Quantum Embedding Theories

Qiming Sun and Garnet Kin-Lic Chan*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

CONSPECTUS: In complex systems, it is often the case that the region of interest forms only one part of a much larger system. The idea of joining two different quantum simulations—a high level calculation on the active region of interest, and a low level calculation on its environment—formally defines a *quantum embedding*. While any combination of techniques constitutes an embedding, several rigorous formalisms have emerged that provide for exact feedback between the embedded system and its environment. These three formulations: *density functional embedding*, *Green's function embedding*, and *density matrix embedding*, respectively, use the single-particle density, single-particle Green's function, and single-particle density matrix as the quantum variables of interest.

Many excellent reviews exist covering these methods individually. However, a unified presentation of the different formalisms is so far lacking. Indeed, the various languages commonly used, functional equations for density functional embedding, diagrammatics for Green's function embedding, and entanglement arguments for density matrix embedding, make the three formulations appear vastly different. In this Account, we introduce the basic equations of all three formulations in such a way as to highlight their many common intellectual strands. While we focus primarily on a straightforward theoretical perspective, we also give a brief overview of recent applications and possible future developments.

The first section starts with density functional embedding, where we introduce the key embedding potential via the Euler equation. We then discuss recent work concerning the treatment of the nonadditive kinetic potential, before describing mean-field density functional embedding and wave function in density functional embedding. We finish the section with extensions to time-dependence and excited states.

The second section is devoted to Green's function embedding. Here, we use the Dyson equation to obtain equations that parallel as closely as possible the density functional embedding equations, with the hybridization playing the role of the embedding potential. Embedding a high-level self-energy within a low-level self-energy is treated analogously to wave function in density functional embedding. The numerical computation of the high-level self-energy allows us to briefly introduce the bath representation in the quantum impurity problem. We then consider translationally invariant systems to bring in the important dynamical mean-field theory. Recent developments to incorporate screening and long-range interactions are discussed.

The third section concerns density matrix embedding. Here, we first highlight some mathematical complications associated with a simple Euler equation derivation, arising from the open nature of fragments. This motivates the density matrix embedding theory, where we use the Schmidt decomposition to represent the entanglement through bath orbitals. The resulting impurity plus bath formulation resembles that of dynamical mean-field theory. We discuss the numerical self-consistency associated with using a high-level correlated wave function with a mean-field low-level treatment, and connect the resulting numerical inversion to that used in density functional embedding.

We finish with perspectives on the future of all three methods.
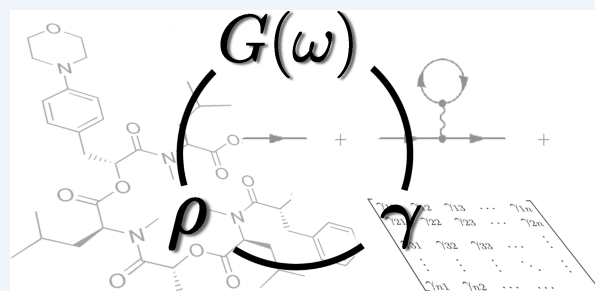
■ INTRODUCTION

Embedding theories provide a natural way to focus computation on a small region within a larger environment, such as atoms near the active site in an enzyme. In any embedding theory, the full problem is partitioned into the fragment of interest (A) and its environment (B). (The terms "subsystem" or "impurity" are commonly used in place of "fragment".) There may be multiple fragments of interest, and the environment may also be partitioned. In any case, the purpose of the embedding is to provide a computational recipe for the properties of A, taking into account its environment, without the computational cost of treating the full problem. The idea is thus very general, and encompasses a wide variety of methods. For example, whenever

A and B are treated at two different levels, for example, when freezing orbitals in a calculation, we are formally performing embedding! What concretely distinguishes one embedding theory from another, is the particular way in which the effects of the environment are communicated to the fragment A, and vice versa.

Here, we will describe a family of three related, rigorous, quantum embedding theories: density functional (DFT) embedding,[1−5] Green's function embedding,[6−11] and density matrix embedding.[12−15] Compared to simpler embedding

techniques, these stand out as they provide for nontrivial communication between the fragment and environment. In the three theories, information is communicated via the density, the single-particle Green's function, and the single-particle density matrix, respectively. Note that we identify the kind of embedding by its functional dependence on a quantum variable, rather than intermediary computational objects. Thus, even if a density matrix is used in the calculation, if it ultimately encodes a density functional (e.g., in a Kohn–Sham theory), then the embedding is a density functional embedding. There are excellent reviews for each of the three techniques individually, for example, refs 3–5, 7, 9, and 14. Here, we will give an introduction to all three together, that emphasizes their common intellectual strands, and provide a summary of their strengths and weaknesses.

