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The Development of Computational Chemistry as an Extension of the Traditional Theoretical or Quantum Chemistry: An Overview

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Abstract

An overview of the development of computational chemistry as an extension of the traditional theoretical or quantum chemistry is discussed. The first published paper on quantum mechanics by Heisenberg in 1925, Schrödinger 1926 theory of quantum mechanics and the Hückel postulated of Pi (π) electron theory in 1931 was an indication that a new field of chemistry is in viewed. The development of computers since 60s, software chemical databases and molecular modelling by Molecular Design, Ltd (1978) and Tripos Associates Inc (1979) respectively stimulate the birth of computational chemistry. The work by Martin Karplus, Michael Levitt and Arieh Warshel which won the 2013 Noble Price in chemistry for the development of "multiscale methods for complex systems" revolutionized the computational chemistry field. The computational chemistry tools: Ab Initio calculations, Semi empirical calculations, Density functional theory (DFT) and Hartree–Fock (HF) method have their roots to traditional quantum chemistry community. Molecular geometry: the shapes of molecules, bond lengths, angles and dihedrals are some applications of computational chemistry. Quantitatively, applications describe the physical and chemical phenomena (energy states, structures, reactivity, positions and momenta of atoms) that occur in a particular system.

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1. INTRODUCTION

Literature studies have showed that academic resources abound on computational Chemistry. Beginning from its definition, goal, origin, the extension from blocks laid by the traditional theoretical or quantum chemistry, to its applications, one thing is common, the use of computers. This paper therefore attempts to give a compendium of computational chemistry with respect to its meaning, goal, origin, its extension from the foundation laid by the traditional theoretical or quantum chemistry, and applications.

1.1 Definition of Computational Chemistry

Several definitions of computational chemistry have been given by researchers. According to Gilbert. (2011) Computational Chemistry is the modelling of chemical phenomenon using computers rather than chemicals. Computational chemistry is a branch of chemistry that uses computer simulation to assist in solving chemical problems (Khilari and Kadam, 2019). Further definition was given as the use of computers to solve the equations of a theory or model for the properties of a chemical system (Parker, 2017). Sudais, (2019) have reported that computational Chemistry is the application of existing computer programme and methodology to specific chemical problems. Computational chemistry (also called molecular modelling; the two terms mean about the same thing) is a set of techniques for investigating chemical problems on a computer. Questions commonly investigated computationally are: Molecular geometry: the shapes of molecules – bond lengths, angles and dihedrals (Lewars, 2011).

1.2 Goal of Computational Chemistry

The goal is to solve the complex equations such as the Schrodinger equation for electronic and nuclear motion which accurately describe natural phenomena. In a practical application of computational chemistry, mathematical equations or algorithms are devised to quantitatively describe the physical and chemical phenomena (e.g., energy states, structures, reactivity, positions and momenta of atoms) that occur in a particular system. These algorithms are then programmed in the appropriate computer languages and linked together so that the many millions of calculations required to effectively describe the phenomena can be quickly computed. For example, it might be necessary to evaluate billions of integrals to accurately describe the repulsion of electrons in a complex molecule. The end result is a set of computational tools that predict the characteristics and behaviour of the chemical system Thompson et al. (1999).

2.0 THE LINK BETWEEN COMPUTATIONAL CHEMISTRY AND QUANTUM CHEMISTRY

2.1 Background to extension

"Karplus, Warshel and Levitt applied these ideas but also developed their own, and then went much beyond the initial work by creating *hybrid* methods that combined classical with quantum mechanics ("QM/MM"). This is a major part of the prize announcement; it took a lot of efforts to refine and troubleshoot such methods and make them accessible to non-specialist chemists. You could use the quantum mechanical technique for describing the core part of a molecular system and then use the classical part for simulating the rest of it. Among other things this would enormously save time, since doing a quantum mechanical calculation on the entire system would be prohibitively expensive in terms of time. The three chemists have also developed purely classical methods to simulate molecular motion. These days most of us who do the calculations take this work for granted, so thoroughly ingrained it is in the language and tools of computational chemistry" (Jogalekar, 2013). This excerpt is taken from the addressed of (2013) noble price in chemistry.

