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Review

The use of quantum chemical methods in corrosion inhibitor studies

Gökhan Gece *

Ankara University, Faculty of Science, Department of Physical Chemistry, Ankara 06100, Turkey

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ABSTRACT

Quantum chemical methods are particularly significant in the study of electrochemistry and provide researchers with a relatively quick way of studying the structure and behaviour of corrosion inhibitors. The originality of this review article is based on the fact that it is the first and unique general reference for all those interested in the use of quantum chemical methods in corrosion inhibitor studies. It begins with a concise summary of the most used quantum chemical parameters and methods and then summarizes the results of research articles in corrosion science over the past 20 years.

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1. Introduction

Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity [1]. Thus, it has become a common practice to carry out quantum chemical calculations in corrosion inhibition studies. The concept of assessing the efficiency of a corrosion inhibitor with the help of computational chemistry is to search for compounds with desired properties using chemical intuition and experience into a mathematically quantified and computerized form. Once a correlation between the structure and activity or property is found, any number of compounds, including those not yet synthesized, can be readily screened employing computational methodology [2] and a set of mathematical equations which are capable of representing accurately the chemical phenomenon under study [3,4].

The study of corrosion processes and their inhibition by organic inhibitors is a very active field of research [5]. Many researchers report that the inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and so on [6,7]. The inhibiting mechanism is generally explained by the formation of a physically and/or chemically adsorbed film on the metal surface [8,9]. It is well known that organic compounds which act as inhibitors are rich in heteroatoms, such as sulphur, nitrogen, and oxygen [10,11]. These compounds and their derivatives are excellent corrosion inhibitors in a wide range of media and are selected essentially from empirical knowledge based on their macroscopic physico-chemical properties. Recently, theoretical predic-

tion of the efficiency of corrosion inhibitors has become very popular in parallel with the progress in computational hardware and the development of efficient algorithms which assisted the routine development of molecular quantum mechanical calculations [12]. Due to the enormous complexity of this type of studies which need to consider the metallic surface, inhibitor and solvent molecules, theoretical calculations of the corrosion inhibition processes cannot be achieved in a rigorous way from the viewpoint of quantum chemistry.

2. Quantum chemical parameters

Quantum chemical methods and molecular modeling techniques enable the definition of a large number of molecular quantities characterizing the reactivity, shape, and binding properties of a complete molecule as well as of molecular fragments and substituents. The use of theoretical parameters presents two main advantages: firstly, the compounds and their various fragments and substituents can be directly characterized on the basis of their molecular structure only; and secondly, the proposed mechanism of action can be directly accounted for in terms of the chemical reactivity of the compounds under study [13].

Quantum chemically derived parameters are fundamentally different from experimentally measured quantities, although there is some natural overlap. Unlike experimental measurements there is no statistical error in quantum chemical calculations. There is inherent error however, associated with the assumptions required to facilitate the calculations. In most cases the direction but not the magnitude of the error is known [13]. In using quantum chemistry-based parameters with a series of related compounds, the computational error is considered to be approximately constant throughout the series. The prominent quantum chemical parameters can be subdivided as follows:

* Tel: +90 312 212 67 20/1020; fax: +90 312 223 23 95.
E-mail address: gokhangc@gmail.com

2.1. Atomic charges

All chemical interactions are either electrostatic (polar) or orbital (covalent). Electric charges in the molecule are obviously responsible for electrostatic interactions. The local electron densities or charges are important in many chemical reactions and for physico-chemical properties of compounds. Thus, charge-based parameters have been widely employed as chemical reactivity indices or as measures of weak intermolecular interactions. Despite its usefulness, the concept of a partial atomic charge is somewhat arbitrary, because it depends on the method used to delimit between one atom and the next. As a consequence, there are many methods for estimating the partial charges. Mulliken population analysis [14] is mostly used for the calculation of the charge distribution in a molecule. These numerical quantities are easy to obtain and they provide at least a qualitative understanding of the structure and reactivity of molecules [15]. Furthermore, atomic charges are used for the description of the molecular polarity of molecules.

2.2. Molecular orbital energies

Highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}) are very popular quantum chemical parameters. These orbitals, also called the frontier orbitals, determine the way the molecule interacts with other species. The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that has room to accept electrons. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants [16]. The energy of the HOMO is directly related to the ionization potential and the energy of the LUMO is directly related to the electron affinity. The HOMO–LUMO gap, i.e. the difference in energy between the HOMO and LUMO, is an important stability index [17]. A large HOMO–LUMO gap implies high stability for the molecule in chemical reactions [18]. The concept of "activation hardness" has been also defined on the basis of the HOMO–LUMO energy gap. The qualitative definition of hardness is closely related to the polarizability, since a decrease of the energy gap usually leads to easier polarization of the molecule [19].

2.3. Dipole moment (μ)

The most widely used quantity to describe the polarity is the dipole moment of the molecule [20]. Dipole moment is the measure of polarity of a polar covalent bond. It is defined as the product of charge on the atoms and the distance between the two bonded atoms. The total dipole moment, however, reflects only the global polarity of a molecule. For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments.

2.4. Energy

The total energy calculated by quantum chemical methods is also a beneficial parameter. The total energy of a system is composed of the internal, potential, and kinetic energy. Hohenberg and Kohn [21] proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy.

3. Semiempirical methods

In principle, any observable property of an atomic or molecular system can be obtained from the Schrödinger equation. Over the past decades the semiempirical molecular orbital methods have been used widely in computational studies. Semiempirical approaches neglect many smaller integrals to speed up the calculations. In order to compensate for the errors caused by these approximations, empirical parameters are introduced into the remaining integrals and calibrated against reliable experimental or theoretical reference data. This strategy can only be successful if the semiempirical model retains the essential physics to describe the properties of interest. Provided that this is the case, the parameterization can account for all other effects in an average sense, and it is then a matter of validation to establish the numerical accuracy of a given approach.

In current practice, semiempirical methods serve as efficient computational tools which can yield fast quantitative estimates for a number of properties. This may be particularly useful for correlating large sets of experimental and theoretical data, for establishing trends in classes of related molecules, and for scanning a computational problem before proceeding with higher level treatments. There remains the need to improve semiempirical methods with regard to their accuracy and range of applicability, without compromising their computational efficiency. In addition, there is a need to develop new algorithms in order to exploit modern computer architectures and extend semiempirical calculations to ever larger molecules.

Over the years, a large number of methods with different acronyms have been developed, including MNDO [22], AM1 [23], PM3 [24]. Semiempirical methods differ in the details of the approximations (e.g. the core–core repulsion functions) and in particular in the values of the parameters. The semiempirical methods can be optimized for different purposes. The MNDO, AM1 and PM3 methods were designed to reproduce heats of formation and structures of a large number of organic molecules. Other semiempirical methods are specifically optimized for spectroscopic properties (e.g. INDO/S or CNDO/S).

3.1. MNDO (modified neglect of differential overlap)

It is based on the NDDO (neglect of diatomic differential overlap) approximation and in turn NDDO is an improved version of INDO (intermediate neglect of differential overlap) method. INDO itself is an improvement over the CNDO (complete neglect of differential overlap) approximation. There are several such semiempirical LCAO MO methods, developed for specific purposes.

3.2. AM1 (Austin model 1)

AM1 is a semiempirical method based on the neglect of differential diatomic overlap integral approximation. Specifically, it is a generalization of the modified neglect of diatomic differential overlap approximation. AM1 was developed by Michael Dewar and co-workers reported in 1985 [23]. AM1 is an attempt to improve the MNDO model by reducing the repulsion of atoms at close separation distances. The atomic core–atomic core terms in the MNDO equations were modified through the addition of off-center attractive and repulsive Gaussian functions. The complexity of the parameterization problem increased in AM1 as the number of parameters per atom increased from seven in MNDO to 13–16 per atom in AM1.

3.3. PM3 (parameterized model number 3)

PM3 is another semiempirical method based on the neglect of differential diatomic overlap integral approximation. The PM3

method uses the same formalism and equations as the AM1 method. The only differences are: (a) PM3 uses two Gaussian functions for the core repulsion function, instead of the variable number used by AM1 (which uses between one and four Gaussians per element); (b) the numerical values of the parameters are different. The other differences lie in the philosophy and the methodology used during the parameterization: whereas AM1 takes some of the parameter values from spectroscopic measurements, PM3 treats them as optimised values. The method was developed by Stewart and first reported in 1989 [24].

