

# Advances in Correlated Electronic Structure Methods for Solids, Surfaces, and Nanostructures

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## Abstract

Calculations of the electronic structure of solids began decades ago, but only recently have solid-state quantum techniques become sufficiently reliable that their application is nearly as routine as quantum chemistry is for molecules. We aim to introduce chemists to the pros and cons of first-principles methods that can provide atomic-scale insight into the properties and chemistry of bulk materials, interfaces, and nanostructures. The techniques we review include the ubiquitous density functional theory (DFT), which is often sufficient, especially for metals; extensions such as DFT +  $U$  and hybrid DFT, which incorporate exact exchange to rid DFT of its spurious self-interactions (critical for some semiconductors and strongly correlated materials); many-body Green's function ( $GW$  and Bethe-Salpeter) methods for excited states; quantum Monte Carlo, in principle an exact theory but for which forces (hence structure optimization and dynamics) are problematic; and embedding theories that locally refine the quantum treatment to improve accuracy.

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**DFT:** density functional theory

**TDDFT:** time-dependent density functional theory

**QMC:** quantum Monte Carlo

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## 1. INTRODUCTION

We are interested in a predictive theory of solids. Although no single theory exists that gives all observables for every material type, the combination of efforts from various disciplines has resulted in a portfolio of methods, each with their respective strengths and weaknesses. In this review, we attempt to summarize some of the currently available methodologies to characterize the electronic structure of solids and related phenomena (e.g., chemisorption). We emphasize the essential approximations that enter into the different approaches and point out their successes and failures.

The discussion begins with density functional theory (DFT) (1–3), which is by far the most widely used tool for the ground-state properties of solids, surfaces, and nanostructures. Much of this popularity is because DFT provides a good balance between simplicity and accuracy. Despite its successes, there are many well-known situations in which DFT is unsuitable, and in this review, we present alternative methods that address some of these deficiencies.

Although information from DFT is often interpreted as approximations to excited states, DFT is formally a ground-state theory. We discuss several routes to excited states that are more firmly grounded in theory. The first is the *GW* method (4–6) for quasiparticle excitations, which are transitions between  $N$ - and  $(N \pm 1)$ -electron states. These directly correspond to excitations probed in photoemission (electron removal) and inverse photoemission (electron addition) experiments. The second class of excited-state methods includes time-dependent DFT (TDDFT) (7) and the Bethe-Salpeter theory (6), which yield neutral particle-hole transitions associated with optical experiments.

DFT also performs poorly in situations involving strong electron correlation effects. The quantum Monte Carlo (QMC) method (8–10) can include electron correlation for periodic systems and can also access individual excited states. In the solid-state community, QMC is largely regarded as essentially exact, although the calculations are rather demanding. As a result, we also comment on less-expensive approaches for strongly correlated electrons, including extensions to DFT such as hybrid functionals and DFT +  $U$  schemes.

Lastly, we discuss embedded cluster models for the solid state, which have a long history in the study of chemisorption. The philosophy behind these models is to subdivide the system into a region of interest described at higher level of theory, whereas the surroundings are accounted for in a more approximate manner. A partitioning of the model into different regions requires a choice for the inter-region coupling. We summarize the most common models, including, e.g., purely electrostatic and DFT-based embedding potentials.

Of course, owing to space limitations, we cannot discuss many other promising avenues of development. These include the dynamical mean field theory to deal with strongly correlated materials (11), recent extensions of traditional quantum chemistry approaches to periodic systems (12–15), and advances in  $O(N)$  electronic structure methods (16), just to name a few.

## 2. DENSITY FUNCTIONAL THEORY

The early foundations of DFT (1–3) are due to Hohenberg and Kohn (17), who established the use of the density  $\rho(\mathbf{r})$  as the basic variable from which all ground state properties, in principle, can be derived. In particular, they showed that there exists a universal energy functional  $E[\rho]$ , whose minimum corresponds to the exact ground-state energy  $E_0$ . Although this represents an enormous simplification of the interacting many-electron problem, unfortunately, the exact functional dependence of  $E[\rho]$  is not known.

Kohn & Sham (18) subsequently devised a practical scheme by mapping the problem of  $N$  interacting electrons in an external potential  $v_{\text{ion}}$  onto a fictitious set of  $N$  noninteracting electrons in an effective potential  $v_s$ . Here, we regard  $v_{\text{ion}}$  as the electron-ion potential provided by the nuclei, although the theory holds for more general external potentials. The noninteracting problem is well-known from Hartree-Fock (HF) theory: The total energy is an explicit functional of the one-electron orbitals  $\psi_j$ , and has the form

$$E[\{\psi_j\}] = T_s[\{\psi_j\}] + J[\rho] + E_{\text{xc}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ion}}(\mathbf{r}), \quad (1)$$

where  $\rho(\mathbf{r}) = \sum_j^{\text{occ}} |\psi_j(\mathbf{r})|^2$  is the density,  $T_s$  is the exact, noninteracting kinetic energy,

$$T_s[\{\psi_j\}] = -\frac{1}{2} \sum_j^{\text{occ}} \langle \psi_j | \nabla^2 | \psi_j \rangle, \quad (2)$$

and  $J$  is the classical Hartree energy,

$$J[\rho] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (3)$$

$E_{\text{xc}}$  is referred to as the exchange-correlation (XC) energy and is defined as containing all remaining quantum effects not captured by  $J$  and  $T_s$ . This quantity is generally unknown; however, useful approximations for  $E_{\text{xc}}$  do exist. The use of an approximate  $E_{\text{xc}}$  represents a major source of uncontrolled errors, for there is no general strategy to systematically improve on  $E_{\text{xc}}$ . The search for high-quality approximations for  $E_{\text{xc}}$  is a subject of ongoing research. Additionally, an active area of research is to forgo orbitals entirely and employ instead an approximate  $T_s[\rho]$  that depends explicitly on  $\rho$ , and employ approximations to both  $T_s[\rho]$  and  $E_{\text{xc}}[\rho]$ . This forms the basis for an orbital-free DFT scheme, which avoids the computational expense of dealing with orbitals (19, 20). Unfortunately, no generally applicable  $T_s[\rho]$  is available; hence orbital-free DFT is still limited in scope.

Minimization of Equation 1 with respect to the orbitals  $\psi_j$  leads to

$$\left\{ -\frac{1}{2} \nabla^2 + v_s[\rho](\mathbf{r}) \right\} \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r}), \quad (4)$$

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**HF:** Hartree-Fock

**XC:** exchange correlation

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**KS:** Kohn-Sham  
**LDA:** local density approximation  
**GGA:** generalized gradient approximation

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where  $\varepsilon_j$  are the orbital eigenvalues, and  $v_s$  is the effective Kohn-Sham (KS) potential,

$$v_s[\rho](\mathbf{r}) = \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{ion}}(\mathbf{r}). \quad (5)$$

The eigenvalue of the highest-occupied KS orbital can be identified with an ionization potential or work function. But beyond this, KS wave functions and eigenvalues are not guaranteed to yield actual one-particle quantities for the real, interacting system, and interpretations based on the explicit use of KS orbitals should be made with caution. It is common to report the DFT energy gap  $\varepsilon_g = \varepsilon_{N+1} - \varepsilon_N$ , where  $\varepsilon_{N+1}$  and  $\varepsilon_N$  are the eigenvalues of the lowest-unoccupied and highest-occupied states obtained from a KS calculation for the  $N$ -electron ground state, respectively. Although Koopmans' theorem provides a physical interpretation for HF eigenvalues as one-electron removal/addition energies, the KS eigenvalues do not correspond to excitation energies of any sort. It can be shown (21–23) that  $\varepsilon_g$  differs from the experimental band gap by the derivative discontinuity  $\Delta$ , which represents the discontinuity of the XC potential with respect to a change in particle number. The presence of  $\Delta$  does not result from a failure of approximate XC functionals, and it remains finite even if the exact XC is known. Little is known about the magnitude of  $\Delta$  in a realistic solid, although it has been suggested that it could constitute a significant portion of the experimental band gap (24). In Sections 3 and 4, we provide an overview of methods to treat excited states in solids that have a firmer theoretical basis than an interpretation of KS eigenvalues.

