Abbreviations

Symbol	***Acronyms***
HF	Hartrree-Fock
DFT	Density Functional Theory
SCF	Self Consistent Field
LDA	Local Density Approximation
GGA	Generalized Gradient Approximation
B3LYP	Beck's Three Parameters with Lee-Yang-Parr
STO	Slater Type Orbital
GTO	Gaussian Type Orbital
IR	Infrared
UV	Ultraviolet
Vis	Visible
MO	Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
BW	Band Width
SOMO	Single Occupied Molecular Orbital
IP	Ionization Potential
EA	Electron Affinity
VB	Valence Band
CB	Conduction Band
D	Doner
A	Acceptor
SCLC	Space-Charge-Limited Current
TFL	Trap-Filled-Limited
LWFE	Large Work Function Electrode
SWFE	Small Work Function Electrode
AEDL	Average Exciton Diffusion Length
OPV	Organic Photovoltaic
PVD	Physical Vapor Deposition
AC	Alternating Current
DC	Direct Current
^{1}H-NMR	Proton Nuclear Magnetic Resonance
DMSO	Dimethyle Sulphoxide
FT-IR	Fourier Transform Infrared
XRD	X-ray Diffraction

Abstract

In this thesis our work is classified as follows:

First, a combined experimental and computational study of 2-(2-furanylmethylene) propanedinitrile (FMN). The equilibrium geometries, harmonic vibrational frequencies, thermo-chemical parameters, total dipole moment and HOMO-LUMO energies are calculated by HF utilizing 6-31G and 6-311G basis sets and DFT/B3LYP utilizing 6-31G and 6-31lG basis sets. Results showed that the scaled frequencies are in good agreement with exprementai values.

Also represent the characterization of Au/FMN/Si/Al heterojunction is investigated: dark and illuminated (J-V) characteristics, transport mechanism and reverse bias (J_R-V) characteristics.

Second, a combined experimental and computational study for 2-chloro-5-(2,5-dimethoxy-benzylidene)-1,3-diethyl-dihydro-pyrimidine-4,6(1H,5H)-dione. The molecular structure and vibrational frequencies of the investigated compound are studied. The equilibrium geometries, harmonic vibrational frequencies, thermo-chemical parameters, total dipole moment and HOMO-LUMO energies are calculated by DFT/B3LYP utilizing 6-31G and 6-31lG basis sets.

The optical properties of 2-chloro-5-(2,5-dimethoxy-benzylidene)-1,3-diethyl-dihydro-pyrimidine-4,6(1H,5H)-dione are studied by investigating transmittance (T), reflectance (R), optical constants (n,k), absorption coefficient (α), molar extinction coefficient (ε_{molar}), oscillator strength (f), electric dipole strength (q^2), energy gap (E_g), single oscillator energy (E_0), dispersion energy (E_d) and dielectric constant (ε_L).

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دراسة عملية ونظرية لأغشية رقيقة من ٢-(٢- فيرنيل مثيلين) بروبان ثنائى النيتريل

رسالة مقدمة من

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Theoretical Background and Literature Review

1.1 Theoretical Background

1.1.1 Computational Physics

Computational physics is a sub-discipline of physics that develops and utilizes computer models of physical systems. As computer power has increased over the last half decades, a variety of models have been created to investigate all types of physical questions. Because of the relative expense of materials and analytic equipments compared to computer power, the inherent safety concerns of working with either carcinogenic, explosive, or toxic material, and the absolute control within the computer, computational methods provide a valuable contribution to scientific research.

Any modeling including computational physics has a particular relation-ship with experiment which often produces very specific information like Fourier Transformation Infrared (FT-IR), Fourier Transformation Raman (FT-Raman), Nuclear Magnetic Resonance (NMR), Ultraviolet Visible (UV-Visible) and Mass spectra.

However, these experimental observations do not usually lend themselves to an unambiguous physical interpretation without the aid of models. Computational physics can help to bring the primary experimental data and provides a complete physical picture.

1.1.2 Computational modeling

Computational modeling aims to enhance the communications between experimental research and theoretical work on both existing and new advanced materials and their applications.

