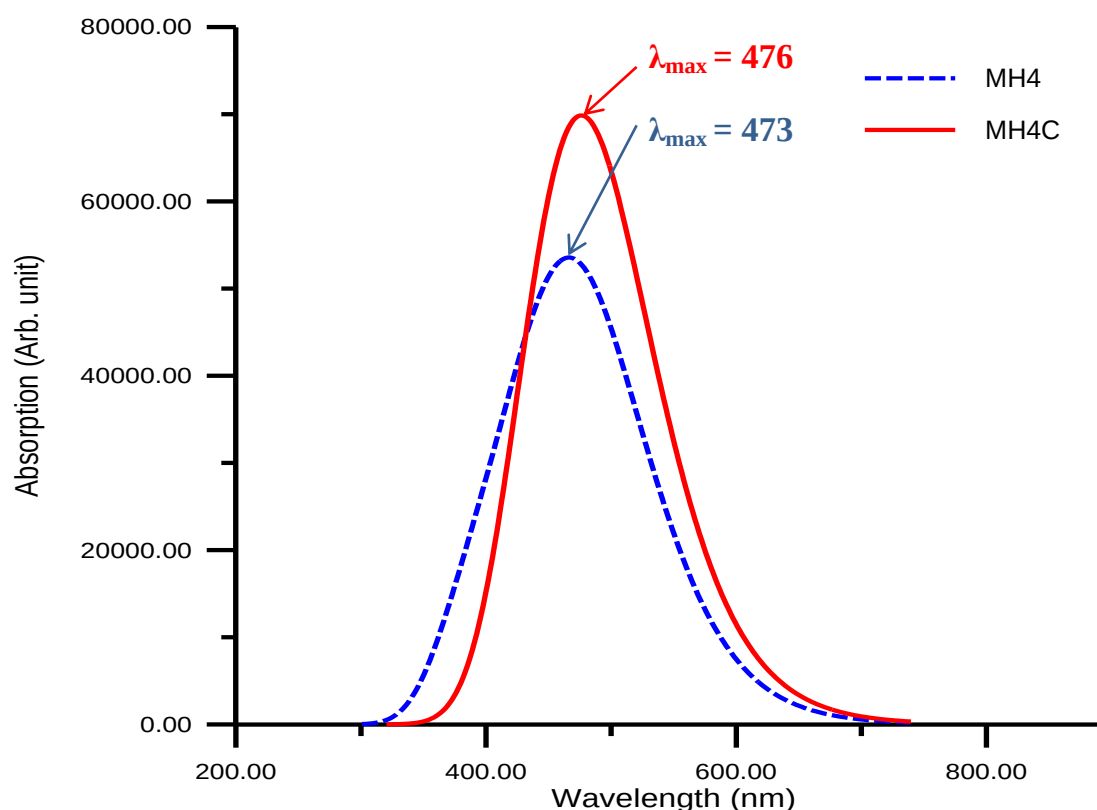


Fig.(3.22): The absorption of dye MH4 before (blue line) and after (red line) addition C .

### 3.3.5 Dye MH5

The next dye has small absorption and we use the same above addition C, as can see from Fig.(3.23) the original electronic transition is (HOMO<sub>-1</sub> to LUMO) whereas after C added, the transition becomes from HOMO<sub>-1</sub> to the different state LUMO<sub>+2</sub> , which has large spatial orbital since the C position is located far away from the O atoms as depicted.