## 2.1. Local and Semilocal Approximations

By far the most common class of approximate XC employed in solid-state problems is the class based on the local density approximation (LDA) and the generalized gradient approximation (GGA). In the LDA, the XC energy is a local functional of the density and has the form

$$E_{xc}^{\text{LDA}}[\rho_{\uparrow}, \rho_{\downarrow}] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}^{\text{unif.}}[\rho(\mathbf{r}), \zeta(\mathbf{r})], \quad \zeta(\mathbf{r}) = \frac{\rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})}{\rho(\mathbf{r})}, \quad (6)$$

where  $\zeta$  represents the spin polarization density, and  $\varepsilon_{xc}^{\text{unif.}} = \varepsilon_x^{\text{unif.}} + \varepsilon_c^{\text{unif.}}$  is the uniform electron gas correlation energy per particle, consisting of an exchange  $\varepsilon_x^{\text{unif.}}$  and correlation  $\varepsilon_c^{\text{unif.}}$  contribution.  $\varepsilon_x^{\text{unif.}}$  is known in closed form (25), whereas the correlation contribution  $\varepsilon_c^{\text{unif.}}$  is not. The versions of the LDA in common use (26–28) are fit to numerical values of  $\varepsilon_c^{\text{unif.}}$  derived from QMC calculations for the unpolarized ( $\zeta = 0$ ) and fully polarized ( $\zeta = 1$ ) uniform electron gas (29). They differ in the details of the functional forms employed for the fits and in the modeling of the  $\zeta$ -dependence in  $\varepsilon_c^{\text{unif.}}$ . Despite its apparent simplicity, the success of the LDA can be attributed to the fact that it satisfies sum rules for the exact exchange and correlation holes (30–32) and provides a good description of the on-top hole density (33).

The GGA considers slowly varying deviations from the uniform electron gas and is a functional of both the density and its gradient,

$$E_{xc}^{\text{GGA}}[\rho_{\uparrow}, \rho_{\downarrow}, |\nabla \rho_{\uparrow}|, |\nabla \rho_{\downarrow}|] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}^{\text{GGA}}[\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r}), |\nabla \rho_{\uparrow}(\mathbf{r})|, |\nabla \rho_{\downarrow}(\mathbf{r})|]. \quad (7)$$

Although sometimes referred to as nonlocal, the GGA is semilocal in the sense that it depends on both the value of the density and its gradient at  $\mathbf{r}$ . Note that the GGA does not represent a systematic improvement over the LDA, and in some cases it can give worse agreement with experiment. Unfortunately, there is no unique way to specify  $\varepsilon_{xc}^{GGA}$ , so a greater variety of GGA functionals is in common usage compared to the LDA. The Perdew and Wang (PW91) functional (34–36) is constructed to satisfy a number of known limits and bounds and is nonempirical. The related Perdew, Burke, and Ernzerhof (PBE) functional (37, 38) represents a simplification of PW91. Zhang & Yang proposed a revised version of PBE (revPBE) (39, 40) by replacing the value of one parameter in PBE with a different value obtained by fitting to a set of theoretical atomic energies, improving its performance for atoms and molecules. An alternative revision of PBE by Hammer, Hansen, and Nørskov (RPBE) (41) yields results comparable to revPBE but does not involve fit parameters. Benchmark studies indicate that both revPBE and RPBE can provide an improved description of chemisorption compared to PW91 and PBE (41).

There is a great deal of accumulated experience with the LDA and the GGA, and from this a few well-known trends are apparent (2, 35, 36, 42–44). Both the LDA and the GGA give good ground-state structural properties (e.g., lattice parameters) to within a few percent of experiment. The LDA tends to overbind: Lattice parameters are underestimated and bulk moduli are too high. The GGA usually (but not always) improves on the LDA structural properties, with a slight tendency to underbind, although the magnitude of the GGA error is typically not as large as the LDA. Cohesive energies are overestimated in the LDA, and this error can be significant. The GGA usually improves on this. Errors in the cohesive energies can often be traced back to a poor description of the isolated reference atom. Band gaps from the LDA are way too small; for example, the LDA gap for Si is approximately 50% of experiment (45). The GGA does not help. Although association of the DFT band gap with the experimental gap is not justified, underestimation of the gap in semiconductors has unfortunate consequences even for the ground state: The conduction band can overlap with the valence band, incorrectly predicting a metallic ground state (e.g., for Ge) (46).

In the case of only one electron, the KS total energy in Equation 1 should simply reduce to a sum of the noninteracting kinetic energy  $T$ , and the electron-ion energy. That is, the exact  $E_{xc}$  should completely cancel out  $J$  when  $N = 1$ . This is true in HF theory, in which the nonlocal Fock exchange,

$$E_x^{\text{HF}} = -\frac{1}{2} \sum_{i,j}^{\text{occ}} \int d\mathbf{r} d\mathbf{r}' \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (8)$$

takes the place of  $E_{xc}$ . But the local and semilocal functionals in standard usage do not exhibit this exact cancellation; the spurious contribution that remains is referred to as the self-interaction error. This error tends to be more severe for strongly localized densities, e.g., the  $d$ - or  $f$ -electrons in late transition metal oxides, in which the self-interaction error tends to favor electron delocalization, leading to a metallic ground state when the correct ground state should be insulating.

Although not in common use for solids, we also mention the meta-GGAs (42, 47). In addition to the usual GGA inputs, these also require the Laplacian of the density,

$\nabla^2 \rho_\uparrow$ ,  $\nabla^2 \rho_\downarrow$ , and the local kinetic energy density,

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_j^{\text{occ.}} |\nabla \psi_j(\mathbf{r})|^2. \quad (9)$$

## 2.2. Hybrid Functionals

One way to minimize the self-interaction error is to simply add back some amount of Fock exchange. The functionals that do this are known as hybrids, and as with the GGAs, there is no unique way to construct a hybrid functional out of  $E_x^{\text{HF}}$ . Instead, the hybrid functionals popular in molecular applications (e.g., B3LYP) take a more pragmatic approach, by introducing parameters (sometimes many) that typically are fit to thermochemical data to achieve chemical accuracy. The simplest of the hybrid functionals in use for solids is the PBE0 functional (48),

$$E_{\text{xc}}^{\text{PBE0}} = E_{\text{xc}}^{\text{PBE}} + a \left( E_x^{\text{HF}} - E_x^{\text{PBE}} \right) = a E_x^{\text{HF}} + (1-a) E_x^{\text{PBE}} + E_c^{\text{PBE}}, \quad (10)$$

where  $E_x^{\text{PBE}}$  and  $E_c^{\text{PBE}}$  are the exchange and correlation components of the semilocal PBE functional, respectively. A mixing factor of  $a = 1/4$  is argued from theoretical grounds and not derived from fits, although other empirical choices for  $a$  have been explored. Although hybrid functionals can deliver better agreement with experiment compared to the LDA/GGA, evaluation of the nonlocal exchange in periodic solids is more computationally expensive compared to the LDA/GGA. Nevertheless, the use of nonlocal Fock exchange with periodic boundary conditions is now available in a number of electronic structure packages (e.g., GAUSSIAN03, CRYSTAL).

