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Review Article

Brief History of Electronic Structure Calculations in Computational Chemistry

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Abstract

The past influence the present and future; for example, in computational chemistry, simplifying assumptions and approximations critical to problem-solving in the pre-computing era remains relevant today in allowing simulation of larger systems using reasonable amount of computational time. By highlighting significant milestones in efforts - from both theoretical and simulation perspectives - aimed at understanding the nature of chemical bond formation, this short essay traces the development and evolution of electronic structure calculation methods over the years. Specifically, Schrodinger equation occupies central place in computational chemistry, where its intractability to easy solution spawned an entire field seeking to develop increasingly refined and accurate methods for obtaining approximate solutions. Such a chronological thread also form the basis for asking counterfactual (“what if”) questions examining, from a historical vantage point, the relative role of computational power and theoretical intuition in the development of computational chemistry.

Keywords: Atomic model; Approximate solutions; Chemical bonding; Computational speed; Intuition; Imagination; Modeling; Schrodinger equation; Science history

1 Introduction

What is a chemical bond? Deceptively simple and yet many aspects remain poorly understood despite intensive investigations, it is one of the fundamental questions that has attracted the interest of many scientists past and present. In particular, gaining an understanding of the nature of chemical bond formation requires specific sub-questions to be answered: for example, are subatomic particles participating in chemical bonding; how do electrons and the nucleus move in relation to each other; and what is the nature of the forces acting between the nucleus and electrons? Science is increasingly pursued via the triumvirate of theory, simulation and experiment – where simulation has emerged, in many fields, to be equal partners to theory and experiment. Advent of various spectroscopy techniques such as Atomic Emission Spectroscopy (AES), Nuclear Magnetic Resonance Spectroscopy (NMR), and X-ray Photoelectron Spectroscopy (XPS) have unveiled many details of electronic interactions previously inaccessible, which prompted the proposal of new theories or refinement of existing models for explaining the new data. Nevertheless, there remain questions not amenable to experimental investigation or, where different scenarios or facets of theoretical models cannot be effectively contemplated without a means for visualizing interactions between myriad parameters in multidimensional space; thus, opening up domains where simulation can step into the fold. Specifically, simulation can serve as tools either for testing hypotheses arising from theoretical studies, or conducting "virtual experiments" for ones which we lack the tools to carry out – particularly in the inability of reconstituting the experimental conditions needed, or the lack of instruments for collecting the necessary data at requisite spatiotemporal scales. A case in point is the prolonged multi-decadal (1964 to 2012) search for the theoretically predicted Higgs boson through a series of particle accelerators of increasing energy levels, where construction of the Large Hadron Collider finally afforded particle physicists an instrument whose energy range encapsulated that of the long sought Higgs field. While computational sciences in general and computational chemistry in particular has long been recognized as an important arm of scientific research, the many jargons, terms, acronyms, and names of methods commonly used in the field are bewildering to most researchers except those active in the field. Particularly, the widespread practice of giving eponymous names to methods – for example, Hartree-Fock or Huckel – in computational chemistry, and the lack of easy to remember and understand acronyms for describing new tools, also adds to the complexity and impenetrability (to outsiders) of the field. Jargons do play an important role in science by expediting communication of complicated concepts between specialists through the use of abbreviated terms or common words conferred with particular context and meaning.

Nevertheless, jargons are not friendly to beginners or students - and usually constitute part of the learning curve for researchers switching between research areas. More important, given the rising importance of computational chemistry in augmenting at least some aspects of theoretical and experimental research, more researchers from other fields such as life sciences and engineering are seriously considering using computational chemistry techniques for either corroborating their experimental findings or, extend their studies to conditions currently not replicable in the lab. Despite much initial enthusiasm and willingness to learn, substantial anecdotal evidence points to frustrated researchers prematurely giving up on incorporating computational chemistry tools and concepts into their research given the significant entry barrier that the esoteric - and sometimes obfuscating - lexicon present. For those who make it through to the next stage, unfamiliarity with meaning of terms and jargons represent a substantial obstacle to time-constrained researchers in learning the idiosyncrasy or working principles of particular methods. Naturally, the problem is most acute for new comers to the field - but active researchers who are switching between sub-fields (for example, from micrometer scale molecular dynamics to sub-nanoscale electronic level calculations) may also be affected.

