First-principles calculations of the electronic structure of open-shell condensed matter systems

Johannes Lischner, Jack Deslippe, Manish Jain, Steven G. Louie

Department of Physics, University of California, Berkeley,
California 94720, USA, and Materials Sciences Division,
Lawrence Berkeley National Laboratory, Berkeley 94720, USA.

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 almost all areas of 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 system was first considered by Cederbaum and coworkers [9, 10] in the 1970's. These authors only applied the formalism to toy problems with few orbitals and employed approximations to the self energy which are not feasible for large systems, such as open-shell defects. Other previous applications of Green's function theory to open-shell systems using the GW approximation had either carefully selected reference states to avoid complications associated with the open-shell [11] or ignored the degenerate ground-state problem [12, 13].

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 $J(\epsilon_{\boldsymbol{k}})$ due to photoelectrons with momentum $\boldsymbol{k}$ and energy $\epsilon_{\boldsymbol{k}}$ is given by [14]

$$J(\epsilon_{\boldsymbol{k}}) = \sum_{ij} \Delta_{\boldsymbol{k}i} \Delta_{j\boldsymbol{k}} A_{ij}(\epsilon_{\boldsymbol{k}} - \omega_{\text{photon}}), \qquad (1)$$

where $\Delta_{\boldsymbol{k}i} = \langle \boldsymbol{k}|\Delta_{\text{dipole}}|\psi_i\rangle$ and $A_{ij}(\omega) = \langle\psi_i|A(\boldsymbol{r},\boldsymbol{r}',\omega)|\psi_j\rangle$ 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)

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

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

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

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 [15]

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

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 [15] 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 [16]. 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 [16, 17]. In our calculations, we avoid this difficulty by carefully choosing a ground state which evolves into a single Slater determinant such that Dyson's equation is valid. 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.

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 [18]. 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 and the $(N-1)$-particle system. The coupling of angular momenta generally produces eigenstates which are sums of *multiple* Slater determinants [19]. 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 of Eq. (3). This important connection between the poles of the self energy and the multiplet structure of open-shell systems was first established by Cederbaum and coworkers [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.

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 [18].

In this work, we employ the GW approximation to the self energy following the first-principles method of Hybertsen and Louie [18]. 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. [20] and [11]. 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

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

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 [20]. Also, V_{jnI} denotes a Coulomb matrix element between the product $\psi_j^* \psi_n$ and the fluctuation charge density ρ_I [20] (see Supplementary Material 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 [18]. 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 [21]. 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 COHSEX approximation [22, 23].

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 partic-

ular ϵ_n in Eq. (5) which determines the position of the self-energy pole under consideration.

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

Nitrogen dioxide (NO_2) has a doublet ground state. We first carry out DFT calculations [24, 25] at the experimental geometry [26] using the spin-polarized LDA exchange-correlation functional, norm-conserving pseudopotentials, a plane-wave basis (50 Ry cutoff) and a cubic supercell with linear dimension of 10.6 $\mathring{A}$.

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 [27, 28] 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.

Figure 1(a) shows the self energy and spectral function for the removal of a *down-spin* electron from the $4b_2$ orbital [see insert 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 $4b_{2\downarrow} \rightarrow 6b_{1\downarrow}$ transition between the two open shells. Hund's rule suggests that the lower energy solution is the triplet state.

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, one from the removal of a *down-spin* electron from the same orbital. These values differ by 0.8 eV and bracket the ex-

TABLE I: Comparison of our results for NO_2 with experiment [26]. All energies are given in eV.

