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Density Functional Theory (DFT) as a Powerful Tool for Designing Corrosion Inhibitors in Aqueous Phase

Dakeshwar Kumar Verma

Abstract

In the current chapter, recent progress has been described in the field of computational quantum chemistry for the development of corrosion inhibitors. The current chapter is divided into several sections and subdivisions. Recently, the development of green and sustainable technologies for corrosion prevention is highly desirable an increase in ecological awareness and strict environmental regulations. In the last decade, the use of quantum calculation based corrosion inhibitors study has attracted considerable attention. Quantum calculation based density function theory (DFT) has been widely accepted as "green corrosion inhibition technique" because of its theoretical based work. DFT can be used to design corrosion inhibitors to prevent corrosion on mild steel, aluminum, copper, zinc, and magnesium in aqueous media. DFT is the simplest way to study the molecular structure and behavior of corrosion inhibitors. Various quantum chemical parameters such as dipole moment (μ), energy difference (ΔE), softness (σ) and global hardness (η), highest occupied molecular orbital (E_{HOMO}) and lowest occupied molecular orbital (E_{LUMO}), etc., of corrosion inhibitors has been calculated using software in order to elucidate the adsorption and corrosion inhibition behavior of inhibitor molecules.

Keywords: adsorption, corrosion inhibition, aqueous solution, metals, DFT

1. Introduction

The damage on the material by corrosion produces not only for the high cost inspection, repair, and replacement, but in addition to these formation of a public risk, thus the need for the development of the novel Substances that treat acid in particular, like corrosion inhibitors Media [1]. The use of corrosion inhibitor molecules is one of the most practical ways to protect the materials against corrosion, and it is becoming increasingly popular in industrial applications.

The atmosphere is affected by various metals and their alloys strikes due to the use of acid like H_2SO_4 and HCl for various industrial processes (acid pickling, oil well-acidification, chemical clean-up, etc.) [2, 3], for these reasons the inhibitors is employed as one of the most practical ways to conserve corrosion. Traditionally, corrosion inhibition performance is evaluated experimentally, such as gravimetric analysis, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). However, these experimental methods are expensive and laborious, and often decrease in the illuminating corrosion mechanism. With the improvements in software and hardware, computer simulation has become a powerful tool to investigate the complex system of corrosion resistance [4]. By checking the structure, electron distribution, and adsorption of molecules on the metal and oxide surfaces, the corrosion mechanism is now deeply detected. In 1971, Vosta and Eliasek [5] introduced quantum chemical methods to investigate the prohibition of corrosion and established the field of quantum corrosion electrochemistry. After this, the main objective of quantum chemistry methods was primarily on the discovery and establishment of relations between molecular structure and prohibition, and many valuable results have now been reported. Quantum chemical study has proven itself very long ago useful in determining the structure of the molecules, the reaction as well as the obvious electronic structures [6]. Thus, it has become a common practice to calculate quantum chemical corrosion study concept of assessment of efficiency a corrosion inhibitors with the help of computational chemistry using chemicals to find compounds with desired properties intuition and experience in a mathematical quantitative and a relation between the structure once computerized and activity or property are found, any number of compounds. Those who have not been synthesized so far can be easily tested planning of computational method [7] and a set of mathematical equations that are capable of displaying correctly chemical incident under study [8, 9].

2. Principles of corrosion

Thermodynamic and electrochemical are two basic principles of corrosion mechanism which describe the transformation of metals and alloys into their stable states like hydroxides, sulfates, oxides and chlorides, etc.

2.1. Thermodynamic principles

Thermodynamics directs the spontaneous direction of a chemical reaction and it is used to determine whether the corrosion on metal surface is theoretically possible or not [10].

2.2. Electrochemical principles

Basically corrosion is the coupled of two half-cell electrochemical reaction, cathodic and anodic reaction. Anodic reaction involves the leaving of free electron by metal ionization however cathodic reaction involves the up taking of free electrons by dissolved oxygen and/or water molecules in the solution. Previous is oxidation type reaction where free electrons are produced while later is reduction reaction in which electrons can be accepted [11]. Corrosion behavior of metals and alloys can be easily determine using electrochemical principles.

Two half-cell reaction can be divided in to following type as given:

2.2.1. Anodic reaction

Anodic reaction is the loss of metal cations as given in examples:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e- \tag{1}$$

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e- \tag{2}$$

$$Cu(s) \rightarrow Cu^{2+} + 2e- \tag{3}$$

Each of the above reactions in Eqs. (1)–(3) is an anodic reaction because there is increase in oxidation number and loss of electrons from metals at the anodic site.

2.2.2. Cathodic reaction

Reduction of cation(s) from free electrons of oxidation reaction is a cathodic reaction. Formation of hydrogen gas (H_2) from the reduction of two hydrogen ions at metal surface is an example of cathodic reaction (Eq. (4)):

$$2H^+(aq) + 2e- \rightarrow H_2(g) \tag{4}$$

Above reactions are shown schematically in **Figure 1**.