■ DFT EMBEDDING

We will begin with the simplest quantum embedding, DFT embedding. We provide a particular perspective to make connections to the subsequent Green's function and density matrix embedding formalisms; other perspectives can be found in the literature.[3–5] The formal groundwork was developed by Cortona[1] and Wesołowski and Warshel.[2] In the ground-state version, the density of A, ρ_A, is adjusted through an external field, v_A, and we view this field as coming from the environment. Further, the energy of A is modified by its interactions with the environment, through the Coulomb term, and indirectly through the exclusion principle. These energetic contributions are contained in a term ΔE.

The DFT embedding formalism provides rigorous foundations for v_A and ΔE as density functionals. We begin with the exact energy density functional for the full system, $E[\rho]$, which determines the ground-state density through the Euler equation

$$\frac{\delta E[\rho]}{\delta \rho} - \mu = 0 \tag{1}$$

where μ is the chemical potential. Partitioning the energy into its Kohn–Sham kinetic, Coulomb, external, and exchange-correlation pieces,[16]

$$E[\rho] = T_s[\rho] + J[\rho] + V_{ext}[\rho] + E_{xc}[\rho] \tag{2}$$

we rewrite the Euler equation

$$\frac{\delta T_s[\rho]}{\delta \rho} + v_J[\rho] + v_{ext} + v_{xc}[\rho] - \mu = 0 \tag{3}$$

$E_{xc}[\rho]$ and $v_{xc}[\rho]$ account for the nontrivial correlation effects and must be approximated. When necessary, we indicate the dependence of these quantities on the approximation scheme S by writing them as $E_{xc}^S[\rho]$, $v_{xc}^S[\rho]$.

We now derive the expressions for v_A and ΔE. Splitting $E[\rho]$ into the fragment energy and its remainder, $E[\rho] = E[\rho_A] + \Delta E[\rho, \rho_A]$ ($E_A = E[\rho_A]$), stationarity with respect to ρ_A implies

$$\frac{\delta}{\delta \rho_A}[E[\rho_A] + \Delta E[\rho, \rho_A]] - \mu = 0 \tag{4}$$

This is the same as the Euler equation for A placed in an external field v_A, if we choose

$$v_A = \frac{\delta \Delta E[\rho, \rho_A]}{\delta \rho_A} \tag{5}$$

Equation 5 thus defines the exact embedding potential, which yields the exact subsystem density ρ_A. Note we use ρ, ρ_A as the

working variables. The use of a global and a fragment quantum variable is a choice common to all three embedding formalisms in this article. However, in DFT embedding, one often works instead with the subsystem and environment densities separately, ρ_A, ρ_B, with $\rho = \rho_A + \rho_B$. This has advantages in practice, for example, if ρ_A and ρ_B are ensemble N-representable, then so is ρ.[17]

We express v_A in terms of its components as

$$v_A = \frac{\delta}{\delta \rho_A}[T_s[\rho] - T_s[\rho_A]] + v_J[\rho - \rho_A] + \frac{\delta}{\delta \rho_A}[E_{xc}[\rho] - E_{xc}[\rho_A]]$$
$$= v_s^\Delta + v_J^\Delta + v_{xc}^\Delta \tag{6}$$

where v_s^Δ is the *nonadditive kinetic potential*, v_J^Δ is the environment Coulomb potential, and v_{xc}^Δ is the nonadditive exchange-correlation potential. v_s^Δ is the largest contribution and expresses the exclusion principle which forces electrons in the fragment to occupy states orthogonal to those in the environment.[1,2]

Commonly in DFT calculations, $E_{xc}[\rho]$ is approximated as an explicit functional of ρ and its derivatives (e.g., as is in the LDA or GGA's). Consequently, $v_{xc}^\Delta[\rho]$ can be obtained by analytical functional differentiation of $E_{xc}[\rho] - E_{xc}[\rho_A]$. $T_s[\rho]$, however, is only known as an *implicit* density functional through the Kohn–Sham orbitals. One way to evaluate v_s^Δ is to approximate T_s by an explicit density functional approximation, such as the Thomas–Fermi (or a related) functional, from which the kinetic potential can be directly derived. This approximation was widely used in the early days of DFT embedding,[1,2] but is limited by the accuracy of the approximate kinetic energy.[18,19] It has found most success in applications where the fragment is weakly bound to the environment, for example, in van der Waals complexes,[20] in highly ionic crystals,[21] and in solvation.[22,23]

