First-Principles Calculations of Quasiparticle Excitations of Open-Shell Condensed Matter Systems

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We develop a Green's function approach to quasiparticle excitations of open-shell systems within the *GW* approximation. It is shown that accurate calculations of the characteristic multiplet structure require a precise knowledge of the self-energy and, in particular, its poles. We achieve this by constructing the self-energy from appropriately chosen mean-field theories on a fine frequency grid. We apply our method to a two-site Hubbard model, several molecules, and the negatively charged nitrogen-vacancy defect in diamond and obtain good agreement with experiment and other high-level theories.

Introduction.—In nature, there exists a wide range of electronic systems with open shells, including most atoms and many molecules, but also defects in crystalline solids. These systems play important roles in many areas of condensed matter physics, chemistry, and biology; for example, the negatively charged nitrogen-vacancy (NV^-) defects in diamond are used for biological imaging [1,2] and are also promising candidates for qubits in quantum computers [3–5].

It is therefore important to develop theoretical methods to study open-shell systems and their properties. While for closed-shell systems a well-established set of methods exists, ranging from wave function–based quantum chemistry approaches to density-functional theory (DFT) and Green's function based many-body perturbation theory, the accuracy of these methods when applied to open-shell systems is less certain: even the application of wave function–based methods to small open-shell molecules is far from straightforward [6], and standard density functionals are known to break the orbital and spin degeneracy of the ground state [7,8].

A Green's function approach to electron excitations in open-shell molecules was first considered by Cederbaum and co-workers [9,10] in the 1970s. Later, highly accurate Green's function approaches were developed for quantum chemistry applications including open-shell systems [11–15]. Previous applications of Green's function theory to open-shell systems using the *GW* approximation [16,17] had either carefully selected reference states to avoid complications associated with the open-shell [18] or ignored the degenerate ground-state problem [19,20].

In this Letter, we extend the *GW* approach to open-shell systems. Calculations on several prototypical systems are performed: a two-site Hubbard cluster, four molecules (nitrogen dioxide, oxygen, nitrogen difluoride, chlorine dioxide), and the NV^- center in diamond. We find our approach is capable of describing these systems with quantitative accuracy. We have identified and implemented two important elements for accurate results in *GW* calculations of open-shell systems: (i) a careful choice of the mean-field starting point providing accurate self-energy pole positions and (ii) a method for evaluating the self energy on a fine frequency grid.

Theory.—In a photoemission experiment with photons of energy ω_{photon} (setting $\hbar = 1$), the photocurrent $J(\epsilon_k)$ due to photoelectrons with momentum k and energy ϵ_k is given by [21]

$$J(\epsilon_k) = \sum_{ij} \Delta_{ki}\Delta_{jk}A_{ij}(\epsilon_k - \omega_{\text{photon}}), \quad (1)$$

where $\Delta_{ki} = \langle k|\Delta_{\text{dipole}}|\psi_i\rangle$ and $A_{ij}(\omega) = \langle \psi_i|A(r, r', \omega)|\psi_j\rangle$ denote matrix elements of the dipole operator and the spectral function, respectively, with ψ_i being an appropriate single-particle orbital. Neglecting off-diagonal matrix elements for an appropriately chosen physical set of orbitals, we obtain $A_{jj}(\omega) = 1/\pi|\text{Im}G_{jj}(\omega)|$ by computing the interacting Green's function (here we give the electron removal part)

$$G_{jj}(\omega) = \sum_{\lambda} \frac{|\langle N-1, \lambda|c_j|N, 0\rangle|^2}{\omega - E_\lambda - i\eta} \quad (2)$$

with $E_\lambda = E_0^{(N)} - E_\lambda^{(N-1)}$. Here, $|N, 0\rangle$ and $E_0^{(N)}$ denote the N-particle ground state and its energy, respectively, while $|N-1, \lambda\rangle$ denotes an $(N-1)$-particle state (with λ being an appropriate set of quantum numbers) with energy $E_\lambda^{(N-1)}$. Also, c_j is the destruction operator for an electron in orbital j and $\eta = 0^+$.

E_λ solves the quasiparticle equation

$$E_\lambda = \epsilon_j + \Sigma_{jj}(E_\lambda) - V_{jj}^{xc}, \quad (3)$$

where ϵ_j and V_{jj}^{xc} denote the orbital energy and a diagonal matrix element of the exchange-correlation potential from a mean-field calculation, respectively, while $\Sigma_{jj}(\omega)$ is a diagonal matrix element of the self-energy operator.