4. Corrosion inhibitors studied by semiempirical methods

The inhibition of corrosion in acid solutions can be affected by the addition of a variety of organic molecules. Compounds containing nitrogen, oxygen and sulphur have shown vast applications as corrosion inhibitors. The studies of Vosta and Eliášek [25] and Chakrabarti [26] can be respected as the first theoretical studies on corrosion inhibitors in the literature. Subsequently, Costa and Lluch [27] reported the results of quantum mechanical calculations of different compounds, such as linear-chain diols, diamines and aliphatic aminoalcohols as corrosion inhibitors of metals. They calculated HOMO and LUMO energies by using the semiempirical MINDO/3 method. A good agreement was found between their theoretical predictions and experimental data. Sayós et al. [28] performed theoretical calculations on several aromatic organic compounds as corrosion inhibitors for titanium and its alloys employing the MNDO method. They also concluded that the agreement with the experimental data was quite good. In the following decades, several studies on various compounds were reported which dealt with correlations of quantum chemical properties obtained with semiempirical tools with experimental findings. For instance, the influence of some heterocyclic compounds, i.e. some oxadiazole derivatives, on the corrosion of mild steel in acid solutions, has been investigated by Lagrenée et al. [29], and Bentiss et al. [30,31]. Beside using experimental methods, they used AM1 semiempirical method to obtain the electronic properties of those compounds. They calculated E_{HOMO}, E_{LUMO}, ΔE ($E_{LUMO} - E_{HOMO}$) and dipole moment (μ) and found a highly significant multiple correlation coefficient between experimental and theoretical data.

Semiempirical calculations to evaluate the efficiency of some imidazole derivatives as acidic corrosion inhibitors for zinc and iron have been performed by Bereket et al. [32,33] using AM1, PM3, MNDO and MINDO/3 methods. Charges on nitrogen atoms, total energy, ionization potential, E_{HOMO}, E_{LUMO}, ΔE ($E_{LUMO} - E_{HOMO}$) and dipole moment (μ) have been calculated and correlated with experimental results. A satisfactory agreement was found between theoretical and experimental data. Similar studies on these compounds have been carried out by Öğretir et al. [34,35] in order to probe the inhibition mechanism of corrosion via metal–ligand interaction using semiempirical methods. According to their conclusion, semiempirical calculations can be used to elucidate the mechanism of inhibition.

Popova et al. [36] investigated the effect of molecular structure of some different azole derivatives as corrosion inhibitors for mild steel in acidic medium by using the AM1 method. The effect of some triazole derivatives (triazole (TA), 3-amino-1,2,4-triazole (ATA) and 3,5-diamino-1,2,4-triazole (DTA)) on copper corrosion in 0.5 M HCl have been studied by El Issami et al. [37] using AM1, MNDO and PM3. They aimed to show the formation of the copper-ATA or copper-DTA complexes and establish a correlation between the highest occupied molecular orbital energy (E_{HOMO}) and inhibition efficiencies. Therefore, they calculated quantum chemical indices such as E_{HOMO}, E_{LUMO} and the energy gap (ΔE) and the energy of formation (ΔH_f). By comparing their experimen-

tal and theoretical results, they concluded that high values of E_{HOMO} indicated a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy of empty atomic orbitals, while the energy of the lowest unoccupied molecular orbitals indicated the ability of the molecule to accept electrons. Also, the less negative HOMO and the smaller energy gap reflected stronger chemisorbed bond and greater inhibitor efficiency.

Zhang et al. [38] also studied some triazole derivatives using Parker, Parr and Pople (PPP) method. They concluded that E_{HOMO}, E_{LUMO} and π-electron density were consistent with the inhibition efficiencies of the compounds. The adsorption behaviour of some thiazole derivatives at Fe surface was studied by Zhang et al. [39] through molecular dynamics simulation and quantum chemical calculations. Furthermore, some pyrazole [40–42] and pyridine [43–46] derivatives have been investigated as corrosion inhibitors in acidic media by means of semiempirical quantum chemical methods.

Due to the presence of the –C=N– group, electronegative nitrogen, sulphur and/or oxygen atoms in the molecule, Schiff bases should be good corrosion inhibitors. Recently, some Schiff bases as effective corrosion inhibitors for steel [47,48], aluminum [49,50] and copper [51,52] in acidic media have been investigated by using semiempirical molecular orbital methods. El Ashry et al. [53] correlated the structural characteristics of hydrazides and Schiff bases with their corrosion inhibition efficiency at different inhibitor concentrations in aqueous acid solutions and investigated the relation between the inhibition efficiency and quantum chemical parameters, such as E_{HOMO}, E_{LUMO}, dipole moment, total negative charge on molecules, and linear solvation energy. These researchers used a non-linear regression analysis to correlate quantum chemical parameters (E_{HOMO}, E_{LUMO}, μ, TE), LSER (Vi, π^*) and inhibitor concentrations (C_i) with the experimental inhibition efficiencies obtained by mass loss methods for the compounds. According to their results, the inhibition efficiency of the Schiff bases increases with increasing E_{HOMO} and decreasing E_{LUMO}, while an opposite trend was observed for the hydrazides. A highly significant multiple correlation coefficient ($r > 0.96$) was obtained between experimental and calculated efficiencies.

Some amides and their derivatives, e.g. urea, thiourea, thioacetamide, and thiosemicarbazide were found to be good inhibitors for mild steel in acid solutions [54–59]. Several quantum chemical studies [54–59] have been carried out on these compounds by using semiempirical methods. Zhang et al. [59], Fang and Li [57] found a strong relationship between inhibition effect and the ΔE ($E_{LUMO} - E_{HOMO}$), whereas Kutsán et al. [58] found a relationship between the dipole moment (μ) and corrosion parameters. According to the reported theoretical data, the inhibition efficiency decreased as the E_{HOMO} level decreased. The urea molecule has the lowest E_{HOMO} value, and, therefore, the lowest inhibition efficiency.

Imidazoline-based corrosion inhibitors are well known as efficient corrosion inhibitors and are used extensively to prevent oilfield corrosion. A considerable number of experimental studies of imidazoline inhibitors has been reported [60,61]. However, there were relatively few theoretical studies [62,63]. Wang et al. [63] measured the averaged percentage protection experimentally and obtained molecular geometry and charge density in MNDO calculations. Their theoretical predictions were in good agreement with experimental results.

The environmental requirements that are currently imposed on the development of "green" chemical inhibitors represent a strong motivation for the study of inhibition by natural tannins. Although anti-corrosive action of natural tannins was known for a long time, only in the past decade tannins were systematically investigated as metal corrosion inhibitors in various media both experimentally and theoretically [64–66].

Martinez et al. [64,65] calculated molecular properties of chestnut and mimosa tannins most relevant to their action as corrosion

inhibitors. These were, namely, the geometrical structure of the molecule, the dipole moment (μ), HOMO and LUMO energies, and the energy gap. According to the results of their work, the analysis of the action of metal corrosion inhibitors by quantum chemical tools may, to a great extent, eliminate an empirical approach to research in this field. Moreover, it may also facilitate a rational selection and design of new inhibitors.

As an alkaloid, berberine could be readily abstracted from natural *coptis* [67], and the hydrochloric berberine has also been commonly used for years as a non-toxic antibiotic in China [68]. Since little is known about the inhibition behaviour of berberine for metals in acidic media, Li et al. [69] used experimental and quantum chemical methods to discuss the correlation of the inhibition effect and molecular structure of berberine. The authors predicted that the adsorption of berberine on the mild steel surface in sulfuric acid may be achieved by the interaction between iron atoms and cyclic molecular π orbital and calculated HOMO and LUMO energies. The density distribution of HOMO/LUMO indicated that there were several feasible absorption sites in one berberine molecule which favored strong adsorption and high inhibition efficiency.

Attempts to connect corrosion inhibition with structural properties of prospective molecules by using semiempirical quantum chemical methods were developed along with the theories of reactivity. Various compounds were investigated i.e. zinc di-alkyl-di-thiophosphates [70,71], potassium ethyl xanthate [72], phthalocyanines [73], polymethylene amines [74], benzyl triphenyl phosphonium bromide [75], nicotinic acid (pyridine 3-carboxylic acid) [76], hydrazine carbodithioic acid derivatives [77], aliphatic amines [78], pyrimidine derivatives [79], piperazine derivatives [80], amino acids and hydroxy carboxylic acids [81], phenyl-*N,N*-dimorpholinemethanes [82], aniline trimers [83], tri-block copolymers [84], quarternary ammonium salts [85], organophosphorus compounds [86], *para*-chlorobenzene nitriles [87], maleimide and its derivatives [88], anhydrides and imides [89] substituted catechols and pyrogallols [90]. Parameters of electron structure have been extensively used for the correlation with corrosion inhibition effect of these organic compounds.