A more recent strategy has been to compute $\delta T_s/\delta \rho_A$ and the nonadditive kinetic potential numerically.[24–27] Since the forward computation of $v_s \to \rho$ (to determine the noninteracting ground-state density in an external potential v_s) is cheap ($O(N^3)$ where N is the number of electrons), the inversion is tractable.[28,29] In practice, there are numerical difficulties,[30] because large changes in v_s can yield only small changes in ρ. This leads to unphysical oscillations in the numerically determined v_s.[30,31]

The above is a basic formulation of ground-state DFT embedding, and extensions exist, for example, to ensemble representations for fragments with noninteger particle number,[32–34] and Kohn–Sham projector formalisms to avoid the nonadditive kinetic potential altogether.[35,36] However, we now consider the two common contexts in which DFT embedding is applied. The first is DFT in DFT embedding,[2] where both the subsystem A and environment B are treated with DFT. This may not seem to result in any simplification, but there are several ways to obtain savings. For example, different levels of DFT can be used for A and B (e.g., functionals with or without exact exchange)[37] or the self-consistency may be approximated (e.g., by replacing the self-consistent ρ_B by a frozen superposition of densities). The latter is particularly appropriate for solvent systems,[22,23] and allows for very large environments, such as protein frameworks, to be considered.

The second common context is where the fragment is described using a high-level wave function, and the environment by DFT, and embedding connects the two.[17,38–41] Wave function in DFT embedding was pioneered by Carter and co-workers[27,38] and has attracted much recent attention, because of

the difficulties of DFT in treating aspects of electronic structure such as excited states and bond-breaking.

In wave function in DFT embedding, two approximations enter for the correlations, S_{WF} and S_{DFT}. The energy functional is defined as

$$E[\rho] = E^{S_{WF}}[\rho_A] + E^{S_{DFT}}[\rho] - E^{S_{DFT}}[\rho_A] \tag{7}$$

where the wave function energy for fragment A is formally expressed through

$$E^{S_{WF}}[\rho_A] = \min_{\Psi^{S_{WF}} \to \rho_A} \langle \Psi^{S_{WF}} | \hat{H}_A | \Psi^{S_{WF}} \rangle \tag{8}$$

Since the effect of the environment is completely contained within v_A, the minimizing Ψ in eq 8 is the ground-state of $\hat{H}_A + v_A$. Any wave function ansatz may be used to approximate this eigenstate,[27,38−41] and existing quantum chemistry programs only need be modified to include the potential v_A, which adds to the attractiveness of the method.

In the simplest scheme, ρ_A and v_A are defined both from the DFT density, and the DFT expression, $\Delta E^{S_{DFT}}[\rho, \rho_A]$ in eq 5. In a more sophisticated scheme, the wave function treatment of correlation is used to improve the density self-consistently. This is achieved by defining the exchange-correlation potential of the full system

$$v_{xc}[\rho] = v_{xc}^{S_{WF}}[\rho_A] + v_{xc}^{S_{DFT}}[\rho] - v_{xc}^{S_{DFT}}[\rho_A] \tag{9}$$

Self-consistent iteration between v_{xc} and v_A then allows for the DFT density ρ_A^{DFT} and the WF density ρ_A^{WF} to become identical.

There is an increasing number of applications using wave function in DFT embedding, such as to molecules adsorbed on surfaces[42,43] and molecular fragments embedded in larger systems.[44] A growing community is exploring these techniques also for excited state properties (see, e.g., ref 45). The simplest way to compute excited states is to assume that the ground-state and excited-state embedding potential and energy functional are identical.[46] This is, however, an approximation, and in principle, the ground-state formalism must be extended. There are two ways to do so. The first is a state-specific DFT embedding, where $E[\rho]$ and v_A acquire an excited state dependence. State-specific DFT embedding has been explored by several workers,[47,48] who find that state-dependence gives significant corrections, especially when the charge character of the excited state differs from the ground-state. A second way is through time-dependent DFT, where excitation energies are poles of the response. Here, the embedding potential becomes time-dependent, with a nonlocal dependence on the density at earlier times, $v_A[\rho_-(t')]$.[49,50] Applications using this second formalism are now beginning to appear.[51]

Despite its conceptual simplicity, wave function in DFT embedding inherits limitations intrinsic to all combinations of wave functions with density functional approximations. For example, in the total energy expression, eq 7, the nonadditive part of the energy is described at the DFT level, while an accurate total energy requires error cancellation between the wave function and DFT descriptions of the system ($E^{S_{WF}}[\rho_A] - E^{S_{DFT}}[\rho_A]$). Incomplete cancellation is sometimes referred to as "double counting". The two sources of error are important if the interface between the fragment and environment cuts across a bond of interest, as they affect the correlation energy of the bond. Similarly, if van der Waals interactions between the fragment and environment are important, such contributions, omitted in many density functionals, will be missed. Both these situations can be remedied formally by increasing the system size treated with the wave function method, albeit at increased cost.

