On the accuracy of the HSE hybrid functional to describe many-electron interactions and charge localization in semiconductors

Mauricio A. Flores, Walter Orellana, and Eduardo Menéndez-Proupin

1 Facultad de Ingeniería y Tecnología, Universidad San Sebastián, Bellavista 7, Santiago, 8420524, Chile.
2 Departamento de Ciencias Físicas, Universidad Andrés Bello, Sazié 2212, Santiago, 0370136, Chile.
3 Departamento de Física, Facultad de Ciencias, Universidad de Chile, Las Palmeras 3425, Núñoa, Santiago, 7800003, Chile.

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Hybrid functionals, which mix a fraction of Hartree-Fock exchange with local or semilocal exchange, have become increasingly popular in quantum chemistry and computational materials science. Here, we assess the accuracy of the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional to describe many-electron interactions and charge localization in semiconductors. We perform diffusion quantum Monte Carlo (DMC) calculations to obtain the accurate ground-state spin density of the negatively charged (SiV)$^-$ and the neutral (SiV)$^0$ silicon-vacancy center in diamond, and of the cubic silicon carbide (3C-SiC) with an extra electron. We compare our DMC results with those obtained with the HSE functional, showing that the latter is unable to describe many-electron interactions beyond the mean-field approximation in systems with moderate correlation, such as (SiV)$^-$. Also, we examine the case of the neutral Cd vacancy in CdTe, for which we assess the performance of HSE against the many-body GW approximation for the description of the position of the defect states in the band gap.

I. INTRODUCTION

Density functional theory (DFT)\textsuperscript{1,2} has become the leading method for electronic structure calculations in materials science, quantum chemistry, and condensed-matter physics.\textsuperscript{3,4} The DFT formalism shows that ground state properties of a many-electron system can be determined from the knowledge of the electron density distribution alone, thereby avoiding the computation of massively complex many-dimensional wave functions. The ground state density is described by a single determinant with all many-body effects included in one term, the exchange-correlation functional. Unfortunately, the exact functional is unknown and it is necessary the use of practical approximations.

Extensive research efforts have been dedicated to obtain better approximations to the exact exchange-correlation functional. Earlier approximations were the local density approximation (LDA),\textsuperscript{5} which considers the exchange and correlation interaction as obtained from a homogeneous electron gas, and the generalized gradient approximation (GGA),\textsuperscript{6,7} which adds gradient terms to the LDA approach. Both approximations are computationally efficient and give reasonable results for ground state properties of molecules and solids, however, they have limitations that hinder their predictive power. They do not property account for the long-range dispersion forces in van der Waals systems,\textsuperscript{8,9} underestimate the energy barriers of chemical reactions, give erroneous dissociation energies of diatomic radicals,\textsuperscript{10} and severely underestimate the band-gap in semiconductors and insulators.\textsuperscript{11} Better approximations can achieved by including additional information to the energy density. In this way, meta-GGAs\textsuperscript{12,13} incorporate the second-order gradient of the density, giving accurate results when the system is near mechanical equilibrium, but still failing when bonds are stretched, as nonlocality dominates.\textsuperscript{14} Hybrid-GGAs\textsuperscript{15,16} include nonlocality information by mixing a fraction of Hartree-Fock exchange with local or semilocal exchange. They improve the description of the energy band gap in semiconductors and insulators, but the results critically depend on amount of Hartree-Fock exchange included in the functional. Although some studies have shown that hybrid functionals such as the Heyd-Scuseria-Ernzerhof (HSE)\textsuperscript{16,17} yield good accuracy for defect energy levels in solids,\textsuperscript{18,19} other calculations revealed serious discrepancies when they are compared with more accurate methods such as diffusion quantum Monte Carlo (DMC).\textsuperscript{20–22} More recently, double-hybrids GGAs have been proposed.\textsuperscript{23–26} In addition of a fraction of Hartree-Fock exchange, they include a fraction of second order Møller-Plesset (MP2) correlation the random phase approximation (RPA).

