Quantum effects in complex systems: Summarizing remarks

Sharon Hammes-Schiffer

Department of Chemistry, Yale University, 225 Prospect Street, New Haven,

Connecticut 06520 United States

Abstract

Quantum mechanical phenomena such as coherence, spin dynamics, and tunneling have been observed in biological, electrochemical, polymeric, and many other condensed phase processes. This paper summarizes the diverse contributions to the Faraday Discussion on quantum effects in complex systems. Various processes exhibiting quantum mechanical behavior were examined using advanced spectroscopic and theoretical methods. An emerging theme was the critical importance of feedback between experiment and theory, particularly in the form of experimental testing of theoretical predictions.

Introduction

Quantum mechanical effects have been observed in a wide range of complex systems, including biological, electrochemical, and polymeric processes. The field of quantum biology has risen in popularity[1] due to measurements and calculations showing evidence of quantum coherence,[2, 3] spin dynamics,[4, 5] and hydrogen tunneling[6, 7] in biological systems. However, an argument could be made that quantum mechanics plays an even more fundamental role than those represented by these phenomena. In particular, all processes involving excited states are intrinsically quantum mechanical because of the quantized energy levels. Moreover, electron transfer reactions are also inherently quantum mechanical, as indicated by electron tunneling and delocalization effects. Even chemical bond breaking and forming is fundamentally a quantum mechanical process in that it requires the rearrangement of electrons. Thus, it is clear that quantum mechanics underlies most chemical and biological processes.

This Faraday Discussion focused on the exploration of the more unusual quantum phenomena such as coherence, spin dynamics, and hydrogen tunneling. This exploration has led to the development of a variety of new experimental and theoretical methods. A theme running throughout this Discussion was the importance of collaboration between experimentalists and theoreticians. Theory or experiment alone cannot address these complex problems. To facilitate progress in this field, experimentalists should measure quantities that can be computed, and theorists should calculate experimental observables that can be measured. Most importantly, theorists should make predictions before the experiments have been conducted, and experimentalists should be willing to test these theoretical predictions. Theorists can help guide the experimentalists in determining the molecules to study, the spectroscopic signatures to probe, and the overall design of the experiments.

Even within the theoretical components of these studies, multiple approaches are needed to address these complex problems. Analytical theories are required for conceptual understanding, and simulations are required for atomic-level understanding. Moreover, simulations provide the input quantities to the analytical theories, and theories predict trends that can be tested via simulations. In general, a single theoretical method will not be suitable for all systems, and systematic comparisons of different methods are useful for determining which method should be used for a particular application. This Faraday Discussion highlighted the diversity of promising theoretical methods and the importance of comparative studies. An emerging theme was the necessity of communication among theorists as well as between theorists and experimentalists in efforts to work together to enhance the level of understanding of complex systems.

Quantum coherence and spin dynamics

Quantum coherence was a central topic in this Discussion. The papers presented by Hutchinson, Troisi, and Saller presented simulations of light harvesting complexes such as the FMO (Fenna-Matthews-Olson) complex[8] (DOI: 10.1039/c9fd00081j, DOI: 10.1039/c9fd00045c, DOI: 10.1039/c9fd00050j). Throughout the literature, this field has been engaged in a debate as to whether the coherence observed in the FMO complex should be characterized as electronic, vibrational, or vibronic. Moreover, regardless of how it is characterized, the biological relevance of quantum coherence has not been established. These papers addressed some of these issues through computer simulations. Furthermore, in addition to probing coherence, these simulations provided insights into other important aspects of light harvesting complexes, such as site variation and conformational sampling. Quantum coherence effects were also investigated for I_2 in solid Kr

by Picconi and coworkers (DOI: 10.1039/c9fd00065h) and for a model dimer system by Datta and coworkers (DOI: 10.1039/c9fd00068b).

The role of spin dynamics in bird magnetoreception was another topic of discussion. The coherent spin dynamics of photochemically formed radicals in the retina have been proposed to serve as a magnetic compass for birds. The paper by Hore and coworkers illustrated that this phenomenon is not adequately described by semiclassical methods but rather requires a fully quantum mechanical treatment (DOI: 10.1039/c9fd00049f). A related paper by Grünbaum and coworkers showed that organic light emitting diodes may be used as models for bird magnetoreception to better understand the fundamental spin dynamics (DOI: 10.1039/c9fd00047j). Although competing theories for bird navigation have been proposed, the concept of spin dynamics playing a significant role in bird magnetoreception is compelling.