Another disadvantage of DFT embedding is that it is difficult, through examining ρ_A alone, to distinguish between a fragment which is bonded with the environment, and one which is not. This is because the density, by definition, does not contain direct information on off-diagonal density matrix correlations (i.e., coherence and entanglement). While, in principle, all effects can be captured by the exact density functional, the lack of the off-diagonal information can pose difficulties for density functional approximations used in practice. One way to surmount this is to consider embedding theories of richer quantum variables with off-diagonal correlations, such as the single-particle Green's function or the single-particle density matrix. We now turn to these embedding formalisms.

GREEN'S FUNCTION EMBEDDING

Green's function embedding has a long history, and is widely used in condensed matter problems.[6−9,11,52] We cannot cover the extensive literature on models, and will restrict ourselves to the aspects of Green's function embedding relevant to ab initio quantum chemistry.[10,11,53−55]

The zero-temperature, time-ordered, single-particle Green's function generalizes the familiar single-particle density matrix, to carry additional information on time-dependent correlations. In a basis labeled by i,j, it is defined as

$$iG_{ij}(t) = \mathcal{T}\langle \Psi_0 | a_i(0) a_j^\dagger(t) | \Psi_0 \rangle \tag{10}$$

where $\mathcal{T}$ denotes time-ordering, Ψ_0 the ground-state wave function, and $a^{(\dagger)}$ are electron annihilation (creation) operators in the Heisenberg representation. It is common also to use $\mathbf{G}(\omega)$, the Fourier transform of $\mathbf{G}(t)$. The imaginary part of the Green's function $-\frac{1}{\pi}\mathrm{tr}\,\mathrm{Im}\,\mathbf{G}(\omega)$ is the single-particle density of states, while the equal-time Green's function $-i\mathbf{G}(t = 0_+)$ (where 0_+ is a positive infinitesimal) is the single-particle density matrix. As an example, the real-space noninteracting Green's function is given by $\mathbf{g}(\mathbf{r}, \mathbf{r}', \omega) = \Sigma_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}') (\omega - \epsilon_i + i0_+)^{-1}$, where ϕ_i, ϵ_i are the single-particle orbitals and energies.

Unlike in DFT, the energy is computable explicitly from the exact Green's function as

$$E = \frac{1}{2} \int_{-\infty}^{\mu} d\omega \,\mathrm{tr}[(\mathbf{h} + \omega\mathbf{1})\mathrm{Im}\,\mathbf{G}(\omega)] \tag{11}$$

(μ is the chemical potential, $\mathbf{h}$ is the single-particle Hamiltonian). For approximate Green's functions, the expression must be modified with additional terms to obtain a variational bound.[56] One example is the Luttinger-Ward functional, from which an embedding formalism can be constructed.[57] However, it is complicated to specify and we do not need all its properties here. Instead, it is sufficient to consider the corresponding Euler equation, namely the Dyson equation.

The Dyson equation relates the Green's function of different Hamiltonians. For example, the Green's function of a non-interacting system $\mathbf{g}(\omega)$ and that of the interacting system $\mathbf{G}(\omega)$ are related by

$$\mathbf{G}(\omega) = \mathbf{g}(\omega) + \mathbf{G}(\omega)\boldsymbol{\Sigma}(\omega)\mathbf{g}(\omega) \tag{12}$$

where $\boldsymbol{\Sigma}(\omega)$, the self-energy, accounts for interactions. Equation 12 is the analog of the DFT Euler equation (eq 3) where $\mathbf{g}(\omega)$ plays a similar role to $\delta T_s/\delta\rho + v_{ext}$, and the self-energy plays the part of the Coulomb plus exchange-correlation potential. In practice, the self-energy must be approximated, and it is

convenient to discuss such approximations in diagrammatic terms. The exact (proper) $\mathbf{\Sigma}(\omega)$ is a sum over all perturbation theory diagrams, where each diagram is a connected graph of Green's function and interaction lines, and no diagram can be cut in two by cutting a single Green's function line. An approximate self-energy will sum over a subset of these diagrams, which can be specified in terms of the diagram skeletons (S), and the Green's functions $\mathbf{G}_\Sigma(\omega)$ and interactions V within them. We thus denote a self-energy approximation by $\mathbf{\Sigma}^S[\mathbf{G}_\Sigma, V]$. A *self-consistent* approximate self-energy is one where the Green's function used in the self-energy diagrams satisfies the Dyson equation, that is, $\mathbf{G} = \mathbf{G}_\Sigma$.