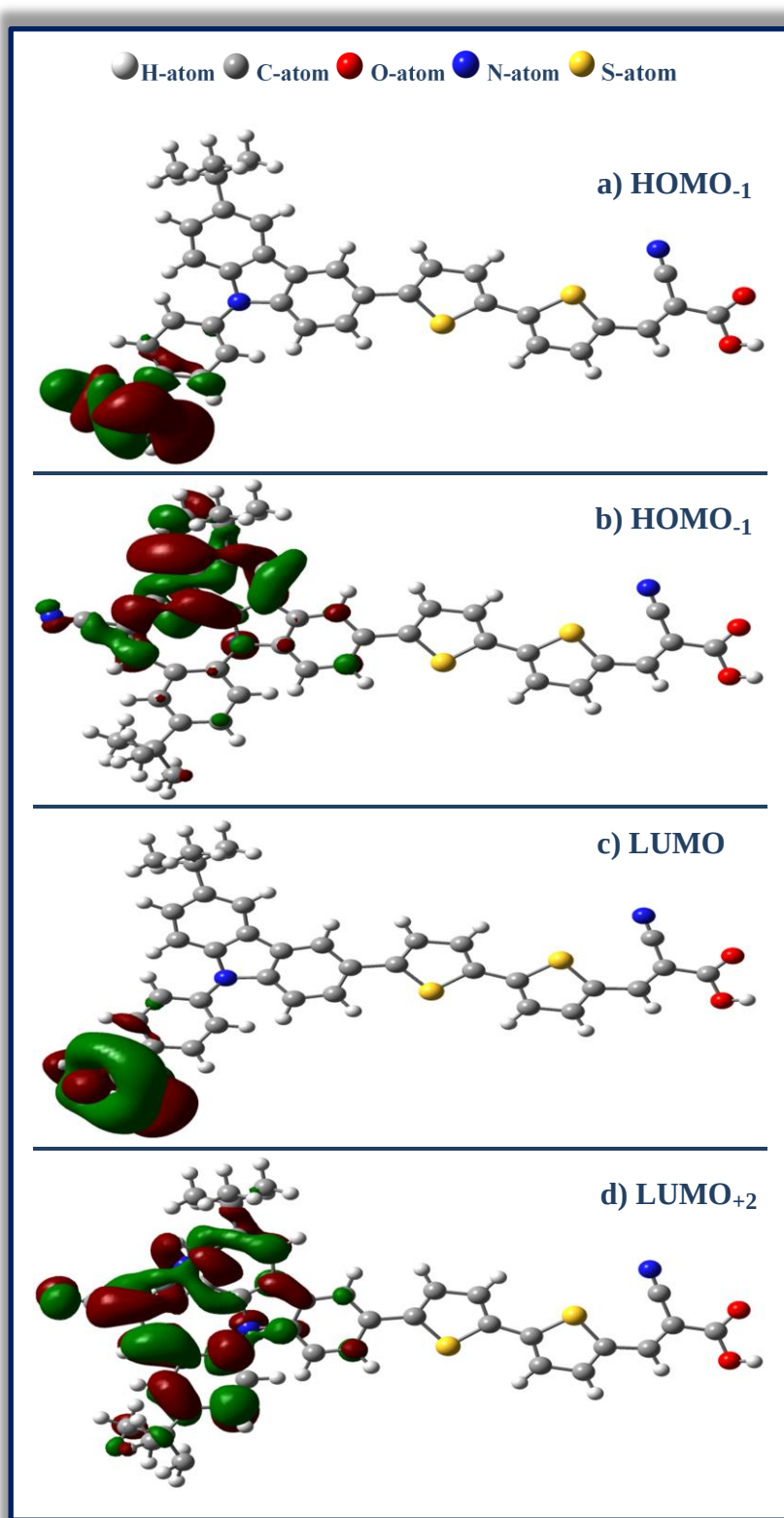


Fig.(3.23): HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH5 .

The numerical data listed in Table (3.6).

Table (3.6): Numerical results of the important electronic properties of dye MH5 before and after improvement.

| <b>Property (unit)</b>                          | <b>Before Addition</b>    | <b>After Addition</b>    |
|-------------------------------------------------|---------------------------|--------------------------|
| <b>H-n ( eV )</b>                               | <b>-5.06</b>              | <b>-4.30</b>             |
| <b>L+n ( eV )</b>                               | <b>-2.81</b>              | <b>-2.12</b>             |
| <b>Eg ( eV )</b>                                | <b>2.25</b>               | <b>2.18</b>              |
| <b>Electronic Transition</b>                    | <b>H-1-&gt;LUMO (84%)</b> | <b>H-1-&gt;L+2 (48%)</b> |
| <b>LT ( eV )</b>                                | <b>1.19</b>               | <b>1.88</b>              |
| <b>HT ( eV )</b>                                | <b>1.06</b>               | <b>0.30</b>              |
| <b>V<sub>oc</sub> ( eV )</b>                    | <b>1.19</b>               | <b>1.88</b>              |
| <b>E<sub>total</sub> ( eV )</b>                 | <b>-68308.20</b>          | <b>-75343.88</b>         |
| <b><math>\lambda_{\text{max}}</math> ( nm )</b> | <b>863</b>                | <b>986</b>               |
| <b>OS ( eV )</b>                                | <b>0.0013</b>             | <b>0.0030</b>            |

