

Perspective Study of *Ab Initio* Quantum Chemical Methodology and Its Applications in Chemistry

A.K. Rastogi*

Department of Chemistry, Ranchi University, Ranchi, Bihar, India

ABSTRACT

This perspective provides a summary of state-of-the-art ab initio quantum chemical methodology and applications. The precision of each approach for fundamental chemical properties is summarized, and the computational performance is analyzed, emphasizing significant advances in algorithms and usage over the past decade. Consolidation of a condensed-phase environment by means of mixed quantum mechanical/molecular mechanics or self-consistent reaction field techniques is discussed. An extensive variety of illustrative applications, focusing on chemical sciences and biology, are discussed briefly.

Keywords: *Ab Initio*, application of *Ab Initio*, chemical properties, quantum chemical methodology

***Corresponding Author**

E-mail: rastogiak32@gmail.com

INTRODUCTION

Ab initio quantum chemistry methods are computational chemistry methods based on quantum chemistry. The term *ab initio* was initially used in quantum chemistry by Robert Parr and coworkers, including David Craig in a semiempirical study on the excited states of benzene. The background is described by Parr [1].

In the course of recent decades, *ab initio* quantum science has turned into a fundamental apparatus in the investigation of atoms and molecules, progressively, in displaying complex frameworks, for example, those emerging in science and materials science. The underlying core technology is computational solution of the electronic Schrodinger equation; given the places of a gathering of nuclear cores, and the aggregate number of electrons in the framework, ascertain the electronic vitality, electron thickness, and different properties by means of a well-defined, automated approximation ("model

chemistry") [1]. The ability to obtain "adequate" answers for the electronic Schrodinger condition for frameworks containing tens, or even hundreds, of atoms has revolutionized the ability of theoretical chemistry to address important problems in a wide range of disciplines; the Nobel Prize granted to John Pople and Walter Kohn in 1998 is an impression of this perception [1, 2].

APPLICATIONS OF *AB INITIO* QUANTUM CHEMICAL METHODOLOGY

For small molecules in the gas phase and in solution, *ab initio* quantum chemical calculations can provide results approaching benchmark accuracy, and they are used routinely to complement experimental studies. A wide variety of properties, including structures, thermochemistry, spectroscopic quantities of various types and responses to external perturbations, can be computed effectively. As discussed above, SCRF

methods (or simply ignoring the solvent entirely, an approximation that is sometimes acceptable, particularly in nonpolar solvents or when a quantity that is insensitive to the dielectric of the environment is being computed) enable a relatively straightforward extension of gas-phase quantum chemical methods to obtaining results for molecules in solution [2].

Chemical-Science Applications

Materials-science applications have grown exponentially over the past decade and now involve exploration of highly complex structures and chemistries. Both bulk and surface properties can be computed for solids, in many cases yielding excellent agreement with experiment. Bandgaps and optical properties of solids have been addressed successfully by DFT-based methods. The interactions of small molecules with surfaces have also been the subject of extensive investigation, with the focus on structures, binding energies, and catalytic chemistry. Calculations of this type are central to practical applications involving industrially relevant catalytic processes, semiconductor processing, and modeling of conductivity for microelectronics applications. Another significant area of both theoretical and practical interest is modeling photochemical applications (*e.g.*, solar energy conversion by dyes adsorbed onto titanium dioxide), as implemented in the Graetzel cell, which has achieved a conversion yield very close to that of amorphous silicon [3].

Applications to Nanotechnology

Applications to nanotechnology are relatively recent but represent a focus of increasing interest. Among the systems that have been investigated are carbon nanostructures (buckyballs and nanotubes) and semiconductor quantum dots. The effects of quantum confinement and structural modification imposed by various

nanostructures on chemical and electrical properties can be investigated in a rigorous fashion, which will be essential as attempts are made to use these materials in various types of devices [3].

Biological Applications

Biological applications have focused principally on the modeling of enzymatic catalysis and active-site chemistry, although interesting investigations of other phenomena, such as cooperativity in backbone hydrogen bonding and modeling of β -sheet formation propensities by a periodic DFT calculation, have been performed recently. The use of QM/MM methods permits incorporation of the full protein environment, which is crucial in an important subset of cases, as has recently been shown in cytochrome P450, for example [4].

A wide variety of enzymatic systems have been investigated, with quantitative comparison with experimental structural and thermodynamic data yielding an encouraging level of agreement in the most accurate modeling efforts. *Ab initio* calculations provide a wealth of detail that is not available from experiment and a degree of confidence in the results that is not available from more empirical approaches. In systems such as methane monooxygenase, in which a substantial number of careful calculations have been performed by several groups and close contact with experiment has been achieved for many aspects of the catalytic process, a comprehensive picture of the functioning of the enzyme is beginning to be assembled by means of the interaction of theory and experiment. Last, the coupling of *ab initio* quantum QM/MM methods with simulation and protein structure prediction techniques permits investigation of events in which reactive chemistry is coupled to substantial conformational changes, such as the catalytic loop motion in triose phosphate isomerase [4, 5].

