Conceptual Density Functional Theory and Its Application in the Chemical Domain

Editors Nazmul Islam | Savaş Kaya

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Nazmul Islam, PhD, is now working as a vice principal at the Government Engineering College, Ramgarh (India). He has published more than 70 research papers in several prestigious peer-reviewed journals and has written many book chapters and research books. In addition, he is the editor-in-chief of *The SciTech, Journal of Science and Technology*; *The SciTech*, *International Journal of Engineering Sciences*; and the *Signpost Open Access Journal of Theoretical Sciences*. He also serves as a member on the editorial boards of several journals, such Journal of *Chemical Engineering and Materials Science*, *International Journal of Physical Sciences, Polymers Research Journal*, and *International Journal of Current Physical Sciences*. He is also as editor of several books: *Handbook of Nano Science and Nano Technology*, *Theoretical and Computational Research* in 21st Century, and more.

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LIST OF ABBREVIATIONS

2-HBP	N,N'-bis(2-hydroxybenzaldehyde)-1,3-propandiimine
2-PCT	2-pyridinecarboxaldehyde thiosemicarbazone
3-HBP	N,N'-bis(3-hydroxybenzaldehyde)-1,3-propandiimine
4-HBP	N,N'-bis(4-hydroxybenzaldehyde)-1,3-propandiimine
4-PCT	4-pyridinecarboxaldehyde thiosemicarbazone
A	electron affinity
AIM	atoms-in-molecules
API	American Petroleum Institute
ATA	anisalicylal-[5-(p-methyl)-phenyl-4-amino-(1,2,4-triazolyl)-2-thiol]-acylhydrazone
B3LYP	hybrid density functional theory
BCP	bond critical point
BDTC	4-(4-bromophenyl)-N'-(2,4-dimethoxybenzylidene) thiazole-2-carbo-hydrazide
BHF	Born–Haber–Fajans
BHTC	4-(4-bromophenyl)-N'-(4-hydroxybenzylidene) thiazole-2 carbohydrazide
BMTC	4-(4-bromophenyl)-N'-(4-methoxybenzylidene)thiazole-2-carbohydrazide
BSSE	basis set superposition error
CDFT	conceptual density functional theory
CG	contragradience
CIT	classical information theory
COMPASS	condensed-phase optimized molecular potentials for atomistic simulation studies
CORE-C	Center of Research Excellence in Corrosion
CSA	charge sensitivity analysis
CT	charge transfer
DFT	density functional theory
DHDFs	doubly hybrid density functionals
DMs	density matrices

DPE	deprotonation enthalpy
EEP	electronegativity equalization principle
EIS	electrochemical impedance spectroscopy
EIS	Electrochemical impedance spectroscopy
ELF	electron localization function
EO	equidensity orbitals
FMM	fast marching method
FMOs	frontier molecular orbitals
FTSC	furoin thiosemicarbazone
GB	gas phase basicities
GC	grand-canonical
GDP	gross domestic product
GGA	generalized-gradient approximation
GIAO	gauge-independent atomic orbital
GSM	growing string algorithm
HBTT	3-[(2-hydroxy-benzylidene)-amino]-2-thioxo-thiazolidin-4-one
HCl	hydrochloric acid
HF	Hartree–Fock
HK	Hohenberg and Kohn
HOMO	highest occupied molecular orbital
HSAB	hard/soft acid/base
HZM	Harriman-Zumbach-Maschke
I	ionization energy
IEF-PCM	integral equation formalism polarizable continuum model
INHB	N'-(phenylmethylene) isonicotinohydrazide
INHC	N'-(3-phenylallylidene) isonicotinohydrazide
INHF	N'-(furan-2-ylmethylene) isonicotinohydrazide
INHS	N'-(2-hydroxybenzylidene) isonicotinohydrazide
IRC	intrinsic reaction coordinate
IRI	intrinsic reactivity index
KACST	King Abdulaziz City for Science and Technology
KFUPM	King Fahd University of Petroleum & Minerals
KS	Kohn–Sham
LCS	low carbon steel
LDA	local density approximation

LPBE	Linearized Poisson–Boltzmann equation
LRD	local reactivity descriptor
LSDA	local spin-density approximation
LUMO	lowest unoccupied molecular orbital
MD	molecular dynamics
MEP	minimum energy path
MEP	molecular electrostatic potential
MHP	maximum hardness principle
MI	3-(4-(4-methoxybenzylideneamino)phenylimino)indolin-2-one
MM	molecular mechanics
MMQT	3-((5-methylthiazol-2-ylimino)methyl) quinoline-2-thiol
MO	molecular orbital
MPP	minimum polarizability principle
MTMP	2-((5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)phenol
NAO	natural atomic orbital
NBO	natural bonding orbital
NMR	nuclear magnetic resonance
NSTIP	National Science Technology Plan
NT	Newton trajectory
NVAO	natural valence atomic orbital energies
OCP	open circuit potential
OCT	orbital communication theory
OMTKY3	turkey ovomucoid third domain
PA	proton affinity
PCM	polarized continuum method
PDTT	5-((E)-4-phenylbuta-1,3-dienylideneamino)-1,3,4-thiadiazole-2-thiol
PEIDs	property enhanced intramolecular distances
PES	photo electron spectroscopy
PES	potential energy surface
PEST	property encoded surface translator
PI	3-(4-(3-phenylallylideneamino)phenylimino)indolin-2-one
PMA	2-(2-{[2-(4-pyridylcabonyl)hydrazono]methyl}phenoxy) acetic acid

PMQ	3-((phenylimino)methyl)quinoline-2-thiol
PPLB	Perdew, Parr, Levy, and Balduz
PT	prototropic tautomerism
PTM	2-(phenylthio)phenyl)-1-(o-tolyl)methanimine
QIT	quantum information theory
QM	quantum mechanics
QMSI	quantum molecular similarity indices
QMSM	quantum molecular similarity measures
QSAR	quantitative structure activity relationships
QSM	quadratic string method
QSPR	quantitative structure-property relationships
SCE	saturated calomel electrode
SCF	self-consistent field
SCRF	self-consistent reaction field
SDP	steepest descent path
SE	Schrödinger equation
SEM	scanning electron microscope
SRL	separated-reactant limit
STA	salicylal-[5-(p-methyl)-phenyl-4-amino-(1,2,4-triazolyl)-2-thiol]-acylhydrazone
TEM	transmission electron microscope
TS	transition states
VBT	volume based thermodynamics
VTA	vanillin-[5-(p-methyl)-phenyl-4-amino-(1,2,4-triazolyl)-2-thiol]-acylhydrazone
WE	working electrode
XC	exchange-correlation
ZPE	zero point energy

PREFACE

The scientific and technological progress in the 20th century was definitely incredible. In this century one of the most outstanding amendment was the shrinkage of the quantum chemical world due to the introduction of a new concept—the density functional theory (DFT). Till then, the evaluation of theoretical concepts has been strongly influenced by density functional theory. The chemical concepts such as chemical potential, chemical hardness, electronegativity, electrophilicity, and nucleophilicity have important applications in topics like prediction of reaction mechanisms and the analysis of chemical reactions.