As we can see the  $\lambda_{\max}$  has shifted by 119nm with OS 0.0013 to 0.0030 (eV) whereas the absorption from 90 to 170 double of the original absorption.

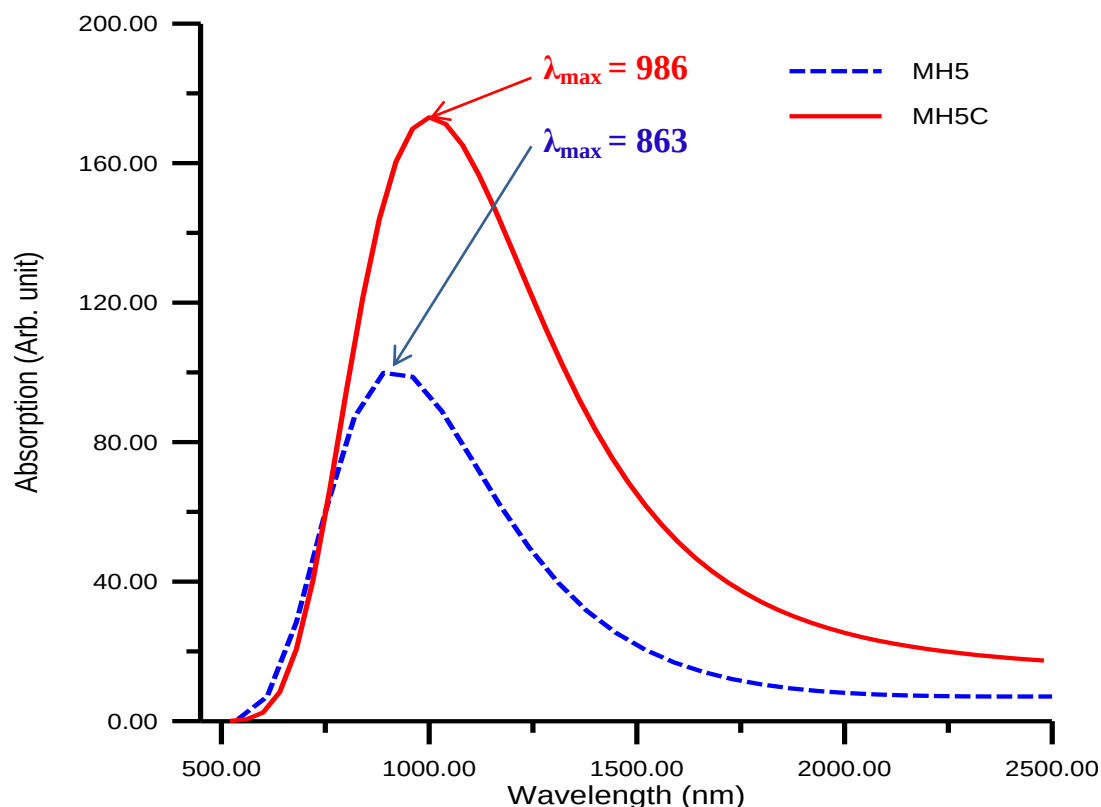


Fig.(3.24): The absorption of dye MH5 before (blue line) and after (red line) addition C .

### 3.3.6 Dye MH6

The famous acceptor is D it can see from Fig.(3.25) since it has 2O atom and 1N atom so the transition of the electron change from HOMO–LUMO to HOMO–LUMO<sub>+2</sub> which has large spatial orbital and this lead to the high OS as can be seen from the Table below.