Besides learning the definition and meanings of terms and acronyms, understanding the underlying principles and assumptions of particular methods or algorithms is de rigueur for gaining the working knowledge necessary for appreciating the limitations of specific methods and range of conditions over which they can be usefully applied. Such understanding would help researchers select the appropriate methods for the task at hand - and, more important, forms the basis from which creative innovations or workarounds can help bridge gaps in capabilities between different methods during problem-solving. Nevertheless, inter-relationships between methods and the determinants driving the evolution of the field as a whole, as well as the motivations potentiating the development of improved incarnations of existing methods are important information generally not emphasized in either formal computational chemistry courses or in research projects – where the focus is on solving a narrowly-defined problem. Partly due to the plethora of methods, and limitations on curriculum time, different methods are usually presented as individual silos with little emphasis on how different methods (obsolete or contemporaneous) fit within an overall framework; thus, leaving students without a deep appreciation of how different methods relate to one another, and the reasons (or motivations) that drove their development. As some of the students eventually become active researchers, the partial or fragmented understanding of computational chemistry methods may negatively impact on their comprehension – and the appreciation of the significance - of research not immediately allied to their sub-field.

The prevailing view has been that computational power drives advances in computational chemistry; however, the role of theoretical thinking in unlocking intractable problems during system/problem definition prior to simulation has received less attention. Thus, is the relationship as straightforward as stated? Or, are there subtle cross-pollination of ideas between theoretical ingenuity and computational advances in solving increasingly complex problems at larger scales (i.e., more atoms) with finer spatiotemporal detail? Using the chronological tread delineated and drawing on examples in the field - where simple but elegant insights, such as the BornOppenheimer approximation, help open up a path to previously inaccessible solutions - an attempt would be made to critically assess the relative importance of theoretical intuition and computational power in seeding new developments and breakthroughs in the field. While retrospective analysis does reveal multiple instances in which increases in computational power potentiated advances in computational chemistry, such as the increasingly facility of simulating larger systems of polyatomic molecules from first-principles; there were also many examples of how theoretical insights - the most prominent of which was the Born-Oppenheimer approximation - laid the groundwork and charted the path to solution for problems thought to be intractable.

Though many detailed historical accounts [1, 2, 3] on the evolution of computational chemistry are available, they are either focused on the scientific personalities associated with specific methods or placed heavy emphasis on technical details. There is a lack of accessible articles describing salient features of particular tools but which also helps highlight relationships between methods within a chronological framework. The current essay aims to fill the gap by providing a short survey of historical development of electronic structure calculations.

Specifically, the focus will be on how theoretical physics and chemistry, and later computational chemistry, has attempted to answer, with increasing accuracy, many of the questions surrounding chemical bond formation through ingenious methodological developments. Besides describing developments in the field - which is centered on solving Schrodinger's equation - along a chronological order, inter-relationships between different methods and the motivations underlying their development would be explained. Finally, the chronological framework encompassing myriad electronic structure calculation methods provides a suitable backdrop for discussing the relative importance of computational power and theoretical insights in advancing computational chemistry research through the lens of "what if" questions.

1.1 Discovery of sub-atomic particles and derivation of Schrodinger equation

The discovery of the electron by J. J. Thomson in 1897, followed by that of the atomic nucleus by Rutherford in 1911, and finally, the neutron in 1932 by James Chadwick4 unveiled the hitherto mysterious world of atoms and confirmed the existence of sub-atomic particles. Building on Rutherford and coworkers' discovery that the atom is made up of a dense positively charged nucleus surrounded by orbiting electrons, Niels Bohr proposed in 1913 a model of the atom similar in concept to the classical planetary model - i.e., electrons orbiting the nucleus in fixed orbits. Nevertheless, the model, based on classical physics, was unable to explain the perplexing observation that orbiting electrons did not spiral into the nucleus - as would have been predicted by electrostatic attraction between the positively charged nucleus and negatively charged electrons. The solution to the conundrum lies in quantum mechanics, which when applied to the atom, stipulates that electrons occupy discrete energy levels. A major breakthrough came in 1926 when the empirical Schrodinger equation was formulated for explaining the emission spectrum of the hydrogen atom - which did not fit classical physics models.4 Although the Schrodinger equation underpins much of chemistry, its solution is highly intractable for all but the simplest systems such as the one electron hydrogen atom; thus prompting the famous remark by Dirac (in 1929) that most problems in chemistry could be solved if there is a general method for obtaining exact solutions to the Schrodinger equation [5, 6].

