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The World of Theoretical Chemistry: Unboxed

Saba Niaz[1*], Altaf Hussain Pandith[1*]

[1]*Department of Chemistry, University of Kashmir, Srinagar - 190006, J&K, India*

[*]**Corresponding authors**
Saba Niaz and Altaf Hussain Pandith, Department of Chemistry, University of Kashmir, Srinagar-190006, J&K, India.

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Abstract

The review paper focuses on the developments that have taken place in the field of theoretical chemistry ranging all the way from different software's, methodologies, equations, theories, basis sets and conceptual reactivity descriptors. We have also discussed their advantages and limitations that made them stand out in the field of study. Theoretical chemistry has gained pace, as it proves highly efficient in the field of hydrogen storage, solar energy storage, non-linear optics and in metal ion toxicity. The said research field has proven beneficial, as now we can easily compare the accuracy of our experimental data with the theoretical one. Theoretical chemistry has revolutionized the world of chemistry, as it has paved the way for a new pathway that's not only time saving but also accurate when it comes to data calculation and interpretation.

Keywords: Theoretical Chemistry, Density Functional Theory, Basis Sets, Reactivity Descriptors

Introduction

Theoretical chemistry is based on the fundamentals of quantum mechanics, classical mechanics and statistical thermodynamics that assist in providing an in-depth understanding of the structure and dynamics of various chemical systems and help in correlating and predicting the thermodynamic and kinetic properties of such systems. The study of chemical structure includes studies of electronic structure, potential energy surfaces, force fields, vibrational-rotational motion, equilibrium properties of condensed-phase systems and macromolecules. Studies on chemical dynamics include molecular dynamics, statistical thermodynamics, kinetics, energy transfer, metastable states, condensed-phase and macromolecular aspects of dynamics. The fundamental basis for understanding materials and phenomena ultimately rests upon understanding of the electronic structure. The electronic structure gives an insight about the chemical structure of the material, as well as the dynamic properties of the structure. The basic reason for introducing theoretical chemistry was to inculcate such concepts and systems that will provide the detailed qualitative information about the electronic structure that assists in understanding both the ground state and excited state of many-body interacting systems. Theoretical chemistry has an advantage as it allows the study of those novel systems that are not possible to investigate at an experimental level and that too in an elaborated manner. Historically, the year 1927 marked the dawn of theoretical study, as in the same year Walter Heitler and Fritz London successfully performed the first theoretical calculations in chemistry.

Computational chemistry employs the principles of theoretical chemistry, such as quantum chemistry etc., incorporated in appropriate computer-based programs to solve the chemical problems related to the structure, properties and reactivity of molecules and condensed matter. The study includes a variety of methods such as ab initio methods, empirical and semi empirical methods which differ from one another in terms of accuracy and computational cost. Computational chemistry proves quite beneficial, when it comes to experiments, as we can not only double check our results but also can study a variety of novel complexes which can prove helpful in designing new molecules for the future.

Theoretical chemistry brings chemists, physicists, and mathematicians together in designing computer algorithms and programs while the computational chemistry simply uses these programs to study or predict the structure, stability and various thermodynamic and kinetic properties of molecules. This field of study came into limelight when in 1998 John pople and 2013 to Walter Kohn, were awarded nobel prize in Density-Functional Theory for designing computational methods that find their applications in quantum chemistry.

Computational Chemistry: An Introduction

1. To check the feasibility of a chemical reaction.
2. To interpret various spectroscopic data (NMR, IR, UV).
3. To study those molecules which are difficult to synthesize.

4. They are widely used in drug designing and to monitor catalytic reactions.
5. It also assists chemists to check the accuracy of a chemical reaction by comparing it with theoretical data.
6. Calculates and predicts the charge distribution, potential energy surfaces, rate constants and the optimized geometries of the molecules both in the ground as well as in the excited states.
7. In addition to this we can also get the polarizabilities, electron density maps and population analyses which provide us an in depth information about the chemical species.

Software Packages

Various computational software packages have been developed over the last several decades which provide the chemists the necessary tools to study various aspects of varied types of chemical systems, ranging from atoms and molecules to condensed systems. These packages get upgraded time and again to include additional computational methods. So, in order to choose a best package we need to look at its computational cost, accuracy, ease of installation and finally the one which can calculate various desired parameters, using optimal computational resources and time (figure 1).

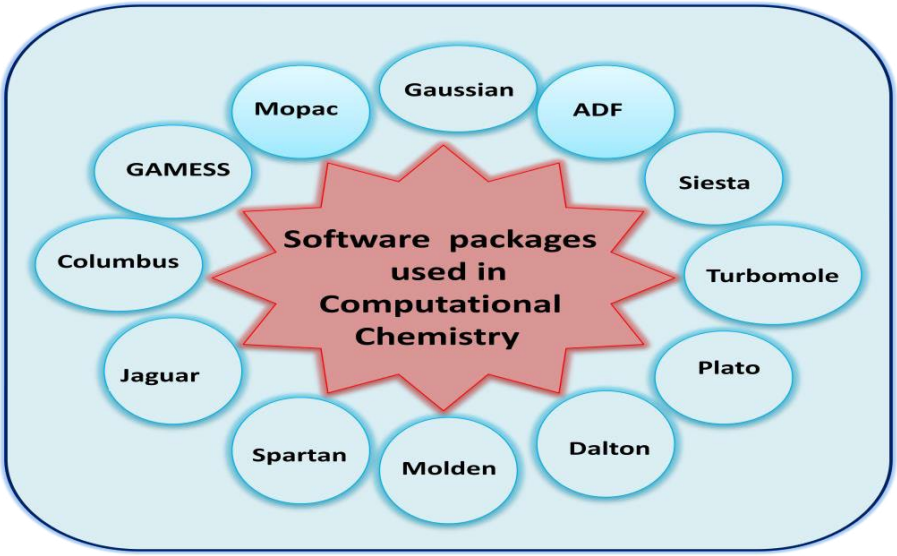


Figure 1: Various Software Packages Used in Computational Chemistry

Jaguar

This software is based on ab *initio* method and finds its application for the calculations that are performed in gas and solution phase [1]. It was designed by Richard Friesner and William Goddard but is being marketed by Schrödinger. The most recent in this series is Jaguar 9.7 which can perform calculations that involve Hartree–Fock, Density Functional Theory and Møller–Plesset perturbation theory. The package performs the geometry optimizations, conformational analysis, calculation of solvation free energies and spectral analysis.