Literature further revealed that the tools which employ computations in quantum scale, that is computations that seek to solve the Schrödinger equation originates from the so call "traditional Theoretical or quantum chemistry". Thus, the quantum mechanical methods, based on the Schrodinger equation: semi empirical, ab initio and Density functional theory (DFT) is traced to quantum chemistry. This authors considered a good extension to the "traditional theoretical or quantum chemistry because it laid the pillars upon which computational chemistry stands. For instance, Lewars (2011) asserted that ab initio, semiempirical, and density functional methods belong to quantum chemistry. Khilari and Kadam, (2019) opined that, building on the founding discoveries and theories in the history of quantum mechanics, the first theoretical calculations in chemistry were those of Walter Heitler and Fritz London in 1927. The books that were influential in the early development of computational quantum chemistry include Linus Pauling and E. Bright Wilson's 1935 Introduction to Quantum Mechanics, with applications to Chemistry, Eyring, Walter and Kimball's 1944 Quantum Chemistry, Heitler's 1945 Elementary Wave Mechanics – with Applications to Quantum Chemistry, and later Coulson's 1952 textbook Valence, each of which served as primary references for chemists in the decades to follow. Thus it can be infer that quantum chemistry is foundational to computational chemistry. Hohenburg and Kohn (1964), Kohn and Sham (1965) reported that electronic structure methods, by definition, attempt to solve the Schrödinger equation at some level of approximation. There are now two broad classes of widely used methodologies; first, Hartree–Fock (HF) methods that have been developed largely in the molecular quantum chemistry community, but which have also been widely and successfully applied to solids; secondly, density functional theory (DFT), which has been extensively applied in condensed matter and increasingly in molecular studies. DFT methods tend to scale with system size better than HF techniques and have become increasingly popular as the field has moved increasingly toward applications to large complex systems. Authors will attempt to give an overview of the tools used in computational chemistry.

2.2 COMPUTATIONAL CHEMISTRY TOOLS

2.2.1. Molecular Mechanics is based on a model of a molecule as a collection of balls (atoms) held together by springs (bonds). If we know the normal spring lengths and the angles between them, and how much energy it takes to stretch and bend the springs, we can calculate the energy of a given collection of balls and springs, i.e. of a given molecule; changing the geometry until the lowest energy is found enables us to do a geometry optimization, i.e. to calculate a geometry for the molecule. Molecular mechanics is fast: a fairly large molecule like a steroid (e.g. cholesterol, $C_{27}H_{46}O$) can be optimized in seconds on a good personal computer.

2.2.2 Ab Initio Calculations (ab initio, Latin: "from the start", i.e. from first principles") are based on the Schrodinger equation. This is one of the fundamental equations of modern physics and describes, among other things, how the electrons in a molecule behave. The Schrodinger equation cannot be solved exactly for any molecule with more than one (!) electron. Thus approximations are used; regardless of its level, an ab initio calculation is based only on basic physical theory (quantum mechanics) and is in this sense "from first principles".

2.2.3 Semiempirical Calculations are, like ab initio, based on the Schrodinger equation. However, more approximations are made in solving it, and the very complicated integrals that must be calculated in the ab initio method are not actually evaluated in semi-empirical calculations: instead, the program draws on a kind of library of integrals that was compiled by finding the best fit of some calculated entity like geometry or energy (heat of formation) to the experimental values (Schaefer, 2001).

2.2.4. Density Functional Theory (DFT) methods based on approximate solutions of the Schrodinger equation, bypassing the wave function that is a central feature of ab initio and semi-empirical methods. Density functional calculations (DFT calculations, density functional theory) are, like ab initio and semi-empirical calculations, based on the Schrodinger equation However, unlike the other two methods, DFT does not calculate a conventional wave function, but rather derives the electron distribution (electron density function) directly

2.2.5. Molecular Dynamics Methods study molecules in motion. Thus one can simulate the motion of an enzyme as it changes shape on binding to a substrate, or the motion of a swarm of water molecules around a molecule of solute; quantum mechanical molecular dynamics also allows actual chemical reactions to be simulated (McKenna, 2006).