In Green's function embedding, the fragment Green's function $\mathbf{G}_A(\omega)$, is adjusted through another self-energy $\mathbf{\Delta}_A(\omega)$, dual to $\mathbf{G}_A(\omega)$. To prevent confusion with the self-energy arising due to interactions in eq 12, we term $\mathbf{\Delta}_A(\omega)$ the hybridization. Together with the self-energy approximation $\mathbf{\Sigma}_A(\omega)$, this gives the fragment Dyson equation

$$\mathbf{G}_A(\omega) = \mathbf{g}_A(\omega) + \mathbf{G}_A(\omega)(\mathbf{\Delta}_A(\omega) + \mathbf{\Sigma}_A(\omega))\mathbf{g}_A(\omega) \quad (13)$$

where $\mathbf{g}_A(\omega)$ is the noninteracting Green's function of the system computed *in isolation*, that is, with no couplings to the environment or any interactions. Inverting eq 13 gives the hybridization as

$$\mathbf{\Delta}_A(\omega) = \mathbf{g}_A(\omega)^{-1} - \mathbf{G}_A(\omega)^{-1} - \mathbf{\Sigma}_A(\omega) \quad (14)$$

$\mathbf{\Delta}_A(\omega)$ is the analog of the DFT embedding potential ν_A, and eq 14 is analogous to eq 6. Similarly to ν_A, $\mathbf{\Delta}_A(\omega)$ contains effects from electron delocalization into the environment as well as environment Coulomb interactions. However, unlike in DFT embedding, the inversion from $\mathbf{G}(\omega) \rightarrow \mathbf{\Delta}(\omega)$ is explicit through eq 14, and no iterative technique is necessary.

We now discuss two different contexts in which Green's function embedding is applied. These correspond to different self-energy approximations for A and the environment B, and parallel the contexts appearing in DFT embedding. The simplest is to describe both A and the full system at the mean-field level. Then, $\mathbf{\Sigma}_A(\omega)$ and $\mathbf{\Sigma}(\omega)$ correspond to the respective mean-field Coulomb and exchange terms (and thus have no frequency dependence). Similarly to DFT in DFT embedding, savings result when we use different levels of mean-field for A and the full-system, for example by forgoing self-consistency in the environment. A common application of the latter is to impurities in crystals, where $\mathbf{G}(\omega)$ is first computed using translational invariance in the periodic crystal, and relaxation of the environment is ignored when the impurity is introduced.[52] In molecular junctions, $\mathbf{\Delta}_A(\omega)$ is similarly obtained for a semi-infinite electrode, and assumed to be unchanged on the introduction of the bridging molecule.[58]

A second context is to perform Green's function embedding with more sophisticated approximations for $\mathbf{\Sigma}_A(\omega)$ and $\mathbf{\Sigma}(\omega)$. This is similar to wave function in DFT embedding, as there are now two different correlation treatments which must be bridged. We denote the "high-level" approximation S_H and the "low-level" approximation S_L. The low-level approximation is used to construct a self-energy including all interactions in the full problem, $\mathbf{\Sigma}^{S_L}[\mathbf{G}, V](\omega)$, and the high-level approximation is used to construct a self-energy considering interactions only in the subsystem A, $\mathbf{\Sigma}_A^{S_H}[\mathbf{G}_A, V_A](\omega)$. The composite self-energy for the full problem is

$$\mathbf{\Sigma}(\omega) = \mathbf{\Sigma}^{S_L}[\mathbf{G}, V] + \mathbf{\Sigma}_A^{S_H}[\mathbf{G}_A, V_A](\omega) - \mathbf{\Sigma}_A^{S_L}[\mathbf{G}_A, V_A](\omega) \quad (15)$$

where $\mathbf{\Sigma}_A^{S_L}[\mathbf{G}_A, V_A]$ indicates the part of $\mathbf{\Sigma}^{S_L}[\mathbf{G}, V]$ involving only Green's functions and interactions within fragment A. eq 15 is analogous to the expression for the exchange-correlation potential eq 9 in wave function in DFT embedding. In fact, one common way to compute $\mathbf{\Sigma}_A^{S_H}[\mathbf{G}_A, V_A](\omega)$ is by carrying out a wave function calculation on the subsystem A in the presence of additional fictitious "bath" orbitals that reproduce the effects of the hybridization $\mathbf{\Delta}_A$.[10] The subsystem plus bath orbitals is known as a quantum impurity problem. We return to impurity problems in the context of density matrix embedding theory. Self-consistency of the Green's functions is obtained by solving eq 14 and eq 15 for the hybridization and self-energy.