2.2.3. Coupled electrochemical reactions

Figure 2 represents coupled electrochemical reactions in which anodic and cathodic reactions exist on the metal surface at different places. There are four different types of conditions causes to corrosion are: (i) an anodic reaction, (ii) a cathodic reaction, (iii) a metallic path between these two reactions, and (iv) electrolyte. Electrolyte is an ionic aqueous solution in which
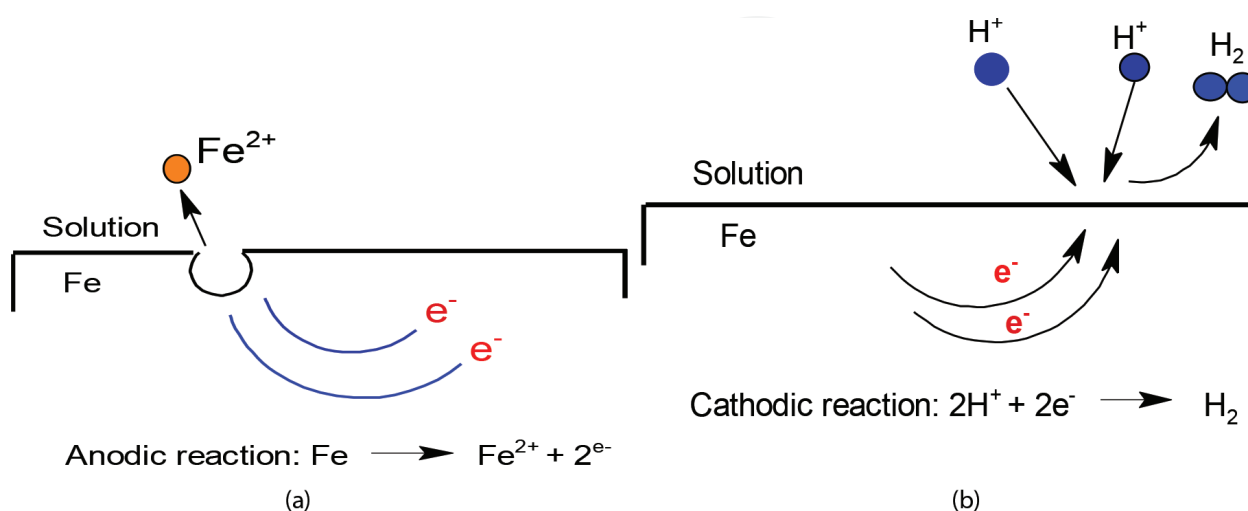

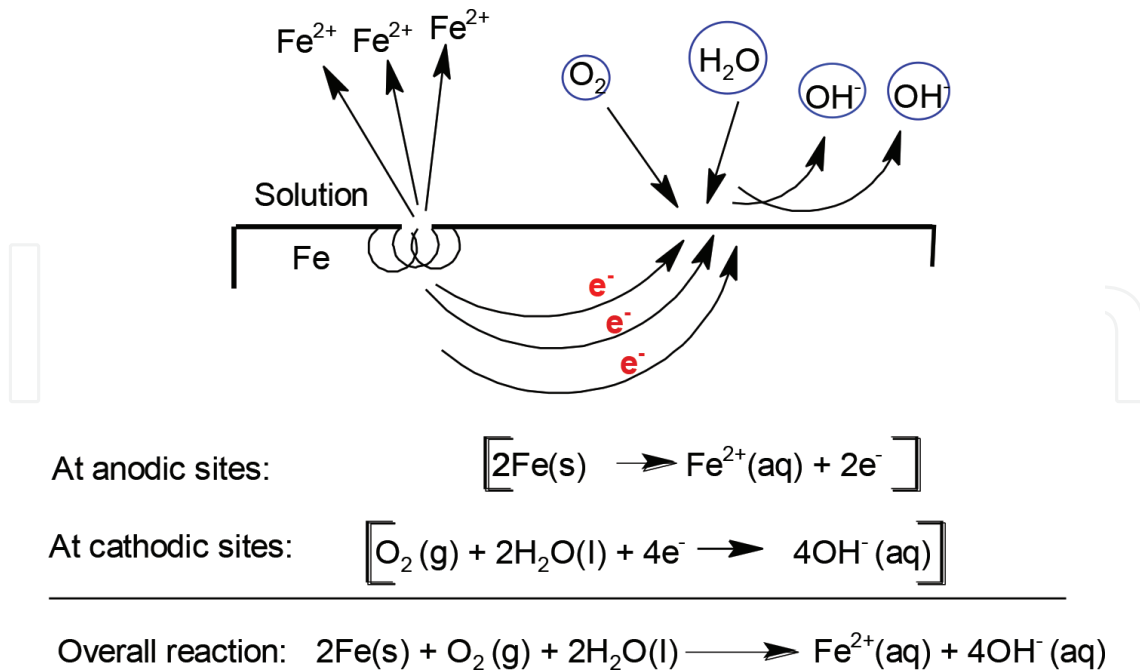**Figure 1.** (a) Anodic reaction and (b) cathodic reaction in metal/solution interface.

Figure 2. Coupled reactions occurring on the metal surface at different sites for iron in a neutral or basic medium.

current can be flow. The coupled reaction for an iron metal dipped in neutral, acidic or basic medium is illustrated in **Figure 2**.

Heterogeneous nature of a metal surface is reason for the orientation of coupled reaction on the same metal surface. Heterogeneity on metal surface can be arise due to defects like screw, steps, dislocation, point defects and kink sites, etc.