Spectroscopic signatures of quantum effects

A variety of spectroscopic methods were discussed in the context of probing quantum effects in complex systems. Fielding and coworkers studied the multiphoton ionization photoelectron spectrum of phenol in water using both experimental and computational methods (DOI: 10.1039/c9fd00079h). Barford and coworkers examined the photoexcited states in π-conjugated polymers (DOI: 10.1039/c9fd00054b), and Scholes investigated exciton delocalization in molecular aggregates (DOI: 10.1039/c9fd00064j). In addition, Marti and coworkers studied the multidimensional spectral lineshapes of water-solvated adenine (DOI: 10.1039/c9fd00072k), and Leonard and coworkers investigated the vibrational coherence and quantum yield of retinal-chromophore-inspired molecular switches (DOI: 10.1039/c9fd00062c). Furthermore, Segatta and coworkers showed that time-resolved near-edge X-ray absorption fine structure spectroscopy is a

powerful tool for probing photoinduced dynamics (DOI: 10.1039/c9fd00073a). All of these papers highlighted advanced spectroscopic tools that are capable of capturing quantum mechanical phenomena.

Zero-point energy and tunneling

Hydrogen tunneling in enzyme reactions was another key topic in this Discussion. Hydrogen tunneling has been shown to occur in many enzymatic reactions, although the biological significance is still debated in the literature.[9] Hay and coworkers investigated hydrogen tunneling in enzymes using a transition state theory framework with a semiclassical tunneling correction prefactor[10] (DOI: 10.1039/c9fd00044e). According to this perspective, the magnitude of the tunneling correction provides an indication of the significance of hydrogen tunneling. A correlation between the hydrogen/deuterium (H/D) kinetic isotope effect (KIE) and the tunneling correction for a series of enzymatic reactions was interpreted to imply that a larger KIE is evidence of a greater extent of hydrogen tunneling. Although such a correlation may be valid for certain restricted classes of systems, other tunneling models suggest that this type of correlation may not be generally applicable.[11] Iyengar and coworker used an *ab initio* molecular dynamics method to investigate the enzyme soybean lipoxygenase and to identify a catalytically important residue (DOI: 10.1039/c9fd00071b). Both of these approaches are valid in the electronically adiabatic regime, in which the reaction occurs on the electronic ground state without contributions from excited electronic states. Such approaches will not be able to describe electronically nonadiabatic enzyme reactions, which involve contributions from excited electronic states. Previous work has provided evidence through several different quantitative diagnostics that the proton-coupled electron transfer (PCET) reaction catalyzed by soybean lipoxygenase is vibronically and

electronically nonadiabatic.[12] In this case, a vibronically nonadiabatic PCET theory[13] can be used to compute the rate constant and KIE, with input provided by mixed quantum mechanical/molecular mechanical molecular dynamics simulations as well as quantum mechanical models.[14]

Hydrogen tunneling can also play a significant role in electrochemical reactions.[15] An advantage of electrochemistry is the ability to modulate the applied potential and thereby tune the driving force.[16, 17] In some aspects, these systems provide a cleaner platform for studying hydrogen tunneling than enzyme reactions. On the other hand, electrochemical reactions are complex and often entail many steps. The complicated structure of the solvent and ions at the electrochemical interface and its dependence on the applied potential, as well as the probability of defects in the surface structure, lead to additional challenges for describing heterogeneous reactions. Sakaushi explored hydrogen tunneling in electrochemical reactions by experimental measurement of the current densities and H/D KIEs for the hydrogen evolution reaction and the oxygen reduction reaction in both acidic and alkaline solutions (DOI: 10.1039/c9fd00032a). The experimental techniques used in these studies alleviated some of the complications associated with heterogeneous systems and provide valuable benchmarks for theoretical calculations.

A variety of theoretical methods for including nuclear quantum effects in simulations of complex systems were presented in this Discussion. The ring polymer molecular dynamics (RPMD) method[18] and its impressive capabilities to describe zero-point energy and tunneling in complex systems were highlighted in the opening lecture presented by Manolopoulos. Burghardt and coworker used the multi-level multiconfigurational time-dependent Hartree (MCTDH) method[19-21] to simulate exciton diffusion along an oligothiophene chain at finite temperature (DOI: 10.1039/c9fd00066f). Iyengar and coworker presented a quantum nuclear wavepacket

method using tensor networks designed to reduce the computational expense of time-dependent wavepacket simulations (DOI: 10.1039/c9fd00071b). The thermostatted path integral molecular dynamics (DOI: 10.1039/c9fd00056a) and forward-backward trajectory solution (DOI: 10.1039/c9fd00069k) methods were discussed by Litman and Kelly, respectively. Althorpe and coworkers compared thermostatted RPMD, two types of centroid molecular dynamics,[22, 23] and the linearized semiclassical initial value representation for computing the infrared spectrum of water in gas, liquid, and ice phases (DOI: 10.1039/c9fd00077a).

In terms of nonadiabatic dynamics, Martens compared a recently developed quantum trajectory surface hopping method[24] to the highly popular fewest switches surface hopping method[25] and exact quantum dynamics for simple model systems (DOI: 10.1039/c9fd00042a). In these calculations, the nuclei were moving on multiple electronic potential energy surfaces, but nuclear quantum effects such as tunneling were not included. Ghosh and coworkers explored approaches for incorporating such nuclear quantum effects into these types of nonadiabatic molecular dynamics simulations. Specifically, the results from three types of ring polymer surface hopping[26] were compared in an application to hole transfer in a molecular dimer model (DOI: 10.1039/c9fd00046a). These types of systematic comparisons among different methods are critical for understanding their strengths and limitations.