Dynamical mean-field theory[8−10] (DMFT) (which here refers to both single-site and cluster extensions) provides a widely used example of a higher-level self-energy embedding within a lower-level treatment. In DMFT, we divide the full problem of interest (commonly a crystal) into multiple fragments A containing strongly correlated orbitals (typically transition metal d and f orbitals) for which a high-level self-energy approximation in each fragment, $\mathbf{\Sigma}_A(\omega)$, is computed. The composite self-energy in eq 15 becomes

$$\mathbf{\Sigma}(\omega) = \mathbf{\Sigma}^{S_L}(\mathbf{G}, V) + \sum_A [\mathbf{\Sigma}_A^{S_H}(\mathbf{G}_A, V_A) - \mathbf{\Sigma}_A^{S_L}(\mathbf{G}_A, V_A)] \quad (16)$$

where the sum over A reflects a summation over the fragments. For a crystal, the self-energy in each cell is identical. Self-consistency of eq 16 with $\mathbf{\Delta}_A(\omega)$ for each cell A yields the cellular DMFT equations.[59]

The low-level approximation in DMFT is often chosen to be a DFT treatment. This combination is called DFT+DMFT,[9] and has been widely applied to correlated materials, especially to compute the density-of-states observed in photoemission experiments.[9] It has also been used, less commonly, in molecular applications, for example, to obtain correlation corrections to the conductance of a molecular junction,[60] and qualitative features of the electronic structure in transition metal clusters and complexes.[54]

Unfortunately, the combination of DFT with DMFT suffers from similar problems to wave function in DFT embedding, such as partial double counting of interactions, and this has been a barrier to chemical accuracy. Combining DMFT with a low-level Hartree−Fock self-energy avoids this issue, as the diagrams can be correctly subtracted in eq 16, and has recently been explored in small molecules,[53] and in a minimal basis cubic hydrogen solid.[10] Unfortunately, this treatment provides no description of correlations outside of the fragments, and is thus also not quantitative. Incorporating "non-local" correlations into a DMFT description is a topic of current research, and strategies include using a random-phase approximation (RPA) for the nonlocal correlations, which modifies both the low-level self-energy, as well as screens the Coulomb interaction $V_A \rightarrow V_A^{\mathrm{RPA}}(\omega)$ appearing in the high-level self-energy approximation; and using a pure self-energy approximation, such as the self-consistent second-order self-energy.[61] The latter has been explored by Zgid and co-workers.[55,62]

The strengths of Green's function embedding are the analytic expressions for the energy and hybridization, and the diagrammatic interpretation of the self-energy approximations. However, fully ab initio applications lag behind those of DFT embedding, because ab initio quantum chemistry methods are primarily developed for single states (such as the ground-state) rather than the Green's function, and computing time-dependent

Green's functions is more expensive than computing time-independent observables.

DENSITY MATRIX EMBEDDING

The practical complexity of working with Green's functions motivates a third formulation of embedding: density matrix embedding, where the quantity of interest is the single-particle density matrix, γ, where $\gamma_{ij} = \langle \Psi | a_i^\dagger a_j | \Psi \rangle$. It appears straightforward to formulate embedding with the density matrix, as it interpolates in complexity between the density and the Green's function. Indeed, one can formally define a density matrix embedding to parallel DFT (and Green's function) embedding, starting from the energy functional of the density matrix, and using stationarity to define an embedding operator $\mathbf{v}_A$,

$$\mathbf{v}_A = \frac{\delta \Delta E}{\delta \boldsymbol{\gamma}_A} \tag{17}$$

which, when substituted into the fragment Euler equation, yields the exact fragment density matrix $\boldsymbol{\gamma}_A$.