DFT is a very popular mainstay of quantum mechanics. It depends upon the electron density (a three variable function) as a basic variable and is developed from the efforts of scientists in search of a simpler method alternative to wave function formalism. The DFT is not only a simpler quantum chemical method based upon a three variable density function but also it has proved its amazing power to put some very important qualitative chemical concepts like electronegativity and global hardness on sound quantum chemical foundation. The DFT is shown to provide a useful balance between accuracy and computational cost.

The chemical reactivity theory can provide important insights into the nature of atoms and molecule. The ultimate aim of the reactivity theory is to provide the answer to the fundamental questions like *Why some molecules are more stable and other more reactive?*, *Is it possible to predict which atomic site is the most susceptible to undergo either a nucleophilic or an electrophilic attack?*, *Why certain atomic sites of a molecule is more reactive?*, etc. Theoretical scientists had the ambition to rationalize those experimental facts with the help of chemical theories. The most fruitful and promising framework so far is probably the DFT. The quest for the theoretical basis of the hard-soft acid base behavior has created such a surge of fundamental research in chemistry that it gave birth of a new branch of density functional based theoretical science known as conceptual density functional theory (CDFT). The framework and some recent

developments of CDFT has been facilitated by the works of conceptual density functional scientists.

In this book, some new developments based on CDFT and some applications of CDFT are discussed. In addition, we have discussed some applications in corrosion and conductivity and synthesis studies based on CDFT. The electronic structure principle such as electronegativity equalization principle, hardness equalization principle, electrophilicity equalization principle, nucleophilicity equalization principle, and studies based on these electronic structure principles are broadly explained.

In Chapter 1, Islam briefly discussed the origin and development of CDFT. In recent years some novel methodologies has been developed in the field of CDFT. These methodologies have been used to explore mutual relationships between the descriptors of CDFT namely electronegativity, hardness, etc. The mutual relationship between the electronegativity and the hardness depend on the electronic configuration of the neutral atomic species. The method of calculation of equalized molecular electronegativity, equalized molecular electrophilicity, and equalized molecular nucleophilicity based on the assumption of charge equalization during the chemical event of molecule formation and by combining electrostatic theorem and CDFT is also reviewed. In Chapter 2, Ramón Alain Miranda-Quintana presented a short introduction to the use of DFT in the study of chemical reactions. In Chapter 3, Ayers et al. computed the unconstrained local hardness using an exact equation for the unconstrained local hardness in Kohn-Sham density-functional theory. In Chapter 4, Ayers et al. analyzed the physical grounds of common approaches used to model the dependency of the ground state energy on the number of electrons in molecular systems (E vs. N models). Ayers et al. elaborated on a recent result indicating that smooth interpolation models are inconsistent with popular grand ensemble approach to open quantum systems and the authors have illustrated this discrepancy using the parabolic and exponential E vs. N models.

In Chapter 5, Kaya et al. revisited the chemical equalization principles and presented some new applications of chemical equalization principles related to hardness, electronegativity, electrophilicity, and nucleophilicity. Prevention of metallic corrosion is a very challenging job and would therefore be a mammoth task considering the enormous role of metals and their alloys in several industrial applications. To prevent solution state metallic

corrosion, suitable small organic molecules as inhibitors are widely used as additive to the aggressive solution. Among the organic inhibitors, different N, O, S donor Schiff base molecules are considerably used due to its low cost starting precursor material, easy to follow synthetic route and environmental friendly manner. In Chapter 6, inhibition of metallic corrosion by N, O, S donor schiff base molecules was analyzed by Saha and Banerjee using CDFT methods. In Chapter 7, Obot et al. showed that the CDFT parameters can be used as a reliable approach to screen and select potential organic corrosion inhibitors prior to experimental validation. In Chapter 8, the equilibrium states of molecular systems, which extremize the system resultant entropy combining the *classical* (probability) and *nonclassical* (phase/current) information contributions, are explored in both the bimolecular complex R = A----B and its acidic(A) and basic(B) reactants by Nalewajski. The failures of embedded cluster models is discussed by Ayers et al. in Chapter 9. In Chapter 10, Ayers and coworkers showed that similarity-based kriging method for property prediction is more appealing than previous approaches. Finding and characterizing the pathways between reactants and products is very important for studying the mechanisms and energetics of chemical reactions, not only in the gas phase but also in complex environments like enzymes. Liu and Ayers, in Chapter 11, discussed three different methods to study chemical reaction using quantum mechanical models. Safi, in Chapter 12, calculated proton affinity, gas phase basicity, and enthalpy of some polyfunctional compounds using DFT method. In Chapter 13, Safi investigated the tautomerization process using the DFT in the neutral, protonated and deprotonated forms. In addition the effect of the interaction with the transition metal cations on the tautomerization process is also considered. In Chapter 14, Islam et al. compared the ionization energies data of the atoms computed using semi-empirical and DFT methods. In the last chapter, Heidar-Zadeh and Paul W. Ayers studied the molecular similarity from manifold learning on D2-property images.

Finally, we would like to thank the governing body of Apple Academic Press along with all authors, reviewers, and the Editorial Board Members for their invaluable contributions.