Although there is no general way to predict the potential of a compound to be good corrosion inhibitor or to find a universal type of correlation, Babić-Samardžija et al. [91] attempted to correlate some molecular parameters of *N*-heterocyclic amines (piperidine (pip), 2-methyl piperidine (2mp), 3-methyl piperidine (3mp), 2,6-dimethyl piperidine (26dp), 3,5-dimethyl piperidine (35dp)) with their corrosion inhibition efficiency. For this purpose, they used PM3, AM1 and MNDO semiempirical methods. The effect of the molecular structure of these compounds on their inhibiting properties has been considered in terms of their electronic and chemical structure. Firstly, they studied the effect of electron density, i.e. charge on the nitrogen atom and on the entire heterocyclic ring. Secondly, they investigated the effect of structural changes in terms of bond distances and angles. The total energy (E_{tot}) was obtained after geometric optimization with respect to all nuclear coordinates. According to the results of their computational study, a relationship between some molecular parameters and the inhibition properties of amino compounds was found. Nevertheless, a number of neglected parameters that could be involved in such correlations, such as surface and solution characteristics, give at least a simplified explanation, though the correlation is not so simple and straightforward as might be expected. However, it is clear that the inhibition properties of these *N*-heterocyclic amines could be related to the charge on nitrogen atom and sum of the net charge of the six atoms from the cyclic ring.

Babić-Samardžija and Hackerman [92] also used molecular modeling to gain insights into structural and electronic effects of polypyrazolylborates; dihydrobis(1-pyrazolyl) borate (Bp) and hydrotris(1-pyrazolyl)borate (Tp) in relation to their inhibition efficiencies and adsorption behaviour. According to the findings of their electrochemical measurements, both polypyrazolylborates were relatively efficient inhibitors against acidic iron corrosion.

Such parameters as the HOMO and LUMO energies, energy gap, total and binding energies and the heat of formation were obtained by the MNDO method. It was obvious that Bp had a lower binding energy (8.231 kJ mol^{-1}) and heat of formation (268 kJ mol^{-1}) as well as lower total energy (171.677 kJ mol^{-1}) than did Tp. The energy gap (Δ) between the E_{HOMO} and E_{LUMO} showed that the greater inhibition effect could be related to the lower energy difference, i.e. to the Bp molecules that could be more readily excited and undergo a charge transfer interaction with the metal surface. The same researchers also studied the inhibition properties of macrocyclic cobalt(III) complexes [93,94] in the corrosion of iron in perchloric acid solutions. They used semiempirical PM3 and ZINDO/1 methods to correlate structural properties of the complex species and their inhibition efficiency. Their theoretical predictions were in good agreement with experimental results.

Detailed experimental and theoretical investigation of 23 different compounds including amines, thiourea derivatives, and acetylenic alcohols as corrosion inhibitors for 22% Cr stainless steel (austenitic-ferritic, duplex) in hydrochloric acid solutions were carried out by Cardoso et al. [95–97] using quantitative structure-property relationship (QSPR) prediction analysis. They used the AM1 method to calculate quantum chemical parameters and obtained excellent correlations.

Recently, Khaled [98] applied molecular simulation tools to optimize the structure of adsorbed triazole derivatives. The iron/inhibitor/solvent interfaces were simulated and the charges on the inhibitor molecules as well as their structural parameters were calculated in the presence of solvent effects. According to the experimental and theoretical data, aminotriazole was the best inhibitor among triazole, aminotriazole and benzotriazole.

Several studies of corrosion inhibitors employing semiempirical methods have been reviewed up to date (Table 1). As mentioned previously, the use of semiempirical methods has been a subject of particularly intense interest in corrosion inhibitor studies in recent years.

Consequently, it can be said that in such studies two different approaches have been used. In the first, empirical, approach each functional group in an inhibitor molecule is assumed to contribute a unique, independent and additive increment of corrosion protection determined from the corrosion rates by correlation of the molecular fragments with inhibitor performance. In the second, semiempirical, approach, quantum chemical properties are correlated with inhibitor performance; determining the descriptor parameters is a most important aspect of this approach [99].

5. *Ab initio* and density functional theory (DFT) methods

Quantum mechanical methods (*ab initio*, density functional theory (DFT) and semiempirical) are all based on solving the time-independent Schrödinger equation for the electrons of a molecular system as a function of the positions of the nuclei. The term *ab initio* indicates that the calculation is from first principles and that no empirical data is used. The simplest type of *ab initio* electronic structure calculation is the Hartree–Fock (HF), in which the instantaneous Coulombic electron–electron repulsion is not specifically taken into account and only its average effect is included in the calculation. This is a variational procedure, and, therefore, the obtained approximate energies, expressed in terms of the system wave function, are always equal to or greater than the exact energy, and approach a limiting value called the Hartree–Fock limit as the size of the basis is increased [100]. Many types of calculations (Møller-Plesset perturbation theory and coupled cluster the-