GAMESS

The package stands for General Atomic and Molecular Electronic Structure System and originated in 1977 but was divided into two groups GAMESS (US) and GAMESS (UK) [2]. Calculations that involve Hartree–Fock, Møller–Plesset perturbation theory (MP2 & MP3), coupled cluster (CCSD & CCSD(T), Density Functional Theory (DFT) and configuration interaction (CI) can be done using this software. The results are accurate but the only issue with gamess is that the procedure for creating an input file is a bit tiresome [1, 3].

Gaussian

The package got its name from Gaussian orbitals that were used in computational chemistry and was designed by John Pople and his group in 1970 [1, 4, 5]. This package gained popularity as it revolutionized the field of quantum chemistry by offering variety when it comes to performing calculations related to Semi empirical, Moller Plesset perturbation theory (MP2 & MP3) and Density functional theory (DFT). The major advantage of this package is that it is user friendly.

Columbus

It is based on ab *initio* method and is used to study atomic and molecular ground and excited states. This package was designed by Isaiah Shavitt, Hans Lischka and Ron Shepard in 1980 at Ohio State University. The programs are based on Fortran where perlsript is used to make the input files which can be used for various calculations. The program is highly flexible but its use gets limited because of difficulty which arises in preparing the input files.

Spartan

Its user friendly and can be used to perform calculations which involve Semi-empirical methods, ab *initio* methods, Density Functional Theory, post-Hartree–Fock models [6-8]. It is easy to use, determines the structure, molecular properties, conformational analysis, spectra's and reactivity of molecules under study [1, 2, 8].

Siesta
It stands for Spanish Initiative for Electronic Simulations with Thousands of Atoms and is used for performing ab *initio* calculations on solids. Its computationally efficient not only as per time but also predicts accurate results.

Turbomole
Prof. Reinhart Ahlrichs designed the package which uses the ab *initio* method for performing calculations and mostly deals with study related to heterogeneous and homogeneous catalysis. It can be used to study based spectroscopy and biochemistry of various molecules.

Plato
It stands for Package for Linear-combination of Atomic Orbitals which is written in C language. It is mostly used to study point defects and electronic structure of transition metals but can also be used to study the behaviour of various clusters and molecules.

Dalton
This is an ab *initio-based* program which has been named after famous chemist John Dalton [9]. The previous version of Dalton can perform calculations that are based on Hartree–Fock, MP2 and coupled cluster theory but the recent Version DALTON 2.0 can also perform density functional theory calculations.

Molden
The word molden comes from molecular density and is an ab initio-based package. The advantage of molden is that it can use the data of either GAMESS / GAUSSIAN output file and can also be used to make contour plots, and 3-d grid plots.

Amsterdam Density Functional (ADF)
The calculations employ the usage of Density Functional Theory (DFT) [1]. The successful efforts of by E. J. Baerends and T. Ziegler group paved the way for ADF. The applications of ADF cover both the industrial and academic sector as it provides an upper edge in spectroscopy. It is mostly recommended to study heavier elements and transition metals. Band is also equivalent to ADF that provides in depth analysis of crystals but can also be used to study the IR, Raman, VCD, UV, NMR and EPR spectroscopy of the molecules.

Mopac
It stands for Molecular Orbital PACkage and was designed by Michael Dewar's research lab. It is based on Windows, Mac, and Linux based operating systems and performs calculations based on Semi-empirical method [1].

Gromacs
It stands for GROningen Machine for Chemical Simulations and was developed at University of Groningen [5]. This is mostly used for study organic compounds such as proteins, lipids and nucleic acids.

Born–Oppenheimer Approximation
The concept of Born-Oppenheimer Approximation (1927) deals with idea that the electronic and nuclear motions of molecules can be considered separately, as the latter motions to be slower as compared to former ones such that it is to be assumed that the electronic motions are independent of nuclear motions (figure 2).

$$\Psi_{molecule} = \Psi_{electron} \times \Psi_{nuclei} \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.1)$$

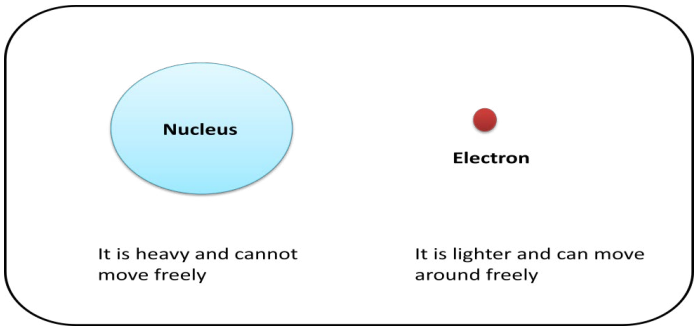


Figure 2: Representation of Born - Oppenheimer Approximation

It is seen that both the electrons and nuclei experience the same force because of same electric charge prevalent over them giving rise to same momentum. But the nuclei possess higher mass which results in lower velocities as compared to the electrons giving the electrons an advantage to easily get relaxed to their ground state configuration. Born-Oppenheimer Approximation implies that energies of molecules arising by virtue of rotational, vibrational and electronic excitations that exists independent of each other. Hence, we can separately deal with electronic and nuclear motions present in the molecule which pays the way for Born-Oppenheimer Approximation. The total energy comprises of various energies as given in equation below.

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{nuclear} \ldots\ldots\ldots (1.2)$$

Ab Initio Methods
Ab *Initio*, is derived from the Latin word meaning " from the beginning ". The foundation of these methods is based on the Schrodinger equation and requires no empirical parameters for performing the desired calculations. Eg: Hartree-Fock (HF), configuration interaction (CI), many-body perturbation theory (MBPT), coupled-cluster (CC) theory. These methods differ in computing electron exchange and correlation energies: the accounting for full correlation interactions along with the use of infinite basis functions leads to Schrodinger limit of accuracy. These methods calculate the electronic state energies and physical properties with respect to the position of the nuclei without taking support of an experimental data. As these methods involve the use of approximations, which can be made more accurate with the further advances in the theory. They were found extremely beneficial during the study of new molecular geometries, energies, spectra, excited states, di-

pole moments of smaller atoms, molecules, radicals and ions. The method becomes limited as it involves exhaustive, involve large number of steps during the calculations, time consuming, occupies more disc space and can't be used in case of concerted reactions, electronic transitions and rearrangement reactions.