3. Adsorption mechanism of corrosion

Corrosion inhibition properties of metals and alloys can significantly change due to adsorption of inhibitor molecules at metal/solution interface. Inhibition of metal corrosion is a surface phenomenon which involves the adsorption of corrosion inhibitors over the metal surface in electrolytic solution. In corrosive solution inhibitor molecules adsorbed on the metal surface by replacing the H_2O molecules at the metal/solution interface according to the given process Eq. (5) [12]:

$$Inh_{(sol)} + nH_2O_{(ads)} \rightarrow Inh_{(ads)} + nH_2O_{(sol)} \tag{5}$$

where Inh $_{(ad)}$ and Inh $_{(sol)}$ are inhibitor molecules in the corrosive medium and adsorbed on the metal surface, respectively, whereas n is the number of H_2O molecules replaced by the molecules of inhibitor. The values of surface coverage (θ) have been used to elucidate the different isotherm to determine the adsorption process at metal/solution interface. The different adsorption isotherms can be characterized by the mathematical models as given in Eqs. (6)–(8) [13]:

$$\left(\frac{c}{\theta}\right) = \log K_{ads} - g\theta \qquad (6)$$

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + C \qquad (7)$$

$$log\left(\frac{\theta}{(1-\theta)C}\right) = \log K_{ads} - g\theta \qquad (8)$$

where θ is the surface coverage, K_{ads} is adsorption constant and C is the equilibrium concentration.

4. Consequences and economics of corrosion

Corrosion is a global problem, which adversely affects the development of both developed and developed countries. According to a highly cited study conducted by the National Association of Corrosion Engineers (NACE) in 1998, the total annual cost of corrosion in the U.S. is estimated at US $ 276 billion, which is approximately 3.1% GDP (GDP; NACE 2002) [14]. In 2011, the total cost of corrosion in the US increased to $ 2.2 trillion. Since the cost of corrosion in India is a matter of concern, it is about two lakh crores (US $ 45 billion) proposed by the 1st Global Corrosion Summit held in New Delhi in 2011 [15]. However, these estimates are outdated and recently the NACE is being closely examined at the cost of the corrosion, according to which the annual global cost of the corrosion is approximately $ 2.5 trillion, which is equivalent to 3.4% of the global GDP. In India, the cost of annual corrosion is more than 100 billion US dollars, whereas in South Africa, direct corrosion costs are estimated to be around 130 billion (i.e., 9.6 billion US dollars) [16, 17]. By applying the existing methods of prevention of corrosion, this cost of the war can be reduced by 35% (US $ 875 billion) to 15% (US $ 375 billion).

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5. Basics and computational aspects of density function theory (DFT)

5.1. The basics of DFT: Hohenberg-Kohn theorem

In Moscow, at the Frumkin Institute of Electrochemistry of the Russian Academy of Sciences, the scientific school of Quantum Electrochemistry was to be started in Revaz Dogonadze in the 1960s. Generally, the ideas that are generated in the field include quantum mechanics, electrodymamics, and electrochemistry; and likewise a very large group of different professional academics is studied. The fields of expertise include chemicals, physics, mechanical and electrical engineering. More specifically, quantum electrochemical electrode surfaces [18] for the study of electrochemical processes, quantum mechanical devices such as DFT are used, including the transfer of electrons from the molecules to the metal electrode surface.

In some previous studies, the basis and importance of DFT [19, 20] has been described. The recent impact of DFT in the development of quantum electrochemistry is significant, and can be linked to achievements in the late 1980s when hybrid functional and gradient-corrected methods were introduced [21]. Based on the famous Hohenberg-Kohn theorem awarded the Nobel Prize in physics for his work on DFT in 1964. DFT concentrates on electron density ρ(r), itself as the carrier of all information in form and/or molecule ground state, rather than an electron wave function, one per electron occurs. In summary, the Hohenberg-Kohn theorem establishes that the base of an electronic system only electronic density is functional. In principle, only need to calculate the electron density in all the properties of the system. In DFT, the ground state total energy for an N-electron system is expressed in terms of the external potential v(r) and the three-dimensional ground-state electronic density ρ(r) in the form (Eq. (9)) [22]:

$$E[\rho] = F[\rho] + \int dr \rho(r) v(r), \tag{9}$$

where $F[\rho]$ is the generalized functional of Hohenberg-Kohn given by the sum of the electronic kinetic energy functional as given in Eq. (10):

$$N = \int dr \rho(r), \tag{10}$$

Eq. (10) pledges the proper normalization of the electron density.

A general DFT formula is given as Eq. (11) [23]:

$$E_{DFT}[\rho] = T_s[\rho] + E_{ne}[\rho] \, J[\rho] \, E_{xc}[\rho], \tag{11}$$

where E_{ne} is the electron-nuclear attraction functional, T_s is the kinetic energy functional, Exc denotes the exchange correlation functional and J is the Coulomb part of the electron-electron repulsion functional. The dependency of each of these terms on the electron density, ρ, is characterized by ρ in brackets following all term.

5.2. Basis sets

The base set, the mathematical description of the orbital within the system used to do theoretical calculations. By putting a low restriction on the location of electrons in large base space,

they make a more accurate orbital estimate. When molecular calculation is done, it is common to use sophisticated finite numbers based on the atomic orbitals cantered on each atomic nucleus within this molecule. Most molecular quantum mechanical methods begin calculating with the choice of a set of base functions. The use of a substantial base set for the success of calculation is a mandatory requirement. Standard basis for electronic computation calculation uses linear combinations of geosynchronous functions of set orbit. In order to accurately represent atomic orbitals, we should use a linear combination of several codgers. Gaussian offers a wide range of predefined base sets, which can be categorized from those numbers and types of works, in which they are included.