1.2 Approximate methods for solving the Schrodinger equation

Thus, the stage is set: where the challenge of solving Schrodinger equation prompted much research activity, particularly in devising approaches for separating the original formalism into sub-components amenable to individual solution, or using approximate methods for solving the full Hamiltonian (a mathematical description of various kinetic and potential energy components of a system). In particular, approximate methods aim to create a simplified model of the system under study for enabling facile computation while capturing most of the useful details.7 In 1927, Max Born (Germany) and Robert Oppenheimer (United States) formulated the Born-Oppenheimer approximation which allows the Hamiltonian to be separated into the constituent electronic and nuclear operators - each amenable to independent solution - thereby eliminating difficulties associated with cross-interactions between the electronic and nuclear components.8 Specifically, given the large mass of the nucleus relative to the electron, the BornOppenheimer approximation, assumes that the nucleus is essentially fixed in space with the electrons orbiting around them - and thus, decouples the motion of the atomic nucleus and electrons [5,9] As expected, the heavier the nucleus under consideration, the closer the approximation is to empirical observation.

In 1932, Huckel made one of the first attempts in using an approximate method for solving the Schrodinger equation, in what is now known as the Huckel method [5] Specifically, the method uses Linear Combination Of Atomic Orbitals (LCAO) for calculating the energies of molecular orbitals containing π electrons - for example, those present in conjugated carboncarbon bonds of molecules such as ethene and benzene. The approach was further refined by Ronald Hoffmann in 1963 in an extension of the Huckel method called the Extended Huckel method, which in addition to π orbitals, also considers the σ orbitals, but ignores electronelectron repulsion [5] During the intervening years, various other approximate methods for solving the Schrodinger equation were also proposed, such as the Hartree approximation, Fock's improvement over the Hartree method, and the self-consistent field method proposed by John Pople.5

The essence of the Hartree approximation is the total neglect of electron-electron repulsion (also known as the electron correlation energy) in the Hamiltonian [9, 10, 11] which proved to be too drastic and motivated the development of improvements to better describe the effect of electron-electron repulsion on total system energy. Fock's improvement on the Hartree approximation, on the other hand, uses a mean (average) field to account for all the interactions (i.e., electron-electron and electron-nucleus), which upon integrating across all electrons, arrives at the electron correlation energy component of the Hamiltonian. This approximate technique belongs to a class of methods known as independent particle approximation or mean field theory [5,9, 10, 11] More specifically, in the Fock's method, a trial wave function is obtained through LCAO, where parameters of the atomic orbitals are adjusted in repeated iterations until the solution converges to the mean field. This variational orbital optimization approach - also known as the self-consistent field method, or the Hartree-Fock Self Consistent Field method (HF-SCF) has been a workhorse for electronic level calculations [12]. Although the HF-SCF method is useful, it runs into computational difficulties because of the need to solve a computationally expensive four-index integral [10]. Thus, efforts were made to implement the HF-SCF method on computers - which had just been introduced in the late 1940s [6]. Significant contributions toward this end were made by Roothaan, and the HF-SCF method is sometimes called the Hartree-Fock-Roothaan Self Consistent Field method [6].