Hartree-Fock Theory

The Hartree-Fock theory deals in determining ground-state wave function and ground-state energy determination of many-body system without taking into consideration correlation effect of electrons [10, 11]. It states that the electrons face an average field that comes from the nearby electrons and gives no consideration to pair-wise correlations. Here the nuclear-nuclear repulsion term has been represented as the sum of one electron operator. The insertion of (1) in the equation 1.3 represents that the operator is 1-electron based.

$$\hat{F}[\{\phi_i\}](1) = \hat{H}^{core}(1) + \sum_{j=1}^{\frac{n}{2}}[2\hat{J}_j(1) - \hat{K}_j(1)] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.3)$$

$$\hat{H}^{core}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{\alpha}\frac{Z_\alpha}{Z_{1\alpha}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.4)$$

$\hat{F}[\{\phi_i\}](1)$is the one electron fock operator ϕ_j orbital, $\hat{J}_j(1)$ being the Coulomb operator includes the electron-electron repulsion energy of the jth electron, $\hat{K}_j(1)$being the exchange operator includes the electron exchange energy. The equation finally leads to the generation of the Hartree–Fock molecular orbitals as can be seen below:

$$\hat{F}(1)\phi_i(1) = \epsilon_i\phi_i(1) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.5)$$

In 1927 D. R. Hartree developed " the Self-consistent Field method " which has been represented in the form of a flow chart (Figure 3). Hartreefock method is the beginning step for most of the methods used in theoretical chemistry, but is poor when it comes to quantitative calculations.

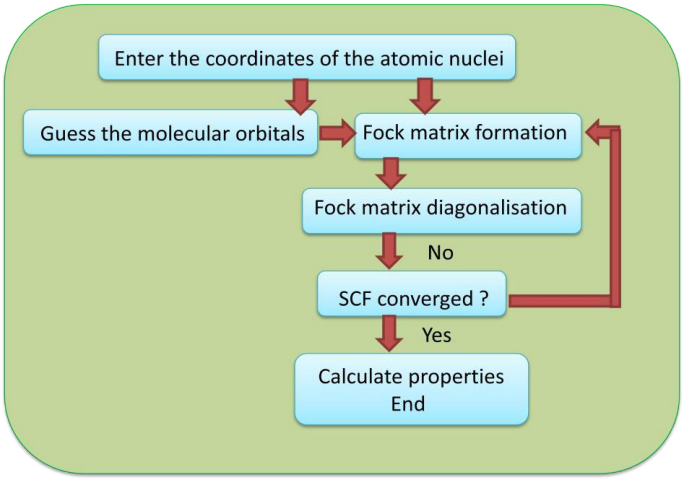


Figure 3: Flow Chart of The Hartree-Fock Self-Consistent Field (HF SCF) Procedure

Limitations of Hartree-Fock Theory

1. Electronic correlations are ignored, accounted for in an average sense.
2. Dispersion interactions are not accounted.
3. Fails to optimize unoccupied orbitals.
4. The bond length details calculated are shorter than expected.
5. It is computationally expensive.

The MP$_n$ Method

The MP2 method was given Møller and Plesset in 1934 and include MP2, MP4 etc [12]. This method gains advantage in computing more accurately the electrostatic interactions and London dispersion interactions where nonlocal electronic correlations are present. These methods only become restricted for application, as they are computationally expensive.

Basis Sets

Basis sets are set of mathematical functions that represent the electronic wave function combined in a linear manner. It was J.C. Slater who laid the foundation of basis sets. These sets represent the molecular orbitals that are located on the centre of the atom. They are mainly divided into two categories, one being minimal basis set and the other being extended basis sets. The ideal basis set should be accurate, flexible, less time consuming and should provide the complete information about the molecular structure.

Minimal Basis Set

This type of basis set involves single function for each orbital and employees' equal number of basis functions for both the core and valence orbital [13-21]. These basis sets utilize minimum basis functions for all the electrons that are present on the atom. They were first given by John Pople and his group and are represented as STO-XG, where STO are Slater Type Orbitals and X represents the number of Gaussian functions. Examples are STO-2G,STO-3G,STO-6G [22-27]. These basis sets involve limited size based atomic orbitals. These basis sets fail to give the proper electronic distribution and hence were replaced by extended basis sets. Some other types of minimum basis sets are MIDIX, MINI and MIDI4 basis sets [28-30].

Slater Type Orbitals (STOs), developed by J. C. Slater possess exponential decay at long range and Kato's cusp condition at short range, but unlike the hydrogen-like Schrödinger orbitals, STOs have no radial nodes [31]. They are not preferred for larger molecules as it takes a lot of time to solve their integrals, hence increase the computational cost. They are mostly used to calculate charge, spin, long range interactions.

The equation that can represent the basis function is given below:

$$\emptyset = Ne^{(-\xi\vec{r})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.6)$$

Here *N* is the normalization constant, ξ being the orbital exponent and $\vec{r}$ is the radius vector.
Slater Type Orbital (STO) are represented by the following equation [31]:

$$STO = \frac{\xi^3}{\sqrt{\pi}} e^{(-\xi\vec{r})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.7)$$

The above equation can also be represented in spherical coordinates (r, θ and ϕ) as:

$$\emptyset(\alpha, n, l, m; r, \theta, \emptyset) = Nr^{n-1}e^{-\alpha r}Y_{l,m}(\theta, \emptyset) \quad \ldots\ldots (1.8)$$

$Y_{l,m}$ = angular momentum and *n,l and m* = quantum numbers.