—Dr. Nazmul Islam
Dr. Savaş Kaya

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CHAPTER 1

THE CONCEPTUAL DENSITY FUNCTIONAL THEORY: ORIGIN AND DEVELOPMENT TO STUDY ATOMIC AND MOLECULAR HARDNESS

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ABSTRACT

In this chapter, we briefly discuss the origin and development of conceptual density functional theory (CDFT). We also review the method of calculating equalized molecular electronegativity, equalized molecular

electrophilicity, and equalized molecular nucleophilicity based on the assumption of charge equalization during the chemical event of molecule formation and by combining the electrostatic theorem and CDFT.

1.1 INTRODUCTION

To solve the Schrödinger wave equation for many electronic systems, in the late 20's, a simple method known as density functional theory (DFT) [1] as an alternative to wave function formalism was developed. In quantum mechanics, we know that all information about a system is contained in the system's wave function, Ψ. Hence, it is known to all readers of quantum mechanics that "if you know Ψ of a system, you know everything about that system." Similarly, the DFT teaches us that all information about a system is coded in the system's wave functional. Pearson [2] has beautifully defined the term "functional" as "a functional is a recipe for turning a function in to a number, just as a function is a recipe for turning a variable in to a number." The DFT has revolutionized the theoretical study of chemical reactivity as it has a good rigid conceptual framework and fundamental concept. The basic idea of DFT is to replace the complicated *N*-electron wavefunction, Ψ, by the electron density, ρ, a three-variable function.

After its introduction, the DFT became the central plenum of quantum mechanics. The DFT is currently a valuable alternative for including correlations effects, without using complicated wave function methods.

1.2 THEORETICAL BACKGROUND OF CONCEPTUAL DENSITY FUNCTIONAL THEORY

The principles of DFT are conventionally developed by the attempts of theoreticians to solve the many-body Schrödinger equation

$$H\Psi = E\Psi \tag{1}$$

where H is the N-electron Hamiltonian, Ψ is the N-electron antisymmetric wave function, and E is the corresponding energy eigenvalue of H.

The first approximation may be considered as the one proposed by Hartree [3] in 1928. Hartree postulated that the *N*-electron wave function can be written as a simple product of *N* one-electron wave functions, each of which verifies a one-particle Schrödinger equation.

The DFT started with the landmark work of Hohenberg and Kohn [4] and the subsequent work of Kohn and Sham [5]. After the introduction of the Hohenberg and Kohn theorem-based DFT, the use of DFT gave a major boost to the field of computational chemistry. Hohenberg and Kohn showed in their first theorem that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only three spatial coordinates.

The Hamiltonian H has the form

$$H=T_N+V_N+U_N$$

where is T_N is the *N*-electron kinetic energy, V_N is the *N*-electron potential energy from the external field, and U_N is the electron-electron interaction energy.

The famous Hartree-Fock approximation, which is considered as the central plenum of most ab initio calculations, transformed the wavefunction Ψ into a Slater determinant of one-electron wavefunctions ψ_i

$$\left(-\frac{1}{2}\nabla^2+v_{ext}(r)+v_H(r)+v_{x,i}^{HF}(r)\right)\psi_i(\mathrm{r})=\in_i\psi_i(\mathrm{r}) \tag{2}$$

In the above equation, $v_{ext}(r)$, $v_H(r)$, and $v_{x,i}^{HF}$ are the external, Hartree, and non-local exchange potentials, respectively, and together are known as the effective HF operator, v_{eff}^{HF}

$$\left(-\frac{1}{2}\nabla^2+v_{eff}^{HF}(r)\right)\psi_i(\mathrm{r})=\in_i\psi_i(\mathrm{r}) \tag{3}$$

where ∇^2 is the Laplacian operator and $\in_i$ is the eigenvalue of electron i in spin-orbital ψ_i.

The problem with the Hartree-Fock method is that it does not account for Coulomb correlation due to the rigid form of the single determinant wave

function. To take correlation into account, the so-called post-HF methods such as configuration interaction, coupled-cluster, or Møller–Plesset perturbation theory [6] must be taken into consideration. In post-HF methods, the wave function is generally represented by a linear combination of determinants accounting for correlation. Moreover, while the post-HF methods offer a systematic way to improve the accuracy of the results, they scale as fifth or even higher power with the size of the system, thus implying a considerable computational effort. Thomas [7] and Fermi [8] made a very important assumption – "Electrons are distributed uniformly in the six-dimensional spaces for the motion of an electron at the rate of two for each h^3 of volume." In 1964, Hohenberg and Kohn [4] provided the very first theorem that established the Thomas–Fermi assumption as an exact theory – the DFT.

The first Hohenberg and Kohn [4] theorem allows us to determine the external potential v_r of a given system under certain conditions by the electron density ρ_r of that system. They also demonstrated that the total energy of the system is stationary with respect to the density ρ_r. Unfortunately, the Hohenberg–Kohn theorems do not provide the exact form of the total energy functional $E[r]$. Among the different components of the total energy, the exact density functional forms of both kinetic and exchange-correlation terms remain unknown. To circumvent the problem of the kinetic part (much larger than the exchange correlation one), Kohn and Sham (KS) [7] proposed to introduce a set of fictitious one-electron wave functions ψ_i to build a Slater determinant. This leads to the KS equation

$$\left(-\frac{1}{2}\nabla^2 + v_{ext}(r) + v_H(r) + v_{x,i}^{KS}(r)\right)\psi_i(r) = \in_i \psi_i(r) \tag{4}$$

In the above equation, $v_{ext}(r)$, $v_H(r)$, and $v_{x,i}^{KS}$ are the external, Hartree, and exchange potentials, respectively, and together are known as the effective KS operator, v_{eff}^{KS}.

$$(-1/2\nabla^2 + v_{eff}{}^{KS}(r))\psi_i(r) = \in_r \psi_i(r) \tag{5}$$

The energy is a functional of the wave function.

$$E[\psi_i(r)] = \int \psi_i(r) H \psi_i(r)^* \, dr \equiv \langle \psi_i(r) | H | \psi_i(r)^* \rangle \tag{6}$$

The variational theorem states that the energy is higher than that of the ground state unless Ψ correspond to Ψ_0. The ground state wave function and energy may be found by searching all possible wave functions for the one that minimizes the total energy. The Hartree-Fock theory consists of an ansatz for the structure of Ψ; it is assumed to be an antisymmetric product of functions, each of which depends on the coordinates of a single electron.