1.3 Evolution of chemical bonding theory

On a parallel front, efforts aimed at approximate solution of the Schrodinger equation also led to improvements in our conceptual understanding of chemical bonding. In particular, drawing from the understanding derived from numerical calculations and theoretical formulation, the chemical bonding theory was proposed and formed the intellectual foundation for the latter emergence of the valence bond and molecular orbital theory. Though dichotomous in approach, both the valence bond and molecular orbital theories are approximate solutions of the Schrodinger equation [6]. The foundation of the valence bond theory was first laid down by Heitler and London in 1927, and was further developed by Slater at MIT, and Linus Pauling at Caltech.6 In essence, the valence bond theory posits that atomic orbitals are centered at the nucleus of atoms, and a covalent chemical bond would be formed when atomic orbitals overlap with each other after appropriate hybridization. Thus, the valence bond theory articulates that each atom has ownership of its own electron density even after forming a covalent bond - although part of it is shared with the bonding partner.

The molecular orbital theory, on the other hand, was developed by Mulliken in the mid1920s as an alternative to the valence bond theory [6]. The main difference between the two revolves around their respective conceptualization of the electron density constituting a chemical bond. Specifically, the molecular orbital theory posits that electron density is not spatially constrained between specific atom pair, but instead electrons move around, under the influence of the nuclei, in the space encompassed by the molecule. Thus, under the molecular orbital theory framework, atoms lose their individual “identity,” and a chemical bond is not defined as localized electron density between pairs of atoms in a molecule - unlike the case of the valence bond theory.

During the period between 1950s and early 1980s, semi-empirical methods for electronic level calculations such as Complete Neglect of Differential Overlap (CNDO) and Modified Neglect of Differential Overlap (MNDO) were very popular because they provide reasonably good estimates while keeping computational cost down. These are parameterized methods for solving the Schrodinger equation where values for the parameters are supplied by experimental studies.10 With greater availability of inexpensive computational power in recent years, the aforementioned methods have become less important in contemporary research - and have largely given way to full ab initio calculations.

1.4 Rise of first-principles methods

The rapid development of ab initio or first-principle electronic level simulation methods – and their application to more complicated systems comprising polyatomic molecules - is largely enabled by the availability of large amount of low-cost computational capacity. Firstprinciple methods refer to the simulation of atoms or molecules from the bottom-up using as little or sometimes no empirical information for either calibrating a model, or supplying requisite values for parameters important in describing system characteristics. Development in the field has focused on two areas: i) creating better basis sets for constructing trial wave functions that enable more efficient approximate solution of the Schrodinger equation, and ii) developing methods that more accurately calculate the critical exchange-correlation energy of the electronic Hamiltonian operator.

The development of basis sets (comprising a number of atomic orbital wave functions) has progressed from the Slater Type Orbital (STO) to the current standard Gaussian Type Orbital (GTO), which was first proposed by Samuel Francis Boys (who also developed the first complete software package) and latter revived by Colin M. Reeves and Malcolm C. Harrison.13 Although using multiple GTOs in a linear combinatorial manner for approximating a single STO would increase the number of basis functions13 - and computational cost needed - the ease of solving GTO relative to STO has made the approach attractive to many researchers.10 Additionally, using a basis set larger than the minimum required for approximating a wave function would also allow the solution accuracy to approach that of the theoretical Hartree-Fock limit10 - though at the expense of computational time.

While the HF-SCF method is able to account for 99% of total system energy (including electron exchange energy), the remaining 1% that accrues to electron correlation is particularly important for explaining the chemical properties of a system.9 Thus, for many years, various methods – with varying levels of success - have been proposed to better account for the exchange-correlation energy of the electronic Hamiltonian operator. One of the more successful methods is the second order perturbation method, MP2 (Moeller and Plesset) [5]. which is a different approach for solving the Schrodinger equation compared to the variational method adopted in HF-SCF. Specifically, MP2 assumes that a given system can be described by an exact and an inexact portion, where, by varying parameters, the sensitivity of the system can be assessed; thereby, allowing a more accurate description of the inexact portion.

Another important method for solving the wave function is Density Functional Theory (DFT). Developed by Walter Kohn in the 1960s, DFT comprises the Hohenberg and Kohn theorem, and the Kohn and Sham method,4, 9 and uses a solution technique significantly different from other methods. Specifically, instead of calculating the wave function in an approximate manner, DFT attempts to solve the electron density of a given system exactly (at least in theory) by exploiting the one-to-one correspondence between electron density and system energy. Nevertheless, the absence of a mathematical relationship between electron density and ground state energy results in the need for its estimation - which constitutes the essence of the DFT method [9]. With its ability of generating more accurate results with lower computational cost, DFT is gaining in popularity and has been applied to the solution of problems in myriad fields.