Gaussian Type Orbitals (GTOs) were introduced by S.F. Boys in 1950 [32]. Here, four-center integrals can be reduced to finite sums of two-center integrals, and in a next step to finite sums of one-center integrals. This take less time in calculating the integrals as compared to calculations based on STOs, hence have low computational cost. As compared to STO's, GTOs have no cusp condition at short range. They are represented as:

$$GTO = \frac{2\xi}{\pi^{3/4}} e^{(-\xi r^2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.9)$$

Extended Basis Sets

They provide much more freedom as compared to minimal basis sets and can readjust themselves as per different molecular environment which involves either contraction or expansion of orbitals. The orbital's get further divided into a compact inner orbital while the outer orbitals remains diffused. These sets use higher orbitals of the molecule and are responsible for size and shape of molecular orbitals. They are broadly divided into four types [13-21]:

Double-Zeta Basis Sets

The double zeta sets use two orbitals and are represented as DZ- or 2ζ-basis sets [33]. We have a single atomic orbital that comprises of two Slater-type orbitals. The zeta value-based function is a direct indication of charge distribution. This leads to the idea that if the charge is distributed mainly at the nucleus we will get higher zeta value while the lower zeta value is an indication of charge distribution being away from the nucleus. The higher zeta value indicates the larger size of the orbital. The value of 'd' present in the equation (1.10) helps us to know about the contribution of the second STO towards the final orbital. Hence, we can say that the value of two STOs will be responsible for determining the size of the atomic orbital. The type of the atom whether its positive or negative is related to the density, which makes it either to expand or contract. The double -Zeta basis sets can be written as:

$$\phi(r) = \phi_{2s}^{STO}(r, \xi_1) + d\phi_{2s}^{STO}(r, \xi_2) \ldots\ldots\ldots\ldots \quad (1.10)$$

We can similarly have triple and quadruple-zeta basis sets if we use three and four STOs.

Split-Valence Basis Sets

The use of double-zeta basis set for each orbital is a tedious task. In addition to that, most of the reactions are mainly focused on the valence orbitals instead of the core orbitals. So, in order to solve this issue, it suffices to use only single basis function for core atomic orbitals (AOs) while double-zeta basis set is used only for the valence AOs. This concept lead to the generation of split valence basis sets. They are represented by X-YZ where X is the core Gaussian while Y and Z are the two basis functions of the valence orbital (figure 4) [34]. Some of the split valence basis sets are 3-21G, 6-31G and 6-311G [22, 34-40]. The addition of split valence basis set offers better description of the valence orbitals. For example, in case of 3-21G basis set we have core orbital that uses three GTOs and a valence orbital that uses two GTOs for contracted valence orbitals with one function and one GTO with extended valence orbitals that has one function. This basis set finds its application in all basis sets till xenon atom. We can similarly have the 6-31G basis set. In case of 6-311G, which is a triple split valence basis sets, the inner orbital possesses three Gaussians, while middle and outer orbital has one Gaussian each. To simplify the calculations, the priority is given to the double zeta of the valence orbital as it improves the flexibility while the core orbital is considered insignificant.

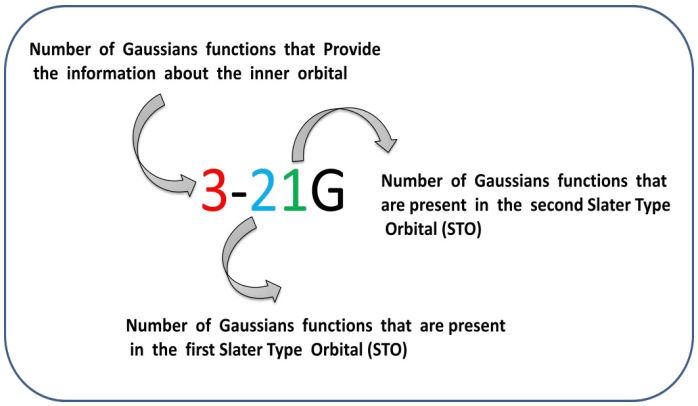


Figure 4: 3-21G Split-Valence Basis Sets

Polarized Basis Sets

The basis sets need to attain some polarization effects to prove

efficient when it comes to performing calculations, as the shape of the orbital gets modified by the effect of polarization which causes "s" orbitals to attain "p" orbital effect and "p" orbitals in turn attain a little of the "d" orbital effect. These Polarized basis sets are denoted by asterisk (*), single asterisk (*) for heavier elements while two asterisks (**) are for lighter elements like hydrogen and helium. In this way, we can add p-functions, d-functions to valence p orbital's, and f-functions to valence d-type orbital's (figure 5). The neighbouring nuclei affect the electronic distribution of an atom, as it now faces an asymmetric environment which causes change in the shape of an orbital. To accommodate this change, we need to add polarization functions which can provide them the orbital flexibility. Examples are 6-31G*(d) basis set, which adds a set of "d" functions and 6-311G **(d, p) basis set that not only adds set of "d" functions to the atoms but also and a set of "p" functions which are added only on hydrogen atom. We can similarly have Double-zeta basis sets (DZP) which possess one d-function and one set of p-functions, while Triple-zeta basis sets (TZVP) contains one set of d-functions with one set of p-function.

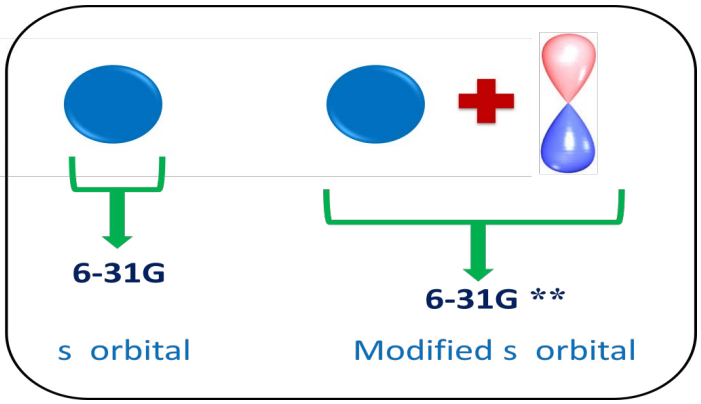


Figure 5: Split-Valence Polarization 6-31G** Basis Set

Diffuse Basis Set

These sets are denoted by a plus sign + (p function for atoms with Z >2), and two plus signs ++ (p and s functions, with an additional larger s function for H atoms), indicating addition on lighter atoms. E.g.: 6-31+G and 6-31++ G. The electrons that are located far away from the nucleus such as anions, lone pairs, excited states, strong electronegative atoms and transition states also effect the electronic density of an atom and in such cases, we use diffuse functions which takes these effects into consideration. These functions are mostly located in distant tail portion of an atomic orbital. It is mostly used to calculate polarizabilities, dipole moment and binding energies of complexes where complexes involve dispersion forces. In addition to that we can also have spin valence basis sets with polarized (3-21G*), or diffused functions (3-21+G), and basis sets that are both polarized and diffused (3-21+G*,6-31+G*, 6-311++G**) are termed as balanced basis sets.