Unfortunately, there is a complication that is unique to the density matrix formulation. In DFT embedding, ΔE and the embedding potential are defined with respect to a closed noninteracting system, and the latter acts to adjust the reference density to match the fragment density. (A similar statement may be made with respect to the Green's function for Green's function embedding). However, the *density matrix* of a closed noninteracting system must be idempotent, while the density matrix of a general (open) fragment need not be, and the two in general cannot be matched via an embedding operator. Instead, one is forced to consider more complex interacting reference systems (to represent nonidempotent fragment density matrices) or more complicated interacting density matrix functionals that minimize to nonidempotent solutions. Some of the more complex reference systems considered include ones where the ground-state is modeled by a geminal wave function,[15,63] as well an impurity-like formulation, where the reference is the size of the full system, but with interactions restricted only to the fragment of interest.[64]

The above complication reflects the essential physical difference between an open system, which is entangled with its environment and should be described by a mixed state, and a closed system, described by a pure state. Rather than using a more complicated pure-state to mimic a nonidempotent density matrix, one can instead model the open fragment as part of a closed system, by introducing additional bath degrees of freedom. This is the same physical idea used in the impurity representation of the hybridization in Green's function embedding. Of course, if the bath has the same complexity as the rest of the system, nothing is gained, but in practice, the size of the bath can be significantly less than the size of the environment.[14,65] A simple example is the link orbitals in QM/MM calculations, a small set of extra atomic orbitals chosen to saturate the dangling bonds of the QM fragment. Other embedding approaches, such as divide and conquer, similarly introduce buffer orbitals,[66] using orbitals spatially close to the fragment region.

The choice of additional bath degrees of freedom appears to have some arbitrariness, but a construction that is provably optimal at the mean-field level has recently been provided by the DMET (density matrix embedding theory) of Knizia and Chan.[12,13] A key property of the DMET bath is that it is (at

most) the same size as the fragment, and thus rigorously removes most of the degrees of freedom in the environment. DMET thus avoids the much larger baths associated with Green's function embeddings.[12] To see that the environment can be compressed to this size, consider the case where one has the exact wave function $|\Psi\rangle$ for the full problem. This wave function may be rewritten (via the Schmidt decomposition) in terms of states that live solely in the fragment, and environment Hilbert spaces, $\{|\alpha_i\rangle\}$, $\{|\beta_i\rangle\}$, respectively

$$|\Psi\rangle = \sum_i^D \lambda_i |\alpha_i\rangle |\beta_i\rangle \tag{18}$$

The summation is over D terms, the dimension of the fragment Hilbert space, and the decomposition defines D exact bath states $|\beta_i\rangle$. The exact wave function can then be expressed within the reduced Hilbert space $\{|\alpha_i\rangle\} \otimes \{|\beta_j\rangle\}$. When $|\Psi\rangle$ is a Slater determinant (e.g., the ground-state of a mean-field Hamiltonian $\hat{f}$) then the Schmidt decomposition takes a particularly simple form. In particular, if the fragment has d orbitals, then the bath states are spanned exactly by the Hilbert space of d (partially occupied) bath orbitals, with all other orbitals either completely filled (core orbitals) or empty. The partially filled bath orbitals are the eigenvectors (with partial occupancy) of the environment block of the mean-field density matrix. This fragment plus bath representation of a mean-field wave function becomes the reference system in DMET, a noninteracting problem of twice the size of the fragment. Projected into this representation, the mean-field ground-state of $\hat{f}$ can reproduce any fragment density matrix by augmenting with a suitable fragment operator, $\hat{f} \rightarrow \hat{f} + \hat{v}_A$. Since the bath orbitals capture the effects of embedding at the mean-field level, $\hat{v}_A$ serves to encode additional correlation effects beyond the mean-field treatment, and is thus analogous to the exchange-correlation potential in DFT, or self-energy in Green's function embedding.

Mean-field in mean-field embedding in DMET can be formulated using different levels of mean-field theory to define bath orbitals from the full problem, and to model the smaller fragment plus bath representation. However, DMET has so far mainly been applied using a correlated wave function description of the fragment plus bath, on top of a mean-field reference. Denoting the mean-field description by S_L, the DMET bath orbitals are obtained from the mean-field reference Ψ^{S_L} (the ground-state of $\hat{f} + \hat{v}_A$) which defines a fragment density matrix $\boldsymbol{\gamma}_A$. The correlated energy of the *full* problem is then

$$E^{S_H}[\boldsymbol{\gamma}_A] = \min_{\Psi_A^{S_H}} \langle \Psi_A^{S_H} | \hat{H} | \Psi_A^{S_H} \rangle \tag{19}$$

where the correlated wave functions are defined in the DMET "active" space of fragment A plus its bath and core orbitals. The functional dependence on $\boldsymbol{\gamma}_A$ enters in eq 19 through the definition of the bath, but $\boldsymbol{\gamma}_A$ is in general different from the high level density matrix $\boldsymbol{\gamma}_A^{S_H}$, obtained from $\Psi_A^{S_H}$. Self-consistency adjusts $\hat{v}_A$ such that $\boldsymbol{\gamma}_A = \boldsymbol{\gamma}_A^{S_H}$. The numerical procedure to do so involves a noninteracting inversion $\boldsymbol{\gamma}_A \rightarrow \mathbf{v}_A$, and is analogous to the inversion $\rho_A \rightarrow v_A$ in DFT embedding, with related issues of representability.[14,63]