The density can then be obtained by squaring $\Psi_i(r)$ and integrating the coordinates of all the electrons (i.e., $i = 1$ to $i = N$)

$$\rho_r = \sum_{i=1}^{N} \left|\psi_i(\mathrm{r})\right|^2 \tag{7}$$

Now, like Hartree's scheme, the KS scheme also failed to account for the exchange correlation $v_{x,i}^{KS}(\mathrm{r})$.

To apply the density scheme to describe atomic and molecular states and properties, Parr et al. [9] have developed an important concept known as conceptual density functional theory (CDFT). The CDFT is a subfield of DFT in which one tries to extract from the electronic density relevant concepts and principles that help to understand and predict the chemical behavior of a molecule. CDFT successfully provides easy computational algorithms for chemical concepts such as electronegativity, hardness, softness, and electrophilicity and provides the framework to use them in the domain of chemical reactivity by proving some principles such as the electronegativity equalization principle [10], the hard soft acid base (HSAB) principle [11], and the maximum hardness principle [12].

DFT methods are in general capable of generating a variety of isolated molecular properties. The commercial exploitation of organic compounds as a medicinal drug, for example, is likely to require, at some stage of its development, the determination of biological or chemical activities or properties related to the intended end use of the compound. It is therefore desirable to have at hand relatively straightforward and inexpensive procedures that enable the efficient and accurate prediction of a molecular activity or property, especially when its direct measurement by experiment is, for any reason, to be avoided if at all possible. The procedures that are conventionally used for indirect determination of activities

employ molecular "descriptors" that have suitable molecular properties and physical-organic constructs obtained from both experimental and computational sources.

1.3 CDFT DESCRIPTORS AND THEIR USES

In 1968, Gyftopoulos and Hatsopoulos [13] following the statistics of ensembles and by considering free atom or ion as a thermodynamic system put forward a quantum thermodynamic definition of electronegativity. Given the electron density function, $\rho(r)$, in a chemical system (atom or molecule) and the energy functional, $E(\rho)$, the chemical potential, μ, of that system in equilibrium is defined as the derivative of the energy with respect to the number of electrons at fixed molecular geometry.

$$\mu = \left[\frac{\delta E(\rho)}{\delta \rho}\right]_{v} \tag{8}$$

where v is the external potential acting on an electron due to the presence of the nucleus.

The differential definition more appropriate to the atomic system is based on the assumption that for a system of N electrons with the ground state energy, $E[N,v]$,

$$\mu = -\chi = \left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{9}$$

where χ is the electronegativity of the chemical species.

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = \left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \tag{10}$$

where η is the hardness of the chemical species.

A distinct breakthrough came with the landmark work of Parr and Pearson [14] in 1983 when they derived operational and approximate definitions of chemical hardness, electronegativity, and chemical potential of

any chemical species (atom, ion, or molecule) by using the method of finite difference approximation. Electronegativity, χ, and chemical hardness, η, are defined mathematically as

$$\chi = -\mu = \frac{(I + A)}{2} \tag{11}$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(r)} = \left(\frac{\partial \mu}{\partial N}\right)_{\upsilon(r)} = \frac{(I - A)}{2} \tag{12}$$

Parr et al. [15] by using an empirical relationship described by Maynard et al. [16] developed another very useful descriptor of CDFT known as electrophilicity index (ω). The mathematical definition of ω is

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \tag{13}$$

Nucleophilicity (ε) is physically the inverse of electrophilicity.

$$\varepsilon = 1/\omega \tag{14}$$

We can calculate the four reactivity descriptors with the operational and approximate formula of all such descriptors in terms of equations (11–14) by using only the ionization energy and electron affinity value of the corresponding atom or molecule. But the problem is that I and A of all molecules are not known experimentally, and the accurate theoretical evaluation is very costly for sizable molecules [17, 18]. To overcome the abovementioned problems, we, following Feynman [19] and relying upon classical electrostatic theorems, have derived [17, 18] radial-dependent formulae for computing atomic χ, η, ω, and ε as follows:

Classically, the energy $E(N)$ of charging a conducting sphere of the radius, r, with the charge, q, is given by

$$E(N) = q^2 / 2r \quad (in\ C.G.S.\ Unit) \tag{15}$$

$$E(N) = q^2 / (4\pi\varepsilon_0)2r \quad (in\ S.I.\ Unit) \tag{16}$$

where $E(N)$ is in ergs, q is in electrostatic unit, and r is in cm.

Now, for an atom, the change in energy associated with the increase of q, on removal of an electron (of the charge, e), would be the ionization energy, I. Similarly, the energy generated on addition of an electron with q would be the electron affinity, A. Hence,

$$I = E(N+1) - E(N) = \left[\left\{(q+e)^2 / 2r\right\} - \left(q^2 / 2r\right)\right] \tag{17}$$

and

$$A = E(N) - E(N-1) = \left[\left(q^2 / 2r\right) - \left\{(q-e)^2 / 2r\right\}\right] \tag{18}$$

Now, putting the value of I and A into the CDFT definition of χ, η, ω, and ε, Eqs. (11, 12, 13, and 14), respectively, we offered the formulae for computing χ, η, ω, and ε as follows:

$$\chi \propto eq / r \tag{19}$$

$$\eta \propto e^2 / 2r \tag{20}$$

$$\omega \propto e^2 / r \tag{21}$$

$$\varepsilon \propto r / e^2 \tag{22}$$

1.4 COMPUTATION OF THE EQUALIZED MOLECULAR DESCRIPTORS

Let us consider the formation of a polyatomic molecule ABC… from its constituents. The polyatomic molecule is assumed to be a cluster of atoms where one atom is at the center and the other atoms are surrounding it. Let us assume that the central atom is A and the ligands surrounding the central atom are B, C… as represented in Eq. (23).

$$A + B + C + \ldots \quad \rightarrow ABC \ldots \tag{23}$$

Let the hardness of the molecule be η and that of the combining atoms be η_A, $\eta_{B,}$ η_C …. η_n, respectively.