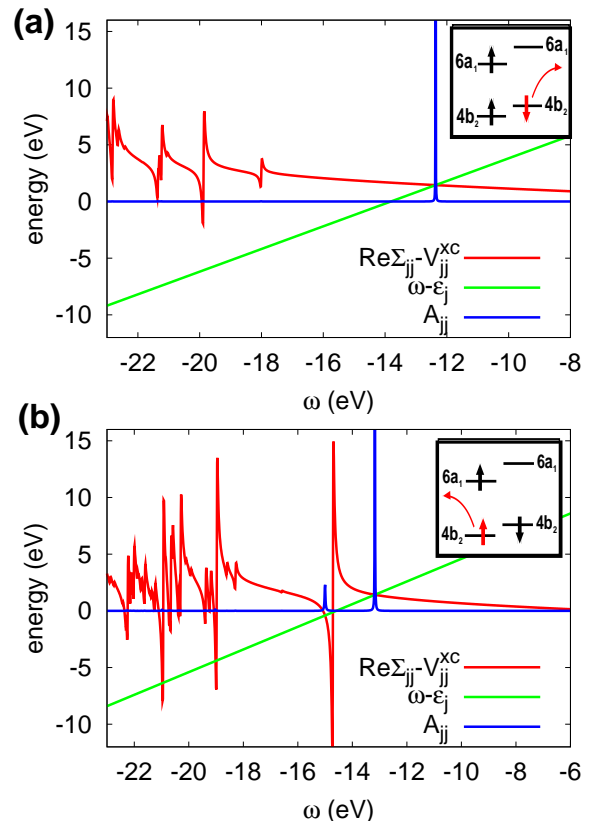| orbital	DFT	COHSEX	$G_{LDA}W_{LDA}$	GW	exp.	state
$6a_1(\uparrow)$	-6.6	-12.0	-10.7	-11.2	-11.2	$^1A_1$
$4b_2(\downarrow)$	-8.7	-14.1	-12.5	-12.8	-13.0	$^3B_2$
$4b_2(\uparrow)$	-9.3	-14.9	-10.5	-13.6	-13.0	$^3B_2$
$4b_2(\uparrow)$	-9.3	-14.9	-13.4	-15.4	-14.5	$^1B_2$

FIG. 1: 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.

perimental 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 [29]. 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*.

The ratio of the areas under the singlet and the triplet peaks in Fig. 1(b) should be the experimentally observed

TABLE II: Comparison of our results for O_2, NF_2 and ClO_2 with experiment [31–33]. All energies are given in eV.

	orbital	state	$G_{LDA}W_{LDA}$	GW	exp.
O_2	$1\pi_g$	$^2\Pi_g$	12.1	12.4	12.3
O_2	$3\sigma_g$	$^4\Sigma_g^-$	15.4	19.2	18.4
O_2	$3\sigma_g$	$^2\Sigma_g^-$	19.5	21.6	20.7
NF_2	$2b_1$	$^1A_1$	11.6	12.0	12.1
NF_2	$6a_1$	$^3B_1$	11.9	15.0	14.6
NF_2	$6a_1$	$^1B_1$	14.7	17.3	16.4
ClO_2	$3b_1$	$^1A_1$	10.2	10.6	10.5
ClO_2	$1a_2$	$^3B_1$	10.5	13.3	13.0
ClO_2	$1a_2$	$^1B_1$	13.5	15.8	15.4

ratio of photoemission intensities, the so-called multiplet ratio [30]. 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 coworkers found a relatively simple analytical procedure for calculating these ratios based on the addition of angular momenta [30]. 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.

Table II shows our results for 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 [31–33]. However, splittings obtained from $G_{LDA}W_{LDA}$ can deviate from experimental findings by several electron volts.

Hubbard cluster.— To further establish the accuracy of our method, we apply it to an analytically solvable model system: a two-site Hubbard cluster containing three electrons with a Hilbert space spanned by four spin-orbitals. We denote the hopping parameter t and the on-site interaction U. This system has a doublet ground state. We compute the mean-field wavefunctions and energies using the spin-polarized Hartree-Fock method and then evaluate the self energy corresponding to the removal of an up-spin electron from the doubly occupied bonding orbital. We find two solutions of the quasiparticle equation due to the occurence of a pole in the self energy: their separation is $1.1U$ for $U/t < 1$ where we expect the GW approximation to give accurate results.