Recently, Medvedev and co-workers\textsuperscript{27} pointed out that DFT is straying from the path toward the exact functional, which should give “the right answer for the right reason.”\textsuperscript{28,29} They shown that modern highly parameterized functionals have improved the energies while not always improving the electron densities. Here, we investigate the performance of the HSE hybrid functional to describe many-electron interactions and charge localization in semiconductors beyond that of pristine bulk materials. We present a comparison of electron densities calculated using the increasingly popular HSE functional with those obtained with the accurate wave function based DMC method.\textsuperscript{30–32} We assess the accuracy of HSE for the description of defective diamond and cubic silicon carbide (3C-SiC) with an extra electron. Additionally, we compare the performance of HSE with the many-body GW approximation\textsuperscript{33,34} for the description of the position of localized defect levels introduced in defective CdTe. In the latter case, we find that the two approaches differ
qualitatively in determining the position of the antibonding orbital introduced by the neutral Cd vacancy with respect to the conduction band edge, irrespectively of the amount of Hartree-Fock exchange included in the hybrid functional.

\[ \text{e}_g \quad \text{e}_u \quad \text{a}_{2u} \quad \text{a}_{1g} \]

**FIG. 1.** On the left, a schematic diagram of the electronic structure. On the right, the electron spin density ($\rho = 20\%$ of the maximum) of the negatively charged silicon-vacancy center in diamond obtained by HSE and DMC calculations.

II. METHODS

A. Computational Details

We performed density functional calculations using the optimized norm-conserving pseudopotential library generated by Hamann, in a plane-wave basis set with an energy cutoff of 80 Ry. We used the HSE hybrid functional with the standard exchange and screening parameters, as implemented in the QUANTUM-ESPRESSO code.

Our DMC calculations were performed using the CASINO code. We used trial wave functions ($\Psi_T$) of the Slater-Jastrow type:

\[ (\Psi_T) = \text{det} \{ \psi_T \} \text{det} \{ \psi_\uparrow \} e^J, \tag{1} \]

where the determinants are composed of single particle orbitals obtained from spin-unrestricted DFT calculations performed using the QUANTUM-ESPRESSO code package. We used Trail and Needs norm-conserving pseudopotentials with a plane-wave energy cutoff of $\sim 4081.71$ eV ($= 150$ Ha). Electron terms, electron-nucleus terms, and electron-electron-nucleus terms were included in the Jastrow correlation factor ($e^J$), whose parameters were optimized through variance minimization of the local energy at the variational Monte Carlo (VMC) level. The calculations were performed using 64-atom supercells for diamond and 3C-SiC, at the R-point only. In the latter case, the trial wave function was generated from the a spin-polarized DFT-PBE calculation. We used a DMC time step $\tau$ of 0.01 a.u. and a target population of 5048 walkers, which resulted in an acceptance ratio grater than 96%. To reduce the bias due to pseudopotential localization, we used the T-move scheme proposed by Casula. Additionally, to establish the difference among the methods under study, we also calculate the dissociation curve of H$_2$ by placing the molecule in a cubic supercell of side 18 Å.

For the Cd vacancy in CdTe, we performed many-body $G_0W_0$ calculations using the ABINIT simulation code. The calculations were performed in 64-atom supercells, using a $2 \times 2 \times 2$ k-point mesh to obtain a converged DFT charge density that was then used as a starting point for a subsequent COHSEX (Coulomb-Hole Screened Exchange) $G_0W_0$ calculation at the $\Gamma$-point only. We used 3200 bands and a 20 Ry energy cutoff to represent the dielectric matrix, in which the plasmon-pole model of Hybertsen and Louie was used to approximate its frequency dependence. To accelerate the convergence with respect to the number of empty states, we applied the extrapolation approximation of Bruneval and Gonze.

III. RESULTS AND DISCUSSION

A. Many-electron interactions in the silicon-vacancy center in diamond

**FIG. 2.** On the left, a schematic diagram of the electronic structure. On the right, the electron spin density ($\rho = 20\%$ of the maximum) of the silicon-vacancy center in diamond in the neutral charge state obtained by HSE and DMC calculations.

