I.INTRODUCTION:

I.1: The Importance of pyridine and its Derivatives:

Pyridine is among the most important nitrogen-containing heterocyclic compound with chemical formula C5H5N. It has a weak base characteristic and it's structure consists of an unsaturated hexagonal ring containing a nitrogen atom, [1,2]. Generally, pyridine is used in many industries such as pharmaceutical, agrochemicals, pesticide, rubber and adhesives; pyridine in the preparation of pyridine cetyl chloride and peridenium lauryl chloride, which are used as sterilizers in oral and dental care used and is also an important solvent and reagent. In addition to that, it is used invitro to synthesis of DNA[3] , in the synthesis of sulfapyridine (a drug against bacterial and viral infections), antihistaminic drugs tripelennamine and mepyramine, as well as water repellents, bactericides, and herbicides[2,4-6], antibacterial [7], anti-Malarial agents [8] and antitumuors[9,10]. Pyridine derivatives have been used in charge transfer complex formation with σ and π acceptors [11, 12].

Hydroxypyridines compounds are of special interest since they can function as n- and π-donors, and studying of their CT interactions can help to explain many chemical and biological phenomena, which they take part. They have various applications in medical and pharmacological filed, in addition to their use in analytical chemistry

The chemical structure of the 3-hydroxypyridine (3HP) and 4-hydroxypyridine(4HP) are given in Fig. 1.
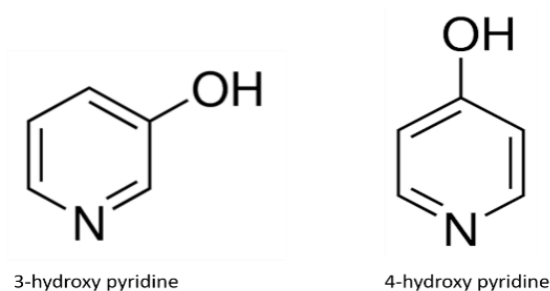

Fig.I.1: Chemical structure of 3-hydroxypyridine and 4-hydroxypyridine

3HP and 4HP have many derivatives that are widely used in medical drug fields and have a great important for uses in antibacterial and antifungal activities against a variety of microorganisms[7,13,14]. In fact, 3HP derivatives are structural analogs of pyridoxine (vitamin B6) compounds, which are important in the metabolism of man and animals thus it have interesting in chemical and pharmacological applications. One of the most effective drugs belonging to this group is ethyl methyl hydroxyl pyridine succinate (mexidol, mexi- cor), which is used in neurology for acute and chronic brain circulatory insufficiency[15], and its derivatives are used as an active antioxidant in many fields like food and pharmaceuticals[16]. 4HP and its derivatives show up optical, chemical properties and antimalarial activity [1,8]. The present investigation report the study of formation CT complexes between possible π- and n-donors (3HP & 4HP) with σ-(Iodine) (I_2) and π- (2,3-dichloro-5,6-dicyano-p-benzoquinone)(DDQ) acceptors.

Compounds that contain bond between an electron donor-electron acceptor is called Charge transfer (CT) complexes which formed through intermolecular electronic charge-transfer transition which accompanied by hydrogen transfer or electron transfer between donor and acceptor. Weak bonds formed between donor and acceptor by Charge transfer interaction. The formation of CT complexes between π- and n-donors with σ- and π-acceptors has been investigated[12,17-21].

I.2 : Literature Review

Mulliken is one of the most important scientists Who worked to explain the intermolecular charge-transfer (CT), where he pointed out that the bond between the components of the complex being postulated to arise from the partial transfer of these electrons from the base (D) to orbitals of the acid (A) (Lewis acid–Lewis base interaction). The donor molecule is an electron-rich aromatic compound, (a molecular with an unshared pair of electrons). The acceptor is an electron deficient molecule, (a proton, a Lewis acid, a halogen, an electron-poor aromatic ring or a transition metal ion)[22,23].

A new absorption band of a D–A complex appears in the the UV or visible part of the spectrum at a longer wavelength than any of the component spectra and are known as CT bands , commonly attributed to an intermolecular CT transition, involving electron transfer from the donor to the acceptor[23].

Charge transfer complexes have been gaining importance due to their individual physio-chemical properties and varied range of appliacation such as optical materials, drug-receptor interaction mechanism, uses in solar energy, surface chemistry and play a role in biological systems[18-20,24]. During the last decade, the drug-acceptor interaction in solid state and in solution have captuerd the attention of many studies due to is cheaper, simpler, and more efficient than the methods of drug determination[21,25]. Also, the study of this type of complexes is important in understanding the drug–receptor interactions and the mechanism of drug action[14,20,26]. These CT complexes show potential antimicrobial properties against Gram-positiveand Gram-negative bacteria as well as fungi[21].

Considerable work has gone into trying to understand the phenomena of charge transfer complexes [27-33] using several spectroscopic techniques and thermal analysis [34-36]. The experimental results obtained were discussed and interpreted with aid of theoretical calculations [36]. The steady advances in computer technologies along with the improvement of computational techniques enabled us to model and to simulate large systems. Nevertheless, it stills a key challenge. Nasrin and Badiadka developed a simple and accurate spectrophotometric method for the analysis of clotrimazole (CLZ) in pure drug and its pharmaceutical products. They found a linear relationships (R=0.9985 – 0.9995) between the absorbance and the concentrations of CLZ for the CLZ-TCE and

CLZ-TCNQ charge transfer complexes [37]. Biswajit Roy et al. used the density functional theory (DFT) to study the ground state of the (1:1) and (1:2) charge transfer complex formed between zinc tetraphenylporphyrin and a set of four aromatic solvents. The association constants have been determined for the ground state charge transfer complex by Benesi–Hildebrand method [38].

Animesh and Bula studied formation of 1:1 synthesized charge transfer (CT) complex between 1-(2-Thiazolylazo)-2-naphthol (TAN) and aromatic nitro compounds by the different spectroscopic technique such as FT-IR, 1H NMR, UV–visible spectroscopy, in addition to elemental analysis. The results obtained experimentally have been analyzed with aid of DFT/B3LYP quantum chemical calculations [39]. Tetra methyl ethyl enediamine (TMEDA) formed a series of charge transfer molecular adducts with σ, π, and vacant orbital acceptors. These adducts were characterized by spectroscopic methods, elemental and thermal analysis. In addition to that, the electrical and biological activity properties of the obtained adducts have been studied and the results have been discussed [40].

Marwa et al. developed spectrophotometric method for determination of fenoprofen calcium drug (FPC) based on the charge transfer (CT) as n-electron donor with (Quinalizarin, QZ) (as π-acceptor) to give highly colored charge transfer complexes [41]. Natália et al. studied the charge transfer complexes formed between N,N-dimethylaniline and N,N-diethylaniline with SO2. Moreover,

the thermochromism property for the solution of these CT complexes was studied using resonance Raman spectroscopy technique. TDDFT quantum calculations have been used to aid in the interpretation of the obtained results [42].

The hydrogen bonded complex formed between amino quinoline (4AQ) as an electron donor chlornilic acid (CLA) as a π acceptor in different solvents was studies by Khairia M. Al-Ahmary et al. [36]. The stoichiometery of the formed adduct has been obtained by job's method. The solid adducts obtained have characterized using elemental analysis as spectroscopic techniques. The results have been explained with aid of quantum chemical calculation using DFT /B3LYP and TDDFT level of theory[36].

The effect of increasing the pressure of oxygen on poly(3-hexylthiophene) shows that the formation of charge transfer complexes between these two species leads to the alteration of some properties such as conductivity (increases), and the charge carrier mobility (lowered) [43]. A series of quinolone derivatives possessing antibacterial activity was determined spectrophotometrically through charge transfer complex formation with TCNQ, DDQ and Chloranilic acid (CL) as π acceptors. The results for Statistical analysis shows no significance between the methods proposed in this study compared to the other official methods [44]. The application of charge transfer interactions in the field of electronic devices with special emphasizes to the light emitting devices in addition to the

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photovoltaic cells has been studied by X. Ji et al. [45]. One of the most electron acceptors that give rise to spectacular CT-complexes with variety of donors are Quinones due to thier importance in biological reactions[12]. Quinones are used in oxidative phosphorilation, photosynthesis, sensi- tised oxidations and involved in processes of energy storage and utilization[13,46-48].

Iodine molecule is a σ electron acceptor from n-donors and has biological significance [3]. Iodine and iodine derivatives are used in a wide range of medical, agricultural, and industrial applications and in the industry of polarizing film in liquid crystal display (LCD) screens, also used during nuclear accidents to protect the thyroid gland against exposure to radioactive. [49-52]. Thus, the mechanism of interaction of these biologically important acceptors is a research topic of significant interest [3]. For this, number of studies were focused on charge transfer complexes with different donors [22, 24,30] .

Likewise DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) is derivative of Quinones commonly known as electron acceptors used in chemical synthesis [13]. Its charge-transfer complexes have been the subjects of an extensive study [13,48]. one of the most important applications of DDQ is that used to determination of caroverine [53]. It has several major functions include the deprotection of thioacetals, acetals and ketals and conversion to aldehydes and ketones, and the deprotection of benzyl, mediated carbon-carbon bond formation for the synthesis

of quinolines from imines and alkynes or alkenes, dehydrogenation of hydroaromatic compounds.[54-56]

The effects of solvent was studied on the spectroscopic and thermodynamic properties of the charge transfer (CT) complexes of different electron acceptors[46,57].   The results showed that the solvent plays an important role by changing both the thermodynamic and spectrophotometric properties of these molecular complexes. These studies pointed out the solvents to compete as electron donors[23,58-60]. Several charge transfer studies on pyridine derivatives were conducted including experimental and theoretical studies [11, 61-65].

Several High level quantum chemical studies have been conducted by several authors and found to provide an excellent prediction for investigating non-covalent interactions[8,10,11,13,66-69,77].