For zero-band-gap systems (metals),  $E_x^{\text{HF}}$  is long-ranged, which presents additional difficulties in its evaluation. This is also the reason why HF theory for metals yields  $\partial \varepsilon(\mathbf{k})/\partial \mathbf{k}$  that diverge logarithmically for states  $\mathbf{k}$  near the Fermi level. It is known that the way to eliminate this divergence is to screen the Coulomb potential  $1/|\mathbf{r} - \mathbf{r}'|$  appearing in the exchange operator. In the Thomas-Fermi theory of screening, this is done by replacing  $1/|\mathbf{r} - \mathbf{r}'|$  in  $E_x^{\text{HF}}$  with  $e^{-k_{\text{TF}}|\mathbf{r} - \mathbf{r}'|}/|\mathbf{r} - \mathbf{r}'|$ , where  $k_{\text{TF}}$  is the Thomas-Fermi screening length. In the many-body Green's function theory, the Coulomb potential appearing in the self-energy operator  $\Sigma$  is screened by the inverse dielectric function  $\varepsilon^{-1}$  (see Section 3). Bylander & Kleinman (49) proposed a hybrid functional that incorporates Thomas-Fermi screening and found band gaps for Si much improved over the LDA. Seidl et al. (50) later argued for the validity of this procedure using a constrained-search formulation of DFT and showed that, in principle, the DFT band gaps derived from such a screened exchange operator can include some amount of the derivative discontinuity  $\Delta$ . More recently, Heyd and coworkers (51, 52) proposed a screened hybrid functional based on PBE0, derived by partitioning the Coulomb operator into short- and long-range contributions, whose relative extents are controlled by an adjustable parameter  $\omega$ .

The performance of hybrid functionals in solids is not as well-established as the LDA/GGA. Probably the most significant improvement provided by the hybrid functionals is in the DFT band gaps. In particular, the narrow-gap semiconductors that are metals in the LDA/GGA are correctly predicted to be semiconductors (50, 53).

Band gaps of large-gap insulators are still underestimated. The performance for metals is not as satisfactory, as cohesive energies are worse than those derived from PBE, and valence bandwidths are too large (54, 55).

### 2.3. The DFT + $U$ Method

Another strategy to deal with the self-interaction error is the DFT +  $U$  method, commonly used to model strongly correlated materials (56). Here an additional ( $U - J$ ) parameter is added to the total DFT energy functional to mimic an effective on-site Coulomb ( $U$ ) and exchange ( $J$ ) between electrons with the same orbital angular momentum. Such an HF-like correction is motivated by the fact that HF theory is free of self-interaction errors. One advantage of DFT +  $U$  over the hybrid functionals described above is that the additional computational expense is minimal, whereas the evaluation of nonlocal Fock exchange in a periodic solid is much more demanding.

Although one can choose the ( $U - J$ ) parameter empirically, a more rigorous approach is to determine ( $U - J$ ) from first principles. One way to do this is via constrained DFT (57), in which the electron occupation on a particular site is held fixed. One can then extract effective  $U$  and  $J$  values from the change in total energy as a function of the number of fixed electrons. Drawbacks are that ( $U - J$ ) is derived from an unphysically constrained situation, and the underlying DFT calculations still suffer from approximate XC problems.

More recently, Mosey & Carter (58) proposed an alternative approach for estimating ( $U - J$ ). They modeled chromia ( $\text{Cr}_2\text{O}_3$ ) as clusters embedded in a classical electrostatic environment (see Section 6.1) and explicitly derived effective  $U$  and  $J$  parameters from unrestricted HF theory, which is strictly self-interaction-free. The resulting parameters were somewhat higher than that obtained from previous constrained DFT estimates, but their subsequent use in a DFT +  $U$  calculation gave results consistent with experiments.

An extension of the DFT +  $U$  method is dynamical mean-field theory (11), which goes beyond the on-site HF description of the correlated electrons. As a result, situations such as metal-insulator transitions can be treated consistently within the same theory. However, dynamical mean-field theory still assumes a Hubbard-Anderson form for the correlation, which ultimately could constrain the resulting physics.

## 3. QUASIPARTICLE EXCITATIONS

In a photoemission experiment, a photon impinges on a solid and ejects an electron. Inverse photoemission is essentially the time reversal of photoemission: An electron is absorbed by a solid, leading to the emission of a photon. The spectra obtained from such experiments correspond to excitations between  $N$ - and  $(N \pm 1)$ -electron states, also known as quasiparticle excitations. We discuss in this section a route to quasiparticle excitations, which is grounded in the theory of many-body Green's functions. The approach is based on the  $GW$  approximation, originally formulated by Hedin (59) in 1965 for the uniform electron gas and later applied to realistic bulk semiconductors in the mid-1980s (24, 60). Today, calculations involving  $GW$  method

are considered routine and can yield accuracy on the order of  $10^{-1}$  eV of experiment for the band structure of bulk semiconductors (4–6).

### 3.1. Basic Theory

In the HF theory for noninteracting electrons, the spectral representation of the one-electron Green's function  $G_0$  has poles that occur at the HF eigenvalues  $\varepsilon_j$ , which, according to Koopmans' theorem, correspond to one-electron removal/addition energies. Thus,  $G_0$  provides a natural way to describe photoemission and inverse photoemission processes. However, the noninteracting Green's function  $G_0$  does not account for orbital relaxation effects; i.e., the electrons of the bulk sample should respond to screen the additional hole or particle added to the system. A proper description of screening needs to take into account many-body effects. For an interacting many-electron system, the one-particle Green's function  $G$  can be related to the noninteracting Green's function  $G_0$  via the Dyson equation,

$$G(\omega) = G_0(\omega) + G_0(\omega)\Sigma(\omega)G(\omega), \quad (11)$$

where  $\Sigma$  is referred to as the self-energy, which encapsulates the complicated effects of XC.

In the presence of interactions, the spectrum associated with  $G$  is no longer guaranteed to be the spectrum of one-electron removal/addition energies associated with  $G_0$ . Nevertheless, if the spectrum can be regarded as a superposition of sharply peaked functions of the energy, it is meaningful to speak of quasiparticle excitations, which are specified by

$$[\hat{T} + v_{\text{ion}}(\mathbf{r}) + v_J(\mathbf{r})]\psi_j^{\text{QP}}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_j^{\text{QP}})\psi_j^{\text{QP}}(\mathbf{r}') = \varepsilon_j^{\text{QP}}\psi_j^{\text{QP}}(\mathbf{r}). \quad (12)$$

Here,  $\psi_j^{\text{QP}}$  and  $\varepsilon_j^{\text{QP}}$  are quasiparticle wave functions and energies, respectively. Note the correspondence with HF theory. The HF exchange potential is now replaced by  $\Sigma$ , which is nonlocal, non-Hermitian, and energy dependent. Consequently, the quasiparticle wave functions are nonorthogonal, and the energies are complex, with lifetimes determined by the imaginary components. In analogy with HF theory, the quasiparticle wave functions can be identified as effective single-particle (hole or electron) wave functions, whereas the quasiparticle energies correspond to energies associated with the removal or addition of an electron.

The basic task is to obtain an approximation for  $\Sigma$ . A practical strategy was provided by Hedin (59), who developed a perturbative expansion for  $\Sigma$  in terms of a dynamically screened interaction  $W(\mathbf{r}, \mathbf{r}'; \omega)$ . Physically,  $W$  represents the potential at  $\mathbf{r}$  due to a test charge at  $\mathbf{r}'$ , taking into account the polarization of the surrounding electrons. For a material with a large polarization, this quantity should be much weaker than the bare Coulomb potential  $1/|\mathbf{r} - \mathbf{r}'|$ , and thus we expect an expansion in  $W$  to behave better than an expansion in  $1/|\mathbf{r} - \mathbf{r}'|$ . The leading term in the expansion of  $\Sigma$  in powers of  $W$  is

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}'; \omega + \omega')W(\mathbf{r}, \mathbf{r}', \omega'). \quad (13)$$

The  $GW$  approximation refers to the use of Equation 13 above for  $\Sigma$  and the neglect of higher-order terms in the expansion (vertex corrections). Here,  $W$  is the bare Coulomb potential screened by the dielectric function  $\varepsilon$ ,

$$W(\mathbf{r}, \mathbf{r}'; \omega) = \int d\mathbf{r}'' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}''; \omega) \frac{1}{|\mathbf{r}' - \mathbf{r}''|}, \quad (14)$$

where  $\varepsilon$  is given by

$$\varepsilon(\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}') - \int d\mathbf{r}'' P(\mathbf{r}'', \mathbf{r}'; \omega) \frac{1}{|\mathbf{r} - \mathbf{r}''|}, \quad (15)$$

and  $P$  is the polarization function. Within the random phase approximation, which describes the mean-field response to the total potential, this is

$$P(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{ij} (f_i - f_j) \frac{\psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{\omega - (\varepsilon_j - \varepsilon_i) + i\eta}, \quad (16)$$

where  $\psi_i$  and  $\varepsilon_i$  are mean-field wave functions and energies, respectively, with occupations  $f_i$ .