Although $E^{S_H}[\boldsymbol{\gamma}_A]$ is an energy for the full problem, correlations are only included close to fragment A, as the bath orbitals are typically localized close to A. This is acceptable for intensive quantities (such as local reactions or excitations). However, for an extensive correlated treatment (as desired in a condensed phase problem) one must embed with multiple fragments. Then,

each fragment A yields a separate high-level wave function for the full problem, $\Psi_A^{S_H}$, and expectation values must be assembled from the different fragment wave functions. It can be expected that expectation values for a given $\Psi_A^{S_H}$ are most accurate close to fragment A, and this is reflected in the partitioning of the contributions. For example, to compute the density matrix element $\gamma_{ij} = \langle a_i^\dagger a_j \rangle$, we define

$$
\gamma_{ij} = \begin{cases} \langle \Psi_A^{S_H} | a_i^\dagger a_j | \Psi_A^{S_H} \rangle & i, j \in A \\ \frac{1}{2}(\langle \Psi_A^{S_H} | a_i^\dagger a_j | \Psi_A^{S_H} \rangle + \langle \Psi_{A'}^{S_H} | & i \in A, j \in A' \\ \quad a_i^\dagger a_j | \Psi_{A'}^{S_H} \rangle) \end{cases}
$$

(20)

Analogous partitionings can be defined for more complicated expectation values.

Because its initial development was motivated by DMFT, the majority of DMET applications have been to correlated lattice models,[63,67,68] where the computational simplicity of the method has enabled very accurate results to be achieved using large fragments, for example, for the 2D Hubbard model.[68] Importantly, self-consistency in DMET, much like in DMFT, allows for nontrivial phases, such as superconductivity in repulsive systems.[68] Related to the physics of such lattice models are problems of strong correlation in chemical settings. The DMET bath allows the formalism to accurately treat fragments when they are bonded to their environment, even when such a bond is stretched or dissociated, as has been demonstrated through accurate calculations of the dissociation curves of molecular chains and rings.[13,14] An exciting area of application is to reduce the cost of high-level correlated wave function calculations in solids, particularly for small-band gap systems such as metals. Here, DMET is used to treat a unit-cell (or a small set of them) while the extra bath orbitals ameliorate the finite size effects associated with the small cell. Demonstrations on crystals in 1, 2, and 3 dimensions by Scuseria and co-workers have shown promise.[69] Recent work has focused on extensions of DMET, for example, to spectra,[70] where the additional bath orbitals are modified to carry a time-dependence that reproduces the linear response of a mean-field wave function. This provides a rigorous way to embed excited states, which are often much more delocalized than the ground-state, and thus more sensitive to the open nature of a chemical fragment.

CONCLUSIONS

Quantum embedding is a natural computational framework in which to think about complex systems. We have focused on three embedding approaches based on the single-particle density, Green's function, and density matrix, respectively. While we have only been able to give a short description of these approaches, we have tried to bring out their common intellectual structure.

There remain many frontier methodological areas: for example, excited states and dynamics in density functional embedding and more efficient ab initio technology in Green's function and density matrix embedding. New application areas are emerging, for example, in biomolecular and condensed phase simulations. In some cases, it is necessary to include classical embeddings, such as through QM/MM, as well. While we cannot predict the future development of the field, the growing activity strongly suggests that quantum embedding methods will remain a key part of simulating complex systems for many years to come.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gkc1000@gmail.com.

Notes

The authors declare no competing financial interest.

Biographies

Qiming Sun received his Ph. D. from Peking University. After postdoctoral work at Princeton University, he joined the California Institute of Technology as a staff scientist. He is the principal developer of the PySCF quantum chemistry package.

Garnet Kin-Lic Chan received his Ph. D. from the University of Cambridge, and carried out postdoctoral work as a Junior Research Fellow at Christ's College, Cambridge, and as a Miller Research Fellow at the University of California, Berkeley. After appointments at Cornell University and Princeton University, he joined the California Institute of Technology, where he is currently the Bren Professor of Chemistry.

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