Table 1
Corrosion inhibitors studied by semiempirical methods

Method	Inhibitor	References
MINDO/3	Linear-chain diols; diamines; aliphatic aminoalcohols; 4-methyl-5-substituted imidazole derivatives; 4-methyl-5-substituted imidazole derivatives; imidazole; benzimidazole; 2-methylbenzimidazole; 2-amino benzimidazole; 2-hydroxymethylbenzimidazole; 2-(3-pyridyl)benzimidazole; 2-benzylbenzimidazole; 2-benzylbenzimidazole-2-ylphenylamine; 2-phenylbenzimidazole; benzylbenzimidazole; 1,2-bis benzylbenzimidazole; butylimidazolidine; 2-(1-methylethyl)-5-hydroimidazole; 2-(2-butylphenyl)-5-hydroimidazole; methyl substituted pyridines; *N*,*N*'-*o*-phenylen-bis(3-mehoxy-salicylidenimine); *N*-2-hydroxyphenyl-(3-methoxy-salicylidenimine); *N*-4-phenylcarbazide-(3-methoxy-salicylidenimine); *N*,*N*'-*o*-phenylen-bis(salicylidenimine); *N*,*N*'-*p*-phenylen-bis(salicylidenimine); *N*-4-phenylcarbazide-(salicylidenimine); aromatic hydrazides; urea; thiourea; thioacetamide; thiosemicarbazide; berberine; piperazine; 1-methylpiperazine; 2-methylpiperazine; *cis*-2,6-dimethylpiperazine; 1-benzylpiperazine; 1-(diphenylmethyl)piperazine; *para*-chloro cinnamonitrile; *para*-chloro benzonitrile; *para*-chloro benzeneacetonitrile; *para*-chloro bsopropyl benzeneacetonitrile	[27,32–34,45,51,53,57,69,80,87]
MNDO	Phenol, nitrobenzene; aniline; toluene; picric acid; 4-methyl-5-substituted imidazole derivatives; 4-methyl-5-substituted imidazole derivatives; imidazole; benzimidazole; 2-methylbenzimidazole; 2-amino benzimidazole; 2-hydroxymethylbenzimidazole; 2-(3-pyridyl)benzimidazole; 2-benzylbenzimidazole; 2-benzylbenzimidazole-2-ylphenylamine; 2-phenylbenzimidazole; benzylbenzimidazole; 1,2-bis benzylbenzimidazole; butylimidazolidine; 2-(1-methylethyl)-5-hydroimidazole; 2-(2-butylphenyl)-5-hydroimidazole; 4-methylimidazole; (4-methylimidazole-5-yl)methan-1-ol; ethyl-4-methylimidazole-5-carboxylate; 4-methylimidazole-5-carboxylic acid; 4-methylimidazole-5-carbaldehyde; triazole; 3-amino-1,2,4-triazole; 3,5-diamino-1,2,4-triazole; pyrazole and bipyrazole derivatives; pyridine; 3-picoline; 2-picoline; 4-picoline; 2,4-lutidine; 3-methyl pyridine; 2-methyl pyridine; 3,5-dimethyl pyridine; 2,6-dimethyl pyridine; 2,5-dimethyl pyridine; 2,4,6-trimethyl pyridine; methyl substituted pyridines; 2-[2-aza-2-(5-methyl(2-pyridyl))vinyl]phenol, 2-[2-aza-2-(5-methyl(2-pyridyl))vinyl]-4-bromophenol; 2-[2-aza-2-(5-methyl(2-pyridyl))vinyl]-4-chlorophenol; aromatic hydrazides; zinc di-alkyl-di-thiophosphate; polymethylene amines; 2-mercaptopyrimidine; 2,4-dimercaptopyrimidine; 2-mercapto-4-methylpyrimidine; 2-mercapto-4-aminopyrimidine; 2-mercapto-4-hydroxypyrimidine; 2-mercapto-4-amino-6-methylpyrimidine; 2-mercapto-4-amino-6-hydroxypyrimidine; 2-mercapto-4-amino-5-nitroso-6-hydroxypyrimidine; piperazine; 1-methylpiperazine; 2-methylpiperazine; *cis*-2,6-dimethylpiperazine; 1-benzylpiperazine; 1-(diphenylmethyl)piperazine; maleimide; *N*-(*p*-aminophenyl)-maleimide; *N*-(*p*-nitrophenyl)maleimide; dihydrobis(1-pyrazolyl)borate; hydrotris(1-pyrazolyl)borate; thiosemicarbazides	[28,32,35,37,40,43–45, 50,53,63,70,71,74,79, 80,88,89,91,92,99]
AM1	2,5-bis(4-nitrophenyl)-1,3,4-oxadiazole (PNOX); 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (PAOX); 2,5-diphenyl-1,3,4-oxadiazoles; 3,5-diphenyl-1,2,4-triazoles; 2,5-di(*n*-pyridyl)-1,3,4-oxadiazoles; 2,5-bis(4-dimethylaminophenyl)-1,3,4-oxadiazole; 2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole; 4-methyl-5-substituted imidazole derivatives; 4-methyl-5-substituted imidazole derivatives; imidazole; benzimidazole; 2-methylbenzimidazole; 2-amino benzimidazole; 2-hydroxymethylbenzimidazole; 2-(3-pyridyl)benzimidazole; 2-benzylbenzimidazole; 2-benzylbenzimidazole-2-ylphenylamine; 2-phenylbenzimidazole; benzylbenzimidazole; 1,2-bis benzylbenzimidazole; butylimidazolidine; 2-(1-methylethyl)-5-hydroimidazole; 2-(2-butylphenyl)-5-hydroimidazole; 4-methylimidazole; (4-methylimidazole-5-yl)methan-1-ol, ethyl-4-methylimidazole-5-carboxylate; 4-methylimidazole-5-carboxylic acid; 4-methylimidazole-5-carbaldehyde; indole; 1,3-benzothiazole; 1H-benzotriazole; 2,1,3-benzothiadiazole; triazole; 3-amino-1,2,4-triazole; 3,5-diamino-1,2,4-triazole; methyl substituted pyridines; benzylidene-pyridine-2-yl-amine; (4-methyl-benzylidene)-pyridine-2-yl-amine; (4-chloro-benzylidene)-pyridine-2-yl-amine; benzylidene-(2-methoxy-phenyl)-amine; (2-methoxy-phneyl)-(4-methyl-benzylidene)-amine; (4-chloro-benzylidene)-(2-methoxy-phenyl)-amine; (4-nitro-benzylidene)-(2-methoxy-phenyl)amine; tributylamine; *n*-octyamine; diphenylamine; dodecylamine; di-*n*-butylamine; cyclohexylamine; *n*-butylamine; triethylamine; hexylamine; *sec*-butylamine; diethylamine; propylamine; isopropylamine; bidentate salicylaldiminato Schiff base ligands; aromatic hydrazides; aniline; thiourea; allylthiourea; *N*,*N*'-diethylthiourea; *N*,*N*'-diisopropylthiourea; phenylthiourea; diphenyl-thiourea; thiocarbanilide; sym-di-o-tolythiourea; 1,3-dibutyl-2-thiourea; 1,3-diethyl-2-thiourea; 1,3-dimethyl-thio-urea; 2-mercaptopyrimidine; 2,4-dimercaptopyrimidine; 2-mercapto-4-methylpyrimidine; 2-mercapto-4-aminopyrimidine; 2-mercapto-4-hydroxypyrimidine; 2-mercapto-4-amino-6-methylpyrimidine; 2-mercapto-4-amino-6-hydroxypyrimidine; 2-mercapto-4-amino-5-nitroso-6-hydroxypyrimidine; piperazine; 1-methylpiperazine; 2-methylpiperazine; *cis*-2,6-dimethylpiperazine; 1-benzylpiperazine; 1-(diphenylmethyl)piperazine; glycolic acid; glycine; malic acid; aspartic acid; valine; lactic acid; alanine; mandelic acid; phenyl-alanine; benzylic acid; citric acid; glutamic acid; *para*-substituted phenyl-*N*,*N*-dimorpholinemethanes; tetrabutyl ammonium chloride; tetraethyl ammonium chloride; phenyltriethyl ammonium chloride; benzyltrimethyl ammonium chloride; benzyltriethyl ammonium chloride; benzyltributyl ammonium chloride; cetyltrimethyl ammonium bromide; alkylbenzyldimethyl ammonium chloride; benzyldimethylbutyl ammonium chloride; polyethylene glycol; substituted *n*-alkyl catechols; propargyl alcohol; 2-pentyn-1-ol, 3-butyn-1-ol; 2-butyn-1-ol; 2-butyne-1,4-diol	[29–31,45,47–49,52,53,55,58,79–82,85,90,91,95–97]
PM3	4-methyl-5-substituted imidazole derivatives; imidazole; benzimidazole; 2-methylbenzimidazole; 2-amino benzimidazole; 2-hydroxymethylbenzimidazole; 2-(3-pyridyl)benzimidazole; 2-benzylbenzimidazole; 2-benzylbenzimidazole-2-ylphenylamine; 2-phenylbenzimidazole; benzylbenzimidazole; 1,2-bis benzylbenzimidazole; butylimidazolidine; 2-(1-methylethyl)-5-hydroimidazole; 2-(2-butylphenyl)-5-hydroimidazole; 4-methylimidazole; (4-methylimidazole-5-yl)methan-1-ol; ethyl-4-methylimidazole-5-carboxylate; 4-methylimidazole-5-carboxylic acid; 4-methylimidazole-5-carbaldehyde; triazole; 3-amino-1,2,4-triazole; 3,5-diamino-1,2,4-triazole; benzotriazole; *N*,*N*'-bis-(2-thionobenzothiazolin-3-yl-methyl)-*n*-dodecylamine (BTBMDA); *N*,*N*'-bis-(2-thionobenzothiazolin-3-yl-methyl)-*n*-octadecylamine(BTBMOA); methyl substituted pyridines; 2-sulfobenzoic acid imide (saccharin); 2-butyne-1,4-diol (butynediol); 1,4-(β,β'-dihydroxy-2-butyn, 4(β-hydroxypropoxy)-butyn-2-ol-1; 1-methylenecaboxypyridinium chloride; *N*,*N*'-methylenedipyridinium dichloride; aromatic hydrazides; thiourea; allylthiourea; phenylthiourea; diphenyl-thiourea; bis-piperidiniummethyl-urea (BMPU); mono-piperidiniummethyl-urea (MPMU); mimosa tannin; chestnut tannin; mangrove tannin; potassium ethyl xanthate; metal-free phthalocyanine (H₂Pc); copper phthalocyanine (CuPc); copper phthalocyanine tetrasulfuric tetrasodium salt (CuPc·S4·Na4); benzyl triphenyl	

Table 1 (continued)