Let us further assume that the absolute atomic radii of the atoms A, B, C …. etc. are $r_{A,}$ r_B, r_C, $_{....}$ r_n, respectively. Rigorous investigation of the status and the physical condition of atoms in molecules has revealed that the atoms remain in a slightly modified state in the molecule [20, 21]. Because the radii of atoms in any molecule is not available and there is no report of any evaluation method of the radius of any atom being part of any molecule, we can, therefore, safely assume that the radius of the atom in a polyatomic molecule is approximately equal to its absolute radius for all approximate purposes.

Now, let us visualize the charge equalization on the process of molecule formation from its constituent atoms or fragments. While the physical process of charge transfer during the event of chemical reaction leading to bond formation takes place, the charge kernel of atoms changes and in the process, it would increase somewhere and decrease elsewhere so that the ultimate values of the charge-dependent parameters of the atomic fragments will equalize to some intermediate values common to all.

The direction of charge transfer mainly depends on the difference in electronegativity, hardness, electrophilicity, or nucleophilicity values of the atoms forming the molecule. However, for the derivation of the necessary formulae of our work, we arbitrarily assume that the central atom has a lower value and the other atoms have higher values of the charge-dependent parameters.

Now, let us assume that during the formation of the polyatomic molecule, δ is the total amount of charge transferred from the central atom A to the n number of the ligands surrounding the central atom. Although the total amount of charge, (δ), is distributed among the ligands, the amount of charge received by the individual atom is governed by the hardness of that atom.

Let B, C,… n^{th} ligands have the charge δ_1, δ_2, ……. δ_n, respectively, in the molecular cluster and let

$$\delta = \delta_1 + \delta_2 + \ldots\ldots + \delta_n \tag{24}$$

Now, after the charge transfer, the hardness of the central atom A in the polyatomic molecule becomes

$$\eta'_A = K_\eta \left(e-\delta\right)^2 / \ 2r'_A \tag{25}$$

and the hardness of the ligands in the molecule becomes

$$\begin{aligned}
&\eta'_B = K_h \left\{e+\left(d_1\right)\right\}^2 / 2r'_B, \\
&\eta'_C = K_h \left\{e+\left(d_2\right)\right\}^2 / 2r'_C, \\
&\ldots\ldots\ldots\ldots\ldots\ldots \\
&\eta_n = K_h \left\{e+\left(d_n\right)\right\}^2 / 2r'_n
\end{aligned} \tag{26}$$

where $r'_A, r'_B, r'_C \ldots\ldots r'_n$ are the radii of atoms in the molecule, respectively. Similarly, $\eta'_A, \eta'_B, \eta'_C, \ldots\ldots \eta'_n$ are the hardness of the atoms in the molecule and K_η is the proportionality constant.

Expanding Eq. (18), $(e–\delta)^2$ and neglecting the δ^2 term, we get the hardness of the central atom A as

$$\eta'_A = K_\eta \left(e^2 - 2e\delta\right) / 2r'_A \tag{27}$$

Similarly, expanding Eq. (19) and neglecting the δ^2 terms, the formulae for hardness of atoms in the molecule are

$$\begin{aligned}
\eta'_B = K_\eta(e^2 + 2e\delta_1) / \ 2r'_B, \eta'_C = K_\eta(e^2 + 2e\delta_2) / \ 2r'_C, \ldots\ldots \eta'_n \\
= K_\eta(e^2 + 2e\delta_n) / \ 2r'_n
\end{aligned} \tag{28}$$

Now, invoking the hardness equalization principle after the formation of the molecule, the hardness of the individual constituents must be equalized, i.e.,

$$\eta_M = \eta'_A = \eta'_B = \eta'_C = \ldots\ldots\ldots = \eta'_n \tag{29}$$

Eq. (22) implies

$$\eta_M = K_\eta(e^2 - 2e\delta) / \ 2r'_A = K_\eta(e^2 + 2e\delta_1) / \ 2r'_B = K_\eta(e^2 + 2e\delta_2) / \ 2r'_C$$
$$= \ldots = K_\eta(e^2 + 2e\delta_n) / \ r'_n = K_\eta\{(e^2 - 2e\delta) + (e^2 + 2e\delta_1)$$
$$+ (e^2 + 2e\delta_2) \ + \ldots + (e^2 + 2e\delta_n)\} \ / \ \left(2r'_A + 2r'_B + 2r'_C \ldots\ldots + \ 2r'_n\right)$$
$$= K_\eta\{(e^2 - 2e\delta) + ne^2 + 2e(\delta_1 + \delta_2 + \delta_3 + \ldots + \delta_n)\}$$
$$/ \ \left(2r'_A + 2r'_B + 2r'_C \ldots\ldots + \ 2r'_n\right)$$
$$= K_\eta(e^2 - 2e\delta + ne^2 + 2e\delta) \ / \ \left(2r'_A + 2r'_B + 2r'_C \ldots\ldots + \ 2r'_n\right)$$

or

$$\eta_M = K_n(n+1)e^2 \ / \ 2\sum_i r'_i \tag{30}$$

Invoking the approximation that atoms retain their identity in the molecule, we can replace the r' term by the absolute radii, r, of the corresponding atom in Eq. (30).

Thus, we obtain

$$\eta_M = \frac{\mathrm{K}_\eta \ \mathrm{e}^2(\mathrm{n}+1)}{2\sum_i r_i} \tag{31}$$

where the atomic radius, r_i, is expressed in Angstrom unit and K is the constant depending on the fundamental nature of hardness.

Similarly, when we consider the electronegativity equalization, electrophilicity equalization, and nucleophilicity equalization processes, we get the molecular equalized electronegativity, electrophilicity, and nucleophilicity as

$$\chi_M = K_\chi \frac{(n+1)eq}{\sum_i r_i} \qquad \text{(in eV)} \tag{32}$$

$$\omega_M = \mathrm{K}_\omega \frac{7.2(\mathrm{n}+1)}{\sum_i r_i} \qquad \text{(in eV)} \tag{33}$$

and

$$\varepsilon_M = \mathrm{K}_\varepsilon \frac{\sum_i r_i}{7.2(n+1)} \qquad \text{(in eV)} \tag{34}$$

where r_i is the atomic radius in Angstrom unit.