The density functional theory (DFT) was found to be an effective tool in the study of the association between structures and spectral properties [36, 78, 79]. Moreover, the time-dependent density functional theory (TD-DFT) has been used to calculate the electronic absorption spectra and spectroscopic properties of charge transfer and hydrogen bonded complexes [80, 81]. Recently, a combination of DFT calculations and different spectroscopic techniques performed on CT complexes has been reported in the literature [72, 82].

Based on the importance of describing the mechanism of the charge transfer complexes under investigation, we here introduce a detailed spectrophotometric study of the charge transfer complexation between 3HP and 4HP as electron donors with DDQ and I_2 as electron acceptors in different solvents (chloroform, acetonitrile, ethanol, methanol). The electronic spectra included the observation of the CT bands, the relevant stoichiometric ratios for the reactions, and the formation constants of the formed complexes were investigated. This also allowed us to study the stability of the CT complexes by measuring spectroscopic physical parameters like transition energy, resonance energy, free energy change, dissociation energy, and ionization potential. In order to provide support to the experimental results, density functional theory (DFT) and time dependent functional theory (TD-DFT) methods were applied using the B3LYP/6-311+ (d,p) basis sets. The optimized structures of the donor, acceptor, and CT complexes were calculated and analyzed. In addition, geometrical parameters were computed and are presented here. The origin of the electronic spectra will be explained through TD-DFT analysis, considering the effect of the solvent using the polarizable continuum model (CPCM).

I.3:The Aim of the work

Chemical reactivity of compounds such as 3-hydroxypyridine and 4-hydroxypyridine molecules could be discussed and interpreted only based on their

accurate structural data, electronic structure, and their molecular forces. The determination of the structural parameters of the preferred conformation and investigation of their electronic structure represent an important task needed to get more understanding about their mode of biochemical action. Such investigations considered an essential step in the projects of designing new derivatives acting as new active derivatives of possible optical and biological activity. Also the accurate geometrical data are very important input in the normal coordinate calculations to investigate quantitatively the fundamental normal vibrations and the determination of the molecular force field of these molecules as well as their derivatives. Literature survey on experimental and theoretical studies carried out on these compounds showed that there is a lack in the experimental as well as on the theoretical systematic study of their geometry as well as their electronic structure.

These classes of compounds are generally electron donors in nature and the formation of charge transfer complexes with electron acceptors represent an important biochemical step in many of the biochemical processes in solutions of these compounds. Quantitative investigation of the formed charge transfer complexes with different acceptors and their expected geometry will shed strong light on the biochemical behavior and stability of these species in solution.

The Objectives of the work covered in this thesis are:

1- Determination of the preference ground state molecular geometry of 3-hydroxypyridine and 4-hydroxypyridine using different theoretical quantum mechanical levels of computations in gas phase and in different solvents and comparing the results with the available reported experimental data for these compounds.

2- Investigating the ground state geometry of the acceptors used in this study including I_2 and DDQ in gas phase and in different solvents. In addition to that, the electron accepting nature of these molecules will be discussed.

3- Investigating the charge transfer complexes formed between 3-hydroxypyridine and 4-hydroxypyridine as donors and Iodine molecule (I_2) as σ-acceptor and with DDQ as π-acceptor, and determining the preference geometrical structure of these complexes using spectrophotometric studies in addition to theoretical studies.
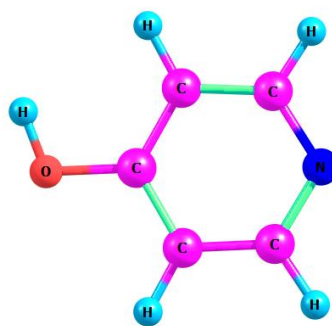
Representation of the different donor compounds and acceptor compounds , which are the subject of our investigation in this work, is given in Fig. I.2.

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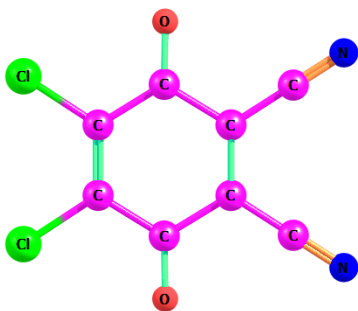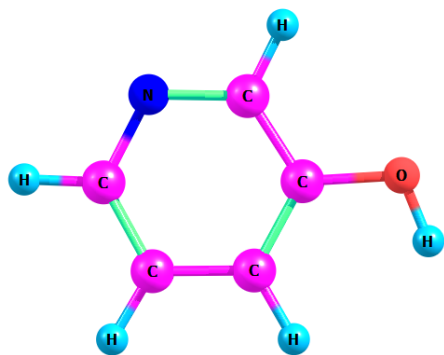
Fig. I.2 : Molecular representation of: (A)3-hydroxypyridine(3HP) ,
(B)4-hydroxypyridine(4HP) and (C) 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ).

I.4 : Theoretical Background

I.4.1: Molecular Orbital Calculations

I.4.1.1: Hartee-Fock MO-Methods: The basic equation in molecular orbital calculations is the time independent Schrödinger equation [83].

$$H \ \psi(q_i,q_\alpha) = E \ \psi(q_i,q_\alpha) \qquad\qquad (1)$$

H is the Hamiltonian which is a differential operator representing the total energy, E is the value of the energy of the state, and $\psi(q_i ,q_\alpha)$ is the wave function which depends on both the spatial as well as the spin coordinates of all particles forming the molecular system.

The Hartee-Fock method is the most common type of calculation (abbreviated HF.In this method the primary approximation is called the central field approximation. This means that the Coulombic electron-electron repulsion is not specifically taken into account. However, its net effect is included in the calculation for closed shell configurations; the molecular HF-wavefunction is expressed as a full antisymmetrized determinant of spin – orbitals (Slater Determinant). Each spin-orbital is the product of the spatial orbital and the spin function (α- or β- function). Within the Born-Oppenheimer approximation (separation of the electronic and nuclear motions) [84] the expression for Hartee-Fock molecular energy E_{HF} is given by the variation theorem[85].

$$E_{HF} = \left(D \left| \hat{H}_{el} + V_{NN} \right| D \right) \tag{2}$$

D is the normalized Slater-determinant Hartree-Fock wave function,

$$E_{HF} = (D|H_{el}|D) + V_{NN}(D/D) \tag{3}$$

V_{NN} is the potential energy due to nuclear repulsion and does not involve electronic coordinates. $\hat{H}_{el}$ is the sum of one-electron operators $\hat{F}_{el}$ and two-electron operators $\hat{g}_{ij}$

$$\hat{H}_{el} = \sum_i \hat{F}_i + \sum_j \sum_{I>j} \hat{g}_{ij} \tag{4}$$

$$\hat{F}_i = -\frac{1}{2}\nabla_i^2 - \sum_a \frac{Z_a}{r_{ia}} \tag{5}$$

$$\hat{g}_{ij} = \frac{1}{r_{ij}} \tag{6}$$

The Hartree-Fock energy of a molecule is

$$E_{HF} = 2\sum_{i=1}^{n/2} H_{ii}^{core} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{NN} \tag{7}$$

$$H_n^{core} \equiv \left(\Phi_i(1) \left| \hat{H}_{(1)}^{core} \right| \Phi_i(1) \right) = \left(\Phi_i(1) \left| -\frac{1}{2}\nabla_1^2 - \sum_u \frac{Z_a}{r_{1a}} \right| \Phi_i(1) \right) \tag{8}$$

$$J_{ij} = \left(\Phi_i(1)\Phi_j(2) \left| \frac{1}{\mathbf{r}_{12}} \right| \Phi_i(1)\Phi_j(2) \right) \tag{9}$$

$$K_{ij} = \left(\Phi_i(1)\Phi_j(2) \left| \frac{1}{r_{12}} \right| \Phi_j(1)\Phi_i(2) \right) \tag{10}$$

where J_{ij} is the coulomb integral and K_{ij} is the exchange integral. The one electron-operator symbol was changed from F_i to $\hat{H}_{(1)}^{core}$. The one-electron core Hamiltonian $\hat{H}_{(1)}^{core}$ omits interaction electron i with other electrons. The sums over i and j are

over the n/2 occupied spatial orbitals Φ_i of the n-electron molecule, each is normalized

$$(\Phi_i(1)|\Phi_i(1)) = 1$$
$$(\Phi_i(1)|\Phi_j(1)) = 0 \qquad \text{for } i \neq j \text{ (orthogonal)}$$

The closed shell orthogonal Hartree-Fock MOs satisfy

$$F(1)\Phi_i(1) = \varepsilon_i\Phi_i(1) \tag{11}$$

Where ε_i is the orbital energy and $\hat{F}$ is the Hartree-fock-operator

$$\hat{F}(1) = \hat{H}^{core}_{(1)} + \sum_{j=1}^{\frac{n}{2}}[2\hat{J}_j(1) - \hat{K}_j(1)] \tag{12}$$

and as given before :

$$\hat{H}^{core}_{(1)} = -\frac{1}{2}V_1^2 - \sum_\alpha \frac{Z_\alpha}{r_{1\alpha}} \tag{13}$$

where, in equation (13), the first term on the right is one electron kinetic energy operator and the second term is the potential energy operators for the attraction between one-electron and the nuclei.