1.5 What drives computational chemistry research forward: Theoretical insights or computational power?

Science more often progresses along torturous - rather than linear - pathways; for example, scientists may propose ideas that we do not yet have tools to examine, while on other occasions, breakthroughs in methodologies help open up entire landscapes for investigation. The paragraphs above have presented the evolution and inter-relationships of methods for electronic structure calculations along a chronological thread; however, what drives computational chemistry research forward? Specifically, which of the two play a more important role: theoretical insights (intuition) or computational power? Or, is the relationship between computational capacity and theoretical imagination more nuanced, where advances in both areas cross-fertilize each other? For example, availability of cheap and plentiful computational capacity enables the simulation of larger systems using theoretical methods developed earlier, but which also spurs the development of new techniques for harnessing possibilities afforded by emerging paradigms such as the transition to highly parallelized graphics processing unit (GPU) powered simulation. Given the calculation intensive nature of computational chemistry, advances in the field are - not surprisingly - intimately intertwined with that of computing in general and computational speed in particular. For instance, in the 1970s, fine-grained quantum mechanical pictures of bond breaking and forming cannot be calculated for more than a few atoms – and even with the vast improvement in both computational capacity and speed over the intervening period, such computations are still unable to attack problems involving hundreds of atoms and, by extension, whole proteins.7 From the mechanical slide rule, to room-sized computers with vacuum tube transistors, to integrated computer chips possessing multiple cores, and current state-of-the-art GPU optimized for parallel computation, the field has constantly tapped on advances in computing concepts and capabilities. While methods had been developed to afford more efficient calculations during the early days when computational power was severely limited, the direction in which the field had developed and evolved in recent decades suggests that availability of requisite computational power had a significant effect on the way researchers thought about problems and possible solution strategies. In particular, insufficient computational power resulted in the use of approximate methods for simulating single atom systems, while subsequent rapid increase in computing capacity enabled the tackling of multi-atomic molecules using methods with higher spatiotemporal resolution, thereby affording interrogation of systems dynamics at finer scales. Despite vast improvement in computational power, attempts at simulating larger molecules over longer duration via first-principles methods inevitably raises computational load. Thus, trade-off between accuracy and computational cost (time) is a perennial concern of computational chemists – even in the current era where there is an apparent overabundance of computational power. Specifically, shortfall in computational capacity and capability for a particular simulation objective (e.g., large number of polyatomic molecules interrogated computationally for long periods) has motivated the development of various techniques of model reduction and system simplification - such as coarse-graining - for answering scientific questions at appropriate level of detail using reasonable amount of simulation time. Hence, although future retrospective analysis of methodological developments may conclude that advent of more powerful computing hardware drove the field of computational chemistry by making possible simulations at scales and complexities previously inaccessible, the effect is decidedly nonlinear