5.3. Basic parameters derived from DFT and their application to corrosion inhibition design

5.3.1. Frontier molecular orbitals

The frontier orbitals are very important in defining the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of molecules. Scientist Fukui [24] recognized the importance of the frontier orbitals of first time because the stereochemistry of the inhibition system and the chemical reactions were key factors in the governing of ease of reaction. A good relationship has been found between E_{HOMO} and corrosion resistance, which is often associated with the electron-sensitivity potential of the molecule. It is well known that the adsorption of the inhibitor on the surface of the metal may be on the basis of donor-acceptable interaction between the heteroatom electrons and/or π electrons and the vacant *d*-orbitals of the metal surface atoms [25]. A high value of E_{HOMO} is likely to indicate the electron donating tendency of the molecule to the vacant orbitals of acceptor molecules whereas the energy of the lower empty orbit shows the electron acceptor ability of the molecule(s). Regarding the value of the interval energy, $\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$, the big values of energy difference mean less reactivity of a chemical species. Good inhibition efficiency will be provided in low values of energy difference, because to reduce the energy from the previously occupied orbital, there is less to donate in the correct orbital of the metal [26].

5.3.2. Dipole moment

The dipole moment is a vector quality which is most extensively used for describing the polarity of a molecule. It is a measurement of the separation of the two opposite electrical charges (positive and negative) and represented as given in Eq. (12) [27]:

$$\mu = q\, R \tag{12}$$

Where μ is a dipole moment, R is the distance between two different charges and q is the extent of the different charge. The dipole moment is applied to the distribution of electrons among the two bonded atoms. The existence of dipole moment, the difference between non-polar and polar bonds is different. With pure dipole moment, the molecule is zero or very small, bond and molecules are considered non-polar and polar molecules with pure bipolar moment. Atoms with similar electronegative values, they produce chemical bonds with very small dipole moment. Total dipole moment, however, reflects only the global prohibition of polarity

of a molecule instead of a single bond notice that the efficiency of inhibitor molecules has decreased with decreasing efficiency. The dipole moment of inhibitors [28] therefore, positive signals of coefficient of μ indicate that the inhibitors can be applied to the metal surface by the physical mechanism [29]. Obot and Obi-Egbedi [30] found a high correlation (0.999) between corrosion inhibition and dipole moment efficiency of benzimidazole and its derivatives; namely, 2-mercaptobenzimidazole and 2-methylbenzimidazole using DFT. The obtained result shows that 2-mercaptobenzimidazole, which has the highest value of dipole moment, exhibits the higher inhibition efficiency. The adsorption strength increase as high value of the dipole moment between the inhibitor molecules and the metal surface.

5.3.3. Electronegativity and the electronic chemical potential

DFT has been found to be successful in providing insight into chemical reactivity and selectivity, in terms of global molecular properties, such as chemical potential ($-\mu$) and electronegativity (χ) [31]. Thus, for an N-electron system with an external potential v(r) and total electronic energy (E) the chemical potential, has been defined as the first derivative of the E with respect to N at constant v(r) as in Eq. (13) [32]:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{13}$$

According to Iczkowski and Margrave [33], it should be noted that, when assuming a quadratic relationship between E and N and in a finite difference approximation, than it can be written as represented in Eqs. (14) and (15):

$$\chi = -\mu \left(\frac{I+A}{2}\right) \tag{14}$$

$$\chi = -\frac{E_{HOMO} + E_{LUMO}}{2} \tag{15}$$

where A and I have the electron affinity and ionization potential, respectively, due to which the electronegative definition of Mulliken can be corrected [34]. In addition, a theoretical justification was provided for the theory of Sanderson's equation of electronegativity, which states that when two or more atoms join together to form a molecule, then their electro negativities is the same intermediate the value is adjusted from [35].

5.3.4. Global hardness and softness

There is total hardness (H) and softness properties, which also facilitate analysis of molecular selectivity and reaction. Correlation between quantum chemical quantities and corrosion inhibition is based on Pearson's hard and soft acids and bases, and the Lewis theory of acid and base [36]. Energy gap, ΔE (i.e., energy difference between E_{LUMO} and E_{HOMO}) also provides information about the reaction of inhibitor molecules. A hard molecule has a high value of ΔE denotes the hard nature of molecules, whereas a soft molecule is a small ΔE. Due to small ΔE value electrons can be easily supplied to acceptor system from soft molecules in comparison to

hard molecule. Hence, the reactive site of the molecule may be absorbed, where, σ has the highest value [37]. For the calculations of quantum chemical parameters, global hardness (Eq. (16)) and softness (Eq. (17)) the following equations can be used [38]:

$$\gamma = \frac{E_{HOMO} - E_{LUMO}}{2} \tag{16}$$

The reverse of the global hardness is written as the softness, σ has given in Eq. (17):

$$\sigma = \frac{1}{\gamma} \tag{17}$$

5.3.5. Mulliken population analysis

To identify the adsorption centers of inhibitors, Mulliken population analysis has been widely reported [39, 40]. All chemical interactions are either covalent or polar (electrostatic). Electric charge in the molecule is obviously responsible for electrostatic interaction. Local electron charge or density is important in the properties of many physical-chemical and chemical reactions of biological molecules. Thus, charge-based parameters have been widely employed as weak intermolecular interaction measures or as chemical reactive indices. Mulliken population analysis [41] is mostly used to calculate the charge distribution in a molecule. These numerical quantities are easy to obtain and provide at least a qualitative understanding of structural reactions of blocking molecules [42]. In addition, atomic charge is used to describe molecular polarization of molecules.