$\hat{J}_j$ (1) is the potential energy of interaction between electron 1 and a smeared-out electron with electronic density $|\Phi_j(2)|^2$; the factor 2 occurs in equation (12), because there are two electrons in each spatial orbital. To obtain the expression for the orbital energies ε_i one multiplies equation (11) by $\Phi_i^*(1)$ and integrate over all space (using the fact that Φ_i is normalized).

$$\varepsilon_i = \int \Phi_i^*(1)\hat{F}(1)\Phi i(1)dv_1 \tag{14}$$

$$\varepsilon_i = \left(\Phi_i(1)\middle|\hat{H}_{(1)}^{core}\middle|\Phi_i(1)\right)$$

$$+ \sum_j \left[2\left(\Phi_i(1)\middle|\hat{J}_j(1)\middle|\Phi_i(1)\right) - \left(\Phi_i(1)\middle|\hat{K}_j(1)\middle|\Phi_i(1)\right)\right]$$

$$\varepsilon_i = \hat{H}_{ii}^{core} + \sum_{j=1}^{\frac{n}{2}}(2J_{ij} - K_{ij}) \tag{15}$$

summation, equation (15), over the n/2 occupied orbitals gives

$$\sum_{i=1}^{\frac{n}{2}}\varepsilon_i = \sum_{i=1}^{\frac{n}{2}}H_{ii}^{core} + \sum_{i=1}^{n/2}\sum_{j=1}^{n/2}(2J_{ij} - K_{ij})$$

Substituting in equation (7)

$$E_{HF} = 2\sum_{i=1}^{\frac{n}{2}}\varepsilon_i - \sum_{i=1}^{\frac{n}{2}}\sum_{j=1}^{\frac{n}{2}}(2J_{ij} - K_{ij}) + V_{NN} \tag{16}$$

Since there are two electrons per MO, the quantity $2\sum_{i=1}^{\frac{n}{2}}\varepsilon_i$ is the sum of orbital

energies.

For accurate SCF wave functions Roothaan[86]proposed to expand the

spatial orbitals Φ_i as linear combination of a set of one electron basis functions χ_s:

$$\Phi = \sum_{s=1}^{b}C_{si}\chi_s \tag{17}$$

(to avoid confusion one uses the letters r, s, t and u to label the basis functions χ;

and letters i, j, k, and ℓ to label the MOs). Substituting equation (17) into equation

(15) gives

$$\sum_s C_{si}\hat{F}\chi_s = \varepsilon_i\sum_s C_{si}\chi_s \tag{18}$$

Multiplication by χ_r^* and integration gives

$$\sum_{s=1}^{b}C_{si}(F_{rs} - \varepsilon_i S_{rs}) = 0 \qquad r = 1,2,\dots,b \tag{19}$$

$$F_{rs} \equiv (\chi_r|F|\chi_s) \qquad\qquad S_{rs} \equiv (\chi_r|\chi_s)$$

$$\det(F_{rs} - \varepsilon_i S_{rs}) = 0 \tag{20}$$

The last equation is called a secular determinant where the roots give the orbital

energies ε_i , and equation (19) is solved by an iterative procedure while the

expression of F_{rs} is given by

$$F_{rs} = H_{rs}^{core} + \sum_{t=1}^{b} \ \sum_{u=1}^{b} \ \sum_{j=1}^{n/2} \ C_{tj}^* C_{uj}[2(rs/tu) - (ru/ts)] \tag{21}$$

The two-electron repulsion integral is defined as

$$(rs/tu) = \int\int \chi_r^*(1)\chi_t^*(2)\left|\frac{e^2}{r_{12}}\right|\chi_s(1)\chi_u(2)dv_1 dv_2$$

Hence

$$F_{rs} = H_{rs}^{core} + \sum_{t=1}^{b}\sum_{u=1}^{b} \ P_{tu}\left[(rs\backslash tu) - \frac{1}{2}(ru\backslash ts)\right]$$

$$P_{tu} = 2\sum_{j=1}^{\frac{n}{2}} \ C_{tj}^* C_{uj} \qquad\qquad t = 1,2,\ldots,b \qquad\qquad u = 1,2,\ldots,b$$

the P_{tu} is an element of electron density matrix (charge density bond order matrix).

The electron probability density ρ is given by

$$\rho(x, y, z) = \sum_j \ n_j \Phi_j^* \Phi_j \tag{22}$$

The sum is over different orthogonal spatial MO_s and n_j is the number of electrons

in the MO Φ_j for closed shell molecule :

$$\rho = 2\sum_{j=1}^{\frac{n}{2}} \ \Phi_j^* \Phi_j = 2\sum_{r=1}^{b}\sum_{s=1}^{b}\sum_{j=1}^{\frac{n}{2}} \ C_{rj}^* C_{sj}\chi_r^*\chi_s \tag{23}$$

$$\rho = \sum_{r=1}^{b}\sum_{s=1}^{b} \ P_{rs}\chi_r^*\chi_s$$

To express the Hartree-Fock energy in terms of integral over the basis functions χ,

one writes

$$E_{HF} = \sum_{i=1}^{n/2} \varepsilon_i + \sum_{i=1}^{n/2} H_{ii}^{core} + V_{NN}$$

$$H_{ii}^{core} = (\Phi_i|H^{core}|\Phi_i) = \sum_r \sum_s C_{ri}^* C_{si}(\chi_r|H^{core}|\chi_s) = \sum_r \sum_s C_{ri}^* C_{si} H_{rs}^{core}$$

$$E_{HF} = \sum_{i=1}^{\frac{n}{2}} \varepsilon_i + \sum_r \sum_s \sum_{i=1}^{\frac{n}{2}} C_{ri}^* C_{si} H_{rs}^{core} + V_{NN}$$

$$E_{HF} = \sum_{i=1}^{\frac{n}{2}} \varepsilon_i + \frac{1}{2}\sum_{r=1}^{b} \sum_{s=1}^{b} P_{rs} H_{rs}^{core} + V_{NN} \qquad (24)$$

Where ε_i are orbitals energies. The nuclear repulsion term V_{NN} is given by

$$V_{NN} = \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}}$$

$r_{\alpha\beta}$ is the internuclear distance.

Because of the central field approximation, the energies from HF calculations are always greater than the exact energy and tend to a limiting value called the HartreeFock limit. The wave function in HF calculations must be described by some functional form, which is only known exactly for few one electron systems. The functions used most often are linear combinations of Slater type orbitals exp (-ax) or Gaussian type orbitals exp (-ax²), abbreviated STO and GTO respectively. The wave function is formed from linear combinations of atomic orbitals or more often from linear combinations of basis functions. Because of this approximation, most HF calculations give a computed energy greater than the HartreeFock limit.

A number of types of calculations begin with a HF calculation then correct for the explicit electron-electron repulsion, referred to as correlation. Some of these

methods are Mohlar-Plesset perturbation theory (MPn, where n is the order of correction), the Generalized Valence Bond (GVB) method, Multi-Configurations Self Consistent Field (MCSCF), Configuration Interaction (CI) and Coupled Cluster theory (CC). As a group, these methods are referred to as correlated calculations.

I.4.1.2: Ab-initio Method: The term "ab-initio" is Latin for "from the beginning". This name is given to computations which are derived directly from theoretical principles, with no inclusion of experimental data. Most of the time is referring to an approximate quantum mechanical calculation. The approximations made are usually mathematical approximations, such as using a simpler functional form for a function or getting an approximate solution to a differential equation.

The most common type of ab-initio calculation is called a HartreeFock calculation (abbreviated HF), in which the primary approximation is called the central field approximation. This means that the Coulombic electron-electron repulsion is not specifically taken into account. However, its net effect is included in the calculation. This is a variational calculation, meaning that the approximate energies calculated are all equal to or greater than the exact energy. The energies calculated are usually in units called Hartree (1 H = 27.2114 eV). Because of the central field approximation, the energies from HF calculations are always greater than the exact energy and tend to a limiting value called the HartreeFock limit.

The good side of ab-initio methods is that they eventually converge to the exact solution, once all of the approximations are made sufficiently small in magnitude. However, this convergence is not monotonic. Sometimes, the smallest calculation gives the best result for a given property. The bad side of ab-initio methods is that they are expensive. These methods often take enormous amounts of computer cpu time, memory and disk space. The HF method scales as N^4, where N is the number of basis functions, so a calculation twice as big takes 16 times as long to complete. Correlated calculations often scale much worse than this. In practice, extremely accurate solutions are only obtainable when the molecule contains half a dozen electrons or less.

I.4.1.2.1: Gaussian Functions and Basis Sets: There is a need for well-defined ab-initio molecular orbital calculations, which are simple enough to be applied systematically to moderately large organic molecules. One such method is the linear combination of atomic-orbital self-consistent-field (LCAO SCF) method using a minimal basis set of Slater-type atomic orbitals, STOs, [87]. For molecules with no atom heavier than fluorine, only ls, 2s, and 2p atomic orbitals are involved and these have the form:

$$\Phi_{1s}(\xi_1, r) = \left(\xi_1 \frac{3}{\pi}\right)^{\frac{1}{2}} exp(-\xi_1 r)$$

$$\Phi_{2s}(\xi_2, r) = \left(\xi_2 \frac{5}{3\pi}\right)^{\frac{1}{2}} r \, exp(-\xi_2 r) \tag{25}$$

$$\Phi_{2p}(\xi_2, r) = \left(\xi_2 \frac{5}{3\pi}\right)^{\frac{1}{2}} r \exp(-\xi_2 r) \cos\theta$$

In general, different values of the exponents ξ_2 may be used for 2s and 2p functions. It is preferable to treat exponents as further variational parameters leading to final optimized ξ values [88].

In variational calculations, each MO is described as a linear combination of atomic orbitals [86], each molecular orbital is written in the form

$$\Psi_i = \sum_\mu C_{\mu i} \Phi_\mu. \tag{26}$$

Where Φ_μ are basis functions and $C_{\mu i}$ are variational coefficients.