Method	Inhibitor	References
	phosphonium bromide; nicotinic acid; N'-furan-2-yl-methylene-hydrazine carbodithioic acid; N'-(4-dimethylamino-benzylidene)-hydrazine carbodithioic acid; N'-(3-nitro-benzylidene)-hydrazine carbodithioic; 2-mercaptopyrimidine; 2,4-dimercaptopyrimidine; 2-mercapto-4-methylpyrimidine; 2-mercapto-4-aminopyrimidine; 2-mercapto-4-hydroxypyrimidine; 2-mercapto-4-amino-6-methylpyrimidine; 2-mercapto-4-amino-6-hydroxypyrimidine; 2-mercapto-4-amino-5-nitroso-6-hydroxypyrimidine; piperazine; 1-methylpiperazine; 2-methylpiperazine; cis-2,6-dimethylpiperazine; 1-benzylpiperazine; 1-(diphenylmethyl)piperazine; glycolic acid; glycine; malic acid; aspartic acid; valine; lactic acid; alanine; mandelic acid; phenyl-alanine; benzylic acid; citric acid; glutamic acid; 2-(diethylamino)ethyl methacrylate-block-2-(dimethylamino)ethyl methacrylate-block-2-(N-morpholino)ethyl methacrylate (PDEA-PDMA-PMEMA); 2-(diisopropylamino)ethyl methacrylate-block-2-(dimethylamino)ethyl methacrylate-block-2-(N-morpholino)ethyl methacrylate (PDPA-PDMA-PMEMA); tetrabutyl ammonium chloride; tetraethyl ammonium chloride; phenyltriethyl ammonium chloride; benzyltrimethyl ammonium chloride; benzyltriethyl ammonium chloride; benzyltributyl ammonium chloride; cetyltrimethyl ammonium bromide; alkylbenzyldimethyl ammonium chloride; benzyldimethylbutyl ammonium chloride; polyethylene glycol; 1-triphenylphosphine; 2-tetraphenylphosphonium chloride; 3-chloromethyltriphenylphosphonium chloride; 4-benzyltriphenylphosphonium; piperidine; 2-methylpiperidine; 3-methylpiperidine; cis-2,6-dimethylpiperidine; 3,5-dimethylpiperidine; 3-hydroxypiperidine; 4-hydroxypiperidine; 4-aminopiperidine; O-,S-,N-dithiocarbamato(1,4,8,11-tetraazacyclotetradecane)cobalt(III) complexes; thiosemicarbazides	[32–35,37–39,45,46,53,58,59,64–66,72,73,75,77,79–81,84–86,91,93,98,99]
ZINDO/1	Aniline trimers; O-,S-,N-dithiocarbamato(1,4,8,11-tetraazacyclotetradecane)cobalt(III) complexes; macrocyclic-bidentate cobalt(III) complexes	[83,93,94]

ory) begin with a Hartree–Fock calculation and subsequently correct for electron–electron repulsion, referred to also as electronic correlation. Density functional theory (DFT) is used to investigate the electronic structure, principally the ground state of many-body systems, in particular atoms, molecules and the condensed phases. The main objective of DFT is to replace the many-body electronic wave function with the electronic density as the basic quantity [101]. Any exchange functional can be combined with any correlation functional in DFT calculations. For example, the notation BLYP/6-31G* denotes a density functional calculation done with the Becke 1988 exchange functional and the Lee-Yang-Parr correlation functional, with the orbitals expanded in a 6-31G* basis set [13].

6. Corrosion inhibitors studied by *ab* initio and DFT methods

Ma et al. [102] attempted to find theoretical parameters to characterize inhibition property of three nitrogen-heterocyclic compounds, namely 3,5-dimethyl-1H-pyrazole, pyridine and 2-(3-methyl-1H-pyrazol–5-yl)pyridine against steel corrosion by using an *ab initio* method employing the HF/LANL2DZ basis set. According to their results, corrosion inhibition efficiency is related to the HOMO energy. They also investigated the interaction between inhibitor molecules and one iron atom and found that the lower the value of combined energy, the more stable the formed complex is, and the inhibitor has better inhibitive property.

A similar interaction energy approach was used for the theoretical study of some aniline derivatives toward the corrosion of copper in hydrochloric acid. Henríquez-Román et al. [103] performed *ab initio* SCF-HF calculations using D95 and D95 V basis sets for aniline derivatives and copper clusters, respectively. Their results showed that corrosion inhibition by aniline molecules can be associated mainly with local properties acting on active sites present in the copper surface.

The electronic and molecular structures of several heterocyclic compounds, 1,3,4-thiadiazole and its derivatives have been calculated by Rodríguez-Valdez et al. [104] by means of B3LYP/STO-3G* method. Such parameters as the total energy, ΔE, the HOMO and LUMO energies, dipole moment (μ) and global hardness (η) were calculated for each one of the derivatives of 1,3,4-thiadiazole, both in the gas and liquid phases. No significant differences were found for the structures of these compounds in gaseous and liquid phases.

Rodríguez-Valdez et al. [105] performed calculations of 4-amino-1,2,3,5-thiatriazole and 5-amino-1,2,3,4-thiatriazole by using a modified density functional, called PBEg, with 3-21G*, CBSB2**, CBSB7, CBSB4 and CBSB1 basis sets. Because of the lack of experimental data for these compounds, they made a comparison of their results with the previous computational results. They found good agreement between the results of these studies indicating that accurate results could be obtained in a reasonable time by using their new DFT method. A similar study on the efficiency of hydroxyethyl, aminoethyl and amidoethyl was also carried out by Rodríguez-Valdez et al. [106] using the PBEg functional with the CBSB2** basis set.

Feng et al. [107] performed calculations of a self-assembled monolayer of 2-mercaptobenzothiazole (MBT) in order to investigate the adsorbate-surface interactions by the B3LYP/6-31+G* method. They calculated such parameters as the atomic charges for two tautomeric forms of the MBT molecule (i.e. thiol and thione), the HOMO and LUMO energies and the interaction energy between MBT and iron. They chose benzothiazole to compare the results obtained by MBT. The HOMO energies of two forms of MBT (-624.1 kJ mol^{-1} for thiol form and -583.5 kJ mol^{-1} for thione form) were larger than that of benzothiazole (-647.9 kJ mol^{-1}). These results showed the importance of the exocyclic sulphur atom in forming the self-assembled monolayers on iron. The interaction energy calculations also predicated that MBT chemically adsorbs on the iron surface most probably via the exocyclic sulphur atom.

To obtain further insights into the adsorbent-surface interactions, Feng et al. [108] also applied B3LYP/6-31+(d,p) method for 5,10,15,20-tetraphenylporphyrin (TTP) and 5,10,15,20-tetra-(4-chlorophenyl)porphyrin (TCIPP) inhibitors for iron corrosion. They computed the HOMO and LUMO energies of these two molecules and found a higher value (-505.67 kJ mol^{-1}) for TTP than that for TCIPP (-543.69 kJ mol^{-1}). They concluded that the interaction between TTP and iron will be stronger than that between TCIPP and iron.

In order to probe the interactions between methionine molecules and metal surface, theoretical calculations were performed by Özcan et al. [109] by using B3LYP/6-311**G(d,p) method. A local type reactivity criterion (Fukui index) was considered and Fukui indices were determined for $N + 1$ and $N - 1$ electron species at the geometry of the reference N-electron methionine molecule. According to their results, it was shown that localization of frontier molecular orbitals (HOMO and LUMO) and condensed Fukui indices (f^- and f^+) analysis of the reactive regions are very useful in characterizing of organic adsorbates.

Li et al. [110] computed the HOMO and LUMO energies, energy gap, molecular orbital densities and dipole moment of newly synthesized three triazole derivatives: 4-chloro-acetophenone-O-1′-(1′,3′,4′-triazolyl)-metheneoxime (CATM), 4-methoxyl-acetophenone-O-1′-(1′,3′,4′-triazolyl)-metheneoxime (MATM) and 4-fluoro-acetophenone-O-1′-(1′,3′,4′-triazolyl)-methenoxime (FATM) as corrosion inhibitors of mild steel in acid media by $ab\ initio$ method employing 3-21G* basis set. They could not find a direct relationship between the inhibition efficiency and the E_{HOMO}, E_{LUMO} and dipole moment of the molecules. Therefore, they tried to reduce the complexity of adsorption process by using just the values of ΔG^o_{ads} obtained from the thermodynamic calculations. According to the free energy of adsorption and calculated quantum parameters, two types of interactions, chemisorption and physisorption, were responsible for the inhibition behaviour of these triazole derivatives.

Gao and Liang [111] investigated the inhibition efficiency of 1-diethylamino-propan-2-ol (EAP) and 1,3-bis-diethylamino-propan-2-ol (DEAP) as corrosion inibitors for brass in simulated atmospheric water. They calculated the Mulliken charges, HOMO and LUMO energies, total energy and dipole moment by using the B3LYP/6-311G** methodology. According to their calculation results, the E_{HOMO} of DEAP (-0.205 a.u.) was higher than in the case of EAP (-0.222 a.u.) and the values of ΔE for EAP and DEAP were -0.258 and -0.242 a.u., respectively. They found a correlation between the inhibition efficiency of DEAP with higher values of E_{HOMO} and lower values of ΔE and dipole moment which was in a good agreement with the experimental findings.