5.3.6. The fraction of electrons transferred (ΔN)

The fraction of electrons transferred (ΔN) has been calculated as given in Eq. (18) [43]:

$$\Delta N = - \frac{\chi_M + \chi_{inh}}{[2(\eta_m + \eta_{inh})]} \tag{18}$$

where χ_{inh} and χ_M and indicate the absolute electronegativity of the inhibitor molecule and metal, respectively. However η_{inh} and η_M denote the absolute hardness of the inhibitor molecule and metal. Usually, ΔN exhibits the inhibition efficiency generated from the electrons transferred, inhibitor molecule to the iron atom. According to Lukovitt et al. [44] if the value of ΔN is less than 3.6, then the inhibition efficiency of the inhibitor molecules increasing with electron releasing ability on metal surface. Improve electron releasing power, was replaced by electron-donating substance ($-OCH_3$ group) by altering a hydrogen atom of the phenyl ring, as in the case of MPTS, which was to improve the prohibition, but on the other hand, a decreasing effect has been observed by electron-attracting group ($-Cl$) in the case of CPTS.

6. Some recent studies of corrosion inhibitor using density function theory

DFT is widely used software designing new corrosion inhibitors of chemical compounds using energy of the highest occupational molecular orbital (E_{HOMO}) energy, the energy of the lowest

unoccupied molecular orbital (E_{LUMO}), ΔE (energy difference), dipole moment (μ), Mulliken population analysis, electronegativity and electronic chemical capacity (χ), global hardness (γ) and softness (σ), the transfer of electrons (ΔN) and molecular polarization potential are most important electronic parameters. As mentioned by some previous researchers [45–47], excellent corrosion inhibitors are usually those compounds that accept electrons from the metal as well as offer electrons in the empty orbital(s) of metal.

During the last two decades, computational methods have been developed as important tools in the corrosion resistance, because in the calculation, large amounts of compounds can be provided in large amounts within a reasonable time frame. The results of such studies can be further used as an appropriate starting point for experimental studies. Computational methods can also be important tools in the development of more suitable compounds used for metal protection, starting with the already available compounds and by identifying derivatives with better metal protection efficiencies through structural modifications. Recently, there are many studies in literature on computational studies of useful organic materials for metal protection. The goal of these studies is to gain insights at the molecular level on the contact of these organic matters with metal surfaces. This important approach is particularly important in the design of new and effective corrosion inhibitors for industrial applications in oil and gas fields. A recent review of some of the research has been given below. They are not enough anywhere because excellent reviews are available elsewhere [48].

6.1. Organic corrosion inhibitors studied using DFT

Using the semi-experimental AM1 method, Mahendra et al. [49], studied the inhibition efficiency of benzimidazole derivatives. Quantum chemical parameters such as E_{HOMO}, E_{LUMO}, ΔE, the fraction of electron transferred (ΔN), dipole moment (μ), and global hardness (γ) and softness (σ) were calculated, which detected a steric hindrance effect of molecules on inhibition efficiency, which was discussed. According to the results obtained (**Table 1**), E_{HOMO} was the most statistically significant term that influenced the inhibition efficiency. The more E_{HOMO}, the more prohibited efficiency was seen experimentally. Hyperchm 8.0 software was used for the use of detailed Quantum Chemical Study program package for the Inh I, Inh II, and Inh III. The experimental abilities of quantum chemical calculation and inhibitors were subject to correlation analysis. Based on HOMO and LUMO energy, HOMO and LUMO coefficients, polarizability, and Mulliken population analysis, it was concluded that considering a parameter is not enough and the synthesis of better corrosion inhibition can be achieved by controlling all the electronic properties and parameters of a selected group of molecules.

Quantum chemical calculation of commercially available drug namely grieseofulvin was calculated towards the corrosion inhibition potential of mild steel using Gaussian 9.0 software package [50]. Quantum chemical parameters has confirmed that the presence of heteroatoms and π electrons increases resistance towards corrosion of the surface of mild steel, which means that the inhibitor shows better inhibition efficiency against metal surface in aqueous solution. Various quantum chemical parameters such as energy gap (ΔE), E_{HOMO}, E_{LUMO}, dipole moment (μ) and hardness (γ) of drug molecule (**Figure 3**) has been evaluated to determine its corrosion inhibition efficiency and corresponding values are depicted in **Table 2**.

Inhibitors	E_{HOMO}(eV)	E_{LUMO}(eV)	ΔE (eV)	σ (eV)	μ (D)	ΔN (e)	η (eV)
Inh I	−8.8459	0.7865	8.0594	0.2462	3.2029	0.2709	4.0297
Inh II	−8.7028	0.7392	7.9636	0.2497	3.4714	0.2896	4.1194
Inh III	−8.6541	0.7069	7.9472	0.2516	5.0267	0.2918	3.9735