The proportionality constant (K) of the above equations plays a significant role in the evaluation of the quantitative values of the molecular reactivity parameters. The K values can be computed using mathematical correlation of the RHS of Eqs. (31–34) with some other sets of corresponding molecular reactivity data [see Refs. 17, 18]. The choice of reference data may improve the results. Hence, the computed molecular reactivity parameters can still be extended and refined. In the last 5 years, we have carried out several attempts [17, 18] to investigate whether the assumption of charge equalization is valid in the real world, and we found that the charge equalization is a valid process during the heteronuclear molecule formation. Our previous investigations also suggest that the CDFT descriptors are useful to study the process of charge equalization during the heteronuclear molecule formation.

1.5 CONCLUSION

It is well known today that the CDFT descriptors can be successfully applied in the atomic and molecular domain. In this book, we have attempted to explore the grand application of the CDFT to study the atomic and molecular properties.

We reviewed the method of calculating equalized molecular electronegativity, equalized molecular electrophilicity, and equalized molecular nucleophilicity based on the assumption of charge equalization during the chemical event of molecule formation and by combining the electrostatic theorem and CDFT.

KEYWORDS

- **CDFT**
- **charge equalization**

- **DFT**
- **electrostatic theorem**
- **quantum mechanics**

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CHAPTER 2

DENSITY FUNCTIONAL THEORY FOR CHEMICAL REACTIVITY

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CONTENTS

ABSTRACT

We present a short introduction to the use of density functional theory (DFT) in the study of chemical reactions (what is termed as conceptual DFT, chemical reactivity theory, or DFT for chemical reactivity). As the

guiding theme for this endeavor, we took the notion of fractional numbers of electrons. The key role of this concept in conceptual DFT will give us a glimpse of the foundations of this theory and its relationship to "traditional" DFT. Our goal is to help the uninitiated reader gain an understanding of the successes and failures of conceptual DFT, and therefore, we focus on the fundamental theoretical aspects of the theory and strive to keep this exposition—which is by no means comprehensive—self-contained.

2.1 INTRODUCTION

The most important problem faced in quantum chemistry is (at least within the nonrelativistic and Born–Oppenheimer approximations) the solution to the electronic Schrödinger equation [1–3]:

$$\hat{H}\left|\Psi\right\rangle = E\left|\Psi\right\rangle, \tag{1}$$

where the electronic Hamiltonian, $\hat{H}$, depends parametrically on the nuclear coordinates, and it is constituted by the sum of the electronic kinetic energy, $\hat{T}_e$, the interaction energy of the electronic cloud with an external potential, $\hat{V}_{Ne}$, and the electron-electron repulsion, $\hat{V}_{ee}$:

$$\hat{H} = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} \tag{2}$$

or, in a simpler and more explicit way, for a system with N electrons and M nuclei (and using atomic units):

$$\hat{H} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{A=1}^{M} -\frac{Z_A}{|r_i - R_A|} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{1}{|r_i - r_i|} \tag{3}$$

where Z_A and R_A represent the charges and coordinates of the nuclei, respectively.

In general, the overall understanding of this problem was what inspired Dirac to say that the underlying mathematical and physical laws necessary to understand the whole of chemistry are completely known. Hyperbole aside, adhering to this point of view is equivalent to reducing chemistry to a mere computation, with the sole purpose of obtaining reliable and

accurate results for Eq. (1). However, we cannot forget Parr's remark that to calculate a molecule is not the same as to understand it.

In order to gain a deeper insight into the chemical behavior of atoms and molecules, obtaining accurate solution to the Schrödinger equation is a necessary and challenging problem, but by no means exhausts all the content of quantum chemistry. We also need tools to interpret the chemical information hidden in these solutions, because concepts so primordial to chemistry like the notion of an atom or chemical bonds inside a molecule are seemingly absent from Eq. (1).

There have been notable efforts to devise methods aimed to retrieve such chemical insight from the solutions of the Schrödinger equation, which focus mainly on the resulting wave function. However, these approaches face many problems, mainly due to the scaling complexity of this function (for a system of N electrons, it depends on $3N$ spatial and N spin coordinates). But perhaps more importantly, as soon as we increase the complexity of our computational approach, moving beyond the simplest molecular orbital and valence bond theories, it becomes harder to regain the chemical information. This is problematic because, in many cases, the use of such simple theories leads to qualitatively wrong results for the system under study, and as such, the interpretation of the resulting wave functions is, at the very best, controversial. This situation prompted Mulliken to say "the more accurate the calculations became, the more the concepts tended to vanish into thin air."

The problem with the wave function, underlying this situation, is that it is not an observable parameter. As such, it seems convenient to find other ways to extract the chemical information from a quantum mechanical calculation. One of the most popular alternatives is to use the electron density, $\rho(r)$ [4–7]. For a system with N electrons, described by a normalized wave function ($\langle \psi \mid \psi \rangle = 1$), this magnitude is defined as:

$$\rho(r) = N \int \Psi^{*}(r, s_1, r_2, s_2 ..., r_N, s_N)\, \Psi(r, s_1, r_2, s_2 ..., r_N, s_N)\, ds_1 dr_2 ds_2 ... dr_N ds_N \tag{4}$$

where s_i denotes the spin variables. From this definition, we can easily infer two properties:

$$\int \rho(r)\,dr = N \tag{5}$$

$$\forall r,\ \rho(r) \geq 0 \tag{6}$$

In other words, the electron density integrates to the number of electrons of the system and, given that it is a probability distribution, is nowhere negative. Contrary to the wave function, $\rho(r)$ only depends on three spatial coordinates, independent of N. Moreover, the electron density is an observable parameter of the system.

For these reasons, there has been an ever-increasing interest in the use of the electron density as a vehicle to rationalize chemical structures and chemical reactivity. We devote this contribution to the latter, making special emphasis on what is known as conceptual DFT (or chemical reactivity theory or DFT for chemical reactivity). We analyze the foundations of this theory, with particular interest in the notion of fractional numbers of electrons. Much of the analysis is devoted to discuss this notion, motivating its introduction, presenting a rigorous framework to work with it in a quantum mechanical sense, and showing its relevance at the time of defining chemical concepts within conceptual DFT. Given our interest that the present chapter could be used by newcomers to this field as an introduction to the machinery of conceptual DFT, we intend it to be as self-contained as possible. For this reason, we begin our exposition with a short introduction of "traditional" DFT, in which we also remark the importance of working with fractional N and present the electronic chemical potential as the common link between computational and conceptual DFT.