The quasiparticle equation [Eq. (3)] follows from Dyson's equation [22]

$$G_{ij}^{-1}(\omega) = G_{0,ij}^{-1}(\omega) - \Sigma_{ij}(\omega) + V_{ij}^{xc}, \qquad (4)$$

which relates the interacting Green's function to the mean-field Green's function $G_{0,ij}(\omega)$ via the self-energy. The standard derivation of Dyson's equation [22] assumes the existence a nondegenerate interacting ground state which evolves into a nondegenerate single Slater determinant state as the interactions are adiabatically turned off. The hallmark of open-shell systems, however, is the existence of multiple degenerate ground states which do not generally evolve into noninteracting single Slater determinant states [23]. If—for a particular ground state—the resulting noninteracting state is a sum of Slater determinants, one has to employ the methods of quantum field theory with initial correlations and replace Dyson's equation with a more complicated expression [23,24]. In our calculations, we avoid this difficulty by carefully choosing a ground state (among the multiple ground states) which evolves into a single Slater determinant such that Dyson's equation is valid. As shown in Ref. [10], the Green's function computed from such a specific ground state provides information on *all* the quasiparticle multiplet levels of the $N-1$ and $N+1$ system in an ensemble averaged measurement. In particular, we work with the ground state with the highest magnetic quantum number because there exists a corresponding single Slater determinant with the same properties (i.e., it is also an eigenstate of the total spin and/or orbital angular momentum operator with the same eigenvalue) [10]. An approximation to this particular ground state is provided by standard spin-polarized mean-field calculations. We note that it is not always possible to find a single determinant ground state. However, such a state must exist whenever Hund's rules apply, indicating a broad range of validity of our approach including many systems containing d and f electrons.

In closed-shell systems, Eq. (3) typically has a single solution leading to a pronounced quasiparticle peak in $A_{jj}(\omega)$ which corresponds to the removal of an electron from orbital j [25]. In open-shell systems, the orbital and spin angular momenta of the electrons in the unfilled shells can couple in various ways resulting in *multiple* low-energy eigenstates of the $(N-1)$-particle system. The coupling of angular momenta generally produces eigenstates which are sums of multiple Slater determinants [26]. As a consequence, multiple eigenstates of the $(N-1)$-particle system can make significant contributions to $G_{jj}(\omega)$ if their matrix element in the numerator of Eq. (2) is large. $G_{jj}(\omega)$ then has multiple poles, and we expect to find multiple solutions to Eq. (3) [9,10].

If $G_{jj}(\omega)$ has multiple poles, Eq. (4) shows that the self-energy $\Sigma_{jj}(\omega)$ must also have poles occurring *between* the poles of $G_{jj}(\omega)$. The occurrence of poles in $\Sigma_{jj}(\omega)$ near E_λ is a particular feature of open-shell systems and a direct

consequence of the electronic multiplet structure. We note that multiple solutions of Dyson's equation can also occur in closed-shell systems where the extra solution results from the coupling of electrons to plasmons [17].

In actual calculations for open-shell systems, a precise knowledge of the *frequency dependence* of the self-energy is necessary to locate its poles and obtain accurate multiplet splittings. In contrast, for closed-shell systems it is usually sufficient to employ a simple linear expression for the frequency dependence of the self-energy in the vicinity of the quasiparticle energy [25].

In this Letter, we employ the GW approximation to the self-energy following the first-principles method of Hybertsen and Louie [25]. To obtain $\Sigma_{jj}(\omega)$ at many frequencies, we make use of a specific form of the evaluation of the frequency dependence of the dielectric response and self-energy as proposed in Refs. [18,27]. In this approach, $\Sigma_{jj}(\omega)$ is separated into a frequency-independent bare exchange part $\Sigma_{jj}^{(x)}$ and a frequency-dependent correlation part $\Sigma_{jj}^{(c)}(\omega)$ given by

$$\Sigma_{jj}^{(c)}(\omega) = \sum_{nI} \frac{|V_{jnI}|^2}{\omega - \epsilon_n - \Omega_I \mathrm{sgn}(\epsilon_n - \mu)}, \qquad (5)$$

where μ denotes the chemical potential, and Ω_I is a neutral excitation energy of the N-particle system obtained by solving Casida's equation in the random-phase approximation [27]. Also, V_{jnI} denotes a Coulomb matrix element between the product $\psi_j^* \psi_n$ and the fluctuation charge density ρ_I [27] [see Supplemental Material [28] for details on the approach].

