

Electronic structure theory: present and future challenges

So Hirata

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Abstract The aim of electronic structure theory is to solve the electronic Schrödinger equation, which is a coupled high-dimensional partial differential equation with numerous singularities in the operator and complex boundary conditions arising from the fermion symmetry. This article briefly summarizes how electronic structure theorists have overcome the immense difficulties of solving this with quantitative accuracy. This has been achieved by elucidating the structure of wave functions and exploiting this knowledge to drastically expedite the numerical solutions, enabling predictive simulations for a broad range of chemical properties and transformations. It also lists some of the outstanding challenges that are to be or being addressed.

Keywords Electronic structure theory · Explicitly correlated methods · Condensed matter · Complex systems · Density-functional theory · Strong correlation

The aim of electronic structure theory is to computationally solve the electronic Schrödinger equation (with modification by the special theory of relativity, if necessary) to understand and even predict the properties and transformations of chemical systems. Since the equation is the exact equation of motion of constituent particles, electronic structure theory can in principle provide complete,

quantitative details of these properties and transformations [1], turning an increasingly wider area of chemistry into a computational science. This may appear to be a hyperbole, but for small gas-phase molecules made of light nuclei, electronic structure theory has indeed begun to predict a variety of their properties (e.g., shape and color) with such high accuracy [2] that it can compete with experimental techniques and change the ways in which research is conducted in areas like combustion and interstellar chemistry. Electronic structure theorists are determined to bring such changes in all areas of chemistry by increasing the accuracy, efficiency, and applicability of their computational methods.

However, the challenges faced by electronic structure theorists to achieve this goal can be immediately seen by inspecting the equation of motion itself (in atomic units):

$$\hat{H}\Psi(\mathbf{x}_1, \dots, \mathbf{x}_n) = E\Psi(\mathbf{x}_1, \dots, \mathbf{x}_n), \quad (1)$$

where Ψ is the wave function, E is the energy, and \hat{H} is the electronic Hamiltonian given by

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_{i=1}^n \nabla^2 - \sum_{i=1}^n \sum_{l=1}^N \frac{Z_l}{|\mathbf{x}_i - \mathbf{x}_l|} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \\ & + \sum_{l=1}^{N-1} \sum_{j=l+1}^N \frac{Z_l Z_j}{|\mathbf{x}_l - \mathbf{x}_j|}, \end{aligned} \quad (2)$$

where n is the number of electrons, N is the number of nuclei, \mathbf{x}_i is the spin-orbital coordinates of the i th electron, and \mathbf{x}_l and Z_l are the spatial coordinates and charge of the l th nucleus. The wave function, $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_n)$, must also satisfy the anti-symmetry requirement:

$$\begin{aligned} \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_n) &= -\Psi(\mathbf{x}_2, \mathbf{x}_1, \mathbf{x}_3, \dots, \mathbf{x}_n) \\ &= -\Psi(\mathbf{x}_3, \mathbf{x}_2, \mathbf{x}_1, \dots, \mathbf{x}_n) = \dots \end{aligned} \quad (3)$$

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S. Hirata (✉)
Department of Chemistry,
University of Illinois at Urbana-Champaign,
600 South Mathews Avenue, Urbana, IL 61801, USA
e-mail: sohirata@illinois.edu

For benzene, Eq. 1 is a coupled 126-dimensional partial differential equation. The corresponding Hamiltonian has 1,365 singularities at electron–nucleus and electron–electron coalescence. Equation 3 is a single equation with $42! \approx 1.4 \times 10^{51}$ terms. Worse still, to achieve predictive accuracy in chemistry, one must solve Eq. 1 with errors in relative energies on the order of one millihartree or less, which is less than 0.001% of $|E|$.

Hence, when viewed naively as a general mathematical or computational problem, it is utterly unthinkable to solve Eq. 1 with such high accuracy for all but the tiniest molecules. One must instead view this as a chemistry or physics problem and eliminate many of these difficulties (the high dimensionality, singularities, and complex dependencies due to anti-symmetry) by elucidating and exploiting the structures of electronic wave functions.