Dunning's Correlation-Consistent Basis Sets

These basis sets were developed by Dunning and co-workers which are represented generally as cc-pVNZ where N=D,T,Q,5,6... (D=double, T=triples, etc.) here cc-p = correlation-consistent polarized' and V = valence only basis sets [41]. In order to calculate geometry and nuclear property, we add augmented functions and for calculations which involve excited state and Van der Waals forces, we prefer diffuse functions to be incorporated in these basis sets (cc-pVTZ+). Examples - cc-pVDZ (Double-zeta), cc-pVTZ(Triple-zeta), cc-pVQZ (Quadruple-zeta) and aug-cc-pVDZ (Augmented) basis set [42-45]. The combined table including different types of basis sets has been given below (figure 6).

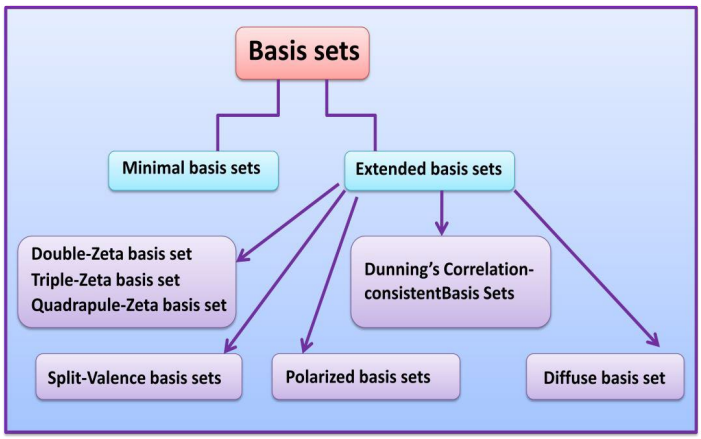


Figure 6: Various Types of Basis Sets Used in Computational Chemistry

Semi-Empirical Methods

Pople and his co-workers gave the concept of semi-empirical method [46]. These methods use the concept of Hartree–Fock formalism, in addition to the experimentally obtained data or the data that has been obtained using from the ab initio methods, for performing the theoretical calculations. They are preferred when dealing with molecules that are of larger in size, as the calculations are performed at faster pace in comparison to ab-initio calculations. Semi empirical methods save time as they don't consider core electrons and prefers minimal basis set for describing the valence orbital's during calculations. They are used for performing geometry optimization, studying intermediates or transition states, calculating heats of formation and for knowing the charge distribution of the molecule. When it comes simpler units like C-C, C-H, C-O, stable conformers, macromolecules, steric interactions and even biopolymers, empirical methods prove quite useful. These methods give accurate results in quantitative and qualitative study and provides better of description of molecular orbitals. In some cases, it also includes electron correlation effects to be taken into consideration. The data related to molecules is already present in database, so when we perform a calculation on a certain molecule and that molecule matches the data set we get accurate results while the ones that fail to match generate inaccurate results. This method doesn't use the variational principle, fails in hydrogen bonding, transition structures and can only be used on certain elements. Pople's NDDO (Neglect of Diatomic Differential Overlap) has been broadly divides into three classes, which include modified neglect

of differential overlap (MNDO), Austin Model 1 (AM1) and Parametric Method 3 (PM3).

1. MNDO: It is based on the NDDO model which involves one-center two-electron integrals in which the two-electron integrals are solved using the concept of multipole-multipole interactions. Earlier the model involved the basis sets based on s and p orbitals but with the passage of time d orbitals have also been introduced in order to describe the transition metals.
2. AM1: It is based on the MNDO model which involves two-electron integrals but also includes the concept of nuclear-nuclear core repulsion that is exactly similar to van der Waals interactions. The model proves helpful to explain the heat of formation of the molecules.
3. PM3: This model evaluates maximum number of molecular properties among which the thermochemistry calculations of elements and transition metals have proven to be more accurate.

Density Functional Theory (DFT)

The Density Functional Theory was developed by Pierre Hohenberg and Walter Kohn in 1964, and were awarded the nobel prize in 1998 [47, 48]. The basic premise of the Density Functional Theory is that any property of a system of many interacting particles can be taken as a functional of the ground state density no(r) ; that means a scalar function of position no(r) determines all the information in the many-body wavefunctions for the ground state and all excited states So by calculating the ground state electron density, we are able to calculate the total energy of the system, which can allow us to determine the ground-state and excited state properties of the system. DFT based calculations are mostly used in case of organometallic systems as it involves many electrons which are accompanied by electronic correlations [49-53]. However, it fails to account for dispersive forces more accurately [54, 55]. DFT provides detailed information about the molecular structures, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths, etc. which goes in agreement with the experimental study.

The Hohenberg-Kohn Theorems

The Density Functional Theory is broadly based on two theorems; (i) The Hohenberg-Kohn Existential Theorem, which takes density as a basic variable and (ii) The Variational theorem, which determines the ground state density no(r); (wavefunction) corresponding to the energy equal to or greater than the ground state energy. The Kohn Sham approach involves independent particles but an interacting density to account for the exchange and correlation effects of multiparticle systems.

Theorem 1: The Hohenberg-Kohn Existential Theorem: For any system of interacting particles in an external potential Vext(r), the potential Vext(r), and hence the Hamiltonian Hˆ, is determined uniquely by the ground state particle density no(r). This means that all properties of the system (including energy) are completely determined, provided the ground state density no(r) is known.
The energy functional is given by equation (1.11):

$$\mathbf{E}[\boldsymbol{n}(\boldsymbol{r})] = \int \boldsymbol{n}(\boldsymbol{r})\boldsymbol{v}_{\boldsymbol{ext}}(\boldsymbol{r})\boldsymbol{dr} + \boldsymbol{F}[\boldsymbol{n}(\boldsymbol{r})] \ldots\ldots\ldots \textbf{(1.11)}$$

$$\mathbf{E}[\boldsymbol{n}(\boldsymbol{r})] = \langle \Psi | \hat{\boldsymbol{H}} | \Psi \rangle \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\mathbf{1.12})$$

$$\hat{\boldsymbol{H}} = \hat{\boldsymbol{F}} + \hat{\boldsymbol{F}}_{\boldsymbol{ext}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(1.13)}$$

$$\hat{\boldsymbol{F}} = \hat{\boldsymbol{T}} + \hat{\boldsymbol{V}}_{\boldsymbol{ee}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(1.14)}$$

$\hat{H}$ = Hamiltonian, $\hat{F}$= Electronic Hamiltonian, $\hat{T}$ = Kinetic energy operator and $\hat{V}_{ee}$ = Interaction operator.