In this model system, analytical evaluation of the Hamiltonian for the three and two particle systems allows for the calculation of the exact many-body Green's function which agrees well with the GW result: it has two poles corresponding to a singlet and a triplet state
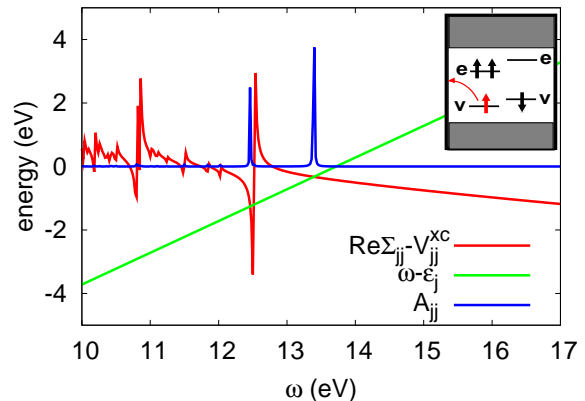

FIG. 2: Self energy $\Sigma_{jj}(\omega)$ and spectral function $A_{jj}(\omega)$ for the removal of an up-spin electron from the $j = \nu$ orbital. A Lorentzian broadening of 5 meV is used for each curve.

TABLE III: Comparison of the calculated multiplet splittings for the NV^- defect in diamond with results from exact diagonalization calculations on the extended Hubbard model[35]. All energies are given in eV.

splitting	GW	Ref. [35]
$E_{(^2E)} - E_{(^2A_2)}$	2.0	1.8
$E_{(^4A_2)} - E_{(^2A_2)}$	0.9	0.9

of the two particle system separated by U.

NV^- center.— Next, we apply our approach to the NV^- center in diamond which has a triplet ground state. This defect complex currently attracts much attention because of its extraordinary properties, such as long coherence times and potential application to quantum computing [3–5].

Again, we carry out DFT calculations as described in the previous sections. We employ a 64-atom supercell and relax all ionic positions. As a test, we first carry out GW calculations with a generalized plasmon pole model [34] and find good agreement with the similarly calculated results of Ma and Rohlfing [12], who use a 256-atom supercell, for the energy differences of the defect levels in the gap. This indicates that our supercell size is sufficient to extract accurate multiplet splittings for the defect levels using the current method.

For the NV^- center we find that the DFT orbital energies are much closer to the static COHSEX results than in NO_2, and we can use the DFT energies and wave functions both for the construction of W_0 and G_0. We use 300 empty orbitals and a 12 Ry momentum space cutoff for W_0 and 300 empty orbitals in conjunction with a modified remainder correction for the self-energy matrix elements. This choice of parameters results in multiplet splittings converged to within ~ 0.1 eV.

Figure 2 shows results for the removal of an *up-spin* electron from the ν level. 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 results to exact diagonalization calculations of the extended Hubbard model of Choi, Jain and Louie[35]. 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 non-vanishing matrix element $\langle \Psi_\lambda | c_{\nu\uparrow} | \nu_\uparrow \nu_\downarrow e_{x\uparrow} e_{y\uparrow} \rangle$ with the ground state. Table III shows that we obtain good agreement with the extended Hubbard model results for the multiplet splittings. Note that the $^4A_2$-$^2A_2$ splitting in Fig. 2 corresponds to the last row in Table III. The first row in Table III shows the splitting between the ^2E state obtained by removing an up-spin electron from the e defect orbital and the $^2A_2$ state. Again, we find good agreement with the extended Hubbard model results.

[1] P. C. Maurer, J. R. Maze, P. L. Stanwix, L. Jiang, A. V. Gorshov, A. A. Zibrov, B. Harke, J. S. Hodges, A. S. Zibrov, A. Yacoby, et al., Nature Physics **6**, 912 (2010).

[2] C.-C. Fu, H.-Y. Lee, K. Chen, T.-S. Lim, H.-Y. Wo, P.-K. Lin, P.-K. Wei, P.-H. Tsao, H.-C. Chang, and W. Fann, Proc. Natl. Acad. Sci. USA **104**, 727 (2007).