Table (3.7): Numerical results of the important electronic properties of dye MH6 before and after improvement.

| Property (unit)               | Before Addition  | After Addition  |
|-------------------------------|------------------|-----------------|
| H-n ( eV )                    | -4.18            | -4.36           |
| L+n ( eV )                    | -2.79            | -2.35           |
| Eg ( eV )                     | 1.39             | 2.01            |
| Electronic Transition         | HOMO->LUMO (96%) | HOMO->L+2 (72%) |
| LT ( eV )                     | 1.21             | 1.65            |
| HT ( eV )                     | 0.18             | 0.36            |
| V <sub>oc</sub> ( eV )        | 1.21             | 1.65            |
| E <sub>total</sub> ( eV )     | -42888.35        | -56737.77       |
| $\lambda_{\text{max}}$ ( nm ) | 1392             | 838             |
| OS ( eV )                     | 0.0492           | 0.1865          |

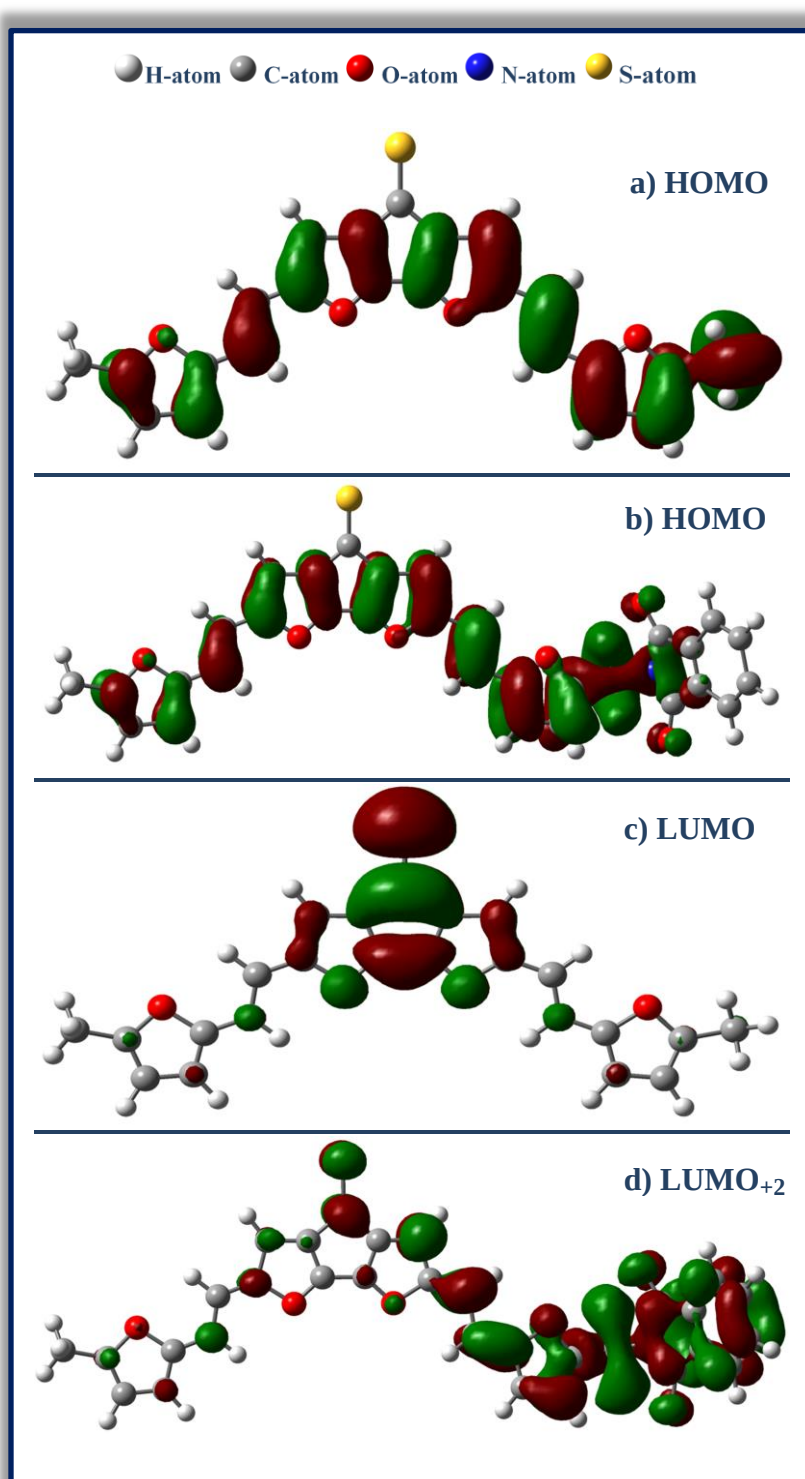


Fig.(3.25): HOMO's and LUMO's before (a,c) and after improvement (b,d) of dye MH6 .

Fig.(3.26) illustrate the increasing of the absorption from 2600 to 8300 . As we can see the  $\lambda_{\max}$  has shifted from 1392 to 838 (nm) with OS 0.0492 to 0.1865 (eV) .

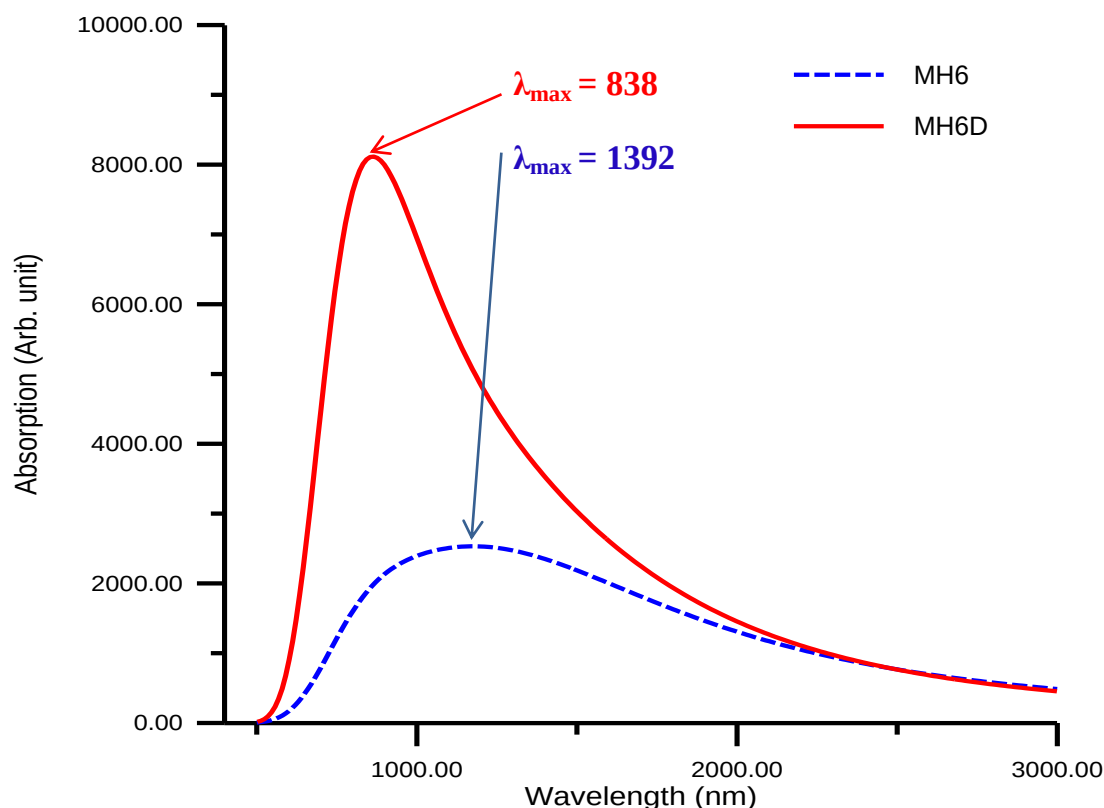


Fig.(3.26): The absorption of dye MH6 before (blue line) and after (red line) addition D .