Equation (5) shows that the poles of $\Sigma_{jj}(\omega)$ are determined by the mean-field electron removal (or addition) energies ϵ_n, which are the poles of G_0, and by the neutral excitation energies Ω_I, which are the poles of the screened interaction W_0 in the random-phase approximation. Both ϵ_n and Ω_I depend on the mean-field theory used to compute G_0 and W_0, implying an analogous dependence on the choice of the mean-field starting point for the poles of $\Sigma_{jj}(\omega)$.

In principle, the self-energy should be computed from the interacting Green's function G, whose poles are at E_λ, and the exact screened interaction W [25]. For closed-shell systems, it is possible to carry out self-consistent GW_0 calculations where the self-energy is recomputed using the iterated Green's functions such that Σ becomes independent of the mean-field starting point [25]. For open-shell systems, self-consistent calculations are more difficult because of the more complicated structure of G and additional problems to be discussed below. To obtain accurate self-energy pole positions we instead carefully choose mean-field theories that yield ϵ_n and Ω_I which are good approximations to E_λ and the poles of the exact W, respectively. In general, one finds that the poles of W_0 obtained from standard density-functional calculations are

good approximations to neutral excitation energies. In contrast, the poles of G_0 obtained from density-functional theory often differ from the exact removal or addition energies (i.e., the quasiparticle energies) by several electron volts. Such an error in the poles of G_0 leads to a similar-sized error in the self-energy pole locations and to a large error in the multiplet splittings. To obtain the best G_0, we construct it from mean-field calculations using the static Coulomb-hole plus screened-exchange approximation (COHSEX) [16,25].

In addition, if the result of a calculation depends on a particular self-energy pole we carry out partially self-consistent calculations where we only update the particular ϵ_n in Eq. (5) which determines the position of the self-energy pole under consideration.

Molecules.—First, we study the quasiparticle multiplet structure of four small molecules for which accurate experimental data are available.

Nitrogen dioxide (NO_2) has a doublet ground state. We first carry out DFT calculations [29,30] at the experimental geometry [31] using the spin-polarized local-density approximation (LDA) exchange-correlation functional, norm-conserving pseudopotentials, a plane-wave basis (50 Ry cutoff), and a cubic supercell with linear dimension of 10.6 Å.

For the construction of W_0, we use wave functions and energies from the DFT calculation. We use 300 empty states and a 15 Ry momentum space cutoff for the dielectric response. For G_0, we use wave functions and energies from a static COHSEX calculation. Table I shows that the COHSEX single-particle energies are much closer to the experimental ionization potentials than the DFT energies, but the multiplet structure is still missing in this calculation. For the calculation of the self-energy matrix element, we use 300 empty states and a modified static remainder correction [32,33] which extends the sum over n in Eq. (5) to all empty states and greatly improves convergence. This choice of parameters results in multiplet splittings converged to within ~0.1 eV.

TABLE I. Comparison of calculated ionization potentials for NO_2 with experiment [31]. Note that the third and fourth rows correspond to the same orbital but different many-body states because the up-spin quasiparticle equation exhibits multiple solutions. The second and third rows correspond to the same many-body state but different orbitals because both up-spin and down-spin quasiparticle equations contain a triplet solution. All energies are given in eV.

Orbital	LDA	COHSEX	$G_{LDA}W_{LDA}$	GW	Expt.	State
$6a_1(\uparrow)$	−6.6	−12.0	−10.7	−11.2	−11.2	$^1A_1$
$4b_2(\downarrow)$	−8.7	−14.1	−12.5	−12.8	−13.0	$^3B_2$
$4b_2(\uparrow)$	−9.3	−14.9	−10.5	−13.6	−13.0	$^3B_2$
$4b_2(\uparrow)$	−9.3	−14.9	−13.4	−15.4	−14.5	$^1B_2$

Figure 1(a) shows the self-energy and spectral function for the removal of a *down-spin* electron from the $4b_2$ orbital [see inset in Fig. 1(a)]. We do not expect any multiplet structure for this process because the up-spin hole can only couple to the up-spin electron in the $6a_1$ orbital to give a triplet state. Indeed, the spectral function exhibits a single peak corresponding to the triplet ($^3B_2$) state.