In order to understand the formation of protective film on iron by alkynol inhibitors (oct-1-yn-3-ol and 2-2-(1,1,-dimethyl-prop-2-ynyloxy)-ethoxy-ethanol) in acidic solutions, Lendvay-Györik et al. [112] calculated the binding energy of both dative iron-triple bond and the iron-alcoholic oxygen bond by using B3LYP/3-21G* and HF/6-311G** methods. They also calculated vibrational frequencies characteristic of the iron-bonded alkynol molecules for comparison with experimental IR spectra. Their calculation results supported the formation of a dative bond between the iron and the carbon–carbon triple bond.

Qafsaoui et al. [113] compared the inhibitive effect of 3-amino 1,2,4-triazole (ATA) with benzotriazole (BTAH) and 1-hydroxybenzotriazole (BTAOH) on the pitting corrosion of copper induced by sulfate and chloride ions by the Hartree–Fock method. They performed calculations to estimate interaction energies between these aggressive anions and ATA supported by Cu^+ ions. They used small Cu^+ clusters to model the copper surface. The binding energy of Cl^- on the ATA-Cu_n^+ system was found to be 13 kJ mol^{-1} higher than the binding energy of Cl^- on clusters of Cu^+ ions. In contrast, the binding energy of SO_4^{2-} on the ATA-Cu_n^+ system was found to be 19 kJ mol^{-1} lower than the interaction energy between SO_4^{2-} ions and the clusters of Cu^+ ions. These calculations showed a significant inhibitive effect of ATA in the presence of chloride ions and that in contrast to the two other inhibitors, ATA was less efficient in sulfate medium than in the chloride one because of the strong interaction with chloride ions.

The correlation between the molecular structures and corrosion inhibition efficiencies of thioacetamide (TAcA), thiourea (TU) and thiobenzamide (TBA) was investigated by Özcan and Dehri [114] using the $ab\ initio$ 6-31G(d) method. To investigate the effect of substituents on the inhibition mechanism and efficiency, they computed the HOMO and LUMO energies, energy gap, the volumes of molecules and molecular orbital densities. Although they could not find a correlation between the LUMO energy and inhibition efficiency for TU molecule, an increase in inhibition efficiencies of molecules was seen when the molecules had higher HOMO energies. Their HOMO energies increased in the order of thiobenzamide > thiourea > thioacetamide, which is in agreement with experimental data. The effects of thiourea (TU), methylthiourea

(MTU) and phenylthiourea (PTU) on the corrosion of mild steel in 0.1 M H_2SO_4 were also investigated by Özcan et al. [115] in relation to the concentration of thioamides. The electronic properties of these compounds were calculated by $ab\ initio$ RHF/6-31G(d) method. The highest E_{HOMO} and the lowest E_{LUMO} and energy gap values were found for PTU which was the most efficient inhibitor according to the experimental data.

Stoyanova et al. [116] investigated the geometrical and electronic molecular structures of α- and γ-pyrophtalone as inhibitors for copper corrosion by using a SVP (split valence plus polarisation quality) basis set which is equivalent to 6-31G*. They calculated bond distances, bond angles, ionisation potentials, dipole moments and net atomic charges. As a result of their calculations they found that the ionisation potential and the dipole moments of the molecules are the parameters that had the strongest influence on the adsorption and inhibition properties of these compounds. It was shown that a decrease in the ionisation potential of the inhibitor molecule and an increase in the dipole moment produce a higher inhibition efficiency toward corrosion.

Lebrini et al. [117] investigated the effect of 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (4-PTH) and its some derivatives (n-PTH; for $n = 2$ and $n = 3$) on the corrosion of mild steel in acidic media by the HF/3-21G method. The energies of HOMO and LUMO and dipole moments were computed. They developed a linear resistance model (LR) relying on dipole moment, E_{HOMO} and E_{LUMO}. They obtained a significant multiple correlation coefficient ($R > 0.93$) that indicated the variation of the corrosion inhibition with the structure of the inhibitors. Şahin et al. [118] investigated the dependence of inhibition efficiencies of three heterocyclic compounds, 3-amino-1,2,4-triazole (3-ATA), 4-hydroxy-2H-1-benzopyran-2-one (4-HQ) and 4-hydroxy-3-(1H-1,2,4-triazole-3-ylazo)-2H-1-benzopyran-2-one (3-ATA-Q), by using the B3LYP/6-31G(d) method. Such parameters as the HOMO and LUMO energies, energy gap, net atomic charges, dipole moments, total and interaction energies were calculated. A good agreement was found between experimental and theoretical data.

Bentiss et al. [119] performed theoretical calculations of 2,5-bis(n-methoxyphenyl)-1,3,4-oxadiazoles (n-MOX) as corrosion inhibitors for mild steel in 1 M HCl and 0.5 M H_2SO_4 to understand if any structural differences induced by different positions of the methoxy group may be related to the experimentally observed differences of corrosion efficiency. They used Monte Carlo method for conformational search and found two conformers of 2-MOX. They calculated the HOMO and LUMO energies, energy gap, charges on nitrogen atoms for these two conformers of 2-MOX, 3-MOX and 4-MOX using the RHF/3-21G* method. They also employed electrostatic potential map calculations to determine the effect of hydrogen bonding on the cationic form of the 2-MOX molecule. Their results revealed that the experimentally found superior inhibition efficiency of 2-MOX can be explained in terms of electronic densities in the neutral molecules and by the cationic form of this molecule highly stabilised by hydrogen bonding. Bentiss et al. [120] also investigated some new 2,5-disubstitued 1,3,4-thiadiazoles as corrosion inhibitors of mild steel in 1 M HCl by using the B3LYP/6-31G(d,p) (2d,2p) method. In order to find a correlation between experimentally determined corrosion inhibition data and a number of quantum molecular properties, inhibition performance of six thiadiazole compounds (2,5-bis(phenyl)-1,3,4-thiadiazole (DPTH), 2,5-bis(4-methoxyphenyl)-1,3,4-thiadiazole (4-MTH), 2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole (4-DATH), 2,5-bis(4-methylphenyl)-1,3,4-thiadiazole (4-MPTH), 2,5-bis(4-nitrophenyl)-1,3,4-thiadiazole (4-NPTH) and 2,5-bis(4-chloroxyphenyl)-1,3,4-thiadiazole (4-CPTH)) was subjected to correlation analysis with the calculated quantum chemical parameters (E_{HOMO}, E_{LUMO}, ΔE and dipole moment (μ)) using linear and non-linear models to establish direct links between them. The linear model was not found to be

satisfactory for correlation. A good correlation (R = 0.98) was found when non-linear model used. The same authors investigated the inhibition properties of 3,5-bis(n-pyrryridyl)-4-amino-1,2,4-triazoles [121], isomers of 3-pyridyl-substituted 1,2,4 and 1,3,4-thiadiazoles [122], some 4H-triazole derivatives [123] and some new macrocyclic polyether compounds as corrosion inhibitors for the corrosion of mild steel using the HF/3-21G*, HF/6-21G*, and B3LYP/6-31G(d,p) methods, respectively. The results of theoretical calculations performed in these studies supported the experimental findings.

Allam [124] tried to establish a quantitative relationship between the inhibition efficiency and the electronic structure of some triazole derivatives (4-amino–5-mercapto-3-methyl 1,2,4-triazole (AMMT), 4-amino-5-mercapto-3-ethyl 1,2,4-triazole (AMET) and 4-amino-5-mercapto-3-propyl 1,2,4-triazole (AMPT)) as new corrosion inhibitors for muntz alloy (60Cu–40Zn) in acidic and neutral solutions. He calculated such parameters as the HOMO and LUMO energies, energy gap, total energy, dipole moment for AMMT, AMET and AMPT compounds by the RHF/3-21G method. A correlation between the E_{HOMO}, energy gap, the charge on nitrogen atom and the inhibition efficiency was found by regression analysis. However, no clear relationship between the E_{LUMO}, dipole moment and the inhibition efficiency could be found according to the results. A similar study was performed for two tautomeric forms of 2-mercapto-1-methylimidazole (MMI) employed to retard corrosion of carbon steel in 1 M HClO$_4$ by Benali et al. [125] using DFT methods. The HOMO and LUMO energies, energy gap and dipole moment were calculated for the thiol and thione forms of MMI. According to the theoretical data, the thione form of MMI is more efficient than the thiol form since the thione form has the highest E_{HOMO} and dipole moment, and the lowest E_{LUMO} and energy gap values.