The electronic operator comes out to be similar in case of n-electron systems, hence we can define it in terms of number of electrons N and the external potential which is represented by $v_{ext}(r)$ as can be seen in equation (1.16). On applying the variational method, we get:

$$\boldsymbol{E}_1^0 < \langle \Psi_2 | \hat{\boldsymbol{H}}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{\boldsymbol{H}}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{\boldsymbol{H}}_1 - \hat{\boldsymbol{H}}_2 | \Psi_2 \rangle \ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(1.15)}$$

$$= \boldsymbol{E}_2^0 + \int \boldsymbol{n}_0(\boldsymbol{r})\left[\boldsymbol{v}_{\boldsymbol{ext},1}(\boldsymbol{r}) - \boldsymbol{v}_{\boldsymbol{ext},2}(\boldsymbol{r})\right]\boldsymbol{dr} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(1.16)}$$

Here $v_{ext,1}(r)$ and $v_{ext,2}(r)$ are the two external potentials with ground state wavefunctions Ψ_1 and Ψ_2 with density $n_0(r)$ and E_1^0 and E_2^0 are the ground state energies of $\hat{H}_1$and $\hat{H}_2$ hamiltonians. the equation finally comes out to be:

$$\boldsymbol{E}_1^0 + \boldsymbol{E}_2^0 < \boldsymbol{E}_2^0 + \boldsymbol{E}_1^0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(1.17)}$$

Theorem 2: The Hohenberg-Kohn Variational Theorem: A universal functional for the energy E[n] in terms of the density *n(r)* can be defined, valid for any external potential $V_{ext}(r)$. For any particular $V_{ext}(r)$, the exact ground state energy of the system is the global minimum value of this functional, and the density *n(r)* that minimizes the functional is the exact ground state density $n_o(r)$.

$$\mathbf{F}[\boldsymbol{n}(\boldsymbol{r})] = \langle \boldsymbol{\psi}|\widehat{\boldsymbol{F}}|\boldsymbol{\psi}\rangle \text{.....(1.18)}$$

$$\mathbf{E}_{\boldsymbol{v}}[\boldsymbol{n}(\boldsymbol{r})] = \int \boldsymbol{n}'(\boldsymbol{r})[\boldsymbol{v}_{\boldsymbol{ext}}(\boldsymbol{r})\boldsymbol{dr} - \boldsymbol{F}[\boldsymbol{n}'(\boldsymbol{r})] \text{.....(1.19)}$$

Here E_v [*n(r)* is the representable energy functional and v_{ext} (r) and *n'* (*r*) being the external potential and density respectively. Using the variation method, we get:

$$\langle \boldsymbol{\psi}'|\widehat{\boldsymbol{F}}|\boldsymbol{\psi}'\rangle + \langle \boldsymbol{\psi}'|\widehat{\boldsymbol{V}}_{\boldsymbol{ext}}|\boldsymbol{\psi}'\rangle > \langle \boldsymbol{\psi}|\widehat{\boldsymbol{F}}|\boldsymbol{\psi}\rangle + \langle \boldsymbol{\psi}|\widehat{\boldsymbol{V}}_{\boldsymbol{ext}}|\boldsymbol{\psi}\rangle \text{.....(1.20)}$$

$$\int \boldsymbol{n}'(\boldsymbol{r})[\boldsymbol{v}_{\boldsymbol{ext}}(\boldsymbol{r})\boldsymbol{dr} + \boldsymbol{F}[\boldsymbol{n}'(\boldsymbol{r})] > \int \boldsymbol{n}(\boldsymbol{r})[\boldsymbol{v}_{\boldsymbol{ext}}(\boldsymbol{r})\boldsymbol{dr} + \boldsymbol{F}[\boldsymbol{n}(\boldsymbol{r})] \text{..... (1.21)}$$

This finally leads to the second Hohenberg-Kohn Theorem.

$$\mathbf{E}_{\boldsymbol{v}}[\boldsymbol{n}'(\boldsymbol{r})] > \mathbf{E}_{\boldsymbol{v}}[\boldsymbol{n}(\boldsymbol{r})] \text{.....(1.22)}$$

Kohn - Sham Equation

The equation has been named after Walter Kohn and Lu Jeu Sham and is based on Schrondinger equation [56]. It considers a system of non-interacting particles that possess the density similar to interacting particles. As we are having the non-interacting particles the wave function (kohn-sham wavefunction) being a single slater determinant generates minimum energy from the Kohn sham orbitals (ϕ_i) .

$$\left[-\frac{\hbar^2}{2\boldsymbol{m}}\boldsymbol{\nabla}^2 + \boldsymbol{v}_{\boldsymbol{eff}}(\boldsymbol{r})\right]\boldsymbol{\phi}_{\boldsymbol{i}}(\boldsymbol{r}) = \boldsymbol{\varepsilon}_{\boldsymbol{i}}\boldsymbol{\phi}_{\boldsymbol{i}}(\boldsymbol{r}) \text{ ... ...(1.23)}$$

ε_i= orbital energy

The ground state density comes out to be equal to:

$$\boldsymbol{\rho}(\boldsymbol{r}) = \sum_{\boldsymbol{i}}^{\boldsymbol{N}} |\boldsymbol{\phi}_{\boldsymbol{i}}(\boldsymbol{r})|^2 \text{ ..... (1.24)}$$

The ground state energy which is represented as the functional of charge density is given in equation below:

$$\boldsymbol{E}[\boldsymbol{\rho}(\boldsymbol{r})] = \boldsymbol{T}[\boldsymbol{\rho}(\boldsymbol{r})] + \int \boldsymbol{\rho}(\boldsymbol{r})\boldsymbol{v}(\boldsymbol{r})\boldsymbol{dr} + \boldsymbol{E}_{\boldsymbol{ee}} \text{ ... ... (1.25)}$$