Figure 1(b) shows results for the removal of an *up-spin* electron from the $4b_2$ orbital. The down-spin hole can now couple to the up-spin electron in the $6a_1$ orbital to yield either a singlet ($^1B_2$) or a triplet ($^3B_2$) state. Indeed, we find two solutions of Eq. (3) resulting in two poles of the Green's function and two peaks in the spectral function with a singlet-triplet splitting of 1.8 eV, which compares favorably with the experimental splitting of 1.5 eV (Table I). In contrast, the singlet-triplet splitting from $G_{LDA}W_{LDA}$ is 2.9 eV, highlighting the importance of an accurate mean-field starting point. To make sure that the two solutions are indeed multiplet states, we traced back the low lying self-energy pole to open-shell features in G_0 and W_0, namely, to the pole in G_0 due to the unpaired up-spin $6a_1$ state and the pole in W_0 due to the $4b_{2\downarrow} \rightarrow 6a_{1\downarrow}$
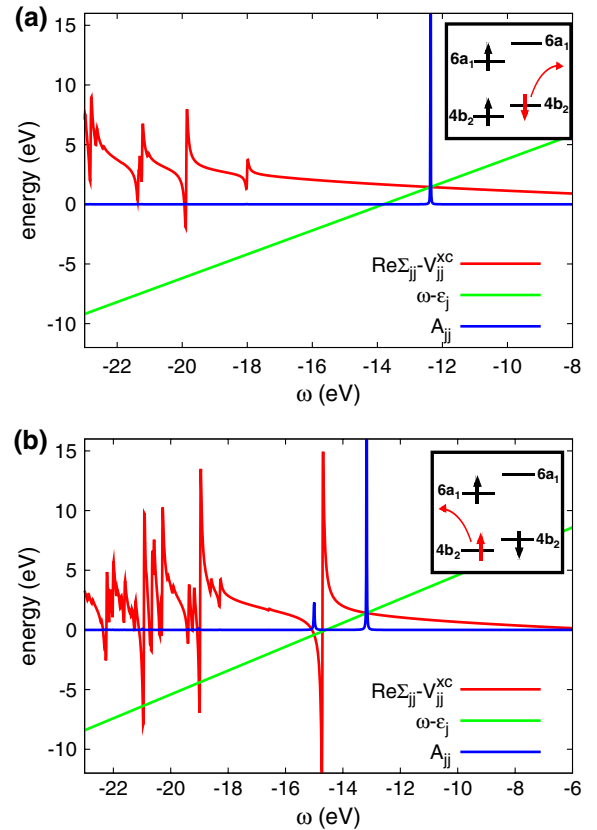

FIG. 1 (color online). Self-energy $\Sigma_{jj}(\omega)$ and spectral function $A_{jj}(\omega)$ for (a) the removal of a down-spin electron from the $j = 4b_2$ orbital in NO_2 and (b) the removal of an up-spin electron from the $j = 4b_2$ orbital. A Lorentzian broadening of 20 meV is used for each curve.

transition between the two open shells. Hund's rule suggests that the lower energy solution is the triplet state: an exact diagonalization analysis in the subspace consisting of the $6a_1$ and the $4b_2$ orbitals shows that the singlet is higher in energy than the triplet solution by $2J$ with J being the positive exchange integral.

Inspection of Table I shows that we obtain *two* values for the energy of the triplet state $^3B_2$: one from the removal of an up-spin electron from the $4b_2$ orbital and one from the removal of a down-spin electron from the same orbital. These values differ by 0.8 eV and bracket the experimental result. There are two factors which contribute to this discrepancy: (i) remaining errors in the positions of the self-energy poles which contaminate only solutions of the up-spin quasiparticle equation and (ii) missing vertex corrections which contaminate solutions of the up- and down-spin quasiparticle equations in different amounts [34]. We expect that the inclusion of vertex corrections will reduce the difference. Nevertheless, as shown above, accurate multiplet splittings can be extracted from our calculations if the energy differences are calculated from solutions of the quasiparticle equation for a *particular spin direction* because errors due to missing vertex correction cancel.

The ratio of the areas under the singlet and the triplet peaks in Fig. 1(b) should be the experimentally observed ratio of ensemble-averaged photoemission intensities, the so-called multiplet ratio [10,35]. We find in our calculations that the multiplet ratios are much more sensitive to the positions of the self-energy poles than the multiplet splittings. We do not expect that these ratios can be computed reliably with our current *GW* approach because of the remaining uncertainties in the self-energy pole locations. However, Schirmer and co-workers found a relatively simple analytical procedure for calculating these ratios based on the addition of angular momenta [35]. We expect that the combination of their approach for the multiplet ratios and the *GW* approach for the multiplet splittings offers a reliable and complete description of the multiplet structure of open-shell systems.