2.2 DENSITY FUNCTIONAL THEORY

Since the early stages of the development of quantum mechanics, it was evident that procedures based on magnitudes rather than on the wave function could provide simpler ways to study quantum phenomena. This motivated Thomas and Fermi, who proposed an heuristic model to study atomic systems, whose fundamental variable was the electron density, $\rho(r)$ [8–11]. However, the many approximations included in this model and the generally poor results (most notably, its inability to account for

the formation of stable chemical bonds) [12–15] diminished the interest of the community of quantum chemists in this approach. The interest in the theory based on $\rho(r)$ was revamped thanks to the work of Hohenberg and Kohn [16], who proved that the electron density of the ground state contains all the information needed to describe a system. Presently, the works of Levy [17–19] and Lieb [76, 79, 82] are considered the most rigorous formulations of the DFT. Its solid theoretical foundation, along with the development, mainly through the Kohn–Sham formalism [20], of attractive computational tools based on it, have contributed to the ever-increasing popularity of DFT as a basic tool in different areas of modern theoretical chemistry.

2.2.1 FOUNDATIONS

It is enough to know the Hamiltonian of a system to determine its state, given that we solve Eq. (1). At this point, we may note that $\hat{H}$ is completely defined by the number of electrons (terms $\hat{T}_e$ and $\hat{V}_{ee}$) and by the external potential (term $\hat{V}_{Ne}$). According to Eq. (5), $\rho(r)$ allows us to determine N; therefore, the only thing that remains is to check whether the ground state electron density, $\rho(r)_0$, is enough to univocally define the external potential acting on the electrons.[1] This potential, as can be seen in the second term of Eq. (3), usually corresponds to the potential associated with the atomic nuclei, even though in a more general formulation, it can include other effects as long as they are local (this means depending on the spatial coordinates as, e.g., $\langle r'|\hat{V}_{Ne}|r\rangle = v(r)\delta(r-r')$. Hohenberg and Kohn (HK) [75, 78] proved that, effectively, each ground state electron density corresponds to at most one external potential. This means that $\rho(r)_0$ contains all the necessary information to build $\hat{H}$ and, therefore, to determine the state of the system. For example, it is possible to write the ground state energy, E_0, using a functional of the electron density:

$$E_0 = E_{HK}[\rho_0] = F_{HK}[\rho_0] + \int \rho(r)_0 \, v(r) dr \tag{7}$$

[1] In general, the external potential will be determined only up to an additive constant. This means that the potentials $v(r)$ and $v(r)+C$ are equivalent, given that the introduction of C only changes the zero of the energy scale.

DFT's biggest attractiveness is that the functional $F_{HK}[\rho]$ (which corresponds to the sum of the kinetic and electron-electron repulsion energies) is universal. In other words, it is independent of $v(r)$, and can, in principle, be used to study any system [74, 77–79].

HK also proved a variational principle in terms of the electron density:

$$E_0 = \min_{\rho:\rho(r)\geq 0, \int \rho(r)dr = N, \rho(r)\to v} E_{HK}\left[\rho\right] \tag{8}$$

In this expression, we highlight that the variational principle will be valid as long as we use density functions that satisfy Eqs. (5) and (6) and that correspond to the ground state of some Hamiltonian with a local external potential ($\rho(r)\to$v). This condition, known as *v*-representability [77–79], is necessary given that $F_{HK}[\rho]$ is defined only over these densities:

$$F_{HK}\left[\rho\right] = E_0\left[\rho\right] - \int \rho\left(r\right)v\left(r\right)_{\rho(r)}dr \tag{9}$$

where we have pointed out that one must use both the ground state energy, $E_0[\rho]$, and the external potential,$v(r)_{\rho(r)}$, of the system where $\rho(r)$ is the ground state. This represents the biggest drawback of the HK formulation, because we do not know the general conditions under which a given $\rho(r)$ is *v*-representable. This implies that the variational principle, Eq. (8), cannot be used in a consistent way.

To solve this problem, Levy proposed formulating DFT starting from the variational principle based on the wave function [17–19]:

$$E_0 = \min_{\Psi} \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle \tag{10}$$

All the admissible wave functions, over which we try to find the minimum of Eq. (10), are normalized, well-behaved, and antisymmetric (given that we are working with fermions). The key step now is to realize that we can separate this minimization into two steps:

$$E_0 = \min_{\rho:\rho(r)\to N} \left\{ \min_{\Psi\to\rho(r)} \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle \right\} \tag{11}$$

First, we consider the set of *N*-representables ($\rho(r)\to N$) electron densities; this set includes those derived from an admissible wave function

according to Eq. (4). Then, for each of these densities, we find the minimum of the mean value of the Hamiltonian over all the wave functions that lead to the selected density. This procedure (known as constrained search) has the advantage that, as opposed to the case of *v*-representability, the conditions for *N*-representability are well understood. In general, $\rho(r)$ will be *N*-representable if it satisfies Eqs. (5), (6), and [77, 78]:

$$\int \left| \nabla \rho(r)^{\frac{1}{2}} \right|^2 dr < \infty \tag{12}$$

Levy's formulation can be presented in a form similar to the one used by HK, which helps to highlight the central role of the electron density [77, 78]:

$$E_0 = \min_{\rho:\rho(r)\to N} E_{LL}[\rho] \tag{13}$$

$$E_{LL}[\rho] = F_{LL}[\rho] + \int \rho(r) v(r) dr \tag{14}$$

$$F_{LL}[\rho] = \min_{\Psi\to\rho(r)} \left\langle \Psi \middle| \hat{T}_e + \hat{V}_{ee} \middle| \Psi \right\rangle \tag{15}$$

Obviously, for a *v*-representable $\rho(r)$:

$$E_{LL}[\rho] = E_{HK}[\rho],\ F_{LL}[\rho] = F_{HK}[\rho] \tag{16}$$

In other words, the functionals of Levy-Lieb, $E_{\mathrm{LL}}[\rho]$ and $F_{\mathrm{LL}}[\rho]$, are extensions of their HK counterparts over the set of *N*-representable $\rho(r)$'s. To simplify the notation, density functionals will be presented without sub-indices, i.e., $E[\rho]$ and $F[\rho]$, unless there is cause for confusion.