[3] P. Neumann, J. Beck, M. Steiner, F. Rempp, H. Fedder, P. R. Hemmer, J. Wrachtrup, and F. Jelezko, Science **329**, 542 (2010).

[4] G. de Lange, Z. H. Wang, D. Risté, V. V. Dobrovitski, and R. Hanson, Science **330**, 60 (2010).

[5] B. B. Buckley, G. D. Fuchs, L. C. Bassett, and D. D. Awschalom, Science **330**, 1212 (2010).

[6] J. F. Stanton and J. Gauss, Adv. Chem. Phys. **125**, 101 (2003).

[7] A. Savin, in *Recent Developments and Applications of Modern Density Functional Theory,* edited by J. M. Seminario, Theoretical and Computational Chemistry Vol. 4 (Elsevier Science, Amsterdam, 1996).

[8] H. A. Fertig and W. Kohn, Phys. Rev. A **62**, 052511 (2000).

[9] L. S. Cederbaum and W. Domcke, Adv. Chem. Phys. **36**, 207 (1977).

[10] L. S. Cederbaum and J. Schirmer, Z. Physik **271**, 221 (1974).

[11] E. Shirley and R. Martin, Phys. Rev. B **47**, 15404 (1992).

[12] Y. Ma, M. Rohlfing, and A. Gali, Phys. Rev. B **81**, 041204(R) (2010).

[13] C. Attaccalite, M. Bockstedte, A. Marini, A. Rubio, and L. Wirtz, Phys. Rev. B **83**, 144115 (2011).

[14] L. Hedin, J. Phys. Condens. Matter **11**, R489 (1999).

[15] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[16] C. Brouder, G. Panati, and G. Stoltz, Phys. Rev. Lett. **103**, 230401 (2009).

[17] A. G. Hall, J. Phys. A **8**, 214 (1975).

[18] M. Hybersten and S. Louie, Phys. Rev. B **34**, 5390 (1986).

[19] C. Cohen-Tannoudji, B. Diu, and F. Laloe, *Quantum Mechanics* (Hermann, Paris, France, 1977).

[20] M. Tiago and J. Chelikowsky, Phys. Rev. B **73**, 205334 (2006).

[21] M. Shishkin and G. Kresse, Phys. Rev. B **75**, 235102 (2007).

[22] J. Deslippe, M. Jain, G. Samsonidze, and S. G. Louie, to be published (????).

[23] F. Bruneval, N. Vast, and L. Reining, Phys. Rev. B **74**, 045102 (2006).

[24] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[25] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[26] O. Edquist, E. Lindholm, L. E. Selin, L. Asbrink, C. E. Kuyatt, S. R. Mulczarek, J. A. Simpson, and I. Fischer-Hjalmars, Phys. Scr. **1**, 172 (1970).

[27] J. Deslippe, M. Jain, G. Samsonidze, and S. G. Louie, to be published (????).

[28] W. Kang and M. S. Hybertsen, Phys. Rev. B **82**, 195108 (2010).

[29] E. L. Shirley, *Ph.D. thesis* (University of Illinois at Urbana-Champaign, 1991).

[30] J. Schirmer, L. S. Cederbaum, and J. Kiessling, Phys. Rev. A **22**, 2696 (1980).

[31] J. A. R. Samson, J. L. Gardner, and G. N. Haddad, J. Electron. Spectrosc. **12**, 281 (1977).

[32] C. R. Bundle and A. D. Baker, *Electron Spectroscopy: Theory, Techniques and Applications* (Academic, London, 1979).

[33] R. Fleisch, E. Ruhl, K. Hottmann, and H. Baumgartel, J. Phys. C **97**, 837 (1993).

[34] J. Deslippe, D. Strubbe, M. Jain, G. Samsonidze, and S. G. Louie, to be published (????).

[35] S. Choi, M. Jain, and S. G. Louie, to be published (????).