We also investigated the multiplet structure of the oxygen (O_2), nitrogen difluoride (NF_2), and the chlorine dioxide (ClO_2) molecules. The *GW* multiplet splittings are 2.4 eV for O_2, 2.3 eV for NF_2, and 2.5 eV for ClO_2. They compare favorably with experimental splittings: 2.3 eV for O_2, 1.8 eV for NF_2, and 2.4 eV for ClO_2 [36–38]. However, splittings obtained from $G_{LDA}W_{LDA}$ can deviate from experimental findings by *several* electron volts (see Supplemental Material [28]).

We also applied our method to a two-site Hubbard model with three electrons, finding good agreement for multiplet splitting between the exact diagonalization result and the *GW* theory over a large range of the interaction parameter (see Supplemental Material [28]).

NV⁻ center.—Next, we apply our approach to the NV⁻ center in diamond, which has a triplet ground state. This
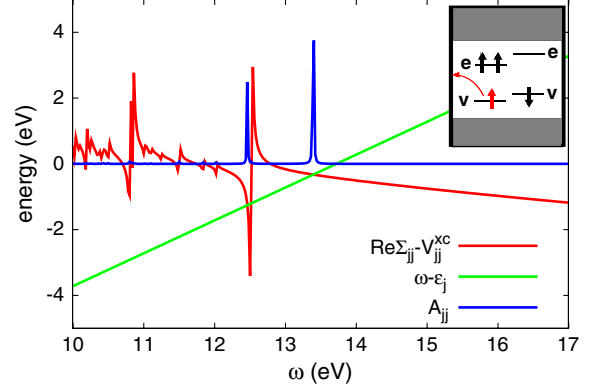

FIG. 2 (color online). Self-energy $\Sigma_{jj}(\omega)$ and spectral function $A_{jj}(\omega)$ for the removal of an up-spin electron from the $j = \nu$ defect orbital of an NV⁻¹ center in diamond. A Lorentzian broadening of 5 meV is used for each curve.

defect currently attracts much attention because of its extraordinary properties, such as long coherence times and potential application to quantum computing [3–5].

Figure 2 shows results for the removal of an up-spin electron from the ν defect level in the band gap of diamond (see Supplemental Material for computational details [28]). As in the NO_2 calculation, the self-energy exhibits a low-lying pole leading to two solutions of the quasiparticle equation. To understand which many-body states these solutions correspond to, we compare our findings to the results of the exact diagonalization of the extended Hubbard model of Choi, Jain, and Louie [39] (see Supplemental Material [28]). These authors fit the parameters of an extended Hubbard model for the defect levels to *ab initio* static COHSEX results and show that this model describes accurately neutral excitations. The model predicts four many-body states Ψ_λ for the $\nu^1 e^2$ configuration. However, only two of the four states, namely, $^4A_2$ and $^2A_2$, are observed in our calculations because by symmetry only these states have a nonvanishing matrix element $\langle \Psi_\lambda | c_{\nu\uparrow} | \nu_\uparrow \nu_\downarrow e_{x\uparrow} e_{y\uparrow} \rangle$ with the ground state. Table II shows that our *GW* multiplet splittings agree well with the results of the exact diagonalization of the extended Hubbard model. Note that the $^4A_2$-$^2A_2$ splitting in Fig. 2 corresponds to the last row in Table II. The first row in Table II shows the splitting between the ^2E state (obtained by removing an up-spin electron from the e defect orbital) and the $^2A_2$

TABLE II. Comparison of the calculated multiplet splittings for the NV⁻ defect in diamond with results from exact diagonalization calculations on the extended Hubbard model [39]. All energies are given in eV.

Splitting	GW	Extended Hubbard model
$E_{(^2E)} - E_{(^2A_2)}$	2.0	1.8
$E_{(^4A_2)} - E_{(^2A_2)}$	0.9	0.9

state. Again, our findings agree well with the result from the exact diagonalization of the extended Hubbard model.

Future work is needed to investigate the performance of the open-shell GW method for systems with more complicated multiplet structures, such as systems containing d and f electrons, where additional low-energy solutions of Casida's equation can give rise to multiple poles of the self-energy.

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