- given that availability of more computing power also spurs the tackling of problems of greater scope and complexity, thereby, creating a circular process requiring more computational capacity. This is not to discount, however, the significant role of theoretical insights and imaginative problem-solving that theorists brought to computational chemistry, without which many intractable problems may not have been unlocked for subsequent solution - independent of steady improvement in both software and hardware. Specifically, theoretical intuition usually has its greatest impact on scientific research by offering fresh perspectives on longstanding conundrums; thereby, opening up new lines of inquiries that emanate from the single incision point that shed light on possible solution path(s). Although such Eureka moments are usually few and far between – and do not guarantee success – they nevertheless put form to ideas by synthesizing abstract concepts into working hypotheses ready for direct testing if requisite computational facilities are available, or which may form the basis for model simplification through various assumptions when contemporary computing power are limited. Focusing on the latter, the various approximations and simplifying assumptions proposed for solving Schrodinger equation, for example, helped move computational chemistry forward in an era of limited computing power – and was critical for informing fundamental understanding of chemical bonding, though, in many cases, the results obtained had less relevance to real-world problems which typically involved larger number of atoms and molecules. One example is the Born-Oppenheimer approximation, which in assuming a stationary nucleus relative to orbiting electrons, is the critical insight that help disentangle the coupled motions of electrons and the nucleus described in the Schrodinger equation - that otherwise would not have been amenable to solution in the pre-computing era given the complicated mathematics involved. More important, even though computational power has seen vast improvement over the decades, the Born-Oppenheimer approximation remains a useful tool in many contemporary studies for simplifying calculations for large atoms or molecules, thereby allowing interactions between more polyatomic molecules to be probed than otherwise possible using similar amount of computational capacity and time. One may ask: is the intractability of Schrodinger equation a theoretical problem awaiting insightful analysis for disentanglement and solution, or one readily solvable by brute force using large amount of computational power? Particularly, were the proposed approximations and simplifying assumptions motivated by a fundamental theoretical difficulty in the mathematical expression of the Schrodinger equation, or were they simply a reaction to the paucity of computational power? Though answers to the above counterfactual questions vary between different investigators, I would argue that the presence of cross-interacting terms in Schrodinger equation and the difficulty of solving many-body problems are both theoretical and computational in nature. Specifically, though increases in computational power may eventually enable the solution of Schrodinger equation without the help of any approximations or simplifying assumptions, the period during which researchers were unable to glean more insights from approximate – but nevertheless useful – models might have impeded research in many areas: from applied material science to fundamental physics and chemistry. As the adage goes: “All models are wrong, but some are useful;” thus, the most important role played by theoretical insights – in the context of model simplification – lies not in generating the exact solution, but rather, is its ability at clarifying a problem by identifying the critical elements needed for model construction. Collectively, theoretical insights and computational capacity would likely continue to interact in driving computational chemistry forward - each bringing their unique strength to problem-solving. Society is continuously evolving and science is responding with innovations or discoveries for explaining new problems or hitherto unknown phenomena. Similarly, as a social science serving to chronicle and synthesize meaning by linking seemingly disparate events, history is a continuous process of interpreting and re-examining old facts in light of new evidence. Hence, with continuous and rapid advances in computational chemistry, the question on the relative importance of computational speed and theoretical thinking in advancing the field elicits different answers at each time-point - where we stood, momentarily, to cast a backward glance on the path travelled. The current exposition hopes to infuse some ideas into the discussion - but deeper analysis would have to await those from science historians. In particular, there will not be one definitive account, but multiple versions examining differing facets of the issue from many perspectives - and arriving at slightly different conclusions.

2 Conclusion

Much progress has been made over the years in understanding the various facets of chemical bonding, especially with the use of computational methods for elucidating deeper understanding via more accurate solution of the governing quantum mechanical Schrodinger equation. From the decoupling of electron and nucleus motion afforded by the BornOppenheimer approximation, to the development and application of molecular orbital theory for first-principle simulation of electronic structure of polyatomic molecules, increases in computational power coupled with theoretical insights has enabled the field to progress from low computational intensive approximate methods applied to monoatomic systems, to more computationally demanding techniques probing interactions between atoms of larger molecules using fewer simplifying assumptions. While the prevailing notion is that increases in computational power are positively correlated with advances in computational chemistry, the reality may be more nuanced. More specifically, several examples, such as the role played by the Born-Oppenheimer approximation in unlocking solution of the Schrodinger equation, highlights the crucial contribution that theoretical intuition brought to problem-solving in computational chemistry; thus, providing evidence that, though unequal in amount, both theory and computational capabilities each help move the field forward. Collectively, with more and cheaper computing power available on the horizon, as well as more effective algorithmic tools and theories for solving the Schrodinger equation, chemical interactions between larger molecules under more realistic conditions will become amenable to study via simulation – thereby, complementing experiment and theory in gaining deeper understanding during exploration of the natural world around us.

Conflicts of Interest

The author declares no conflict of interest.

Author’s contribution

Wenfa Ng conceived the idea for the manuscript, performed the literature review, and wrote the paper.

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