Evaluation of two-electron integrals over STOs is time consuming. One way to overcome this problem is to represent each Slater-type orbital, equation (24), by a linear combination of a small number of Gaussian-type

orbitals Φ_μ each of which is a sum of K Gaussian functions (K = 2-6). The representation of STOs by a small sum of Gaussian functions provides a rapidly convergent method for finding self-consistent molecular orbitals simulating those directly based on an STO set. These combinations are obtained for Slater-type orbitals with $\xi = 1$ and then uniformly scaled. Thus

$$\Phi_\mu'(\xi, r) = \xi^{\frac{3}{2}} \Phi_\mu'(1, \xi_r)$$

where

$$\Phi_{1s}'(1, r) = \sum_k^K d_{1s,k} g_{1s}(\alpha_{2k}, r)$$

$$\Phi'_{2s}(1,r) = \sum_k^K d_{2s,k} g_{1s}(\alpha_{2k},r) \tag{27}$$

$$\Phi'_{2p}(1,r) = \sum_k^K d_{2p,k} g_{2p}(\alpha_{2k},r)$$

Here the constants d and α are chosen to minimize the integrals

$\varepsilon_{1s} = \int(\Phi_{1s} - \Phi'_{1s})^2 d\tau$ and $\varepsilon_{2s} + \varepsilon_{2p} = \int(\Phi_{2s} - \Phi'_{2s})^2 d\tau + \int(\Phi_{2p} - \Phi'_{2p})^2 d\tau$,

which are subjected to normalization constraints while g_{1s} and g_{2s} are the Gaussian-type orbitals:

$$g_{1s}(\alpha, r) = (2\alpha/\pi)^{3/4} \exp(-2\alpha r)$$

$$g_{2p}(\alpha, r) = (128 \, \alpha^5/\pi^3)^{1/4} \, r \exp(-2\alpha r^2)\cos\theta \tag{28}$$

Two points should be noted about the expressions (27). In first place, the 2s exponential function is replaced by a linear combination of 1s Gaussians. This is because integrals involving 2s-type Gaussian functions can not be handled by such elementary methods. Second, the combinations of Φ'_{2s}, and Φ'_{2p} share the same set of Gaussian exponents

In practical calculations, the basis functions Φ'_μ are frequently chosen to be contracted Gaussian functions [89], which is fixed linear combinations of Gaussian functions equation (28). The use of such functions permits explicit integration of Hamiltonian operator [90].

Some of the terms used to describe STO basis sets[91-94] are indicated below .

i- Minimal basis set: Where each atomic orbital is represented by one basis function for the shells occupied or partly occupied in the atomic ground state. For

organic molecules with only first-row atoms, a minimal set consists of a 1s function for hydrogen and 1s, 2s, 2p functions for heavy atoms. One problem with minimal basis sets is that they do not allow alteration of the basis orbitals in response to changing molecular environment. Therefore, the minimal basis sets is unreliable in comparison between charged and uncharged species. Anisotropic environments are another problem for minimal basis sets.

ii- Double-and triple-Zeta basis set : The double-Zeta basis set is obtained by replacing each STO of a minimal basis set by two STOs that differ in their orbital exponents ξ (Zeta). The triple-Zeta is the same as double-Zeta but three STOs are used and differ in their orbital exponents.

iii- Double-Zeta polarization set(DZ+P or DZP): It adds to a double-Zeta basis set an additional set of five 3d functions on each heavy atom and a set of three 2p functions on each hydrogen atom.

iv- Split-valence basis set: This basis set uses two STOs for each valence atomic orbital and only one STO for each inner-shell atomic orbital. The coefficients of these two kinds of orbital can be varied independently during contraction of the MOs.

Gaussian-type orbitals (GTO)

The radical part has the form

$$R_n(r, \alpha) = N_\alpha r^{n-1} e^{-\alpha^2} \tag{29}$$

These functions are easily integrable but they have the disadvantage of the poor description of the properties near the nucleus, therefore, more than one GTO are needed to describe the atomic orbitals. The GTO has the following form in Cartesian coordinates:

$$g_{ijk} = N x_\alpha^i y_\alpha^i z_\alpha^k e^{-\alpha^2} \qquad (30)$$

Where N is the normalization constant, α is a positive parameter (orbital exponent), i, j and k are integers ≥ 0; the sum of these three integers is some how related to the angular momentum quantum number for the atom.

Thus, when

i + j + k = 0 the GTO is called a s-type Gaussian (zero-order Gaussian function)

i + j + k = 1 the GTO is called a p-type Gaussian (first-order Gaussian function)

i + j + k = 2 the GTO is called a d-type Gaussian (second-order Gaussian function)

Contraction of Gaussian basis set: Contraction of basis set is a method used to reduce the number of basis functions and so reduce the time of calculation. Each basis function is taken as a linear combination of small Gaussians

$$\chi_r = \sum_n d_{ur} g_u \qquad (31)$$

Where g_u is a primitive Cartesian, d_{ur} is a coefficient and is constant during calculations. The coefficients of the Gaussian functions are adjusted to give as good a fit as possible to the Slater orbitals. χ_r is called a contracted Gaussian type

function (CGTF), where the latter is used instead of the primitive Gaussian as basis set. The total energy is related to the number of primitive Gaussians, when the number of the primitive Gaussians increases this leads to expand inner-shell atomic orbitals and the iner- and outer-components of the valence-shell functions [95] and this is reflected on the total energy of a molecule and tends toward improving. Some types of basis sets that use CGTF are indicated below.

1- STO-NG [87,96]**:**
Each STO, CGTF$_s$, is a linear combination of N primitive Gaussians, where N = 2-6 Gaussian functions (STO-2G, STO-3G…. STO-6G). The STO-3G set, in particular, is very economical to use as a minimal basis and can be applied to quit large organic molecules. However, minimal basis sets, such as the STO-3G, do not give good descriptions of relative energies; force constant and electric dipole moments.

2- N-21G [97,98]**:**
This basis set commonly uses split-valence basis sets of CGTF. Each inner-shell AO is represented by a single CGTF, which is a linear combination of N primitive Gaussians; for each valence-shell AO, there are two CGTFs one of them is a linear combination of two primitive Gaussians and other is a single diffuse Gaussian. Both the widely used minimal STO-3G and split-valence 3-21G basis sets are moderately successful in reproducing the experimental equilibrium geometries of a

variety of compounds incorporating normal-valent second-row elements, both methods are very bad in their attempted description of the structures of hyper valent species.

3- N-31G[91,99]:

In this basis set, the inner-shell AO is represented by a single CGTF, that is a linear combination of N primitive Gaussians. The valence-shell AO is represented by two CGTFs one of them is a linear combination of three primitive Gaussians and the other is only one primitive Gaussian. This basis set yields hydrogenation energies significantly in better agreement with experimental than those obtained using N-21G basis sets.

4- 6-311G [100]:

Each inner-shell orbital is represented by three CGTF (that is a linear combination of six primitive Gaussians) and each valence-shell orbital is represented by three CGTFs; one CGTF is a linear combination of three primitives and two CGTFs each of them contains one primitive. This basis set is generally applicable to molecules of moderate size.

5- Polarization basis functions[95,99]:

The polarization functions are added to give additional flexibility to the description of MOs. These polarization functions are second-order Gaussian for non hydrogen (d-type) and first-order (p-type) Gaussian for hydrogen atoms. Such

functions have been added to STO-NG*, N-21G*, N-31G* and N-311G* (polarization functions on heavy atoms) and to STO-NG**… and N-311G** (polarization functions on heavy and hydrogen atoms). The d-type functions are important in contributing to electron correlation within the atomic valence shell as well as acting as polarization functions for UHF occupied orbitals, in some compounds exist and often exhibit high thermochemical stability and this is due to the availability for bonding of unfilled but low-lying d-type atomic orbitals on the second-row element. The concept of d-orbital participation in the bonding of hypervalent compounds has been repeatedly confirmed by quantitative molecular orbital calculations.

Selection of basis sets:

Some observations that one has to keep in mind when choosing a basis set are:

i-   Bond length errors for STO-3G calculations are generally somewhat larger for the larger basis sets, but do not change appreciably from 3-21G* through 6-311G*.

ii- STO-G generally provides a poor account of bond distance in hypervalent molecules such as inter halogen, because d-functions are absent.

iii- Correlated methods generally provide bond length improvement over simple HF methods, except for hypervalent molecules.

iv- HF and correlated models generally give comparable results for bond angle, regardless of the basis set.

v- All levels of HF and correlated methods describe well the energetics of isodesmic reactions, even with small basis sets. Errors for semi-empirical methods are much larger (isodesmic processes are reactions in which the number and types of bonding and non-bonding electron pairs are held constant).

1.2.1.5: Population analysis: Mulliken proposed a method to analyze the SCF wave function. Each MO has the form [101]

$$\Phi_i = \sum_s C_{si} \chi_s = C_{1i}\chi_1 + C_{2i}\chi_2 + \cdots \ldots + C_{3i}\chi_3 \qquad (32)$$

The probability density associated with one-electron in Φ_i is

$$|\Phi_i|^2 = C_{i1}^2 \chi_1^2 + C_{i2}^2 \chi_{i2}^2 + \cdots ..2C_{1i}C_{2i}\chi_1\chi_2 + 2C_{1i}C_{3i}\chi_1\chi_3 + \cdots \ (33)$$

Integration over three-dimensional space and using the fact that Φ_i and the χ_s are normalized, one gets

$$1 = C_{1i}^2 + C_{2i}^2 + \cdots ..2C_{1i}C_{2i}S_{12} + 2C_{1i}C_{31}S_{13} + \cdots. \qquad (34)$$

where $S_{12}^{\prime s}$ are the overlap integrals: $S_{12} = \int \chi_1\chi_2 dv_1 dv_2,$ and so on. Mulliken proposed that the terms in equation (34) be apportioned as follow: one electron in MO Φ_i contribute C_{1i}^2 to the net population in χ_1, C_{2i}^2 to the net population in χ_2, and so on. Let n_i electrons occupy the MO Φ_i (n_i = 0, 1, 2) and let $n_{r,i}$ and $n_{r\text{-}s,i}$

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represent the contributions of electrons in MO Φ_i to the net populations in χ_r and

to overlap population between χ_r and χ_s respectively, one gets

$$n_{r,i} = n_i C_{ri}^2, n_i(2C_{ri}C_{si}S_{rs}) \tag{35}$$

Summing over the occupied MO$_s$

$$n_r = \sum_i n_{r,i} \, and \, n_{r-s} = \sum_i n_{r-s,i} \tag{36}$$

n_r is called the net population in χ_r. The sum of all the net overlap populations

equal the total number of electrons in the molecule (n)

$$n = \sum_r n_r + \sum_{r=s} \sum_s n_{r-n} \tag{37}$$

The gross population N_r inχ_r is given by

$$N_r = n_r + \frac{1}{2}\sum_{s \neq r} n_{r-s} \tag{38}$$

The sum of gross population for all basis functions centered on atom A is given by:

$$N_A = \sum_{r \in A} \quad N_r \tag{39}$$

$r \in A$ means all functions centered on atom A.