### 3.2. Standard Implementation

Many technical issues arise when applying the  $GW$  method to realistic materials. Most  $GW$  band-structure calculations begin with KS-DFT within the LDA for XC. This yields a set of KS wave functions  $\psi_{n\mathbf{k}}$  and energies  $\varepsilon_{n\mathbf{k}}$ , where  $n$  is a band index, and  $\mathbf{k}$  lies in the first Brillouin zone. The quasiparticle equation (Equation 12) becomes

$$\left[ \hat{T} + v_{\text{ion}}(\mathbf{r}) + v_J(\mathbf{r}) + v_{\text{xc}}^{\text{LDA}}(\mathbf{r}) \right] \psi_{n\mathbf{k}}^{\text{QP}}(\mathbf{r}) + \int d\mathbf{r}' \Delta\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_{n\mathbf{k}}^{\text{QP}}) \psi_{n\mathbf{k}}^{\text{QP}}(\mathbf{r}') = \varepsilon_{n\mathbf{k}}^{\text{QP}} \psi_{n\mathbf{k}}^{\text{QP}}(\mathbf{r}), \quad (17)$$

where  $v_{\text{xc}}^{\text{LDA}}$  is the LDA XC potential, which is local and independent of the energy, and

$$\Delta\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_{n\mathbf{k}}^{\text{QP}}) = \Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_{n\mathbf{k}}^{\text{QP}}) - v_{\text{xc}}^{\text{LDA}}(\mathbf{r}). \quad (18)$$

The reason for starting with the LDA is that if  $v_{\text{xc}}^{\text{LDA}}$  is a good approximation for the true XC potential, then the difference  $\Delta\Sigma$  should be small, and the LDA wave functions  $\psi_{n\mathbf{k}}$  are close to the quasiparticle wave functions  $\psi_{n\mathbf{k}}^{\text{QP}}$ . Initial  $GW$  applications to simple, bulk  $sp$ -bonded semiconductors found that the overlap  $\langle \psi_{n\mathbf{k}} | \psi_{n\mathbf{k}}^{\text{QP}} \rangle$  is better than 99% (61). Note that more recent work involving surfaces (62) and finite-sized systems (63–65) does find appreciable differences between the KS and quasiparticle wave functions.

An approximation for the self-energy  $\Sigma$  (Equation 13) is constructed starting with the noninteracting Green's function  $G_0$  and the dynamically screened interaction  $W$  (Equations 14–16), both evaluated using the KS wave functions  $\psi_{n\mathbf{k}}$  and energies  $\varepsilon_{n\mathbf{k}}$ . This is referred to as  $\Sigma = G_0 W_0$ . These quantities are typically evaluated in reciprocal space, although real-space implementations are possible. The most straightforward way to accomplish the frequency-domain convolution for  $\Sigma$  is via a numerical integration over the frequency (24, 66), which requires a time-consuming construction

and inversion of  $\varepsilon(\mathbf{k}, \omega)$  at each value of  $\omega$  in the quadrature. Alternatively, model dielectric functions have been proposed (61, 67, 68) that provide a functional form for the frequency dependence of  $\varepsilon^{-1}(\mathbf{k}, \omega)$  so that the frequency integration can be done analytically. They can work reasonably well for *sp*-bonded materials but are less successful for materials with localized *d*- and *f*-electrons. More recent work evaluates  $W$  and  $\Sigma$  without resorting to model dielectric functions, either by working in the space-time domain (69) or in the wave vector–frequency domain (70–72).

The Dyson equation (Equation 11) relates  $G_0$  to the interacting Green’s function  $G$  via  $\Sigma$ . In principle, starting with an initial  $\Sigma = G_0W_0$ , one should self-consistently solve the Hedin’s equations (59) for the operator quantities  $G$ ,  $\Sigma$ ,  $P$ , and  $W$ . In practice, however, this is not done; most studies stop at  $\Sigma = G_0W_0$  and do not explicitly solve Equation 17. Instead, the quasiparticle energies  $\varepsilon_{n\mathbf{k}}^{\text{QP}}$  are obtained by perturbatively correcting the KS energies  $\varepsilon_{n\mathbf{k}}$  to first order in  $\Delta\Sigma$ , in the basis of the KS wave functions  $\psi_{n\mathbf{k}}$ . Whereas early reports on simple, bulk *sp*-bonded semiconductors indicate that second-order perturbation corrections are small (24), later work showed that the quality of the quasiparticle energies is tied to the quality of the input KS quantities (73, 74).

Although the non-self-consistent  $G_0W_0$  approximation has the obvious advantage of requiring much less numerical effort than a fully self-consistent solution, a non-self-consistent  $G$  leads to a formal violation of some important sum rules (e.g., particle conservation). The role of self-consistency in the  $GW$  method and how it should be imposed are ongoing topics of discussion (75–82). A series of studies (83–86) involving the homogeneous electron gas with non-self-consistent  $G_0W_0$ , partially self-consistent  $GW_0$ , and fully self-consistent  $GW$  found that the description of the quasiparticle spectrum deteriorates with increasing levels of self-consistency. Yet the fully self-consistent  $GW$  yields total energies for the homogeneous electron gas that agree well with QMC results. For the purpose of band-structure calculations, it appears that the non-self-consistent  $G_0W_0$  approximation is preferred.

A second question concerns the validity of the pseudopotential approximation. Most  $GW$  work to date relies on the use of pseudopotentials to represent core electrons, which neglects the core-valence contribution to the self-energy  $\Sigma$ . More recently,  $GW$  has been implemented within the various all-electron schemes: linearized augmented plane wave (LAPW) (66), full-potential linearized augmented plane wave (FLAPW) (78, 87), full-potential linear muffin-tin orbital (LMTO) (74, 88), and projector augmented wave (PAW) (71, 72). Although a number of technical differences exist between the different all-electron methodologies, they do appear to consistently underestimate band gaps relative to pseudopotential-based  $GW$  calculations. While it has been argued that the errors due to the lack of self-consistency cancel the errors due to the neglect of vertex corrections (79), the body of all-electron work suggests that the significance of pseudopotential errors has not been fully appreciated.

#### 4. NEUTRAL EXCITATIONS

Excitations observed in optical spectroscopy and EELS (electron energy loss spectroscopy) do not change particle number and are fundamentally distinct from the

quasiparticle excitations discussed in Section 3. These single neutral excitations can be regarded as a two-(quasi)particle excitation involving a (quasi)electron and a (quasi)hole, which are allowed to interact. This information is contained in the poles of the two-particle Green's function (6), and the equation whose solution corresponds to these poles is known as the Bethe-Salpeter equation (BSE). The BSE is closely related to the linear-response formulation of TDDFT (7, 89–91, 92, 93–95), which is in widespread use for the optical excitations of molecules and finite clusters. A comparison of the BSE and TDDFT has been thoroughly discussed by Onida et al. (6).