Outcome data reveals that the absorbency in the same range has three times from 2000 to 8000 .

Finally, we summarized the data in Table (3.8), and the plot in Fig.(3.27) in order to study deeply how the additions type is suitable to get high DSSC<sub>s</sub> performance.

Table (3.8): Outcome results for all dyes under study.

| Dye  | H-n <sup>*</sup><br>(eV) | L+n <sup>*</sup><br>(eV) | $E_g$<br>(eV) | Electronic<br>transition | $E_{total}$<br>(eV) | LT<br>(eV) | HT<br>(eV) | $V_{OC}$<br>(eV) | $\lambda_{max}$<br>(nm) | OS<br>(eV) |
|------|--------------------------|--------------------------|---------------|--------------------------|---------------------|------------|------------|------------------|-------------------------|------------|
| MH1  | -4.53                    | -1.80                    | 2.73          | HOMO->L+1<br>(92%)       | -76903.99           | 2.20       | 0.53       | 2.20             | 498                     | 0.0257     |
| MH1A | -4.45                    | -1.93                    | 2.52          | HOMO->L+2<br>(80%)       | -101808.25          | 2.07       | 0.45       | 2.07             | 573                     | 0.0303     |
| MH2  | -6.41                    | -2.54                    | 3.87          | H-2->LUMO<br>(74%)       | -65923.91           | 1.46       | 2.41       | 1.46             | 367                     | 0.2765     |
| MH2B | -5.98                    | -2.36                    | 3.62          | H-1->LUMO<br>(90%)       | -69999.06           | 1.64       | 1.98       | 1.64             | 382                     | 0.3717     |
| MH3  | -6.09                    | -3.07                    | 3.02          | H-2->LUMO<br>(91%)       | -76532.84           | 0.93       | 2.09       | 0.93             | 424                     | 0.9140     |
| MH3B | -5.98                    | -2.93                    | 3.05          | H-2->LUMO<br>(84%)       | -80603.20           | 1.07       | 1.98       | 1.07             | 424                     | 1.6607     |
| MH4  | -5.76                    | -2.88                    | 2.88          | HOMO->LUMO<br>(99%)      | -67014.13           | 1.12       | 1.76       | 1.12             | 473                     | 1.2225     |
| MH4C | -5.85                    | -3.04                    | 2.81          | HOMO->L+1<br>(98%)       | -74099.68           | 0.96       | 1.85       | 0.96             | 476                     | 1.7194     |
| MH5  | -5.06                    | -2.81                    | 2.25          | H-1->LUMO<br>(84%)       | -68308.20           | 1.19       | 1.06       | 1.19             | 863                     | 0.0013     |
| MH5C | -4.30                    | -2.12                    | 2.18          | H-1->L+2<br>(48%)        | -75343.88           | 1.88       | 0.30       | 1.88             | 986                     | 0.0030     |
| MH6  | -4.18                    | -2.79                    | 1.39          | HOMO->LUMO<br>(96%)      | -42888.35           | 1.21       | 0.18       | 1.21             | 1392                    | 0.0492     |
| MH6D | -4.36                    | -2.35                    | 2.01          | HOMO->L+2<br>(72%)       | -56737.77           | 1.65       | 0.36       | 1.65             | 838                     | 0.1865     |

\* H-n (n = 0,1,2,...)

L+n (n = 0,1,2,...)

n = 0 , refers to basic HOMO and LUMO.