Computational modeling simulates molecular structures and reactions numerically, based in full or in part on the fundamental laws of physics. It can provide information about molecules and reactions which is impossible to obtain through observations such as transition states and unstable intermediates [1]. It computes the energy of a particular molecular structure, geometry optimization and computes the vibrational frequencies of molecules [2]. It covers the interest of many researchers and engineers involved with molecular phenomena [3].

Computational methods are dealing with modeling molecules using software package [4]. In recent years, computational methods have been seen in rapid growth. The continuous improvements in computational methods software have allowed researchers to different theories of molecular systems[5]. Molecular modeling consists of two branches namely: molecular mechanics and electronic structure method[6].

i. Molecular Mechanics

It applies the laws of classical physics to predict the structures and the properties of the molecules. In addition, it performs computations based upon the interaction among nuclei. Electronic effects are approximated, this makes the computations quite inexpensive and used for very large systems [4].

ii. Electronic Structure Method

Electronic structure method is based on the bases of Schrödinger wave equation. But practically the exact solution of Schrödinger equation is not enough so that, it has several approximations to its solution [4]. According to this concept it has the following classes:

a. Semi-Empirical Method

Semi-Empirical Methods use parameters that are derived from experimental data to simplify the computations. This class is inexpensive and provides researchers with reasonable qualitative descriptions of the molecular systems. Moreover, it provides fairly accurate quantitative predictions of energies and structures for systems where good parameters sets are chosen [4].

b. ab Initio Method

ab initio method is based only on quantum mechanics. It provides high quality quantitative predictions for a broad range of systems [4]. Such as Hartree-Fock theory (HF) which is the least expensive ab initio method as well as Density Functional Theory (DFT) which become a popular class of electronic structure methods [7]. DFT method is accurate and attracts many researchers because it includes the effect of electron correlation in their models [8]. It is concerned with modeling the properties of atomic and molecular systems such as energies, structures and vibrational spectra. Inter-atomic bond distances and bond angles can be predicted using DFT to within 0.05 Å and 2 degrees, respectively. Bond energies are estimated accurately to within 5 kcal/mol [9].

1.1.3 Many-Body Problem

The many-body problem may be defined as the study of the effects of interaction between bodies on the behavior of many-body system. The non-relativistic time-independent Schrödinger equation for a system consist of electrons and nuclei is,

$$\mathrm{H}\Psi = \mathrm{E}\Psi \tag{1.1}$$

where H, Ψ and E are Hamiltonian operator for a system of nuclei, the many-particle wavefunction and the total energy of the system, respectively.

i. Hartree Method

Since each electron in a solid is dictated by the behavior of all the other electrons in the solid, the motion of any one electron is strongly coupled to the motion of the other electrons in the system. So, the Born-Oppenheimer approximation is not acceptable. Solving Schrödinger equation for all these electrons requires us to solve a system of around 10^{23} differential equations and such a calculation is beyond the capabilities of present-day computers.

Hartree simplified the problem by assuming that the many-electron wavefunction was just the product of a set of single-electron wavefunctions. In a uniform system these wavefunctions would take the form of simple plane waves. By making this assumption, it was possible to proceed using the variational principle Hartree found that the Hamiltonian equation of the many-electron system which contain *N* electrons is the product of N equations, one for each of the *N* single electron wavefunction. These equations turned out to look very much like the time independent Schrödinger equation. This means that it was possible to treat each electron separately as a single particle. While the potential is no longer coupled to the individual motions of all the other electrons, because of the initial assumption of a product wavefunction. Since some particles as fermions has antisymmetric wavefunction while Hartree assume a symmetric wavefunction.

ii. Fock Method

V.A. Fock [10] pointed out that the Hartree method did not respect the principle of antisymmetry of the wavefunction. The Hartree method used the Pauli exclusion principle in its older formulation, forbidding the presence of two electrons in the same quantum state. However, this was shown to be fundamentally incomplete in its neglect of quantum statistics.

iii. Hartree-Fock Method

The Hartree-Fock method is an improvement over the Hartree and Fock theories in which it treated the many-electron wavefunction as a single-electron wavefunctions (Hartree method) in such a way as to be antisymmetric for fermions and as single permanent for bosons (Fock method). Starting from this assumption it is once again possible to derive the Hamiltonian equation for the system through the variational principle, while in this assumption there are two types of potentials influencing the electrons which are Hartree potential and exchange potential. Where Hartree potential describes the direct Coloumb interaction between an electron and the average electron distribution and exchange potential is a direct consequence of including the Pauli exclusion principle through the use of antisymmetried wavefunction.