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**BSE:** Bethe-Salpeter equation

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The excitonic effects due to the interaction of a particle and hole can be described as a mixing of particle-hole pair states  $\sum_{pb} c_{pb} |pb\rangle$ , where  $|pb\rangle$  is an antisymmetrized product containing a particle in state  $p$  and a hole in state  $b$ . The particle-hole amplitudes  $c_{pb}$  and excitation energies  $E$  are obtained from the BSE, which one can write as an eigenvalue equation (96, 97)

$$\left[ (\varepsilon_p^{\text{QP}} - \varepsilon_b^{\text{QP}}) - E \right] c_{pb} + \sum_{p',b'} K_{pb,p'b'} c_{p'b'} = 0, \quad (19)$$

where  $\varepsilon_p^{\text{QP}}$ ,  $\varepsilon_b^{\text{QP}}$  are quasiparticle energies, and the kernel

$$K_{pb,p'b'} = K_{pb,p'b'}^{\text{Coul.}} + K_{pb,p'b'}^{\text{dir.}} \quad (20)$$

The first term above is the Coulomb (also known as exchange) kernel involving the bare Coulomb interaction,

$$K_{pb,p'b'}^{\text{Coul.}} = 2 \int d\mathbf{r} d\mathbf{r}' \psi_p^*(\mathbf{r}) \psi_b(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_{p'}(\mathbf{r}') \psi_{b'}^*(\mathbf{r}'), \quad (21)$$

and the second term is known as the direct kernel and involves a Coulomb interaction screened by the inverse dielectric function  $\varepsilon^{-1}$  (evaluated at  $\omega = 0$ ),

$$K_{pb,p'b'}^{\text{dir.}} = - \int d\mathbf{r} d\mathbf{r}' \psi_p^*(\mathbf{r}) \psi_b(\mathbf{r}') \varepsilon^{-1}(\mathbf{r}, \mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_{p'}(\mathbf{r}) \psi_{b'}^*(\mathbf{r}'). \quad (22)$$

In practice, the procedure involves (a) a KS-DFT calculation to obtain a set of KS orbitals  $\psi_j$  and eigenvalues  $\varepsilon_j$ ; (b) a *GW* calculation (Section 3) for the quasiparticle energies  $\varepsilon_j^{\text{QP}}$ , using the KS quantities as input; and (c) the solution of Equations 19–22 using  $\varepsilon_j^{\text{QP}}$  from *GW* and  $\psi_j$  from KS-DFT.

The linear-response formulation of TDDFT leads to a set of equations for the excitation energies similar to Equations 19–22 above, except the direct kernel  $K_{pb,p'b'}^{\text{dir.}}$  is replaced by the TDDFT XC kernel

$$K_{pb,p'b'}^{\text{xc}} = - \int d\mathbf{r} d\mathbf{r}' \psi_p^*(\mathbf{r}) \psi_b(\mathbf{r}') \frac{\delta^2 E_{\text{xc}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \psi_{p'}(\mathbf{r}) \psi_{b'}^*(\mathbf{r}'). \quad (23)$$

Due to the local nature of most approximations for  $E_{\text{xc}}$ , the two-electron integral over  $\mathbf{r}$  and  $\mathbf{r}'$  above reduces to a one-electron integral over  $\mathbf{r}$ . The widespread use of TDDFT for molecular and cluster problems largely results from the fact that it requires relatively little effort compared with other excited-state wave function-based methods and it is available in many quantum chemistry packages. However, the application of TDDFT to periodic systems is problematic (6, 91, 93), providing

little improvement over KS energies, and the reasons for this can be traced back to the locality of  $E_{xc}$ . One line of work to overcome these issues with solids is to go to a time-dependent current density functional theory using the functional of Vignale & Kohn (98), in which the current density replaces the density as the central quantity of interest. However, the general applicability of the Vignale-Kohn functional is still under debate (99).

## 5. QUANTUM MONTE CARLO

The QMC method (8–10, 100) is fundamentally different from the other quantum many-body techniques discussed in this review. Here one computes the expectation value of an observable  $\hat{O}$  by stochastically sampling from a distribution function given by the full,  $3N$ -dimensional wave function  $\Psi$ . Unlike other wave function-based methods,  $\Psi$  is not restricted to the usual Slater determinantal form, and thus one can incorporate more efficient ways of describing electron correlation. QMC is a general means of treating electron correlation in periodic crystals, beyond that provided by DFT with current XC functionals, and in some cases, specific excited states can also be accessed. An attractive feature of QMC is that it scales as  $O(N^3)$ , similar to KS-DFT (although the prefactor is considerably larger), and is easily parallelized.  $O(N)$  implementations have also been reported (101, 102). Other methods that include comparable levels of electron correlation effects or treat excited states (e.g., correlated quantum chemistry techniques) typically exhibit far worse scaling and can be difficult to apply to periodic systems. Most successful applications of QMC to the solid state have been for covalently bonded semiconductors and insulators, for example, C and Si nanoclusters and their bulk counterparts (103–108).

Two types of QMC methodologies are in common use for solids. The first is variational Monte Carlo (VMC), which refers to the Monte Carlo optimization of a many-body trial function  $\Psi_T$  and the evaluation of expectation values of an observable  $\hat{O}$  with respect to  $\Psi_T$ . Here, the choice of  $\Psi_T$  is not restricted to forms that are easily integrated, e.g., Slater determinantal wave functions. The only requirement is that we have to be able to evaluate  $\Psi_T$  and the action of  $\hat{H}$  on  $\Psi_T$ . QMC trial functions are usually of the Slater-Jastrow form, in which electron correlation effects are included by multiplying a Slater determinantal function by a factor  $e^J$ , where  $J$  is a Jastrow correlation function.  $J$  consists of a sum of one- and two-electron terms,

$$J(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N t_1(\mathbf{r}_i) + \sum_{i<j}^N t_2(\mathbf{r}_i, \mathbf{r}_j). \quad (24)$$

Details of Slater-Jastrow functions are discussed further in Reference 9. The Slater determinantal part of  $\Psi_T$  is taken from a standard HF or KS-DFT calculation, and the VMC optimization process then varies the parameters in  $\Psi_T$  to minimize some estimator; this can be the energy, the variance of the energy, or some combination of both.

The main utility of VMC is to obtain an optimized  $\Psi_T$  for use in a subsequent fixed-node diffusion Monte Carlo (DMC) calculation. Fixed-node DMC provides

expectation values of the form

$$\langle \hat{O} \rangle = \frac{\langle \Psi_T | \hat{O} | \Psi_0 \rangle}{\langle \Psi_T | \Psi_0 \rangle}, \quad (25)$$

where  $\Psi_0$  is the wave function that minimizes the total energy, subject to the constraint imposed by the nodes of  $\Psi_T$ . If the nodes of  $\Psi_T$  correspond to the nodes of the exact ground state, then  $\Psi_0$  will be the exact ground state, regardless of the details of  $\Psi_T$  away from the nodes. In this case,  $\langle \hat{O} \rangle$  is exact if  $\hat{O}$  is the Hamiltonian  $\hat{H}$  or if  $\hat{O}$  commutes with  $\hat{H}$ . The many-electron wave function has nodes due to fermion antisymmetry, and in general these nodes are complicated and not well understood. Most DMC applications employ a  $\Psi_T$  with an approximate nodal structure, and the use of this is known as the fixed-node approximation. In practice, Slater-Jastrow trial functions provide a reasonable description of the nodal structure, and fixed-node DMC can recover  $\sim 95\%$  of the correlation energy (109). The availability of a high-quality  $\Psi_T$  is critical to the success of DMC in at least two ways: (a) The nodal structure of  $\Psi_T$  determines the accuracy of the fixed-node approximation, and (b)  $\Psi_T$  serves as a guiding function for importance sampling, and thus it controls the efficiency of the algorithm.

A number of implementation issues arise in the application of QMC to solids. First, near the atomic core regions, the wave function is rapidly varying, and thus it is difficult to sample the wave function efficiently and accurately in these regions. Although this can be somewhat ameliorated with the use of pseudopotentials (110), transition metals pose a problem, as the strongly localized *d*- and *f*-electrons have to be treated as valence. To date, only a few QMC studies of solids containing transition metals have been reported, e.g., transition metal oxides (111, 112). Nonlocal pseudopotentials in DMC need to be localized in an approximate manner; this introduces additional complications, which can be minimized by using an accurate trial function (113). Second, QMC with periodic boundary conditions suffers from finite-size effects not seen in mean-field methods such as KS-DFT. Unlike mean-field methods, electrons in QMC are explicitly correlated in real space, and thus the problem cannot be reduced to a single real-space primitive cell via Bloch's theorem. Periodic QMC calculations are done in a large supercell, and steps need to be taken to correct for finite-size errors. Finally, it is difficult to obtain accurate forces, as the QMC Hellmann-Feynman estimator gives an infinite variance. Other attempts at forces include finite differencing, using correlated sampling techniques to reduce the variance (114), and adding Pulay corrections to the Hellmann-Feynman forces (115), to name a few.