3.0 BACKGROUND TO HISTORICAL DEVELOPMENT OF COMPUTATIONAL CHEMISTRY

Authors gathered from literature that computational Chemistry has its root to the so called advent of digital age (Khilari and Kadam , 2019). Hardware has become far cheaper than it was even a few years ago, and powerful programs previously available only for expensive workstations have been adapted to run on relatively inexpensive personal computers (Lewars, 2011). Wenfa (2017) asserted that increases in computing speed and capacity, and the availability of user friendly software packages signal the arrival of the third era of electronic structure calculations. Specifically, greater computing power allows the calculation, from first principles, of most system properties with minimal reliance on simplifying assumptions, in systems comprising large numbers of polyatomic molecules. Catlow (2005) reported that during the last 20 years, computer modelling techniques have had substantial impact on almost all areas of science and technology. Further, advances in mathematical sciences have been indispensable allies and has provided vital tools for computational Chemistry. The mathematical sciences provide the language for quantitative science, and this language is growing in many directions as computational science in general continues its rapid expansion (NRC, 1995).

3.1 Chronological Development in History of Computation Chemistry

According to Wenfa (2017) the past influences the present and future; for example, in computational chemistry, simplifying assumptions and approximations important in the pre-computing era remains relevant today in allowing simulation of larger systems with reasonable amount of computer time. Specifically, chronological examination of computation chemistry's development shed light on three major overlapping periods:

(i) Theory development for explaining observations of spectroscopic emission lines of elements and prediction of their atomic structure.
(ii) Utilization of simplifying assumptions and experiment data for circumventing problems associated with lack of computing power in solving the Schrodinger equation in the pre-computing era.
(iii) Dramatic increase in low cost computing power giving rise to first principles (ab initio) methods for solving, with few or no simplifying assumptions, large systems comprising polyatomic and long chain molecules.

3.2 An overview of the History of Computational Chemistry

Literature has revealed that from the first published paper on quantum mechanics, Richon, (2001) by Heisenberg in 1925, to Schrödinger first paper publication in 1926 on the theory of quantum mechanics, to Pi (π) electron theory postulated by Hückel in 1931, to the development of computers since 60s, to software chemical databases and molecular modelling by Molecular Design, Ltd. (1978) and Tripos Associates, Inc. (1979) respectively stimulate the birth of computational chemistry. Review has also indicated that the development of "multiscale methods for complex systems" Jogalekar (2013), a work by Martin Karplus, Michael Levitt and Arieh Warshel which won the 2013 Noble Price award in chemistry, revolutionized the computational chemistry field. 'It's always very nice to wake up and see your own professional working field win a Nobel Prize. I am very happy to note that this year's prize in chemistry has been awarded to Martin Karplus, Michael Levitt and Arieh Warshel for their development of "multiscale methods for complex systems'' (Jogalekar, 2013). More simply put, these three chemists have been recognized for their development and application of methods to simulate the behavior of molecules at various scales, from single molecules to proteins. The work sheds light on phenomena as diverse as protein folding, catalysis, electron transfer and drug design. It enables chemists like me to calculate a variety of things, from the rates of chemical reactions and the stability of molecules to the probability that a drug will block a crucial protein implicated in a disease'. This excerpt taken from 2013 Noble Price award in chemistry.

3.2.1 Quantum Period

Computational chemistry has its roots in the early attempts by theoretical physicists, beginning in 1928, to solve the Schrödinger equation.

$$-(\hbar/i)\,\partial\psi(\mathbf{r},t)\,/\,\partial t = \mathbf{H}\,\psi(\mathbf{r},t)\,, \qquad \text{----------------------} \tag{1}$$

where **H** is the linear Hermitian Hamiltonian operator:

$$\mathbf{H} \equiv -(\hbar^2/2m)\,\nabla^2 + V(\mathbf{r})\,. \qquad \text{-----------------------------} \tag{2}$$