The Hartree-Fock method neglected the electron correlation which can lead to large deviations from experiment results than the Hartree method, because in Hartree approach the exchange effect cancels out the electron correlation effect while Hartree-Fock approach includes the exchange effects and ignores the correlation effects. So, Hartree-Fock approach fails for solids while gives quite creditable results for small molecules. This is because there are fewer electrons involved than in a solid and so correlation effects are minimal compared to exchange effects.

iv. Density Functional Theory

Density Functional Theory (DFT) was introduced by Hohenberg and Kohn [11] (1964), then by Kohn and Sham [12] (1965). DFT method has one solution to reduce the computational time and to allow studying system with a large number of atoms, compared to post-HF methods. The relation between the external potential and the ground state electron density in DFT is one to one, i.e. Ψ is a unique functional of n. The DFT is described by the charge density which is only dependent on three special and one spin variables (these variables are repeated for every electron in the HF method). Hence, the Schrödinger equation can be solved as a function of n, i.e. the true electron density is the value that gives the ground state energy.

In DFT, the total energy ($E[\rho]$) consists of five terms, the kinetic energy of electrons($T[\rho]$), the Coulomb energy due to electron-ion interaction ($E_{e-ion}[\rho]$), ion-ion interaction($E_{ion-ion}[\rho]$), the Hartree energy($E_H[\rho]$), and the exchange-correlation energy($E_{xc}[\rho]$). The total energy is a function of the charge density,

$$E[\rho] = T[\rho] + E_{e-ion}[\rho] + E_{ion-ion}[\rho] + E_H[\rho] + E_{xc}[\rho] \qquad (1.2)$$

where

$$E_{e-ion}[\rho] = -\int \rho(r) \sum_{\alpha} \frac{Z_\alpha}{|r - R_\alpha|} dr \qquad (1.3)$$

$$E_{ion-ion}[\rho] = \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|} \qquad (1.4)$$

$$E_H[\rho] = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 \qquad (1.5)$$

To express the kinetic energy term, T[ρ], Kohn and Sham introduced a set of orthonormal orbitals as basis for the charge density,

$$\rho(r) = \sum_{i=1}^{N} |\Psi_i(r)|^2 \qquad (1.6)$$

Using equation (1.4), the kinetic energy can be written as:

$$T[\rho] = -\frac{1}{2} \sum_{i} \Psi_i^*(r) \nabla^2 \Psi_i(r) dr \qquad (1.7)$$

The exchange-correlation is the electron-electron interaction term that is not included in the one-particle equation. The Kohn-Sham equation can be solved in a self-consistent way, by guessing an initial charge density. Then, the Coulomb and $E_{xc}[\rho]$ are obtained and used afterward to solve the Kohn-Sham equation to obtain the new charge density and so on until the charge density is converged. The exact exchange-correlation energy is still unknown, and the Kohn-Sham equation is a subject for a better approximation to the exchange-correlation energy. In the early years, the most often approximation used for the exchange-correlation energy was the Local Density Approximation (LDA).

v. The Local Density Approximation (LDA)

The exchange-correlation energy consists of two terms,

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \tag{1.8}$$

where $E_x[\rho]$ and $E_c[\rho]$ are the exchange and correlation energies, respectively. In DFT within LDA, ε_{xc} at a point r in inhomogeneous electron density is replaced by ε_{xc} for a homogeneous electron gas of the same density, $\varepsilon_{xc}^{hom}(\rho(r))$.

$$E_{xc}^{LDA}[\rho(r)] = \int \rho(r)\, \varepsilon_{xc}^{hom}(\rho(r))dr \tag{1.9}$$

$\varepsilon_{xc}^{hom}(\rho(r))$ is divided into two terms (exchange and correlation),

$$\varepsilon_{xc}^{hom}(\rho(r)) = \varepsilon_{x}^{hom}(\rho(r)) + \varepsilon_{c}^{hom}(\rho(r)) \tag{1.10}$$

The exchange energy at a point r can be calculated via an analytic Hartree-Fock treatment of the uniform electron gas,