## 6. EMBEDDED CLUSTER METHODS

Many solid-state phenomena of interest involve a single, localized inhomogeneity in an extended background (e.g., vacancies, impurities, adsorbates). A natural strategy in this case is to focus the modeling effort in the neighborhood around the inhomogeneity. Typically, this is a small, embedded cluster consisting of the inhomogeneity and some of the nearby atoms, while the effects of the background are incorporated

in a more approximate manner. The difficulty with embedding methods is that they tend to be highly system specific, as there is no unique way to define the cluster-background partitioning and their coupling interaction. The possibility of artifacts due to finite-size effects is always a concern, and computed properties often do not converge smoothly as a function of cluster size and morphology.

Although periodic supercell models are easy to define and converge for supercell sizes up to  $\sim 10^2$  atoms, one can envision cases in which supercell models become impractical and embedded cluster models provide a useful alternative. Moreover, local refinement of the physical model becomes possible in such schemes, e.g., improved descriptions of quantum mechanical effects in a local region.

Bare and embedded cluster models for the solid state have a long history, particularly in the study of adsorbates on surfaces, and many different embedding strategies have been proposed (116–119). Below we review four classes of embedded cluster schemes: purely electrostatic, wave function partitioning, density based, and hybrid quantum/classical force field approaches.

### 6.1. Electrostatic Embedding

Ionic crystals possess relatively localized electron densities, and thus small clusters can provide a reasonable description of local phenomena, provided that the surrounding long-ranged electrostatics are accounted for properly. The simplest embedding models involve a small cluster of ions embedded in a set of point charges (typically several thousand) representing the background. The electronic structure of the embedded cluster is solved using standard, real-space quantum chemistry methods, and thus the point-charge lattice is necessarily finite. Unfortunately, the long-range nature of the Coulomb potential means that the Madelung potential within the cluster converges slowly in real space with respect to the number of point charges. If this is not specified carefully, one can get a Madelung potential that disagrees with standard Ewald summation techniques. The easiest way to define the charges is Evjen's (120) method. For a perfect cubic lattice, formal ionic charges are placed at lattice positions within a large box around the cluster, and fractional charges are assigned to sites at vertices (1/8), edges (1/4), and faces (1/2). More sophisticated procedures employ the Ewald summation to compute the exact Madelung potential at various sampling points throughout the solid and then fit the background charges to these values (121, 122).

The presence of a bare Coulomb potential at sites that are nearest neighbors of the embedded cluster can artificially distort the wave function at the cluster boundary. One can minimize this edge effect by putting an effective core potential at these positions (123) to mimic the Pauli repulsion due to electrons on the nearest-neighbor ions. An extension of this is to embed the cluster in a set of *ab initio* model potentials (AIMPs) (124), in addition to the usual point-charge array representing the Madelung potential. Typically several hundred AIMP sites are included. In short, the AIMP can be viewed as a type of HF effective core potential containing (*a*) long-range and (*b*) short-range Coulombic potentials, (*c*) an exchange potential, and (*d*) a projection operator to enforce core-valence orthogonality.

## 6.2. Orbital Space Partitioning

Orbital space partitioning begins with a mean-field HF or KS-DFT description for the total system and then subsequently partitions the space of one-electron orbitals. The orbitals from an HF or KS-DFT calculation are typically delocalized over the entire system. However, because a single Slater determinant wave function is invariant under a unitary transformation of the orbital basis, the key step is to find an appropriate transformation that localizes a subspace of orbitals on the predefined embedded region, and a complementary subspace on the background. Many ways have been proposed to do this (e.g., 125).

A Green's function formulation of the embedding problem can be traced as far back as the work of Pisani and coworkers (126–130) in the 1970s. These methods begin by first finding a mean-field solution for the total, defect-free system (e.g., the clean substrate, in the case of chemisorption). These orbitals are subsequently transformed into a set localized in the embedded region and a set localized in the background. The Green's function for the total system with the defect is solved in terms of the Green's function of the background, whose matrix elements are assumed to be those from the defect-free system in the basis of localized background orbitals. A related approach for surface problems is the surface Green's function methods (131, 132), which yield a proper description of surface states, unlike models involving periodic slabs of finite thickness. The surface Green's function approaches consider a few surface layers in the presence of a DFT effective potential derived from the bulk solid, whose role is to force the surface wave functions to match the electronic structure of the bulk region.

These Green's function-based approaches all involve a mean-field description of the embedded region and do not easily allow for the explicit introduction of correlated wave functions. To this end, Whitten and coworkers (133) developed an embedded configuration interaction (CI) method. In short, the procedure involves (*a*) finding an HF solution for a large cluster surrounding the defect of interest, (*b*) localizing orbitals in or near a smaller, embedded region within the large cluster, (*c*) constructing effective Coulomb and exchange operators out of these localized orbitals, (*d*) augmenting the basis set within the embedded region, and (*e*) performing a CI calculation using orbitals localized in the embedded region. Thus, the presence of electrons outside the embedded region is accounted for approximately; however, the background environment is taken to be a larger cluster, which may not reflect accurately a true bulk environment.

## 6.3. Density-Based Embedding

Orbital-based embedding schemes that rely on localizing orbitals to span a finite, embedded subregion are difficult to apply to metals because the conduction electrons in a metal are delocalized by nature (134). Alternatively, one can formulate the embedding in terms of the density. The essential idea behind this class of embedding schemes is to begin with a DFT-based description and to model the unknown subsystem-environment interaction with a known, but approximate, density functional.

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CI: configuration interaction

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The development of density-based embedding can be traced as far back as Cortona (135), who sought a reduced-scaling DFT method for the cohesive energies of bulk solids. This work, and much of the subsequent work based on it (136–150), can be understood as a partitioning of the total system density  $\rho_{\text{tot}}$  into an embedded region of interest  $\rho_{\text{I}}$ , and a background  $\rho_{\text{II}}$ , such that  $\rho_{\text{tot}} = \rho_{\text{I}} + \rho_{\text{II}}$ . A KS solution for the embedded region (I) is given by

$$\left\{ -\frac{1}{2}\nabla^2 + v_s[\rho_{\text{I}}](\mathbf{r}) + v_{\text{emb}}[\rho_{\text{tot}}, \rho_{\text{I}}](\mathbf{r}) \right\} \psi_{\text{I},j}(\mathbf{r}) = \varepsilon_j \psi_{\text{I},j}(\mathbf{r}), \quad (26)$$

where  $v_s$  is the usual KS potential for region I, and  $v_{\text{emb}}$  is an effective, one-electron potential representing the embedded region/background coupling and has the form

$$v_{\text{emb}}[\rho_{\text{tot}}, \rho_{\text{I}}](\mathbf{r}) = v_{\text{Is}}[\rho_{\text{tot}}, \rho_{\text{I}}](\mathbf{r}) + v_{\text{J}}[\rho_{\text{tot}}, \rho_{\text{I}}](\mathbf{r}) + v_{\text{xc}}[\rho_{\text{tot}}, \rho_{\text{I}}](\mathbf{r}) + v_{\text{ion}}^{\text{tot}}(\mathbf{r}) - v_{\text{ion}}^{\text{I}}(\mathbf{r}). \quad (27)$$

Here,  $v_{\text{Is}}$ ,  $v_{\text{J}}$ , and  $v_{\text{xc}}$  are the kinetic, Hartree, and XC contributions, respectively:

$$v_{\text{Is}}[\rho_{\text{tot}}, \rho_{\text{I}}](\mathbf{r}) = \frac{\delta T_s[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}(\mathbf{r})} - \frac{\delta T_s[\rho_{\text{I}}]}{\delta \rho_{\text{I}}(\mathbf{r})}, \quad (28)$$

$$v_{\text{J}}[\rho_{\text{tot}}, \rho_{\text{I}}](\mathbf{r}) = \frac{\delta J[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}(\mathbf{r})} - \frac{\delta J[\rho_{\text{I}}]}{\delta \rho_{\text{I}}(\mathbf{r})}, \quad (29)$$

$$v_{\text{xc}}[\rho_{\text{tot}}, \rho_{\text{I}}](\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}(\mathbf{r})} - \frac{\delta E_{\text{xc}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}(\mathbf{r})}. \quad (30)$$

Unlike region I, the kinetic energy contribution to the embedded region/background coupling is modeled with an approximate  $T_s$ , which is an explicit functional of the density. Cortona’s original work employed the Thomas-Fermi model (1) for  $T_s$ , although other approximations can be used as well. Thus, the determination of the density of the total system is recast into a problem involving a smaller region of interest in an embedding potential,  $v_{\text{emb}}$ . The embedding potential is an explicit functional of the total density  $\rho_{\text{tot}}$  and the subsystem density  $\rho_{\text{I}}$ , and is solved for self-consistently.