Each of these methods has advantages and disadvantages, and typically a higher level of accuracy is accompanied by greater computational expense. Thus, the optimal method depends on the size and complexity of the system, the physical property being calculated, the required level of accuracy, and the computing resources available. Selection of this optimal method requires an understanding of the strengths and limitations of each method.

Nuclear-electronic orbital (NEO) method

The nuclear-electronic orbital (NEO) framework represents an alternative approach for describing nuclear quantum effects, particularly in the context of quantum chemistry calculations. In this approach, specified nuclei are treated quantum mechanically on the same level as the electrons, and the mixed nuclear-electronic time-independent Schrödinger equation is solved with molecular orbital techniques.[27] Typically only key hydrogen nuclei are treated quantum mechanically, and at least two nuclei are treated classically to avoid complications with translations and rotations. The NEO approach includes proton delocalization and zero-point energy during geometry optimizations, reaction paths, and dynamics in a computationally practical manner. It also includes the non-Born-Oppenheimer effects between the electrons and the quantum nuclei. Both density functional theory (DFT) and wavefunction-based methods have been developed within the NEO framework.

In multicomponent DFT, the energy functional depends on the electron and proton densities, and the Kohn-Sham equations for both electrons and protons are solved iteratively.[28, 29] A challenge within this field has been the development of accurate electron-proton correlation functionals that provide physically reasonable proton densities. Recently, electron-proton correlation functionals have been derived based on a multicomponent extension of the Colle-Salvetti formulation.[30-32] The NEO-DFT method in conjunction with these functionals has been shown to provide accurate proton densities, energies, optimized geometries, and molecular vibrational frequencies that incorporate the anharmonic effects associated with the quantum nuclei. The computational expense of a NEO calculation is similar to the corresponding conventional electronic DFT calculation with the same formal scaling. To calculate excited states within the NEO framework, the linear response time-dependent DFT (TDDFT) equations have been derived

and implemented.[33] The NEO-TDDFT method produces accurate electronic and proton vibrational excitations in a single calculation at a similar cost as electronic TDDFT. In addition to these multicomponent DFT approaches, a series of wavefunction-based approaches has been developed. In particular, the NEO coupled cluster singles and doubles (NEO-CCSD) method[34] has been shown to be highly accurate and computationally accessible.

These NEO approaches are not designed to replace the path integral and wavepacket methods that treat all nuclei quantum mechanically, such as RPMD and MCTDH. Instead, they are designed to be accessible to non-experts striving to incorporate the most essential nuclear quantum effects into their quantum chemistry calculations. The only additional requirements to perform a NEO-DFT calculation are to specify the quantum mechanical nuclei and select a nuclear basis set and electron-proton correlation functional. The computational cost of a NEO-DFT or NEO-TDDFT calculation is similar to the cost of the analogous conventional electronic calculation. Moreover, this approach includes non-Born-Oppenheimer effects that are often neglected in approaches assuming electronic adiabaticity (i.e., assuming the Born-Oppenheimer separation between the electrons and the nuclei). Thus, this approach fills a niche that is distinct from the other available methods. On the other hand, it is not suitable for applications that must treat all nuclei quantum mechanically. As discussed above, the selection of the optimal theoretical method for a given application requires consideration of the strengths and limitations of the available methods.

Outlook

Recent advances in experimental and theoretical methods for investigating quantum effects in complex systems have opened up many new directions. Further improvements in the temporal

and spatial resolution of spectroscopic methods, in conjunction with improvements in the quantitative accuracy and computational efficiency of theoretical methods, will lead to additional progress. Continual feedback between experiment and theory will be a critical component of the developments in both arenas. This feedback will include the benchmarking of theoretical methods by comparison to experimental data and the experimental testing of theoretical predictions.

Complex systems are prevalent in biology, electrochemistry, and materials science. The processes associated with these systems often involve multiple steps, which are coupled to each other in an intricate manner. For example, photoreceptor proteins frequently require the absorption of light, electron and proton transfer, protein conformational changes, and long-range signaling. Enzyme reactions typically involve the binding of a substrate and possibly a cofactor to the enzyme, a chemical reaction that could entail multiple steps, and product release, as well as significant protein conformational changes along this catalytic pathway. Electrochemical processes generally involve diffusion of molecules to and from the electrode, a redox reaction near the electrode, electric fields that vary with applied potential and distance from the electrode, and many other complicating factors. A complete understanding of these types of complex systems requires a combination of experimental and theoretical methods that can probe different time and length scales and can describe these diverse phenomena within a single, unified framework.

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