The net charge q on A is given by:

$$q_A = Z_A - N_A$$

where Z_A is the atomic number of atom A.

I.4.2: Overview of the Density Function Theory:

In the Density Functional Theory (DFT), the total energy is expressed in terms of

the total electron density, rather than the wave function (as in HF ab-initio

method). In this type of calculation, there is an approximate Hamiltonian and an approximate expression for the total electron density.

Density functional theory (DFT) is equivalent to solving Schrödinger's equation and is, therefore, an exact theory for describing the electronic structure and properties of matter. An important difference between DFT and Wave Functional Theory (WFT) is the principle quantity of interest. In DFT this quantity is the electron density which, unlike the wave function, is an observable. The computational advantage of DFT originates with the fact that the electron density has three spatial coordinates, regardless of the number of electrons in the chemical system. Thus, DFT allows the calculation of structures and properties of molecules with a couple hundred atoms, a feat not generally possible with high-level WFT methods.

In 1964 the perception of density functional theory was forever changed. That year, Höhenberg and Kohn [102-104] provided the long sought after Proof that density functional theory is in fact an exact theory for describing the electronic behavior of matter. This was accomplished by considering the theorem: There exists a variational principle in terms of the electron density which determines the ground state energy and electron density. Further, the ground state electron density determines the external potential, within an additive constant.

The Kohn-Sham (KS) scheme [105] reintroduces the orbital (one-electron wave function), and may at first glance seem similar to HF. However, the KS-orbitals are used as a means for calculating the correct electron density. As in HF the expression for the energy can be divided into contributions (Eq. 40):

$$E = T + E_{ee} + E_{ne} \qquad (40)$$

The ansatz in the KS scheme is to divide the true system into a hypothetical system of non-interacting electrons for which an exact functional can be found, and a small correction. The hypothetical system is fully described by a single Slater determinant wave function, so that orbitals can be reintroduced.

As a consequence, the electron density is defined as the sum of orbital densities. The functional can now be written as:

$$E = T_s + E_{ne} + J + E_{xc} \qquad (41)$$

Where Ts is the kinetic energy of the hypothetical system, E_{ne} and J are the classical expressions for nucleus-electron: attraction and electron-electron repulsion and E_{xc} is the so-called exchange correlation term. The first three terms of Eq. (41) are known, and if E is defined as the true energy it will also define E_{xc}. So, E_{xc} is thus the energy not accounted for in the three first terms. It comprises the kinetic energy not within Ts and the different two-electron contributions to the total energy E not included in J. As in HF a set of one-electron equations are

solved iteratively using an SCF procedure leading to the optimal KS orbitals. These orbitals lack strict physical meaning and are only used as tools to calculate the density and energy. It is noteworthy that even though the Kohn-Sham scheme is a single determinant approach it includes electron correlation. Just as with HF, DFT can be extended to allow for spin dependence. A separation of the spatial parts leads to an unrestricted scheme, where the spin densities vary.

It is the quality of the exchange-correlation term that determines the quality of the method. Usually this term is divided into one correlation contribution and one exchange contribution (Eq. 42).

$$E = E_c + E_x \qquad\qquad (42)$$

There is no physical motivation for this separation but it is widely used. The method is then constructed by combining one functional for the correlation and one for the exchange. There are three common ways to model the E_{xc} functional; the local density approximation (LDA). The generalized gradient corrected (GGA), and the hybrid functional methods.

In LDA, the system is locally treated as a uniform electron gas, and the density therefore varies very slowly or not at all. This leads to simple functionals that only depend on the local density, p. A common local exchange functional is that of

Slater (S), and a common local correlation functional is that of Vosko, Wilk and Nusair (VWN) [106].

Since a uniform electron gas is insufficient for a molecule, this method is improved by treating the system as non-uniform. To do this the variations in the density s accounted for through the gradient of the density, and such methods are known as generalized gradient approximation (GGA) methods or gradient corrected methods. The GGA's are sometimes referred to as non-local methods. Several functionals have been developed, e.g. the Becke[107] exchange correction (B) and the Perdew and Wang (PW91) and Lee, Yang and Parr (LYP)[108,109] correlation functionals.

The last methods that will be discussed here are hybrid methods, which are a combination of different methods. The adiabatic connection formula gives the possibility to include exact HF exchange with LSDA and GGA models. The extent of HF exchange is not known and the different contributions are therefore fitted to experimental data. The most well-known is the B3LYP[107-109]functional.

A particular DFT method is constructed by combining functionals for exchange and correlation, and the method is named as the combination, i.e. SWVN, BPW91 and B3PW91. GGA often performs better than LDA, and gives geometries and vibrational frequencies of similar or better quality than MP2, but at a

computational cost similar to HF. The low cost of DFT methods makes them very attractive.

But DFT also has several drawbacks. The first one is that the approximate functionals used are not variational, and they cannot be improved systematically like the wave function approach can by applying more rigorous corrections. Much work therefore goes into verifying that a specific functional is suited for the problem at hand. Another drawback is that it cannot describe excited states of the same symmetry as the ground state [110]. Yet another one is that it sometimes has problems in describing systems of multi reference character[111].

I.4.3: Potential Energy Surface and Geometry Optimization:

The Concept of potential energy surface is the consequence of the Born and Oppenheimer[112-114] proposal of separating the motion of nuclei and electrons in the molecular system. Therefore, the nuclei may be considered to move under the influence of a potential field due to the electrons and consequently many molecular configurations in terms of many dimensional potential energy surface is expected.

Geometry optimizations typically attempt to locate a minimum on the potential energy surface in order to predict equilibrium structures of molecular systems (although they may also be used to locate transition structures). For this

reason, geometry optimizations to a minimum are also called minimizations.

Potential Energy Surface specifies the way in which the energy of a molecular system varies with small changes in its structure. In this way, a potential energy surface is a mathematical relationship linking the molecular structure and the resultant energy. For a diatomic molecule, the potential energy surface can be represented by a two-dimensional plot with the internuclear separation on the X-axis and the energy at that bond distance on the Y-axis; in this case the potential energy surface is a curve. For larger systems the surface has as many dimensions as there are degrees of freedom within the molecule

A minimum is a point at the bottom of a valley in the potential energy surface, from which motion in any direction leads to a higher energy. There are two types for these minima: the local minimum, which corresponds to the lowest point in some limited region of the potential surface, and the global minimum, which is the lowest energy point anywhere on the potential surface. Different minima correspond to different conformations or structural isomers of the molecule under investigation. The illustration also shows two maxima and a saddle point (the latter corresponds to a transition state structure). At both minima and saddle points, the first derivative of the energy, known as the gradient, is zero. Since the gradient is the negative of the forces, the forces are also zero at such points. A point on the potential energy surface where the forces are zero is called a stationary point. All

successful optimizations locate a stationary point, although not always the one that was intended. Geometry optimizations usually locate the stationary point closest to the geometry from which they started. When you perform a minimization, intending to find the minimum energy structure, there are several possibilities as to the nature of the results: you will find the global minimum, a local minimum but not the global minimum, or a saddle point.

Characterizing Stationary points: A geometry optimization alone cannot tell you about the nature of the stationary point that it finds. In order to characterize a stationary point, it is necessary to perform a frequency calculation on the optimized geometry. In order to distinguish a local minimum from the global minimum, it is necessary to perform a conformational search. You might begin by altering the initial geometry slightly and then performing another minimization and modification of the dihedral angles is often a good place to start. There are also varieties of conformational search tools that can help with this task.

The completed frequency calculation will include a variety of results: frequencies, intensities, the associated normal modes, the structure's zero point energy, and various thermo chemical properties. If any of the frequency values are less than zero, these frequencies are known as imaginary frequencies. The number of imaginary frequencies indicates the sort of stationary point to which the given molecular structure corresponds. By definition, a structure that has n imaginary

frequencies is an n<u>th</u> order saddle point.

Thus, the global minimum will have zero imaginary frequencies. An ordinary transition structure will have only one imaginary frequency since it is a first order saddle point.

To begin the process of optimization, one must specify an initial geometry (initial set of Cartesian or internal coordinates), initial basis set and then the chemistry program completes a series of computations [115,116]. These computations not only give you a new geometry, but also a new energy for the molecule. This process is repeated until the molecular energy reaches its minimum. The flow chart that explains the sequence of events which occur in order to optimize a basis set [117] is given in Fig. I.3.
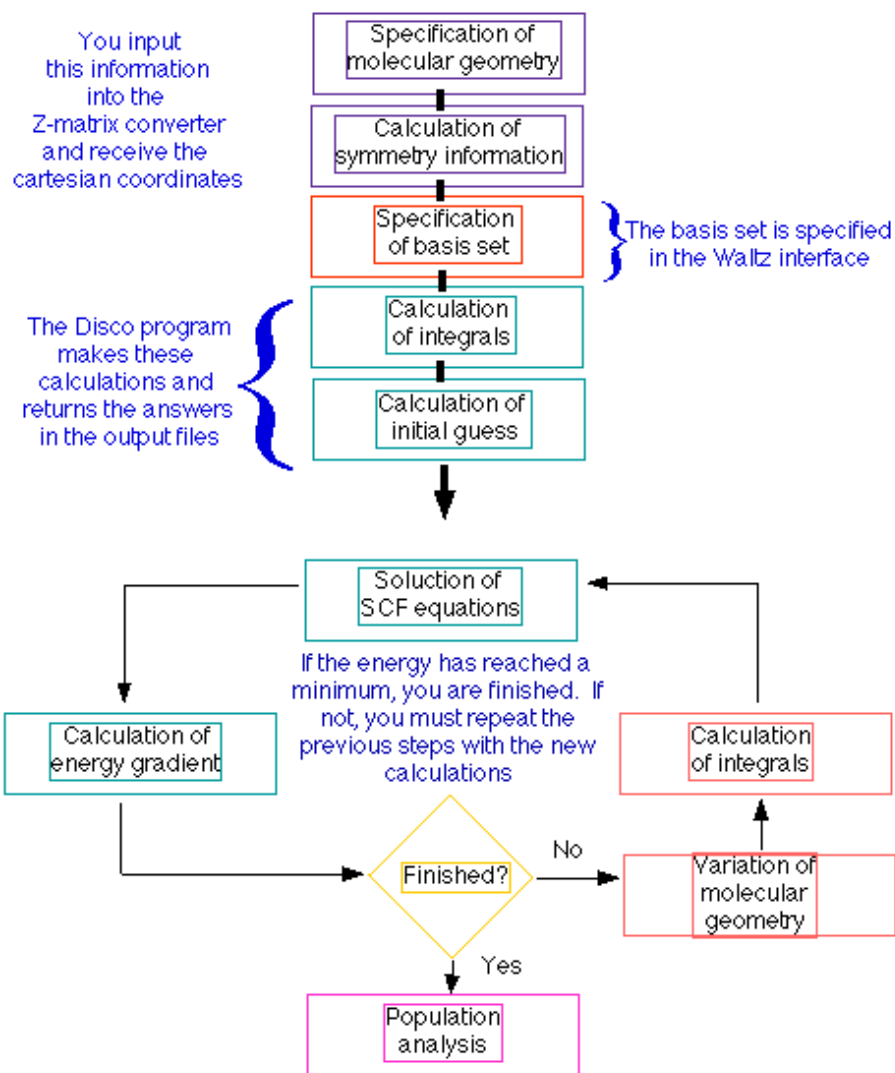
Fig. I.3: The flow chart that explains the sequence of optimization of a basis set.