Ma et al. [126] studied the inhibition efficiency of self-assembled films of 1-methyl-5-mercapto-1,2,3,4-tetrazole (MMT) for iron using the B3LYP/LANL2DZ method. In order to investigate the adsorption between MMT and iron, they calculated the enthalpies, entropies and free energy changes of the MMT/iron system. Taking into account the results of these calculations, they concluded that MMT molecule is bound to the iron surface by sharing electrons between the nitrogen and iron atoms.

Blajiev and Hubin [127] investigated the efficiency of 2-amino-5-mercapto-1,3,4-thiadiazole (AMTD) and 2-methyl-5-mercapto-1,3,4-thiadiazole (MMTD) as copper corrosion inhibitors in neutral chloride environments. They performed calculations by means of SIESTA method [128], which is based on the density functional theory, to reflect the relaxation and adsorption interactions of ions and inhibitors on the (0 0 1) Cu$_2$O surface. They compared their results with benzotriazole inhibitor and came to the conclusion that AMTD and MMTD are better corrosion inhibitors than benzotriazole.

The inhibitive action of some thiadiazole derivatives, namely 2,5-bis(2-thienyl)-1,3,4-thiadiazole (2-TTH) and 2,5-bis(3-thienyl)-1,3,4-thiadiazole (3-TTH) against the corrosion of mild steel in 0.5 M H$_2$SO$_4$ was investigated by Lebrini et al. [129] using the B3LYP/6-31+G(d,p) (2d,2p) method. They calculated the HOMO and LUMO energies, energy gap and the dipole moment (μ) of the molecules. Since a small energy difference was found between E_{HOMO} and E_{LUMO} and no direct correlation could be seen between the dipole moment, energy gap and inhibition efficiency, they used a linear resistance model (LR) to correlate the corrosion inhibition properties with the calculated quantum chemical parameters. A good correlation ($R \approx 0.91$) was found between the coefficient of E_{HOMO}, E_{LUMO}, and inhibition efficiency.

Zhang et al. [130] studied the inhibition efficiencies of imidazole, benzimidazole and their derivatives using the B3LYP/6-31G* method. They calculated a number of quantum chemical parameters, such as E_{HOMO}, E_{LUMO}, energy gap, charge distribution, dipole moment, and molecular connectivity index (MCI) which reveals the steric hindrance effect of the molecule. According to their results, the E_{HOMO} was the most statistically significant term influencing the corrosion inhibition efficiencies The greater the E_{HOMO}, the greater is the inhibition efficiency.

Wang et al. [131] studied the protection offered by self-asssembled films of carbazole (CZ) and N-vinylcarbazole (NVC) against copper corrosion in NaCl solution using ab $initio$ HF/LANL2DZ method. They calculated the HOMO and LUMO energies and total atomic charges of the molecules. Their calculations showed that the HOMO energy (-743.6 kJ mol^{-1}) of NVC was higher than that of CZ (-754.7 kJ mol^{-1}). The LUMO energy (230.68 kJ mol^{-1}) was lower than that of CZ (245.7 kJ mol^{-1}). These results provided a theoretical confirmation that NVC has stronger bonding affinity for copper than CZ, which was consistent with the experimental results. Kandemirli and Sagdinc [132] performed a detailed quantum chemical studies for urea (U), thiourea (TU), acetamide (A), thioacetamide (TA), semicarbazide (SC), thiosemicarbazide (TSC), methoxybenzaldehyde thiosemicarbazone (MBTSC), 2-acetylpyridine-(4-phenyl)thiosemicarbazone (2AP4PTSC), 2-acetylpyridine-(4-methyl)thiosemicarbazone (2AP4MTSC), benzointhiosemicarbazone (BZOTSC) and benzylthiosemicarbazone (BZITSC) using ab $initio$ RHF/6-31G(d) and MP2/6-31G(d) methods and B3LYP/STO-3G, B3LYP/3-21G and B3LYP/6-31G(d) DFT methods. The results of quantum chemical calculations and experimental efficiencies of inhibitors were subjected to correlation analysis. On the basis of the HOMO and LUMO energies, HOMO and LUMO coefficients, polarizability, Mulliken population analysis, they reached the conclusion that considering one parameter is not sufficient and the synthesis of better corrosion inhibitors can be achieved by controlling all electronic properties and parameters of a selected group of molecules.

Szeptycka [133] investigated the effect of saccharin, 2-butyne-1,4-diol, 1-4-β,β′-dihydroxyethoxy-2-butyne, 4-(β-hydroxyprop-oxy)-2-butyne-1-ol, 1-methylenedipyridinium chloride and 1,1'-methylenedipyridinium dichloride, on the corrosion inhibition of steel in two acids, 6.3 N hydrochloric acid and 4.28 N sulfuric acid using ab $initio$ and PM3 methods. All quantum chemical calculations were done using the ab $initio$ method with full geometrical optimization using a STO-3G basis set. The HOMO, LUMO energies and energy gap were calculated and correlated with experimental data. Good fit of data were obtained and it was concluded that such calculations seem useful in assessing the degree of pickling inhibition.

Since the use of polyaniline (PAni) as an alternative anti-corrosion material is well known, Sein et al. [134] investigated the electronic behaviour of aniline oligomers which parallels that of PAni. They determined the thermodynamic parameters for several competing reaction sequences occurring during the interaction of an iron (or aluminum) surface and aniline trimers by using B3LYP/6-311G(2d,p) and B3LYP/6-31G+ methods. The calculation of thermochemical properties of aniline trimers in various oxidation states, in conjuction with similar calculations on cluster models of iron and aluminum surfaces, has shown that the emeraldine dihydrochloride is the most effective form for corrosion inhibition. Furthermore, it was shown that a model based on the analysis of equilibrium and rate for corrosion inhibition by aniline trimers can be supported by density functional theory.

A detailed calculation of the molecular structure of benzimidazoles was performed by El Ashry et al. [135] using the B3LYP/6-31G* method to explore possible correlations between corrosion inhibition efficiencies and a number of quantum molecular properties, such as E_{HOMO}, E_{LUMO}, total negative charge on molecules and linear solvation energy relationship parameters. Furthermore, bivariate correlations using two trial personal correlation coefficient and linear regression analyses were performed by stepping method. A comparison of the inhibition efficiencies of a series of benzimidaz-