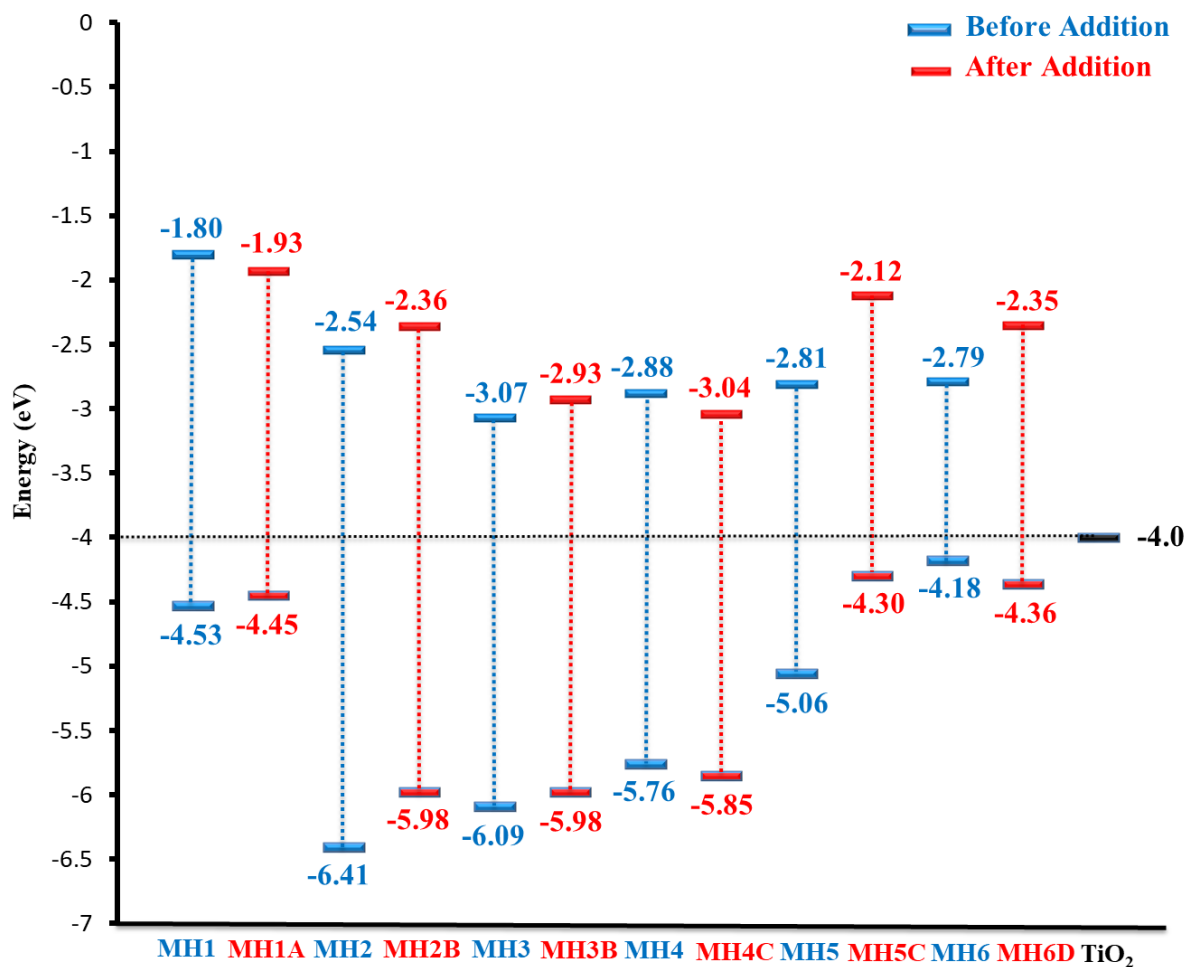


Fig.(3.27): HOMO's and LUMO's of dyes and  $\text{TiO}_2$  (blue-plot before addition, red-plot after addition).