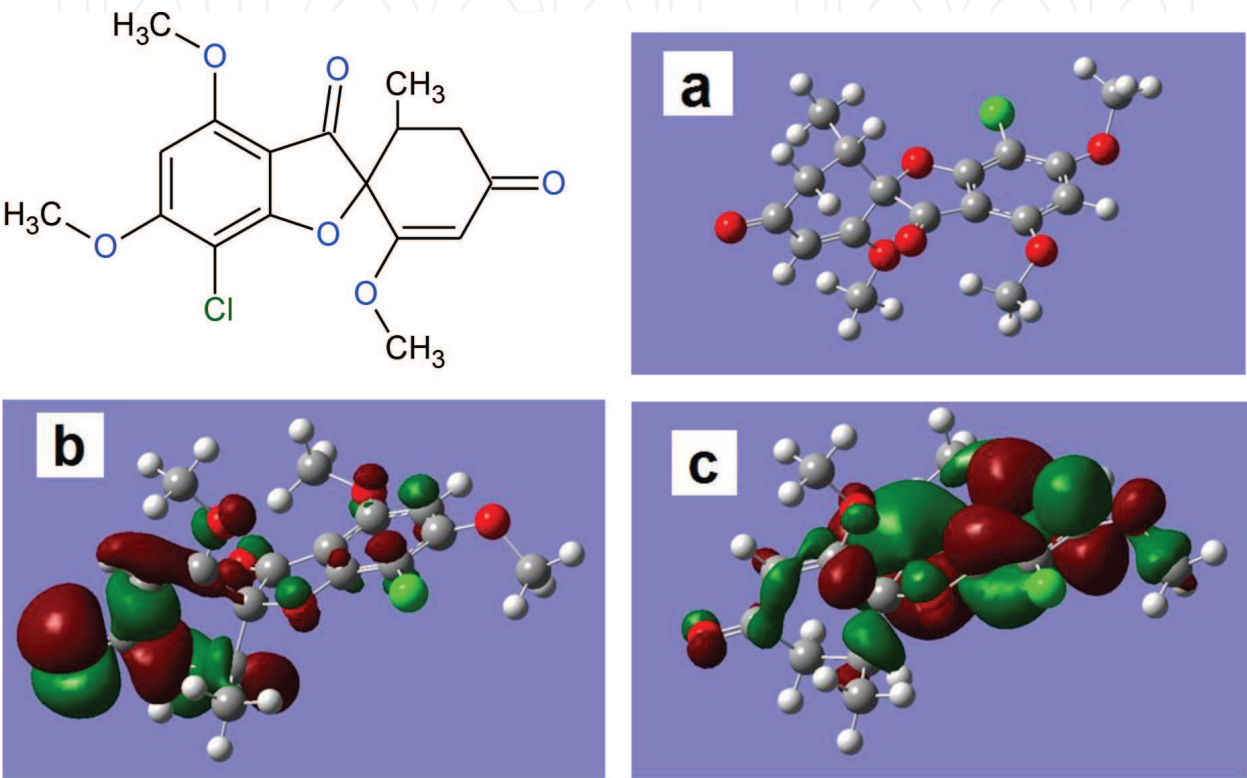**Table 1.** Quantum chemical parameters for the benzimidazole derivatives.

Figure 3. Molecular structure of griseofulvin with the (a) the optimized structure, (b) LUMO and (c) HOMO structures.

All parameters exhibited that griseofulvin acts as a good corrosion inhibitor towards mild steel in HCl solution.

Verma et al. [51] describes the effect of ring and ring size of three 3-amino alkylated indoles (AAIs) namely, N-((1H-indol-3-yl)(phenyl)methyl)-N-ethylethanamine (AAI-1), 3-(phenyl (piperidin-1-yl)methyl)-1H-indole (AAI-3) and 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) on mild steel corrosion acidic solution using experimental as well as theoretical calculations such as quantum chemical calculations and molecular dynamics simulations methods. Experimental results revealed that the inhibition efficiency increases with increased concentration of the corrosion inhibitors. Maximum inhibition efficiencies of 94.34% for AAI-1, 96.08% for AAI-2 and 96.95% for AAI-3 were obtained at 0.862 mM concentrations of inhibitors. Both experimental and theoretical calculations show that 3-amino alkylated indole with cyclic amino groups exhibit high corrosion inhibition efficiency compared with open-chain amino groups. Experimental results explains that resistance efficiency increases with increased

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (eV)	Υ
Griseofulvin	−0.0423	−0.0059	0.0364	3.2396	0.0182

Table 2. Quantum chemical parameters for the griseofulvin.

concentration of the inhibitors. Maximum inhibition efficiency of 94.34% for AAI-1, 96.08% for AA-II and 96.95% for AAI-3 was obtained in 0.862 mm concentrations of inhibitor. Quantum chemical calculations such as dipole moment (μ), E_{HOMO}, E_{LUMO}, ΔE, the fraction of electron transferred (ΔN), global electronegativity (χ), and global hardness (γ) and softness (σ) were calculated. Optimized structure, E_{HOMO} and E_{LUMO} of inhibitors are shown in **Figure 4** and calculation values are given in **Table 3**.

6.2. Plant extracts based corrosion inhibitors studied using DFT

Emeka et al. [52] studied the Inhibition efficiency of green and sustainable biomass extract of *capsicum* on mild steel in acidic solution. Capsaicin (**Figure 5a**) is the major phytoconstituents of capsicum, whose quantum calculation has been studied extensively. Chemical computations of Capsaicin were performed using the S-Mulliken Population Analysis through the DFT electronic structure program DML^3 [40–43]. Various quantum chemical parameters like E_{HOMO}, E_{LUMO}, ΔE, dipole moment (μ), global hardness (γ), softness (σ) and Fukui functions have been studied extensively. Investigation correlation between experimental and quantum chemical calculations and inhibition efficiency was discussed at this work.