Here $\hbar$ is Planck's constant divided by 2π and has the very small value 1.05×10^{-27} erg-second characteristic of the submicroscopic quantum regime. The wavefunction ψ generally is complex; its amplitude squared $|\psi|^2$ provides the probability distribution for the position of the particle at time *t*. The linearity of the Schrödinger wave equation and the Hermiticity of **H** guarantees conservation of probability Wenfa (2017). The discovery of sub-atomic particles such as the electron, proton and neutron sowed the seeds of computation chemistry as an independent field of scientific inquiry. Realization that electrons, or more accurately, electron densities, are arranged in defined energy levels and spatial regions led to the proposal of the atomic and molecular orbital concepts. From a quantum mechanical perspective, these are regions where electrons of specific energies are located. This era was defined by the promulgation of many of the foundation concepts and tools of computation chemistry, where the theoretical tools of quantum mechanics illuminated spectroscopic observations, highlighting that theory lagged behind experiment. the second era of computation chemistry was also characterized by the emergence of many semi-empirical methods, where experiment data (usually from spectroscopy studies) were used in calibrating essential parameters in system models. These parameters describe key characteristics of atoms and could not be calculated from first principles in the pre -computing era (Khilari and Kadam, 2019).

3.2.2 Computer Period

The first computer, the ENIAC (Electronic Numerical Integrator and Computer) is built for the US Army Ordnance Department in 1943. The first UNIVAC (Universal Automatic Computer) is delivered to the Census Bureau in 1951(Richon, 2001). Computers have been applied in chemistry since the 1960s. They were a direct outgrowth of theoretical techniques that calculated all kinds of molecular properties, from a molecule's stability and movement to its reactions with other molecules. For the longest time these calculations could be done only for simple systems, and it was only in the 90s or so that computing power and algorithms began catching up with theory to enable the application of calculations to large, practically relevant molecules like proteins, drugs and materials. It was Karplus, Warshel and Levitt among others who made this possible (Jogalekar, 2013).

3.2.3 Chemical Software molecular modelling period

Several well-known quantum chemistry software packages; General atomic and molecular electronic structure system (GAMESS) , GAUSSIAN, Molecular orbital package (MOPAC), UniChem, TURBOMOL, NWChem) are available to academic and industrial users directly or through commercial vendors. At the present time, the translation of new developments into readily available codes occurs relatively rapidly and through well-established networks. Over the next few years computer codes available through general release will include most aspects of ab initio molecular orbital theory and density functional theory for molecular electronic structure and molecular dynamics. Currently, ab initio molecular orbital theory provides the most accurate prediction of molecular properties. There is no part of chemistry which is now not impacted by computational chemistry (Thompson et al., 1999). Quantum Chemistry Program Exchange (QCPE) formed at Indiana University to distribute quantum chemistry codes in 1963. Westheimer (1946) reported the calculation of racemization ratios for ortho-bibromobiphenyls. In 1950, Roothaan publishes the description of the linear combination of atomic orbitals-molecular orbital self consistent field (LCAO-MO-SCF) method. Hansch and Fujita (1964) describe a new approach to analyzing drug actions: Quantitative structure activity relationship (QSAR).

3.2.4 Puting it all: Quantum period-Computer age-chemical Software

From the forgoing, it can be said that the pillars laid by quantum mechanics, quantum chemistry, digital computing age, chemical software databases were vital to the emergence of computational chemistry.

4. Applications.

Questions commonly investigated computationally are: Molecular geometry: the shapes of molecules – bond lengths, angles and dihedrals. Energies of molecules and transition states: this tells us which isomer is favoured at equilibrium, and (from transition state and reactant energies) how fast a reaction should go. Chemical reactivity: for example, knowing where the electrons are concentrated (nucleophilic sites) and where they want to go (electrophilic sites) enables us to predict where various kinds of reagents will attack a molecule. Infrared (IR), ultraviolet (UV) and nuclear magnetic resonance (NMR) spectra: these can be calculated, and if the molecule is unknown, someone trying to make it knows what to look for (Lewars, 2011).

5. Conclusion

An overview of the development of computational chemistry as an extension of the traditional theoretical or quantum chemistry is presented. It was noted that quantum mechanics, quantum chemistry, digital computing age, chemical software databases laid the foundation to computational chemistry. Further, computational chemistry is an extension of the traditional quantum chemistry from its working tools: semiempirical, ab initio and Density functional theory (DFT) used in computation.

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