Let us consider the singularities in the Hamiltonian due to electron–nucleus coalescence in this regard. The presence of these singularities mean that the electrons sufficiently near a nucleus in a molecule experience only the nucleus' strong attractive forces and thus largely behave like atomic electrons. This suggests the use of atomic-orbital (AO) basis functions and linear-combination-of-atomic-orbital (LCAO) expansions of molecular spin-orbitals (MO) as a rational description of molecular wave functions. The electron–electron interactions also cause many singularities in the Hamiltonian, but they are repulsive. This means that the electrons try to be as far away as possible from one another and their motions are, therefore, only weakly correlated. This suggests an approximation of a wave function by an anti-symmetrized product (Slater determinant) of LCAO MOs, each of which accommodates one electron. This product form of the wave function introduces an approximate separation of variables, drastically reducing the effective dimension of the equation of motion. The Hartree–Fock (HF) method is defined as such and consistently recovers *ca.* 99% of E for a broad range of chemical systems.

Though the HF method achieves remarkable accuracy at a small computational cost, the accuracy is far from satisfactory for quantitative chemistry. One must recover the so-called electron-correlation energy, which is defined as the difference between the HF and exact energies. One mathematically straightforward, but physically unappealing way (see below for an explanation) to do this is to add excited determinants to the many-electron basis in the wave function expansion:

$$\Psi = c_0 \Phi_0 + \sum_a \sum_i c_i^a \Phi_i^a + \sum_{a < b} \sum_{i < j} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{a < b < c} \sum_{i < j < k} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots, \quad (4)$$

where i , j , and k (a , b , and c) are occupied (unoccupied) MOs in the HF determinant (Φ_0) and Φ_i^a , Φ_{ij}^{ab} , and Φ_{ijk}^{abc} are one-, two-, and three-electron excited determinants. This mathematical description of the wave function raises the difficult question as to how one should determine the expansion coefficients, c_i^a , c_{ij}^{ab} , etc. and the correlation energy. The answer comes from a rather unexpected direction: scaling properties of energy with respect to system size [3]. The time-tested methods to determine these coefficients in a physically sound fashion are based on diagrammatic many-body theories that are *size extensive* in the sense that they maintain uniform accuracy across various system sizes and are applicable equally to problems in quantum chemistry as well as in nuclear, atomic, solid-state, and condensed-matter physics. The many-body perturbation (MBPT) and coupled-cluster (CC) methods [4] are perhaps the most successful examples in this category and are used predominantly in quantitative chemical simulations today. This is in contrast with the configuration-interaction (CI) method, which is neither a diagrammatic many-body method nor size extensive and thus slowly exiting from the essential electron-correlation arsenals.

Despite the substantial progress in the field, challenges remain. In the following are listed some of the most significant research problems today, some nearly resolved and others still being in an earlier stage of investigation. The three invited articles [5–7] in the section of electronic structure theory describe the cutting edges of research addressing different aspects of these.

1 Explicitly correlated methods

The weak electron correlation is captured by CC and MBPT that describe mutually avoiding motion of electrons as a superposition of excited determinants. This is an awkward physical picture of correlation, which has a grave practical drawback: the convergence of correlation energies thus obtained is extremely slow with respect to the size of the AO basis set. A more physically appealing and efficient approach is to introduce a basis function that depends explicitly on interelectronic distances (r_{12}), which can describe cusps in wave functions that occur because of the electron–electron singularities in the Hamiltonian [8]. The last decade has seen remarkable progress in this class of methods (the R12 method [9], in particular), virtually eradicating the problem of slow basis-set convergence. Two of the breakthroughs behind this progress are the discovery [10] of a nearly optimal form of the r_{12} -dependent basis function (the so-called Slater-type correlation factor, introducing the F12 method) and the proposal [11]

to determine the expansion coefficient multiplying the r_{12} -dependent basis function analytically, both of which have been made by Ten-no [5].