T[ρ(r)] kinetic energy, $\int \rho(r)v(r)dr$ = electron-nuclei interaction along with the external potential andE_ee= electron-electron interaction

$$\boldsymbol{E}_{\boldsymbol{ee}}[\boldsymbol{\rho}(\boldsymbol{r})] = \frac{\boldsymbol{1}}{\boldsymbol{2}}\int \frac{\boldsymbol{\rho}(\boldsymbol{r})\boldsymbol{\rho}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\boldsymbol{drdr}' + \boldsymbol{E}_{\boldsymbol{xc}}[\boldsymbol{\rho}(\boldsymbol{r})] \text{.....(1.26)}$$

$\frac{1}{2}\int \frac{\rho(r)\rho(r')}{|r-r'|}drdr'$= electron-electron electrostatic interaction, E_{xc} *[ρ(r)]*= exchange–correlation energy

Using the equation 1.24, we introduce the wavefunction(ψ_i) and can now be written as:

$$\boldsymbol{\rho}(\boldsymbol{r}) = \sum_{\boldsymbol{i}=\boldsymbol{1}}^{\boldsymbol{n}} \boldsymbol{\psi}_{\boldsymbol{i}}^{*}(\boldsymbol{r})\boldsymbol{\psi}_{\boldsymbol{i}}(\boldsymbol{r}) \text{.....(1.27)}$$

The kinetic energy comes out to be equal to:

$$T\,[\rho(r)] = -\frac{\hbar^2}{2m}\sum_i^n \langle \psi_i|\nabla^2|\psi_i\rangle \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.28)$$

Assuming wavefunctions to be orthonormal we use lagrange multipliers (ϵ_ij)

$$\int \psi_i^*(r)\psi_j(r)dr = \delta_{ij} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.29)$$

The functional of wavefunctions comes out to be equal to:

$$\Omega[\psi_i] = E[\rho(r)] - \sum_i \sum_j \epsilon_{ij} \int \psi_i^*(r)\psi_j(r)dr \ldots\ldots\ldots\ldots\ldots(1.30)$$

The next step leads to the production of kohn sham equation which is only possible, if we decrease the functional of wavefunction with respect to the wavefunction ψ_i* (r) .

$$\left. -\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(r)\right]\psi_i(r) = \varepsilon_i\psi_i(r) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.31)$$

$$v_{eff}(r) = v(r) + \int \frac{\rho(r')}{|r-r'|}dr' + v_{xc}(r) \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.32)$$

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.33)$$

v_{eff} = effective local potential and v_{xc} (r)= exchange-correlation potential.

Hence, we can say that the above equation shows a resemblance with the equation given by Schrondinger but with an effective local potential. We have in addition also described the Kohn-Sham Self-consistent Field (KS SCF) procedure through a flow chart which has been given below (figure 7).

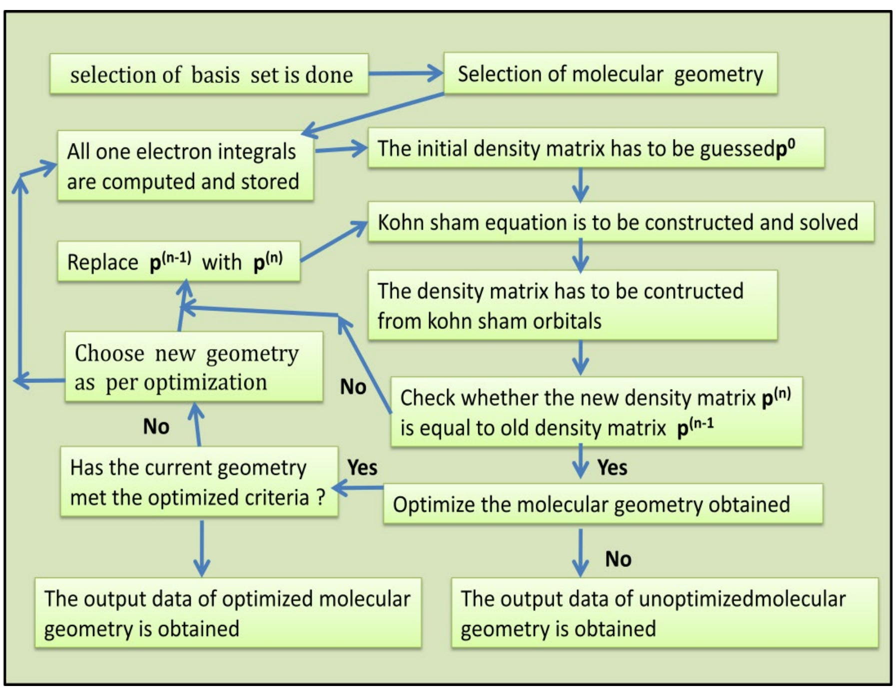


Figure 7: Flow Chart of Kohn - Sham Self- Consistent Field (KS-SCF) Procedure

Functional

A functional in simpler words means function of a function. In computational chemistry we have broadly two types of functionals which are used to perform computational calculations. These include traditional functionals and hybrid functionals.

Traditional Functionals: These are divided into two types:

a) Local exchange and correlation functional: They mainly focus on local spin densities that are present on the molecule.

b) Gradient correlation functional: They use both the electron spin densities and their gradients during calculations. They are also known as non-local gradients.

These functionals include PBE (Perdew, Burke and Ernzerhof, Perdew-86 and Perdew-Wang 91(PW91) [57-59].

Hybrid Functionals: These functionals combine the concept of exact exchange energy (Hartree Fock theory) and exchange-correlation energy concept (empirical / ab *initio* method). Hybrid functionals are combinations of local and gradient–corrected correlation functional. Examples: B3LYP (Becke-3 Lee, Yang and Parr) and B3PW91 (Becke-3 Perdew-Wang 91) [60, 61].

