A Modern Quantum Chemistry Sampler: From Algorithms for the Schrodinger Equation, to Medium Effects, to Large-Scale *In Silico* Molecule Design

Arguably, quantum electronic structure theory is one of the most important and successful branches of theoretical chemistry. Dating back to the advent of quantum mechanics, the work of Heitler and London (1927), Thomas and Fermi (1927), and Hund and Mulliken (1929) created the foundation of the valence bond, density functional, and molecular orbital theories that enjoyed a long and fruitful history, culminating in the Nobel Prize to Pople and Kohn in 1998. Modern quantum chemistry has become a common tool for studying structure, spectra, reaction rates, catalytic activities, dynamics, and other properties of systems ranging from atoms and small molecules to condensed phase, nanoscale, and biological objects composed of many thousands of particles. Multiple new questions have arisen in the field, which continues to experience rapid and fertile development. The current issue of *JPC Letters* includes three Perspectives that illustrate the current quantum chemistry efforts, starting from algorithm development for solving the Schrodinger equation,[1] and extending to medium effects on molecular properties[2] and large-scale *in silico* design of organic systems for solar energy harvesting.[3]

The Perspective by Sergei Manzhos, Tucker Carrington, and Koichi Yamashita[1] describes so-called nonspectral methods for solving the electronic and vibrational Schrodinger equation. Typically, the Schrodinger equation is treated by choosing a basis set, thereby reducing the quantum chemical problem to that of linear algebra. However, the number of basis functions required to obtain converged results is large and grows very rapidly with increasing system size. In order to circumvent the computational difficulty, a number of alternative (nonspectral) techniques have been introduced, including finite-difference, grid, pseudospectral, collocation, neural network, and other algorithms. By abandoning the basis functions for which exact matrix elements are available, one drastically broadens the range of available numerical techniques. Potentially, this can result in smaller, optimized basis sets, efficient parallel computation, and reduced memory requirements. Pseudospectral techniques can be used to address the electron self-interaction problem of density functional theory.[4] Nonspectral approaches are employed in other areas of theoretical physical chemistry, for instance, in electrodynamics calculations of plasmonic properties of noble metal crystals, time-domain modeling of nanoparticle optical properties, dynamic theory of membrane proteins, computation of solvation free-energies, and drug-lead optimization.[5−7]

The Perspective by De Fusco et al.[2] discusses the calculation of electronic excited state properties in condensed phase environments, such as liquid solutions, solid-state matrices, and soft-matter biological systems. Dielectric continuum models provide the simplest level of description; however, they are applicable only to structureless media and cannot include specific interactions, such as hydrogen bonding. Among the explicit solvent models, the effective fragment potential approach developed by the authors ensures that all model parameters can be derived from the first principles. Each solvent molecule is represented as a fragment whose properties are determined from a preparatory *ab initio* calculation. The interaction energy is the sum of electrostatic, polarization, dispersion, Pauli exchange, and charge transfer terms. The fragments can interact with each other and the solute. The iterative convergence of the polarization energy accounts for the inductive many-body effects. The method reproduces structures and binding energies in hydrogen- and π-bonded systems with high accuracy. It has been interfaced with many electronic structure techniques, including both wave function and density-functional methods. The system-environment interactions described by the effective fragment approach of Mark Gordon and co-workers play important roles in many areas of physical chemistry, including electronic and vibrational spectroscopy, biological chromophores, molecular motors, carbon nanotubes, nonlinear optics, and transfer of energy, population, protons, and electrons.[8−10]

The Perspective from the Alan Aspuru-Guzik's group[3] outlines an ambitious project aimed at computational design of organic chromophores for solar energy harvesting using the computational resources available across the world. The project is motivated by the rapidly evolving energy crisis that has risen due to a combination of predicted fossil fuel shortage and emergence of new economic regions that require additional energy. Solar light is the single largest source of power available to mankind; however, its harvesting necessitates development of cheaper and more efficient photovoltaic materials. Organic molecules carry multiple advantages. Most notably, they allow for low-cost and high-volume production and can merge the flexibility and versatility of plastics with electronics. Low efficiencies and a limited lifetime constitute two major drawbacks of organic photovoltaics. Hachmann et al. take advantage of the distributed computing platform, organized by IBM and involving over a million computers, in order to screen an astronomical set of molecular candidates *in silico* for photovoltaic applications. The initial calculations eliminate unfit candidates and provide predictions for promising materials and structural trends. Subsequent and more sophisticated quantum-chemical techniques are used for a detailed characterization of the selected molecules. Similar efforts of *in silico* physical-chemical design, albeit on a much smaller scale, are under way for Gratzel and quantum dot solar cells, hydrogen storage, biomimetic materials, and peptide recognition.[11−14]

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