Development of Molecular Mechanics Force Fields

Last, a key application of quantum chemical methods is in the development of molecular mechanics force fields. The quality of force fields has improved enormously in the past two decades, and a principal reason has been the ability to fit parameters to the results of high-level *ab initio* calculations for larger and more complex model systems. For fixed-charge force fields, torsional parameters can be fit to computations of conformational energy differences of model molecules, whereas charge distributions can be fit to quantum chemical electrostatic potentials. Dimer-interaction energies have typically been used as a heuristic guide to modeling nonbonded interactions; however, for a polarizable force field, these quantities can be fit directly as well, because the model is supposed to represent nonbonded interactions accurately in both the gas phase and the condensed phase. Polarizability parameters can also be fit to quantum chemical data, although there are some issues associated with basis set size that must be considered when doing so [6].

At this point, it is useful to summarize how advances in theory and computational implementation have enabled the tremendous growth in the important applications described above. Small molecules in the gas phase are now typically addressed by high-level methods such as CCSD(T), which in many cases are more accurate than experiment. As systems increase in size, one has to at some point switch over to DFT and/or MP2 [7]. Multireference perturbation methods are typically applied when there are particular difficulties associated with near degeneracies, or for properties such as excited states for which specific multireference approaches (such as CASPT2) have proven to be superior to DFT in a wider subset of cases. The overwhelming majority of large-scale

material science and biological applications have been performed with DFT; this state of affairs is mandated by the large size of the systems that are being considered, the need in some cases for periodic boundary conditions, and the availability of QM/MM and SCRF methods principally for DFT based approaches. Last, for force-field development, localized MP2 is the method of choice because of its acceptable treatment of dispersion interaction and higher accuracy for conformational energies and hydrogen bonding energies than DFT while maintaining a similar (if somewhat larger) computational cost [8].

CONCLUSION AND FUTURE DIRECTIONS

Over the succeeding years, we assume to see noteworthy upturns in accuracy in all four of the principal quantum chemical directions described above. Improvement in developing DFT functionals has been challenging since the innovations of the early 1990s; nevertheless, several favorable approaches and main systematic complications, for examples problems in predicting barrier heights of small molecule radical reactions, have been recognized. Coupled-cluster and multi-reference algorithms comprise attempts to use localized reference states that potentially could lead to the same huge reductions in scaling with system size that have been realized with localized MP2. Continued reductions in the cost/performance of computing and improvements in algorithmic details should continue to yield shorter time to solution for increasingly larger systems.

Likewise, development can be expected in treatment of the condensed phase environment. Optimization of the correct of continuum solvation methods is far from a solved problem; moreover, there is some suggestion that the inclusion of a small number of explicit water molecules

can increase results, but methods of this type must be formulated very cautiously to avoid double counting. QM/MM methods can be made more accurate, robust, cost-effective, and easy to use. Last, sampling algorithms in the condensed phase are essential for many large-scale applications, and substantial advances can be anticipated as more ambitious problems are addressed.

Even if the technology were to stand still, one would expect a large number of important new applications to be carried out over the next decade; with advances in theory, software, and computational hardware, larger data sets and systems of increasing size, will be amenable to study. However, the most exciting possibility is that the parallel advances in theory and experiment will enable fully explanatory and predictive models to be constructed for the complex, condensed-phase processes that govern most of the natural world. *Ab initio* quantum chemical methods are not the only technology that will be a component of such a development, but they surely are an essential one, as demonstrated by the progress and prospects outlined above.

Regardless of the possibility that the innovation was to stop, one would expect a substantial number of essential new applications to be done throughout the following decade; with progresses in principle, programming, and

computational hardware, larger data sets and systems of increasing size, will be amenable to study. Nonetheless, the most energizing plausibility is that the parallel advances in theory and experiment will enable fully explanatory and predictive models to be constructed for the complex, condensed-phase processes that govern most of the natural world. *Ab initio* quantum chemical methods are not the only technology that will be a component of such a development, but they surely are an essential one, as demonstrated by the progress and prospects outlined above.

REFERENCES

- [1] S. Saeb, P. Pulay. *Annu Rev Phys Chem.* 1991; 44: 213–36p.
- [2] R.J. Bartlett. *J Phys Chem.* 1989; 93: 1697–708p.
- [3] B.O. Roos, K. Andersson, M.P. Fulscher, P.A. Malmqvist, L. Serrano-Andres, K. Pierloot, M. Merchan. *Adv Chem Phys.* 1996; 93: 219–331p.
- [4] P. Hohenberg, W. Kohn. *Phys Rev.* 1964; 1326: B864–71p.
- [5] L.J. Sham, W. Kohn. *Phys Rev.* 1964; 145: 561–7p.
- [6] W. Kohn, A.D. Becke, R.G. Parr. *J Phys Chem.* 1996; 100: 12974–80p.
- [7] B.G. Johnson, P.M.W. Gill, J.A. Pople. *J Chem Phys.* 1993; 98: 5612–26p.
- [8] A.D. Becke. *Phys Rev A.* 1998; 38: 3098–100p.