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I.4.4: Time-dependent DFT (TD-DFT)

Time-dependent density functional theory (TD-DFT) uses the same Kohn-Sham approach in DFT of replacing interacting particles with independent particles with an interacting density. It is described by a time-dependent Schrödinger-like equation:

$$i\hbar \frac{\psi_i(t)}{dt} = \hat{H}(t)\psi_i(t)$$

where, $\psi_i(t)$ is the electronic wave function at a particular time t, and $\hat{H}$ is the electronic Hamiltonian. In this work, we use TD-DFT to calculate excitation energies of molecules. The influence of the solvents used in this study on the lowest singlet states of the charge transfer complexes was evaluated using TDDFT [118]. The solvent dependence of the absorption spectra was studied by performing TDDFT calculations on the optimized ground in combination with the CPCM [119].

REFRENCES:

[1] M. Subha, K. Anitha, and R. Jauhar, "The effect of malonic acid on the physico-chemical characterisation of 4-hydroxy pyridine : A new third order NLO single crystal," J. Mol. Struct., vol. 1179, pp. 469–476, 2019.

[2] M. D. Hill, "Recent strategies for the synthesis of pyridine derivatives," Chem. - A Eur. J., vol. 16, no. 40, pp. 12052–12062, 2010.

[3] M. Pandeeswaran, E. H. El-Mossalamy, and K. P. Elango, "Spectroscopic studies on the interaction of cilostazole with iodine and 2,3-dichloro-5,6-dicyanobenzoquinone," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 78, no. 1, pp. 375–382, 2011.

[4] K. M. Al-ahmary, M. M. Habeeb, and S. H. Aljahdali, "Synthesis , spectroscopic characterization and DFT / TD-DFT computations of a novel charge transfer complex via hydrogen bonding between 3-amino-1 , 5-dimethylpyrazole with chloranilic acid in different solvents," J. Mol. Struct., vol. 1181, pp. 48–60, 2019.

[5] K. M. Al-ahmary, M. M. Habeeb, and A. H. Al-obidan, "Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy Charge transfer complex between 2 , 3-diaminopyridine with chloranilic acid . Synthesis , characterization and DFT , TD-DFT computational studies," Spectrochim. Acta Part A Mol. Biomol. Spectrosc., vol. 196, pp. 247–255, 2018.

[6] K. M. Al-ahmary, M. M. Habeeb, and S. H. Aljahdali, "Synthesis , spectroscopic studies and DFT / TD-DFT / PCM calculations of molecular structure , spectroscopic characterization and NBO of charge transfer complex between 5-amino-1 , 3-dimethylpyrazole (5-ADMP) with chloranilic acid (CLA) in different s," J. Mol. Liq., vol. 277, pp. 453–470, 2019.

[7] A. Fassihi et al., "Synthesis, antimicrobial evaluation and QSAR study of some 3-hydroxypyridine-4-one and 3-hydroxypyran-4-one derivatives," Eur. J. Med. Chem., vol. 44, no. 5, pp. 2145–2157, 2009.

[8] M. Flores-Sumoza, J. Alcázar, E. Márquez, J. Mora, J. Lezama, and E. Puello, "Classical QSAR and Docking Simulation of 4-Pyridone Derivatives for Their Antimalarial Activity," Molecules, vol. 23, no. 12, p. 3166, 2018.

[9] A. G. Iksanova et al., "In-vitro antitumor activity of new quaternary phosphonium salts, derivatives of 3-hydroxypyridine," Anticancer. Drugs, vol. 29, no. 7, pp. 682–690, 2018.

[10] A. A. Altaf, A. Shahzad, Z. Gul, N. Rasool, A. Badshah, and B. Lal, "A Review on the Medicinal Importance of Pyridine Derivatives," no. October 2016, 2015.

[11] A. Mostafa and H. S. Bazzi, "Synthesis and spectroscopic studies of the charge transfer complexes of 2- and 3-aminopyridine," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 74, no. 1, pp. 180–187, 2009.

[12] P. Gogoi , U. Mohan , M. P. Borpuzari , A. Boruah , S. K. Baruah , "UV-Vis spectroscopy and density functional study of solvent effect on the charge transfer band of the n → σ* complexes of 2- Methylpyridine and 2- Chloropyridine with molecular iodine, " J. Mol. Struct. vol.1131, pp. 114-123, 2017.

[13] M. M. Habeeb, A. S. Al-Attas, and D. S. Al-Raimi, "Spectroscopic studies and molecular orbital calculations of charge transfer complexation between 3,5-dimethylpyrazole with DDQ in acetonitrile," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 142, pp. 196–203, 2015.

[14] M. S. Refat, A. M. A. Adam, and M. Y. El-Sayed, "Biomarkers charge-transfer complexes of melamine with quinol and picric acid: Synthesis, spectroscopic, thermal, kinetic and

biological studies," Arab. J. Chem., vol. 10, pp. S3482–S3492, 2017.

[15] V. V. Yasnetsov, S. Y. Skachilova, L. N. Sernov, T. A. Voronina, and V. V. Yasnetsov, "Search for new drugs: Synthesis and pharmacological properties of a new 3-hydroxypyridine derivative," Pharm. Chem. J., vol. 46, no. 4, pp. 199–202, 2012.

[16] A. Nazmi, "Evaluation of the 3-hydroxy pyridine antioxidant effect on the thermal-oxidative degradation of HTPB," no. June 2018, pp. 28–36, 2019.

[17] M. S. Refat, H. A. Saad, and A. M. A. Adam, "Spectral, thermal and kinetic studies of charge-transfer complexes formed between the highly effective antibiotic drug metronidazole and two types of acceptors: σ- And π-acceptors," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 141, pp. 202–210, 2015.

[18] O. R. Shehab, H. AlRabiah, H. A. Abdel-Aziz, and G. A. E. Mostafa, "Charge-transfer complexes of cefpodoxime proxetil with chloranilic acid and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone: Experimental and theoretical studies," J. Mol. Liq., vol. 257, pp. 42–51, 2018.

[19] M. Hasani and M. Shariati-rad, "Kinetic and Thermodynamic Studies of Charge-Transfer Complex Formation between Imipramine and Acetonitrile and Dichloromethane Solutions," no. Dcm, pp. 208–214, 2015.

[20] S. Soltani, P. Magri, M. Rogalski, and M. Kadri, "Charge-transfer complexes of hypoglycemic sulfonamide with π-acceptors: Experimental and DFT-TDDFT studies," J. Mol. Struct., vol. 1175, pp. 105–116, 2019.

[21] H. H. Eldaroti, S. A. Gadir, M. S. Refat, and A. M. A. Adam, "Charge-transfer interaction of drug quinidine with quinol, picric acid and DDQ: Spectroscopic characterization and biological activity studies towards understanding the drug-receptor mechanism," J. Pharm. Anal., vol. 4, no. 2, pp. 81–95, 2014.

[22] T. M. El-Gogary, M. A. Diab, and S. F. El-Tantawy, "Spectroscopic and quantum mechanical studies of substituted anilines and their charge-transfer complexes with iodine in different solvents," Monatshefte fur Chemie, 2006.

[23] A. M. A. Adam, M. S. Refat, H. A. Saad, and M. S. Hegab, "Charge transfer complexation of the anticholinergic drug clidinium bromide and picric acid in different polar solvents: Solvent effect on the spectroscopic and structural morphology properties of the product," J. Mol. Liq., 2016.

[24] E. M. Nour, S. Y. Alqaradawi, A. Mostafa, E. Shams, and H. S. Bazzi, "Synthesis, characterization and spectroscopic structural studies of charge-transfer complexes of 1,4,8,11-tetraazacyclotetradecane-5,7-dione with iodine, TCNE and DDQ," J. Mol. Struct., vol. 980, no. 1–3, pp. 218–224, 2010.

[25] R. Rathore and J. K. Kochi, Donor/acceptor organizations and the electron-transfer paradigm for organic reactivity, vol. 35. 2000.

[26] M. S. Refat and S. Abou-Melha, "Spectroscopic and thermal studies on charge-transfer complexes of perhydroisoquinoline with p-chloranil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, and 7,7′,8,8′-tetracyanoquinodimethane," J. Appl. Spectrosc., vol. 79, no. 1, pp. 11–21, 2012.

[27] P. Hemmerich, "Charge Transfer Interactions of Biomolecules. Von M. A. Slifkin. Academic Press, London—New York 1971. 1. Aufl., XX, 271 S., zahlr. Abb. und Tab., geb. £ 16.50," Angew. Chemie, 1973.