In the formulations of HK and Levy, there appear variational principles where the electron density plays a key role (Eqs. (8) and (13)). In both cases, we should be careful to use only densities that integrate to the number of electrons of the system, as given in Eq. (4), and we should also note that this number is usually a non-negative integer. This is certainly not convenient from a conceptual and practical point of view. Therefore, the variational principle is re-formulated using Lagrange multipliers. Now, the equation to solve is [77, 78]:

$$\delta\left\{E[\rho]-\mu\left[\int\rho(r)dr-N\right]\right\}=0 \tag{17}$$

In this expression, the Lagrange multiplier μ, associated with the constraint of constant N, is identified as the electronic chemical potential. The advantage of this procedure is that the test densities can now integrate to an arbitrary real (non-negative) number of electrons. In the forthcoming sections, we will discuss both about the justification for introducing fractional numbers of electrons in this formalism and about the relevance of the chemical potential.

2.2.2 KOHN–SHAM TREATMENT

In the preceding section, we presented the basic formulation of DFT; however, none of the previously discussed functionals has practical applications. For example, even if we can write the energy functional as:

$$E[\rho]=T_e[\rho]+V_{Ne}[\rho]+V_{ee}[\rho] \tag{18}$$

Only the second term can be calculated easily:

$$V_{Ne}[\rho]=\int\rho(r)v(r)dr \tag{19}$$

Of the remaining terms, the most difficult to approximate is the kinetic energy. A possible strategy to overcome this is to re-write Eq. (18) as:

$$E[\rho]=T_S[\rho]+V_{Ne}[\rho]+J[\rho]+\left(T_e[\rho]-T_S[\rho]+V_{ee}[\rho]-J[\rho]\right) \tag{20}$$

Now, the functional, $J[\rho]$, represents the interaction energy of a (classical) electron cloud with itself:

$$J[\rho]=\int\frac{\rho(r)\rho(r')}{|r-r'|}drdr' \tag{21}$$

The functional, $T_S[\rho]$, is chosen such as it contains a considerable fraction of the exact kinetic energy of the system, while having a simple closed form. The most popular choice (albeit not the only one) [21, 22] is the proposal of Kohn and Sham [20] of taking $T_S[\rho]$ as the kinetic energy of a fictitious system of noninteracting electrons with the same density as that of the real system. The wave function of this ideal system is given by a Slater determinant [33, 34]:

$$\Phi_{KS}\left(x_1,...,x_N\right)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\varphi_1^{KS}\left(x_1\right) & \varphi_2^{KS}\left(x_1\right) & ... & \varphi_N^{KS}\left(x_1\right)\\ \varphi_1^{KS}\left(x_2\right) & \varphi_2^{KS}\left(x_2\right) & ... & \varphi_N^{KS}\left(x_2\right)\\ ... & ... & ... & ...\\ \varphi_1^{KS}\left(x_N\right) & \varphi_2^{KS}\left(x_N\right) & ... & \varphi_N^{KS}\left(x_N\right)\end{vmatrix} \tag{22}$$

where χ_i represent the spatial and spin coordinates of each electron and φ_i^{KS} are the spin-orbitals of the auxiliary system, also known as Kohn–Sham (KS) orbitals. Then:

$$T_S\left[\rho\right]=\sum_{i=1}^{N}-\frac{\nabla_i^2}{2}\varphi_i^{KS}\left(x_i\right) \tag{23}$$

The term in parentheses in Eq. (20) is identified, in analogy with the Hartree-Fock (HF) [2] treatment, with the exchange-correlation functional [74, 77]:

$$E_{xc}\left[\rho\right]=T_e\left[\rho\right]-T_S\left[\rho\right]+V_{ee}\left[\rho\right]-J\left[\rho\right] \tag{24}$$

In this case, despite containing the nonclassical effects of the interaction between the electrons, $V_{ee}[\rho]$-$J[\rho]$, (correlation and exchange), we have the kinetic contribution, $T_e[\rho]$-$T_S[\rho]$, due to the approximate characteristic of $T_S[\rho]$.

Up to this point, we have not introduced any approximation, and the KS spin-orbitals can be obtained solving the single-particle equations [20]:

$$\left\{-\frac{\nabla_i^2}{2}+v_{KS}\left(r\right)\right\}\varphi_i^{KS}\left(x_i\right)=\varepsilon_i^{KS}\varphi_i^{KS}\left(x_i\right) \tag{25}$$

being:

$$v_{KS}(r) = v(r) + \int \frac{\rho(r')}{|r - r'|} dr' + v_{xc}(r) \tag{26}$$

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \tag{27}$$

Given that the electron density appears in the left hand side of Eq. (25) (i.e., second term in Eq. (26)) and that, by construction:

$$\rho(r) = \sum_{i=1}^{N} \left| \varphi_i^{KS}(r_i) \right|^2 \tag{28}$$

the KS equations (Eq. (25)) must be solved self-consistently. Like other standard wave function-based methods, the most usual approach is to expand the spatial part of φ_i^{KS} on the basis of approximate basis functions and then solve the resulting algebraic equations [35, 131].

What is left is to know the exchange-correlation functional, $E_{XC}[\rho]$, or its associated potential, $\nu_{XC}(r)$. Given the complexity of the terms included in $E_{XC}[\rho]$, its exact form is unknown. In modern DFT [74, 132], finding accurate, yet computationally feasible, approaches for this functional is considered the central problem of DFT. Among the different strategies devised to accomplish this, we have:

Local functionals: Estimate $E_{XC}[\rho]$ starting with the local density approximation (LDA) [74, 77] taking the expressions derived for the homogeneous electron gas. The Dirac exchange functional [10] and the correlation functional VWN (Vosko, Wilk, and Nusair) [23] are examples of local functionals.

Generalized gradient functionals: Add information concerning the nonlocal behavior of the density, through the use of its gradient, $\nabla\rho(r)$. In a sense, this is equivalent to expanding the functional $E_{xc}[\rho]$ in a power series around the LDA expressions, thus imposing some extra conditions known to hold for the exact functional (e.g., the sum rules for the Coulomb and Fermi holes) [4]. The Perdew, Burke, and Ernzerhof (PBE) functional [24], which does not contain any empirical parameter, belongs to this family.