Anupama et al. [53] examine the *Phyllanthus amarus* leaf extract (PAE) as the mild steel corrosion inhibitor in 1 M HCl. Weight loss, EIS and PDP techniques used to investigate corrosion behavior of PAE under various exposure time and temperature and successfully correlated with different parameters of quantum chemical analysis. Since extracting components are adsorbed on metal surface, inhibitive efficiency increases as concentrations increased and finally reached up to >90%. Computational calculations corresponding to phyllanthin (**Figure 5b**) a major component of PAE was made in order to understand the involvement of the component in the inhibition efficiency of the plant extract. Quantum chemical parameters; ΔE, E_{LUMO}, E_{HOMO}, dipole moment (μ), the fraction of electron transferred (ΔN), global hardness (γ) and softness (σ) and global electronegativity (χ) were calculated and stabilized the effect of structural features on the electron donating ability of major component phyllanthin of PAE.

Raja et al. [54] investigated Isoreserpiline (**Figure 5c**) as active molecule against corrosion protection of mild steel. Isoreserpiline is the major component of leaves and bark extracts of *Ochrosia oppositifolia*. Quantum calculation shows that the density (HOMO and LUMO) of ISR is located within the vicinity of the aromatic indole moiety. This study shows that π electron cloud of ring and lone pair on nitrogen atom of indole ring have high electron donating ability to metal surface. This can be well correlated with FTIR analysis that shows the coordination of ISR with the mild steel surface through electron rich moieties of indole ring. An ideal corrosion inhibitor can be donated electrons in metal surface through HOMO, as well as obtaining
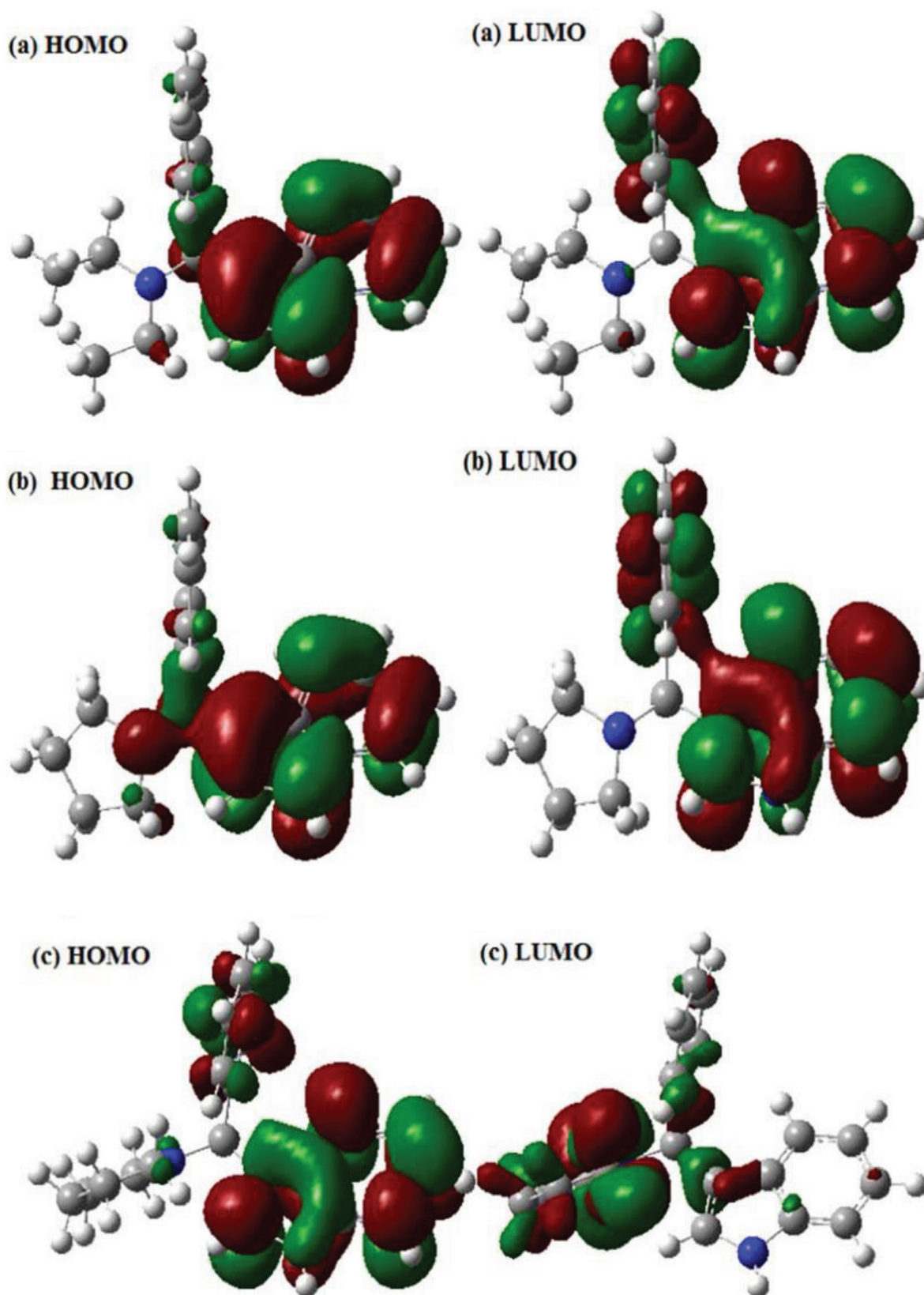
Figure 4. The frontier molecular orbital (left-hand side: HOMO; and right-hand side: LUMO) of the studied inhibitor APQDs derivatives (a) AAI-1, (b) AAI-2, and (c) AAI-3 [reprinted with permission].