[28] "Essentials of medicinal chemistry, 2nd edn.by A. Korolkovas. John Wiley & Sons Ltd., Chichester, 1988, pp. 1204, £ 110," Eur. J. Med. Chem., 1989.

[29] R. Morales, G. C. Diaz, and J. A. Joens, "Thermochemistry of charge-transfer complexes.

1. Enthalpy of formation of charge-transfer complexes of molecular iodine with chlorinated benzene derivatives," J. Phys. Chem., 1988.

[30]   P. J. Trotter and P. A. White, "Resonance Raman Determination of the Triiodide Structure in Bis(Tetrathiotetracene)Triiodide Organic Conductor Compared with the Poly(Vinyl Alcohol)-Iodine Complex," Appl. Spectrosc., 1978.

[31]   S. Licht, "Electrolyte modified photoelectrochemical solar cells," Sol. Energy Mater. Sol. Cells, 1995.

[32]   I. M. Khan and A. Ahmad, "Spectrophotometric and spectroscopic studies of complexation of 8-hydroxyquinoline with π acceptor metadinitrobenzene in different polar solvents," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., 2009.

[33]   P. Y. Cheng, D. Zhong, and A. H. Zewail, "Femtosecond real-time probing of reactions. XXI. Direct observation of transition-state dynamics and structure in charge-transfer reactions," J. Chem. Phys., 1996.

[34]   A. A. Rzokee and A. Ahmad, "Synthesis, spectroscopic studies and thermal analysis of charge-transfer complex of 2,2′-bipyridine with 4-hydroxybenzoic acid in different polar solvents," J. Mol. Struct., 2014.

[35]   N. B. S. Ismail, B. Narayana, and K. Divya, "Validated spectrophotometric methods for the determination of bifonazole in pharmaceuticals by charge transfer complexation," J. Assoc. Arab Univ. Basic Appl. Sci., 2016.

[36]   K. M. Al-ahmary, M. S. Alenezi, and M. M. Habeeb, "Synthesis , spectroscopic and DFT theoretical studies on the hydrogen bonded charge transfer complex of 4-aminoquinoline with chloranilic acid," J. Mol. Liq., vol. 220, pp. 166–182, 2016.

[37]   N. B. S. Ismail and B. Narayana, "Spectrophotometric and spectroscopic studies on charge transfer complexes of the antifungal drug clotrimazole," J. Taibah Univ. Sci., 2017.

[38]   B. Roy et al., "Ground state charge transfer complex formation of some metalloporphyrins with aromatic solvents: Further theoretical and experimental investigations," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., 2018.

[39]   A. Karmakar and B. Singh, "Charge-transfer complex of 1-(2-Thiazolylazo)-2-naphthol with aromatic nitro compounds: Experimental and theoretical studies," J. Mol. Liq., vol. 247, pp. 425–433, 2017.

[40]   A. M. A. Adam, M. S. Refat, T. Sharshar, and Z. K. Heiba, "Synthesis and characterization of highly conductive charge-transfer complexes using positron annihilation spectroscopy," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., 2012.

[41]   M. E. Mohamed, E. Y. Z. Frag, A. A. Hathoot, and E. A. Shalaby, "Spectrophotometric determination of fenoprofen calcium drug in pure and pharmaceutical preparations. Spectroscopic characterization of the charge transfer solid complexes," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., 2018.

[42]   N. M. Monezi, A. C. Borin, P. S. Santos, and R. A. Ando, "The thermochromic behavior of aromatic amine-SO2 charge transfer complexes," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., 2017.

[43]   M. S. A. Abdou, F. P. Orfino, Y. Son, and S. Holdcroft, "Interaction of oxygen with conjugated polymers: Charge transfer complex formation with poly(3-alkylthiophenes)," J. Am. Chem. Soc., 1997.

[44]   S. Mostafa, M. El-Sadek, and E. A. Alla, "Spectrophotometric determination of enrofloxacin and pefloxacin through ion-pair complex formation," J. Pharm. Biomed. Anal., vol. 28, no. 1, pp. 173–180, 2002.

[45]   M. A. El-Ries, F. M. Abou Attia, and S. A. Ibrahim, "AAS and spectrophotometric

determination of propranolol HCl and metoprolol tartrate," J. Pharm. Biomed. Anal., 2000.

[46] M. Pandeeswaran and K. P. Elango, "Solvent effect on the charge transfer complex of oxatomide with 2,3-dichloro-5,6-dicyanobenzoquinone," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 65, no. 5, pp. 1148–1153, 2006.

[47] K. M. Al-Ahmary, M. M. El-Kholy, I. A. Al-Solmy, and M. M. Habeeb, "Spectroscopic studies and molecular orbital calculations on the charge transfer reaction between DDQ and 2-aminopyridine," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 110, pp. 343–350, 2013.

[48] C. Society, "In order to obtain UV-Vis spectra , 3 mL of 1 . 65 x 10 -3 M DDQ or 1 . 41 x 10 -3 M of iodine solution was transferred to a 1-cm quartz cell and titrated with a standard C222 solution by a 100- μ L Hamilton syringe . The same procedure was followed for o," vol. 20, no. 2, pp. 183–192, 2006.

[49] N. A. Al-Hashimi and Y. H. A. Hussein, "Ab initio study on the formation of triiodide CT complex from the reaction of iodine with 2,3-diaminopyridine," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 75, no. 1, pp. 198–202, 2010.

[50] and Applications. .

[51] G. Aksu, E. Temel, and H. Altay, "Comparison of iodine application methods in Rocket Plant," vol. 15, no. 1, pp. 5–10, 2017.

[52] "Iodine production and industrial applications," pp. 8–9, 2016.

[53] A. Raza and T. M. Ansari, "Application Of 2,3-Dichloro-5,6-Dicyano-P-Benzoquinone (DDQ) For Spectrophotometric Determination Of Caroverine In Pharmaceutical Formulations," no. c, pp. 2–5, 2017.

[54] L. Chen, S. Li, P. Chen, H. Chang, and T. Wang, "dehydrogenation of 2-aroyl-3 , 4-dihydro-2 H -benzopyrans : synthesis of 2-aroylbenzopyran-4-ones," vol. 2010, no. xi, pp. 64–76, 2010.

[55] Y. Zhang, X. Yang, W. Wang, X. Wang, and L. Sun, "DDQ as an effective p-type dopant for the hole-transport material X1 and its application in stable solid-state dye-sensitized solar cells," vol. 27, pp. 413–418, 2018.

[56] U. Kucklaender, R. Bollig, W. Frank, A. Gratz, and J. Jose, "Bioorganic & Medicinal Chemistry A novel application of DDQ as electrophile in the Nenitzescu reaction," Bioorg. Med. Chem., vol. 19, no. 8, pp. 2666–2674, 2011.

[57] B. B. Bnowmik and P. K. Srimani, "Solvent effect on charge transfer complexes and their spectra-n *," vol. 29, no. 7, pp. 935–942, 1973.

[58] "Gmax," vol. 42, pp. 1217–1222, 1986.

[59] "Solvent effect on charge transfer complexes of iodine with some pyrimidines," vol. 2, pp. 1017–1021, 1991.

[60] P. Chemistry, "Since charge-transfer emission from pyrene and anthracene has been observed only with aromatic N-aIky1 amines , it has been surmised that the ._ - n-orbitals of the aromatic amines are involved in the complex formation [l]. If we assume for charge-trans," vol. 4, pp. 307–308, 1975.

[61] N. A. Abdalla, "Conductometric Studies of Charge Transfer Complexes Interaction of Amino Pyridine with π- Acceptors," IOSR J. Appl. Chem., vol. 7, no. 8, pp. 01–11, 2014.

[62] A. S. Gaballa, "Preparation and spectroscopic studies on charge-transfer complexes of 2-hydroxypyridine with electron acceptors," J. Mol. Struct., vol. 1043, pp. 91–102, 2013.

[63] K. M. Al-Ahmary, M. M. Habeeb, and A. H. Al-Obidan, "Spectrophotometric study on the charge transfer reaction between 2-amino-4-methylpyridine with chloranilic acid in

43

polar solvents," Phys. Chem. Liq., 2016.

[64]   S. Y. Alqaradawi and E. M. Nour, "Synthesis and spectroscopic structural studies of the adducts formed in the reaction of aminopyridines with TCNQ," vol. 794, pp. 251–254, 2006.

[65]   K. M. Al-Ahmary, S. M. Soliman, M. M. Habeeb, and A. H. Al-Obidan, "Spectral analysis and DFT computations of the hydrogen bonded complex between 2,6-diaminopyridine with 2,6-dichloro-4-nitrophenol in different solvents," J. Mol. Struct., vol. 1143, pp. 31–41, 2017.

[66]   B. J. Lynch, Y. Zhao, and D. G. Truhlar, "Effectiveness of diffuse basis functions for calculating relative energies by density functional theory," J. Phys. Chem. A, 2003.

[67]   S. E. Wheeler and K. N. Houk, "Substituent effects in cation/π interactions and electrostatic potentials above the centers of substituted benzenes are due primarily to through-space effects of the substituents," J. Am. Chem. Soc., 2009.

[68]   E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen, and W. Yang, "Revealing noncovalent interactions," J. Am. Chem. Soc., 2010.

[69]   J. Deng, A. T. B. Gilbert, and P. M. W. Gill, "Communication: Efficient counterpoise corrections by a perturbative approach," J. Chem. Phys., 2011.

[70]   K. M. Al-Ahmary, M. M. Habeeb, and E. A. Al-Solmy, "Spectroscopic and thermodynamic studies on charge transfer complex formation between 2-aminopyridine and 2,5-dihydroxy-p-benzoquinone," J. Solution Chem., vol. 39, no. 9, pp. 1264–1277, 2010.