Table 2
Corrosion inhibitors studied by *ab initio* and DFT methods

Method	Inhibitor	References
HF/LANL2DZ	3,5-Dimethyl-1*H*-pyrazole, pyridine, 2-(3-methyl-1*H*-pyrazol-5-yl)pyridine; 1-methyl-5-mercapto-1,2,3,4-tetrazole; carbazole; *N*-vinylcarbazole;	[102,126,131]
HF/D95	Aniline derivatives	[103]
B3LYP/STO-3G*	2-Methyl-1,3,4-thiadiazole; 2,5-dimethyl-1,3,4-thiadiazole; 2-ethyl-5-methyl-1,3,4-thiadiazole; 2-propyl-5-methyl-1,3,4-thiadiazole; 2-aminoethyl-5-methyl-1,3,4-thiadiazole; 2-(2-hydroxyethyl)-5-methyl-1,3,4-thiadiazole; 2-(2-carboxyethyl)-5-methyl-1,3,4-thiadiazole; 2-(2-tioethyl)-5-methyl-1,3,4-thiadiazole; 2-(2-chloroethyl)-5-methyl-1,3,4-thiadiazole; saccharin; 2-butyne-1,4-diol; 1-4-β,β'-dihydroxyethoxy-2-butyne; 4-(β-hydroxypropoxy)-2-butyne-1-ol; 1-methylenedipyridinium chloride; 1,1'-methylenedipyridinium dichloride	[104,133]
PBEg/CBSB2**,CBSB7,CBSB4,CSBS1	4-Amino-1,2,3,5-thiatriazole; 5-amino-1,2,3,4-thiatriazole; hydroxyethyl imidazoline; aminoethyl imidazoline; amidoethyl imidazoline	[105,106]
B3LYP/6-31+G*	2-Mercaptobenzothiazole; thiourea; methylthiourea; phenylthiourea;2-(α-pyridyl)-indandione-1,3(α-pyrophthalone); 2-(γ-pyridyl)-indandione-1,3(γ-pyrophthalone); 2-(α-pyridyl)-perinaphthinindandione-1,3(α-pyronaphthalone); 6-(α-pyridyl)-6,7-dihyydro-5H-dibenzo[a,b]cycloheptendione; 6-(γ-pyridyl)-6,7-dihyydro-5H-dibenzo[*a*,*b*]cycloheptendione; 2-mercapto-1-methylimidazole; imidazole and benzimidazole derivatives; urea; acetamide; thioacetamide; semicarbazide; thiosemicarbazide; methoxybenzaldehyde thiosemicarbazone; 2-acetylpyridine-(4-phenyl)thiosemicarbazone; 2-acetylpyridine-(4-methyl)thiosemicarbazone; benzointhiosemicarbazone; benzylthiosemicarbazone; aniline trimers; 2-{[(4-methoxyphenyl)imino]methyl}phenol; 1-{[(4-methoxyphenyl)imino]methyl}-2-naphthol; (*E*)-2-(1-(2-(2-hydroxyethylamino)ethylimino)ethyl)phenol; 2,2'-(1*E*,1'*E*)-1,1'-(2,2'-azanediylbis(ethane-2,1-diyl)bis(azan-1-yl-1-ylidene))bis(ethan-1-yl-1-ylidine); 2,2'-((2*E*,12*E*)-3,6,9,12-tetraazatetradeca-2,12-diene-2,13-diyl)diphenol; guanine; adenine; 2,6-diaminopurine; 6-thioguanine; 2,6-dithiopurine	[107,115,116,125,130,132,134,135,137,138,142]
B3LYP/6-31+G(d,p)	5,10,15,20-tetraphenylporphyrin; 5,10,15,20-tetra-(4-chlorophenyl)porphyrin; thioacetamide; thiourea; thiobenzamide;3-amino-1,2,4-triazole; 4-hydroxy-2H-1-benzopyran-2-one; 4-hydroxy-3-(1H-1,2,4-triazole-3-ylazo)-2H-1-benzopyran-2-one; 2,5-bis(phenyl)-1,3,4-thiadiazole; 2,5-bis(4-methoxyphenyl)-1,3,4-thiadiazole; 2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole; 2,5-bis(4-methylphenyl)-1,3,4-thiadiazole; 2,5-bis(4-nitrophenyl)-1,3,4-thiadiazole; 2,5-bis(4-chloroxyphenyl)-1,3,4-thiadiazole; 4H-triazole derivatives; 2,5-bis(2-thienyl)-1,3,4-thiadiazole; 2,5-bis(3-thienyl)-1,3,4-thiadiazole; 2,3,8,9-dibenzo-4,7-dioxa-13-thia-11,12-diazabicyclo[8.2.1]trideca-10,12-diene; 2,3,11,12-dibenzo-4,7,10-trioxa-16-thia-14,15-diazabicyclo[11.2.1]hexadeca-13,15-diene; 2,3,14,15-dibenzo-4,7,10,13-tetraoxa-19-thia-17,18-diazabicyclo[14.2.1]nonadeca-18,18-diene; 2,3,17,18-dibenzo-4,7,10,13,16-pentaoxa-22-thia-20,21-diazabicyclo[17.2.1]docosa-19,21-diene; 2,3,20,21-dibenzo-4,7,10,13,16,19-hexaoxa-25-thia-23,24-diazabicyclo[20.2.1]pentacoza-21,24-diene;	[108,114,118,120,123,129,139]
B3LYP/6-31G**(d,p)	Methionine; triazole,oxadiazole, thiadiazole derivatives; pyridine derivatives	[109,136,141]
B3LYP/3-21G*	4-Chloro-acetophenone-*O*-1'-(1',3',4'-triazolyl)-metheneoxime; 4-methoxyl-acetophenone-*O*-1'-(1',3',4'-triazolyl)-metheneoxime; 4-fluoro-acetophenone-*O*-1'-(1',3',4'-tr,azolyl)-metheneoxime; prop-1-yn-3-ol; 2,5-bis(4-pyridyl)-1,3,4-thiadiazole; 2,5-bis(*n*-methoxyphenyl)-1,3,4-oxadiazoles; 3,5-bis(*n*-pyrryridyl)-4-amino-1,2,4-triazoles; isomers of 3-pyridyl-substitued 1,2,4 and 1,3,4-thiadiazoles; 4-amino–5-mercapto-3-methyl 1,2,4-triazole; 4-amino-5-mercapto-3-ethyl 1,2,4-triazole; 4-amino-5-mercapto-3-propyl 1,2,4-triazole;urea; acetamide; thioacetamide; semicarbazide; thiosemicarbazide; methoxybenzaldehyde thiosemicarbazone; 2-acetylpyridine-(4-phenyl)thiosemicarbazone; 2-acetylpyridine-(4-methyl)thiosemicarbazone; benzointhiosemicarbazone; benzylthiosemicarbazone; 3,5-bis(2-thienyl)-1,3,4-thiadiazole; 3,5-bis(3-thienyl)-1,3,4-thiadiazole; 2,5-bis(4-pyridyl)-1,3,4-thiadiazole;	[110,112,117,119,121,122,124,132,140]
B3LYP/6-311G**	1-Diethylamino-propan-2-ol; 1,3-bis-diethylamino-propan-2-ol	[111]

oles indicated that their inhibition effect has been closely related to the orbital energies (E_{HOMO} and E_{LUMO}), Log P, dipolar-polarizability factor (π^*) and the total negative charge on the molecule. It has been concluded that a composite index of more than three quantum chemical parameters should be considered to characterize the inhibition efficiency of molecules. Quantum chemical studies of corrosion inhibition of steel in acidic medium by some triazole, oxadiazole and thiadiazole derivatives were conducted by El Ashry et al. [136] in a similar manner.

Increased attention has been paid in recent years to Schiff bases as corrosion inhibitors for various metals in typical acidic environments. Hasanov et al. [137] investigated the inhibition effects of two Schiff base compounds, (2-{[(4-methoxyphenyl)imino]-methyl}phenol and 1-{[(4-methoxyphenyl)imino]methyl}-2-naphthol), on steel corrosion in sulfuric acid solution. Such parameters as frontier orbital energies, Mulliken charges of possible adsorption

sites and dipole moments were calculated by the B3LYP/6-31G (d) method. All theoretical data were found to be in good agreement with the experimental findings. Furthermore, Ju et al. [138] presented a theoretical study of electronic and molecular structures of aminic nitrogen-containing polydentate Schiff base compounds and calculated their HOMO and LUMO energies, charge distributions, the absolute electronegativity (χ) values, and the fraction of electrons (ΔN) transferred from inhibitors to iron by the B3LYP/6-31G* method. It was concluded that the inhibition efficiency increased with an increase in E_{HOMO} and decrease in $E_{LUMO}-E_{HOMO}$. This conclusion simply restates the results of various studies of different inhibitor molecules, such as macrocyclic polyether compounds [139], thiadiazole derivatives [140,117] and pyridine derivatives [141].

In a very recent study, purines and their derivatives, such as guanine, adenine, 2,6-diaminopurine, 6-thioguanine and

2,6-dithiopurine, were investigated as corrosion inhibitors for mild steel in 1 M HCl solution by Yan et al. [142] using the 6-31G* DFT method. The Mulliken partial charges, HOMO and LUMO energies, energy gap and dipole moments were calculated and the inhibition efficiency was correlated with the energy gap and the electron density of the frontier orbital. It was concluded that purines were physically adsorbed by π stacking on mild steel.

For the inhibition of aqueous metallic corrosion with an organic compound, it is necessary to design a ligand that adsorbs strongly on the metal. There are some theoretical studies in the literature concerning the corrosion inhibition of metals taking into account the role of the metallic surface. Since the scope of this review article is limited only for the studies of corrosion inbihition compounds, these studies will not be reviewed here. It is noteworthy to emphasize that the general aim of such studies is to set up a model of the interactions that embody the adsorption of a compound with a particular metal [143–152].

7. Conclusions

The survey of theoretical corrosion literature presented in this review (Tables 1 and 2) demonstrates that quantum chemistry is a powerful tool to study the fundamental, molecular-level processes related to corrosion inhibition. However, much care must be taken in planning these studies, as calculations performed with inaccurate methods or with an insufficient dataset can easily lead to erroneous conclusions. The role of quantum chemistry in corrosion inhibitor studies is likely to increase in the future, as the focus of investigations shifts toward complicated chemical mechanisms. However, the restrictions caused by the high computational effort of the calculations mean that quantum chemical methods will not in the foreseeable future be able to replace experimental corrosion studies or computationally less expensive methods for the processes related to corrosion inhibition.

Acknowledgement

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