Reactivity Descriptors

Conceptual Density Functional Theory assists in understanding the electronic properties of the molecules by using the reactivity descriptors that include electronegativity, electrophilicity, chemical potential and hardness [41, 54, 62-79]. These have a direct effect in understanding the chemical reactivity and the reaction mechanisms of the molecule [80-84]. The reactivity descriptors are broadly divided into global and local reactivity descriptors [85-92]. These descriptors help in understanding both the intermolecular and intramolecular reactivity trends that occur inside the molecule. Koopmans' theorem represented ionisation potential (I) and electron affinity (A) [41] as:

$$IE \approx -\epsilon_{HOMO} \; ; \; EA \approx -\epsilon_{LUMO} \qquad \ldots\ldots\ldots\ldots 1.34$$

ϵ_{HOMO} = Highest occupied molecular orbital energy, ϵ_{LUMO} = Lowest unoccupied molecular orbital energy

Chemical potential (μ) is the escaping tendency of electrons and can be represented as:

$$\mu = \frac{\partial E}{\partial N}, \qquad \ldots\ldots\ldots\ldots 1.35$$

$$\mu = \left(\frac{\partial E}{\partial \rho}\right)_{v(\vec{r})} \qquad \ldots\ldots\ldots 1.36$$

E = Total energy, N = Number of electrons and $v((r))^{\rightarrow}$ = External potential Chemical potential is also related to electronegativity and can be represented as:

$$\mu = -\chi = -\frac{IE + EA}{2} \qquad \ldots\ldots 1.37$$

$$\mu = -\chi = -\frac{1}{2}(\epsilon_{HOMO} + \epsilon_{LUMO}) \qquad \ldots\ldots 1.38$$

It was Pauling who defined electronegativity first but the concept was later modified by Mulliken [93-95]. Electronegativity in simpler words can be defined as the capability of an atom to attract electrons towards itself [74].

$$\chi = -\mu = \frac{\partial E}{\partial N}, \qquad \ldots\ldots\ldots 1.39$$

$$-\chi = \left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} = \left(\frac{\partial E}{\partial \rho}\right)_{v(\vec{r})} = \mu \qquad \ldots\ldots 1.40$$

Hardness (η), is an indication of a molecule to resist charge transfer [7, 47, 70]. It also provides an idea about the polarizable nature of the species. Electrophilicity calculates the energy change that occurs during the addition or removal of electrons [66, 96, 97].

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})} \qquad \ldots\ldots\ldots 1.41$$

$$= \frac{1}{2}(IE - EA) = \frac{1}{2}(\epsilon_{LUMO} - \epsilon_{HOMO}) \qquad \ldots\ldots\ldots 1.42$$

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \qquad \ldots\ldots\ldots 1.43$$

The reactivity descriptors are among the important parameters which are used to study and compare the efficiency of different hydrogen storing materials [98-100]. Hydrogen technology is seen as one of the best options for meeting the growing energy crisis demand [100]. It is seen that the increase in hardness and decrease in both electronegativity and electrophilicity values is the direct indication of stability of the complex upon hydrogen adsorption.

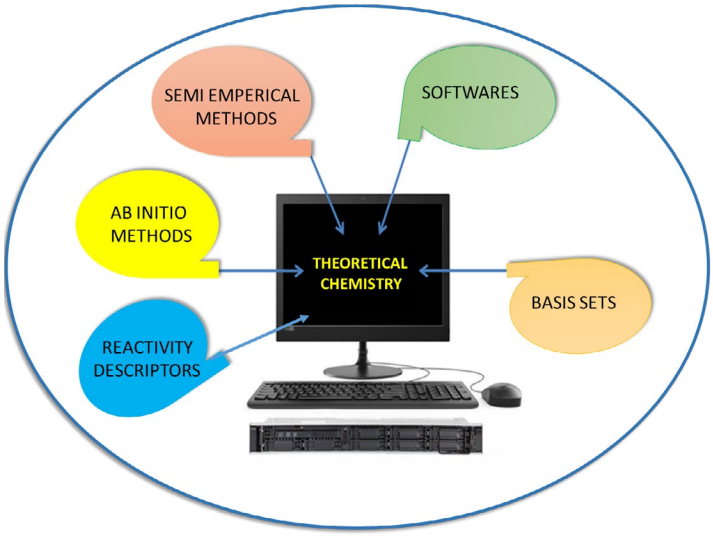
Summary

The field of theoretical chemistry is rapidly emerging as a great alternative when it comes to data calculation and interpretation. The said review paper covers all the theoretical aspects that includes different software's, methodologies, theories, basis sets and conceptual reactivity descriptors. Theoretical chemistry combines the efforts of chemists, physicists, and mathematicians in designing computer algorithms and programs while computational chemis-

try simply uses these programs to study or predict the structure, stability and various thermodynamic and kinetic properties of molecules. Computational software packages are also available for studying the chemical systems, atoms, molecules and condensed systems but they differ with one another with respect to their computational cost, accuracy, ease of installation and time. The study includes a variety of methods such as ab *initio* methods, empirical and semi empirical methods. Ab *initio* methods calculate the electronic state energies without taking support of an experimental data. The method is highly useful for molecular geometries, energies, spectra, excited states, dipole moments of smaller atoms, molecules, radicals and ions. The method becomes limited as it involves large number of steps, time consuming and occupies more disc space. Hartree-Fock theory determines the ground-state wave function and energy of many-body system without considering correlation effect of electrons and gives no consideration to pair-wise correlations. Basis sets are used to represent the molecular orbitals that are located on the centre of the atom and provide the complete information about the molecular structure. Although many basis sets are available but the choice of basis set determines the accuracy of data. Semi empirical methods are faster and preferred in case of large molecules for their geometry optimization, studying intermediates or transition states, calculating heats of formation and for knowing the charge distribution of the molecule. The method fails to study hydrogen bonding, transition structures and can only be used on certain elements. DFT based calculations find its applications mostly in case of organometallic systems, as it involves many electrons which are accompanied by electronic correlations. It covers the parameters such as vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths, etc. However, it fails to account for dispersive forces more accurately. Here is when MPn method gains advantage as it covers the electrostatic interactions and London dispersion interactions but become restricted for being computationally expensive. Reactivity descriptors such as electronegativity, electrophilicity, chemical potential and hardness assists in understanding the electronic properties, chemical reactivity and the reaction mechanisms of the molecule. Every method has proven efficient for calculating certain parameters. But the need of the hour is to find a method that can provide an in depth analysis of the molecule. Finally, we can say that theoretical chemistry proves highly advantageous, when it comes to experiments, as we can not only double check our results but also can study a variety of novel complexes which can prove helpful in designing new molecules for the future.

Graphical Abstract

The said review paper covers all the theoretical aspects that includes different software's, methodologies, theories, basis sets and conceptual reactivity descriptors to study or predict the structure, stability and various thermodynamic and kinetic properties of molecules. This field of chemistry can be used to study a variety of novel complexes which can prove helpful in designing new molecules for the future.



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Dr. Saba Niaz dedicates this review paper to her Mother, for her constant support and encouragement.

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