[71]   M. Belfaragui, A. Seridi, J. Y. Winum, M. Abdaoui, and M. Kadri, "A spectrophotometric and thermodynamic study of the charge-transfer complexes of N-aryl-N'-isopropyloxycarbonylsulfamides with DDQ and TCNE," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 108, pp. 55–61, 2013.

[72]   O. R. Shehab and A. M. Mansour, "Charge transfer complexes of 2-arylaminomethyl-1H-benzimidazole with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone: Experimental and DFT studies," J. Mol. Struct., vol. 1047, pp. 121–135, 2013.

[73]   A. S. Al-Attas, D. S. Al-Raimi, and M. M. Habeeb, "Spectroscopic analysis, thermodynamic study and molecular modeling of charge transfer complexation between 2-amino-5,6-dimethyl-1,2,4-triazine with DDQ in acetonitrile," J. Mol. Liq., vol. 198, pp. 114–121, 2014.

[74]   Y. Büyükmurat and S. Akyüz, "Theoretical and experimental IR spectra and assignments of 3-aminopyridine," J. Mol. Struct., vol. 563–564, pp. 545–550, 2001.

[75]   L. Shahada, A. Mostafa, E. M. Nour, and H. S. Bazzi, "Synthesis, spectroscopic, thermal and structural investigations of charge-transfer complexes of 4,4???-trimethylenedipiperidine with chloranil, TBCHD, DDQ, TCNQ and iodine," J. Mol. Struct., vol. 933, no. 1–3, pp. 1–7, 2009.

[76]   N. Singh, I. M. Khan, A. Ahmad, and S. Javed, "Synthesis, spectrophotometric and thermodynamic studies of charge transfer complex of 5,6-dimethylbenzimidazole with chloranilic acid at various temperatures in acetonitrile and methanol solvents," J. Mol. Liq., vol. 221, pp. 1111–1120, 2016.

[77]   G. García Liñares, G. Parraud, C. Labriola, and A. Baldessari, "Chemoenzymatic synthesis and biological evaluation of 2- and 3-hydroxypyridine derivatives against Leishmania mexicana," Bioorganic Med. Chem., vol. 20, no. 15, pp. 4614–4624, 2012.

[78]   R. Wrzalik, K. Merkel, and A. Kocot, "Ab initio study of phenyl benzoate: Structure, conformational analysis, dipole moment, IR and Raman vibrational spectra," J. Mol.

Model., 2003.

[79] T. Imase, S. Kawauchi, and J. Watanabe, "Conformational analysis of 1,3-benzenediol dibenzoate as a model of banana-shaped molecules forming chiral smectic phases," J. Mol. Struct., 2001.

[80] N. A. Wazzan, E. S. H. El-Mossalamy, and L. M. Al-Harbi, "DFT calculations of charge transfer complexes of N-aryl-N′-4-(-p-anisyl-5-arylazothiazolyl)thiourea derivatives and benzoquinones," Asian J. Chem., 2015.

[81] G. Lei, J. Qiang, B. Dong, and T. Wang, "Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy UV spectroscopic studies and charge transfer properties of azobenzene-containing cyclopentadienyliron complexes of arenes : A combined experimental and density functional theoretical stu," Spectrochim. ACTA PART A Mol. Biomol. Spectrosc., vol. 104, pp. 287–291, 2013.

[82] W. Sawka-Dobrowolska et al., "X-ray and neutron diffraction, IR and INS spectroscopic and DFT theoretical studies on the tetramethylpyrazine-1,2,4,5-tetracyanobenzene complex," Chem. Phys., 2006.

[83] R. Ahlrichs, " R. Daudel, G. Leroy, D. Peeters, and M. Sana: Quantum Chemistry , John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore 1983. 558 Seiten, Preis: £ 48.50 ," Berichte der Bunsengesellschaft für Phys. Chemie, 1984.

[84] M. Born and R. Oppenheimer, "Zur Quantentheorie der Molekeln," Ann. Phys., vol. 389, no. 20, pp. 457–484, 1927.

[85] A. Strich, "Quantum chemistry, 4th ed. By Ira N. Levine, Prentice-Hall, Englewood Cliffs, NJ, 1991, X + 629 pp. Elementary quantum chemistry, 2nd ed. By Frank L. Pilar, McGraw-Hill International Editions, New York, 1990, XVI + 599 pp.," Int. J. Quantum Chem., 1992.

[86] C. C. J. Roothaan, "New developments in molecular orbital theory," Rev. Mod. Phys., 1951.

[87] W. J. Hehre, R. F. Stewart, and J. A. Pople, "Self-consistent molecular-orbital methods. I. Use of gaussian expansions of slater-type atomic orbitals," J. Chem. Phys., 1969.

[88] J. C. Slater, "Atomic shielding constants," Phys. Rev., 1930.

[89] E. Clementi and D. R. Davis, "Barrier to internal rotation in ethane," J. Chem. Phys., 1966.

[90] "Electronic wave functions - I. A general method of calculation for the stationary states of any molecular system," Proc. R. Soc. London. Ser. A. Math. Phys. Sci., 1950.

[91] K. B. Wiberg, "Ab Initio Molecular Orbital Theory by W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, John Wiley, New York, 548pp. Price: $79.95 (1986)," J. Comput. Chem., 1986.

[92] R. Ditchfield, W. J. Hehre, and J. A. Pople, "Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules," J. Chem. Phys., 1971.

[93] W. J. Hehre, Practical strategies for electronic structure calculations. Wavefunction Incorporated, 1995.

[94] A. Hinchcliffe, Computational quantum chemistry. John Wiley & Sons, Inc., 1988.

[95] M. M. Francl et al., "Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements," J. Chem. Phys., vol. 77, no. 7, pp. 3654–3665, 1982.

[96] W. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, "self-consistent molecular orbital methods. iv. use of Gaussian expansions of Slater-type orbitals. Extension to second-row

molecules," J. Chem. Phys., vol. 52, no. 5, pp. 2769–2773, 1970.

[97] J. S. Binkley, J. A. Pople, and W. J. Hehre, "Self-consistent molecular orbital methods. 21. Small split-valence basis sets for first-row elements," J. Am. Chem. Soc., vol. 102, no. 3, pp. 939–947, 1980.

[98] W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople, and J. S. Binkley, "Self-consistent molecular orbital methods. 24. Supplemented small split-valence basis sets for second-row elements," J. Am. Chem. Soc., vol. 104, no. 19, pp. 5039–5048, 1982.

[99] W. J. Hehre, R. Ditchfield, and J. A. Pople, "Self—consistent molecular orbital methods. XII. Further extensions of Gaussian—type basis sets for use in molecular orbital studies of organic molecules," J. Chem. Phys., vol. 56, no. 5, pp. 2257–2261, 1972.

[100] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, "Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions," J. Chem. Phys., vol. 72, no. 1, pp. 650–654, 1980.

[101] R. S. Mulliken, "Overlap populations, bond orders and covalent bond energies," J. chem. Phys, vol. 23, pp. 1841–1846, 1955.

[102] T. Clark, A handbook of computational chemistry: A practical guide to chemical structure and energy calculations. Wiley-Interscience, 1985.

[103] H. J. Lindner, " R. E. Christoffersen: Basic Principles and Techniques of Molecular Quantum Mechanics . Springer-Verlag Berlin, Heidelberg, New York 1989, 686 Seiten, Preis: DM 172,-, ISBN 3-540-96759-1 ," Berichte der Bunsengesellschaft für Phys. Chemie, 1990.

[104] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," Phys. Rev., vol. 136, no. 3B, p. B864, 1964.

[105] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," Phys. Rev., vol. 140, no. 4A, p. A1133, 1965.

[106] S. H. Vosko, L. Wilk, and M. Nusair, "Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis," Can. J. Phys., vol. 58, no. 8, pp. 1200–1211, 1980.

[107] A. D. Becke, "Completely numerical calculations on diatomic molecules in the local-density approximation," Phys. Rev. A, vol. 33, no. 4, p. 2786, 1986.

[108] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," Phys. Rev. B, vol. 37, no. 2, p. 785, 1988.

[109] A. D. Becke, "Phys. Re V. A 1988, 38, 3098.(b) Becke," J. Chem. Phys, vol. 98, no. 1372, p. 5648, 1993.

[110] O. Gunnarsson and B. I. Lundqvist, "Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism," Phys. Rev. B, vol. 13, no. 10, p. 4274, 1976.

[111] W. Koch and M. C. Holthausen, A Chemist's Guide to Density Functional Theory. 2001.

[112] M. Born and R. Oppenheimer, "Zur Quantentheorie der Molekeln," Ann. Phys., 1927.

[113] H. A. Jahn and E. Teller, "Stability of polyatomic molecules in degenerate electronic states-I—Orbital degeneracy," Proc. R. Soc. London. Ser. A-Mathematical Phys. Sci., vol. 161, no. 905, pp. 220–235, 1937.

[114] R. Renner, "Zur Theorie der Wechselwirkung zwischen Elektronen-und Kernbewegung bei dreiatomigen, stabförmigen Molekülen," Zeitschrift für Phys. A Hadron. Nucl., vol. 92, no. 3, pp. 172–193, 1934.

[115] J. W. McIver Jr and A. Komornicki, "Rapid geometry optimization for semi-empirical

molecular orbital methods," Chem. Phys. Lett., vol. 10, no. 3, pp. 303–306, 1971.

[116] J. PancíŘ, "Study of reaction mechanisms by semiempirical methods I," Theor. Chim. Acta, vol. 29, no. 1, pp. 21–28, 1973.

[117] J. Foresman and E. Frish, "Exploring chemistry," Gaussian Inc., Pittsburg, USA, 1996.

[118] O. Gritsenko and E. J. Baerends, "Asymptotic correction of the exchange–correlation kernel of time-dependent density functional theory for long-range charge-transfer excitations," J. Chem. Phys., vol. 121, no. 2, pp. 655–660, 2004.

[119] Y. Takano and K. N. Houk, "Benchmarking the conductor-like polarizable continuum model (CPCM) for aqueous solvation free energies of neutral and ionic organic molecules," J. Chem. Theory Comput., vol. 1, no. 1, pp. 70–77, 2005.