Wesolowski & Warshel (136) applied a similar density-based embedding to the study of single-molecule solvation. Although the subject of liquid-state simulations is beyond the scope of this review, their methodology is general and relevant to our discussion of the solid state. The total system density  $\rho_{\text{tot}} = \rho_{\text{I}} + \rho_{\text{II}}$  is partitioned into the electron density of the embedded solute,  $\rho_{\text{I}}$ , and the electron density of the surrounding solvent,  $\rho_{\text{II}}$ . The electron density of each solvent molecule is determined individually in advance and frozen at this initial value, and  $\rho_{\text{II}}$  is constructed as the sum over all solvent molecules. Cortona’s approach is followed in an analogous manner, to arrive at a set of KS equations whose structure is identical to Equations 26–30, except now  $\psi_{\text{I},j}$  are the orbitals of the solute molecule, and the subscripts I and tot refer to the solute molecule and the combined solute/solvent system, respectively. More recently, this approach has been extended to include a TDDFT treatment of the embedded solute molecule to evaluate solvent-induced spectral shifts (137). Clearly, the use of a model  $T_s$  is a significant approximation in the theory, and various approximations to  $T_s$ , in the context of atomic and molecular systems have been explored (138).

All the density-based embedding applications described above represent a DFT-in-DFT embedding, in the sense that they begin with a DFT estimate for the background region  $\rho_{\text{II}}$  and solve for the embedded DFT density  $\rho_{\text{I}}$  in the presence of  $\rho_{\text{II}}$ . Carter and coworkers (141–149) developed a related density-based embedding method that includes electron correlation within the embedded region beyond the DFT level to address problems ranging from chemisorption to strongly correlated Kondo physics. The derivation of the working set of embedding equations differs somewhat from Cortona’s approach, although the structure of the resulting embedding potential is the same. Cortona’s derivation involves the functional minimization of the total DFT energy with respect to the set of one-electron orbitals  $\psi_{\text{I},j}$  spanning the embedded region (I). To move beyond a one-electron picture, Carter and coworkers began by writing the total energy functional as

$$E_{\text{tot}}[\rho_{\text{tot}}] = E_{\text{I}}[\rho_{\text{I}}] + E_{\text{II}}[\rho_{\text{II}}] + E_{\text{int}}. \quad (31)$$

$E_{\text{int}}$  is a generally unknown cluster-background interaction and is modeled as

$$E_{\text{int}} \approx E_{\text{tot}}^{\text{DFT}}[\rho_{\text{tot}}] - E_{\text{I}}^{\text{DFT}}[\rho_{\text{I}}] - E_{\text{II}}^{\text{DFT}}[\rho_{\text{II}}], \quad (32)$$

where  $E_i^{\text{DFT}}$  ( $i = \text{tot}, \text{I}, \text{II}$ ) are known, within the context of approximate density functionals,

$$E_i^{\text{DFT}}[\rho_i] = T_s[\rho_i] + E_{\text{xc}}[\rho_i] + J[\rho_i] + \int d\mathbf{r} v_{\text{ion}}^i(\mathbf{r})\rho_i(\mathbf{r}). \quad (33)$$

We emphasize that no approximation is introduced for  $E_{\text{I}}$  and  $E_{\text{II}}$ ; only the cluster-background coupling  $E_{\text{int}}$  is approximated with a model DFT functional. Instead of searching for a mean-field solution that minimizes a DFT total energy, one considers a more general variation with respect to the embedded region density  $\rho_{\text{I}}$ . If the influence of the inhomogeneity is sufficiently contained within the embedded region I, and the background region II is large, it is reasonable to assume that  $\delta E_{\text{II}}[\rho_{\text{II}}]/\delta\rho_{\text{I}} = 0$ . This leads to the Euler equation

$$\frac{\delta E_{\text{tot}}[\rho_{\text{tot}}]}{\delta\rho_{\text{I}}(\mathbf{r})} = \frac{\delta E_{\text{I}}[\rho_{\text{I}}]}{\delta\rho_{\text{I}}(\mathbf{r})} + v_{\text{emb}}[\rho_{\text{I}}, \rho_{\text{tot}}](\mathbf{r}) = \mu, \quad (34)$$

where  $\mu$  is a Lagrange multiplier associated with the constraint  $\int d\mathbf{r} \rho_{\text{I}}(\mathbf{r}) = N_{\text{I}}$ , and  $v_{\text{emb}}$  is an effective embedding potential,

$$v_{\text{emb}}[\rho_{\text{I}}, \rho_{\text{tot}}](\mathbf{r}) = \frac{\delta E_{\text{tot}}^{\text{DFT}}[\rho_{\text{tot}}]}{\rho_{\text{tot}}(\mathbf{r})} - \frac{\delta E_{\text{I}}^{\text{DFT}}[\rho_{\text{I}}]}{\rho_{\text{I}}(\mathbf{r})}. \quad (35)$$

Substituting Equation 33 into  $E_{\text{tot}}$  and  $E_{\text{I}}$  above leads to an embedding potential  $v_{\text{emb}}$  identical to that given by Equations 27–30.

The density  $\rho_{\text{I}}$ , which satisfies Equation 34, equivalently can be found by solving the Schrödinger equation for the embedded cluster,

$$\left\{ \hat{H}_{\text{I}} + \sum_{j=1}^N v_{\text{emb}}[\rho_{\text{I}}, \rho_{\text{tot}}](\mathbf{r}_j) \right\} \Psi_{\text{I}} = E\Psi_{\text{I}}, \quad (36)$$

where  $\hat{H}_{\text{I}}$  is a many-body Hamiltonian involving the ions and electrons of the embedded cluster region, and  $\Psi_{\text{I}}$  is a many-body wave function from which  $\rho_{\text{I}}$  can be

derived. At this point, the stage is set for the application of well-established ab initio methods (e.g., CI) to systematically include electron correlation within the embedded cluster region.

Of the quantities  $\rho_{\text{tot}}$ ,  $\rho_{\text{I}}$ , and  $\rho_{\text{II}}$ , only two are independent, so in principle one should minimize the energy with respect to the two chosen independent variables, subject to the constraint that  $\rho_{\text{tot}} = \rho_{\text{I}} + \rho_{\text{II}}$ . So far this has not been possible in practice, and a number of approximate schemes have been tried. Early efforts (141–145) chose to begin with a  $\rho_{\text{tot}}$  obtained from a periodic KS-DFT calculation. The intention was to then input this  $\rho_{\text{tot}}$  into the embedding potential  $v_{\text{emb}}$  and solve Equation 36 self-consistently for  $\rho_{\text{I}}$ . However, numerical difficulties arose in the self-consistent update of  $v_{\text{emb}}$ , so the kinetic energy contributions  $\delta T_s[\rho_{\text{I}}]/\delta\rho_{\text{I}}$  and  $\delta T_s[\rho_{\text{tot}}]/\delta\rho_{\text{tot}}$  were held fixed at some initial estimates (from bare cluster and periodic DFT densities) and not solved for self-consistently. Later work (146, 147) adopted the strategy taken in the DFT-in-DFT approaches described above, by explicitly constructing an estimate for the background density  $\rho_{\text{II}}$  and then holding this quantity fixed. Equation 36 is then solved self-consistently for  $\rho_{\text{I}}$ , with  $\rho_{\text{tot}}$  evaluated as a sum of the embedded cluster density  $\rho_{\text{I}}$  and the initial estimate for the background density  $\rho_{\text{II}}$ . This led to a much more numerically stable procedure, allowing all terms in  $v_{\text{emb}}$  to be solved self-consistently. Lahav & Klüner (150) also recently reported an implementation of a similar self-consistent embedding scheme.