***Chapter Four***

***Conclusions***

***and***

***Future Works***

## Chapter Four

### Conclusions and Future Works

#### 4.1 Conclusions

1. DFT is a good approximation method for sensing performance.
2. Depending on the FH value, the ranking of the sensors are Coronene+Al , Coronene+Cu , Coronene+Ge and pristine Coronene for both TNT and NQ molecules.
3. Al is the best substitutional atom for TNT and NQ detecting.
4. The coronene and its modification are suitable device sensor.
5. The adsorption energies for TNT molecule is in the order: Coronene-TNT < Coronene+Cu-TNT < Coronene+Al-TNT < Coronene+Ge-TNT , and for NQ molecule is: Coronene-NQ < Coronene+Cu-NQ < Coronene+Ge-NQ < Coronene+Al-NQ .
6. Total energy values calculated of coronene-doped are higher compared to those of pristine coronene , this refers to high stable.
7. The density of states shows the probability of the electron transfer crossing the energy gap.
8. A TD-DFT is a good approximation method for DSSC<sub>s</sub> as a performance test.
9. The LUMO of modified dyes still higher than that of TiO<sub>2</sub> with high efficient charge transfer.
10. The terminal additions that have nitrogen reveal to the high efficiency of the DSSC<sub>s</sub> .
11. Presently the addition D was very suitable for rising the absorption to 3 times when compared with original dye.

12. The changing of the transition states after the improvement gives low energy that needs, as comparison with the must original dyes.
13. The total energy increased in all modification dyes after addition, this refers to high stable.

## **4.2 Future Works**

1. Study the circumcoronene as a TNT, NQ sensor with Al, Cu and Ge substitution atom.
2. Study the carbon nanotube sensor with suitable substitution atom for TNT and NQ detecting.
3. Study the effect of another terminal addition with high electronegativity with N, O, and S atoms.
4. Study the absorption of the dyes and the electron transition with DSSC<sub>s</sub> collector charge.

# ***References***

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## الخلاصة :

تلعب المركبات العضوية دورا كبيرا في حياتنا. في هذه الدراسة ، تم استخدام طريقة DFT مع دالية B3LYP ومجموعة الأساس 6-31G لغرض ترشيح متحسس نانوي لمركبين عضويين هما TNT و NQ في حزمة برامج Gaussian09 من خلال معرفة عاملين اساسيين لكل متحسس وهما: المسافة بين الجزيئة العضوية والمتحسس الكرافين ، وكذلك التغير لفجوة الطاقة للمتحسس حيث ستتغير عندها التوصيلية لجهاز التحسس. كما قمنا بتطوير المتحسس الكرافيني عن طريق ذرات تعويضية وهي Al، Cu و Ge ، وظهرت النتائج تحسن في الاداء لوحظ من خلال التغير الحاصل في فجوة الطاقة ، حيث وجدنا أن فجوة الطاقة تتأثر بشدة بجميع الجزيئات العضوية ، وكان عنصر Al الافضل لمتحسس TNT و NQ. وتم كذلك حساب بعض الصفات الإلكترونية مثل توزيع HOMO و LUMO ، طاقة الاضافة ، الطاقة الكلية ، كثافة الحالات ، طيف الأشعة تحت الحمراء وكذلك التحسين الهندسي للجزيئات العضوية والمتحسس. ثم استخدمنا نظرية دالية الكثافة (DFT) و نظرية دالية الكثافة المعتمدة على الزمن (TD-DFT) مع دالية B3LYP ومجموعة الاساس 6-31G لفحص بعض الصبغات العضوية التي تستخدم في الخلايا الشمسية المتحسسة للضوء عن طريق دراسة طيف الاشعة UV-Vis ومعرفة مستويات الطاقة الانتقالية للالكترونات ومدى طيف الامتصاص. وقمنا بتطوير هذه الصفات عن طريق اضافات طرفية لجزيئات عضوية حيث زادت الامتصاصية وقلت طاقة الانتقال في  $DSSC_s$  التي تستخدم  $TiO_2$  كجامع للشحنات. وتم دراسة بعض الصفات الإلكترونية مثل توزيع HOMO و LUMO وفجوة الطاقة وشدة التذبذب والتحسين الهندسي لهذه الصبغات العضوية.



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## دراسة $DFT$ و $TD-DFT$ للجزيئات العضوية: تطبيقات المتحسسات النانوية و صبغات الخلايا الشمسية المتحسسة

رسالة مقدمة الى مجلس كلية العلوم - جامعة ذي قار وهي جزء من متطلبات  
نيل درجة الماجستير في علوم الفيزياء

من قبل

حمود مرداس ياسر

بكالوريوس علوم الفيزياء – جامعة ذي قار ٢٠١٦

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