Inhibitors	μ	E_{HOMO}	E_{LUMO}	ΔE	η	σ	χ
AAI-1	1.6927	−8.5748	−5.1214	3.4534	1.7267	0.57913	6.8481
AAI-2	1.9680	−8.5262	−5.2214	3.4504	1.7252	0.57964	6.8376
AAI-3	2.3671	−7.8036	−5.1236	2.6800	1.3350	0.74903	6.4636

Table 3. Quantum chemical parameters of inhibitors resultant from the B3LYP/6-31+G(d,p) method.
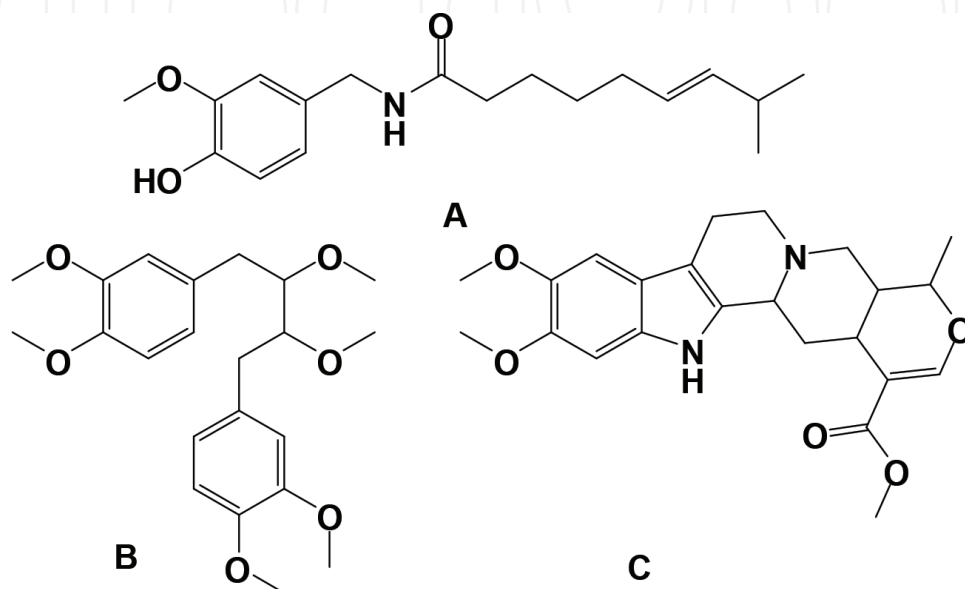

Figure 5. Molecular structure of (A) capsicum, (B) phyllanthin, and (C) Isoreserpiline.

electrons via LUMO through metal surfaces (Fe through Fe^{2+}, Fe^{3+} conversion) or bind mild steel surface strongly, which states that the ISR can donate and accept electrons through induction movement. On the other hand quantum calculation represents the energy level E_{HOMO}, E_{LUMO} and ΔE ($E_{HOMO} - E_{LUMO}$) for iron and inhibitor molecule. ΔE for ISR −0.3083 EV was found, which was more (less negative) than FE^{2+} and Fe^{3+} (−1.2178 and − 2.0712 EV); While E_{LUMO} values were found in ISR Fe, Fe^{2+} and Fe^{3+}. This result indicates that ISR can donate electrons to MS surface but in turn, MS cannot obtain donation electron from the surface. Quantum chemical analysis well supported the result of FTIR analysis and evidenced the possibility of electron transfer from inhibitor molecules to mild steel.

7. Future developments

Density functional theory (DFT) has become an attractive theoretical method, because it provides accurate, basic and important parameters for at least complex and molecules cost. Apart from this, by implementing the DFT methodology, we can understand reactionary behavior conditions of hard and soft acid/base (HSAB) principles that provide a systematic way interrupter/analysis of surface interaction and prediction. Survey of theoretical corrosion literature

presented in chapter (Sections 6.1 and 6.2) shows that density function theory (DFT) is a powerful tool to study fundamental, molecular-level processes regarding the corrosion barrier. However, it should be very careful with these calculations, these studies should be taken in planning can easily lead with inaccurate or inadequate data-sets for the wrong findings. Role of quantum chemistry in corrosion focus is likely to increase in future inhibitory studies moves towards the investigation of complex chemical mechanisms. However, due to high computational effort restrictions calculations mean that there will be no quantum chemical methods be able to replace experimental corrosion in the near future less expensive methods of study or computerized procedures regarding the corrosion inhibition.

8. Conclusion

This chapter focuses on the use of modern quantum chemical methods, primarily to describe the adsorption of corrosion-resistant molecules on a metal surface in the aqueous solution as the functional principle of density. It is evident that DFT can be used as powerful technique with a unique ability to make practical calculations on many complex bodies system, such as large organic molecules, drugs, ionic liquids those are widely used as inhibitor. Hydrophobic/hydrophilic nature of corrosion inhibitor has been identified as an important factor in determining the ability of the resistant to prevent corrosion. Finally, the idea of an important future in the design of new and effective corrosion inhibitors using DFT will identify organic structures, which have less toxicity besides having high corrosion protection capacity.

Acknowledgements

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