2 Condensed-phase and complex systems

Systematic, size-extensive electron-correlation approximations (CC, MBPT, and their combinations) converging toward the exact basis-set solutions of the Schrödinger equation have been developed (increasingly with the aid of computer algebra [12]). Systematic basis sets converging toward completeness are also available. They have been instrumental in making electronic structure theory, a predictive science at least for small molecules in the gas phase. Today, these methods also raise the prospect of having condensed-phase systems and large complex systems (such as biological systems, in which the strengths of the pertinent interactions, including dispersion and stacking interactions [13], span three orders of magnitude) in the applicable domain of predictive simulations, potentially transforming quantitative aspects of these fields. Considerable progress has already been made to the use of spatially local basis functions that exploits the essentially local nature of correlation and speeds up these calculations dramatically [14]. In addition to the speedup procedures that benefit all these methods, a diagrammatic many-body method that strikes superior balance between accuracy and computational cost and is subject to an extension to metallic solids or to an integration with statistical thermodynamics (e.g., a finite-temperature extension) continues to be warranted. The random-phase approximation (RPA), introduced to chemistry by Furche [6, 15], is one such method which is only marginally more expensive than HF yet is capable of capturing much of electron correlation. RPA, like CC [16], includes the sum of perturbation corrections of a certain type to an infinite order and can thus resist a breakdown typical of MBPT when quasi-degenerate states are present near the ground state such as occur in metals. It promises to be a practical, systematic, and size-extensive electron-correlation method useful for small and large molecules as well as solids alike.

3 Density-functional theory

Density-functional theory (DFT) does not conform to the framework of wave-function theory (WFT), namely, the one based on the expansion of an exact wave function by determinants. It instead aims at recovering the exact energy as a functional of electron density. Abolishing at least partly the high-dimensional wave function as a quantity to be determined, DFT tends to achieve superior cost-

accuracy performance and greater practical utility than the existing counterparts in WFT. While neither systematic nor predictive in the sense of CC, MBPT, or RPA, approximations in DFT have seen an explosive advance in the past two decades, eliminating such shortcomings in earlier approximations as their poor descriptions of ionization energies [17], Rydberg excitation energies [17], charge-transfer states [18], (hyper)polarizabilities [19], and dispersion [20] and stacking interactions [21]. The use of electron density in lieu of wave functions as a basic variable must, therefore, somehow exploit a hidden structure of wave functions, the detail of which has not been understood. Further theoretical studies of fundamental nature are thus still warranted to elucidate why some approximations of DFT perform so well for a range of problems. Ultimately, like WFT, DFT needs to be characterized by systematic series of approximations converging toward the exactness, in which electron density may be a low-rank member of a new hierarchy of basic physical variables such as density matrices [22], intracules, and two-electron density parameters, the last two of which have been advocated by Gill and coworkers [7, 23].

4 Strong correlation

Strongly correlated systems are ones in which there are two or more (quasi-)degenerate states that are interacting with one another. They include such systems as spin lattices, transition-metal complexes with many metal centers, and breaking and formation of chemical bonds. The HF method, in which electron correlation is assumed implicitly to be weak (see above), becomes a poor approximation, rendering MBPT and occasionally even CC based on a single reference determinant also inadequate. There has been an impressive array of original methods recently proposed to resolve this problem. Some [24], including various multi-reference and active-space electron-correlation methods, selectively sum critical determinant contributions within the framework of WFT. Others [25] do so by allowing the number of electrons to be varied! Perhaps the most successful ones thus far essentially resort to the full CI method but with vastly improved algorithms based on quantum Monte Carlo [26], density matrix renormalization group [27], graphically contracted functions [28], etc. These methods and algorithms imply that certain regular structures exist in strongly correlated wave functions, which are yet to be fully understood.

The field of electronic structure theory has undergone steep, linear growth since 1990, capitalizing upon the foundational work in the preceding decades, into a new level of maturity. It has transformed neighboring experimental fields of chemistry, which, as a result, rely increasingly

heavily on black-box computational methods and software electronic structure theorists have developed. It also continues to serve as an essential infrastructure of higher quality and greater convenience for the sister fields of theoretical chemistry that is quantum dynamics and statistical thermodynamics. There is hardly any question that this trend will continue, and the prime of electronic structure theory is still ahead.

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