#### 6.4. Solid-State QM/MM

QM/MM refers to a class of hybrid methods in which an embedded region of interest is treated quantum mechanically (QM), while the background region is described using classical force field models [molecular mechanics (MM)] (151). This is a popular strategy in biomolecular simulations, and an increasing effort has been made over the past decade to apply these ideas to the solid state. The motivation is to allow for the embedded structure to relax while accounting for the mechanical and polarization response of the background, and models that attempt to do this can become quite complex. There are two general issues with which all QM/MM approaches need to cope: (a) how to define the QM/MM boundary and (b) how to deal with the mismatch of forces across the QM and MM regions. The nonuniqueness of the solution to these two problems has spawned a myriad of QM/MM-type methods.

In an ionic or molecular solid, there is a natural separation between ions or molecules, and interatomic interactions are largely dominated by classical electrostatics. Thus, the specification of the QM/MM boundary is relatively straightforward. An important consideration is a proper treatment of long-range polarization effects, which is typically done for ionic materials via shell model potentials for the background ions (152). In the shell model (153), each ion is assigned an effective positive core and a negative shell that are connected via a harmonic potential, and polarization manifests as a redistribution of the effective charges. The AIMP embedding (Section 6.1) has also been combined with shell models in a self-consistent manner (154). More recently, Rösch and coworkers (155) developed an elastic polarizable environment model to study the adsorption of a Pd atom at oxygen vacancies of

MgO(001), in which the background is described with effective core potentials, point charges, shell models, a dielectric continuum, and special short-range potentials designed to handle the embedded cluster/background boundary region.

Covalently bonded materials present additional problems because it is not so obvious how to determine the QM/MM partitioning. One common approach is to choose the QM/MM boundary to cut across covalent bonds, which leaves dangling bonds associated with undercoordinated boundary atoms. These dangling bonds are typically saturated with a fictitious pseudoatom (116), a strategy that follows from early efforts by Goddard and coworkers (156) to study the reactivity of Si surfaces with finite Si cluster models. Examples of this include the studies of Carmer et al. of the reaction of acetylene on the Si(111) surface (157); the QM-Pot method of Sauer & Sierka (158); and the SIMOMM (surface-integrated molecular orbital molecular mechanics) method of Gordon and coworkers (159), which is an extension of the IMOMM method of Maseras & Morokuma (160) to deal with surfaces. Alternatively, there are schemes in which the QM/MM boundary is chosen to pass through atoms, which are split into pseudoatoms common to both the QM and MM regions. Recent examples of this include a study of lattice deformations around a neutral oxygen vacancy in  $\alpha$ -quartz (161) and an extension of the elastic polarizable environment model for ionic solids (see above) to treat covalent solids (162). Effective model atomic potentials have also been proposed to represent boundary atoms (166).

To date, comparatively fewer attempts to apply a QM/MM-type strategy for metals have appeared. The existing ones (163–165) are all based on the density-based embedding scheme discussed in Section 6.3. The background region is modeled with classical EAM (embedded atom method) potentials. The background density  $\rho_{\text{II}}$  is constructed as a superposition of atomic DFT densities computed for the free atom, and Equation 32 is used to define the coupling between the QM and MM regions.

## 7. CONCLUSIONS

As should now be evident, the palette of solid-state electronic structure techniques is richly textured and substantive. We believe this is the sign of a healthy field of science, in which multiple strategies are simultaneously developed to probe the same phenomena or states of matter. Even for formally exact theories such as DFT or QMC, approximations are necessary to render them usable. Because all practical implementations therefore involve some level of approximation, it is our strongly held belief that no one technique should ever dominate to the exclusion of all others. Competing techniques in theory, similar to competing experimental instruments, provide multiple windows on phenomena that will always give a more complete picture in the end.

Of late, DFT has been anointed as the method of choice for the quantum description of molecules and materials. Although often sufficient and even remarkably accurate at times, it is best trusted only as a qualitative indicator because its quantitative accuracy is still (and probably always will be) limited by approximate XC functionals. Moreover, there are cases in which DFT fails completely, even in a qualitative sense. Photochemistry, optical and photoemission spectra, HOMO-LUMO and band gaps,

physisorption (even chemisorption at times), strongly correlated materials, molecular solids, biomolecules, and polymers are all at best poorly described within standard implementations of DFT, even with the most accurate XC functionals available today (GGA, meta-GGA, etc.).

For photochemistry and optical and photoemission spectra, the issue is that DFT is a ground-state theory and these phenomena involve excited states. Therefore, one should employ theories that properly account for electron excitations (embedded CI, TDDFT, *GW*, or BSE). As outlined above, approximations inherent in TDDFT (lack of XC functionals designed for excited states, problems applying it to periodic systems), *GW* and Bethe-Salpeter (choice of self-energy evaluation, self-consistency, and expense), and embedded CI (limited to local excitations, use of an approximate kinetic energy density functional) still limit the impact of these methods somewhat. Clearly, much room exists for improvements to all these methods in terms of algorithmic efficiency as well as breakthroughs to reduce the extent of approximations made.

For HOMO-LUMO and band gaps, chemisorption such as CO on transition metals, and strongly correlated electron materials, the failure of DFT results from the approximate XC functional. Without exact exchange as in HF theory, a single electron interacts with itself in DFT. In HF, this spurious self-Coulomb repulsion is exactly canceled by an exchange energy. Without the exact nonlocal exchange term, however, some self-repulsion remains. As a result, the LUMOs or conduction band minima are artificially too low, and some semiconductors become metals by accident in an attempt to reduce electron repulsion by forming a more delocalized electron distribution. Hybrid functionals that mix in some exact exchange counteract this effect, as does the DFT + *U* and embedded CI methods. Again, it is good for the field to have multiple approaches to probe the same phenomena.

Polymers, biomolecules, molecular solids, and physisorption all are dominated by dispersion forces, which again are not described by ground-state DFT. Dispersion involves induced dipole-induced dipole interactions, which can be thought of as resulting from two simultaneous single-electron excitations. Periodic Møller-Plesset perturbation theory is likely to be one of the methods of choice for such systems, as well as embedded CI calculations, at least for the physisorption case. Progress in *O(N)* QMC algorithms may also provide another excellent option for studying such systems.

As we look to the future, we are enthusiastic that these theories, as well as new ones to come, will continue to evolve in accuracy, efficiency, and generality. In addition, we envision that these approaches will also make connections to higher length scale theories that hunger at the moment for information from the atomic scale. A truly gestalt understanding of solid-state behavior will undoubtedly result.

#### SUMMARY POINTS

1. KS-DFT provides a good qualitative description of ground-state properties for simple metals and covalently bonded materials. Interpretation of KS quantities for excited states should be made with caution.

2. KS-DFT fails for strongly correlated materials (e.g., transition metal oxides) due to the self-interaction error in approximate XC functionals. Methods that incorporate exact exchange (hybrid functionals, LDA +  $U$ , and embedded CI) can alleviate these problems.
3. Excited states are rigorously described within the many-body Green's function formulation. The  $GW$  approximation can provide photoemission/inverse photoemission spectra and solution of the BSE yields optical spectra for insulators, semiconductors, and metals. Both methods yield descriptions of excited states that are significantly improved over a naive interpretation of KS eigenvalue differences.
4. Correlation effects beyond DFT, as well as excited states, can be achieved with QMC. However, QMC calculations are demanding, and the availability of a good trial function is critical. Most solid-state applications of QMC have been restricted to simple, covalently bonded materials. To date, a few results for transition metal oxides have been reported, and little to no results have been reported for metallic crystals.
5. Embedding models are a highly versatile strategy for the description of localized phenomena, and they allow for a local refinement of theory in the embedded region of interest. They can grow to be complex, however, and special care must be taken to ensure that results are free of model bias.

## DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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