Defects in diamond have been proposed as promising candidates to realize single photon sources with applications in quantum cryptography, magnetic field sensing, and quantum optics. In particular, the negatively charged silicon-vacancy center (SiV)$^-$ has attracted considerable interest due to its exceptional optical properties. The (SiV)$^-$ has a split-vacancy configuration wherein the Si atom adopts a position equidistant from two carbon vacancies. This configuration has $D_3d$ symmetry and six carbon dangling bonds, which combine into $a_{1g}, a_{2u}, e_u,$ and $e_g$ defect orbitals. Eleven electrons fill these orbitals: six electrons are provided by the dangling bonds, four $sp^3$ electrons are donated by the Si impurity and one additional electron is captured by the defect center, leading to the $a_{1g}^2a_{2u}^2e_u^6e_g^3$ open-shell electronic configuration. As the $e_g$ state is partially filled, the (SiV)$^-$ should, in principle, undergo a Jahn-Teller distortion to a lower symmetry point group. However,
photoluminescent emission (PL) and excitation (PLE) experiments, as well as Zeeman studies suggest that the defect center keeps the $D_{3d}$ symmetry. The origin remains unclear, but it has been suggested that the $e_g$ state in $D_{3d}$ symmetry may be split by a dynamic Jahn-Teller effect.

One way to assess the accuracy of the HSE hybrid functional for the description of many-electron interactions is by computing the spin-density and compare the results with more accurate DMC calculations. In DMC, the dependence of the many-electron wave function on electron-electron separations is taken into account by including an optimized Jastrow correlation factor. The schematic representation of the electronic structure of (SiV)$^0$, based on a simple molecular orbital model, is shown in Figure 1. There are three electrons in the $e_g$ level, leaving a single hole with $e$ symmetry and a many-body state with $^2E$ total spin symmetry. Figure 1 also shows the spin-density obtained by HSE and DMC calculations. Interestingly, both methods give a qualitative different result that we attribute to the different treatment of electron-electron interactions. A deviation from the mean-field electron density of DFT is a characteristic of correlated systems, in which the wave function strongly depends on the electron-electron separations.

It is also suitable to investigate the silicon-vacancy in the neutral charge state (SiV)$^0$. The (SiV)$^0$ complex has a $a_1^2g_2^0e_g^4e_g^2$ electronic configuration, which according to the Hund’s rule, results in a $S=1$ ground-state electron spin configuration. The schematic representation of the electronic structure as well as a comparison between the spin-density obtained by HSE and DMC calculations are shown in Figure 2. In contrast to (SiV)$^-$, we observe a qualitative agreement between HSE and DMC. Although the HSE spin-density is slightly over localized as compared with the DMC result, in both cases the distribution has its maxima equally centered on the six carbon dangling bonds.

To analyze why HSE gives a good approximation for (SiV)$^0$ but fails in the case of (SiV)$^-$, we first discuss about how many-electron interactions are treated in Kohn-Sham density functional theory and within the DMC approximation. In the case of electrons with parallel spins, the antisymmetry requirement of the wave function fulfills the Pauli exclusion principle and keeps electrons apart, introducing the so-called Fermi hole. However, the Pauli exclusion principle exerts only a small influence in electrons of opposite spin and thus Coulomb interactions should be explicitly taken into account. Therefore, we should note that correlation errors mainly affect the description of electrons having opposite spins. In DFT, electron interactions are approximated by a mean-field potential and the many-body wave function is represented by a single Slater determinant composed of single-particle orbitals. This is a good approximation for systems of slowly varying density, but is insufficient for situations of degeneracy or near degeneracy, or when electron correlations depend on the shape of the ground-state vacant orbitals or excited-state orbitals. In these cases, the system is poorly described by a single Slater determinant. On the other hand, in DMC the effect of short-range correlations is accounted by a Jastrow correlation factor, which reduces the amplitude of the wave function when electrons are close to each other, thereby making the wave function explicitly dependent on the position.

The difference between the two approximations can be clearly seen in the stretched H$_2$ molecule, the simplest case of a strongly correlated system, where the true (interacting) ground state is a singlet. Figure 3 shows the calculated dissociation curve of H$_2$ obtained within the DFT approximation (employing both PBE and HSE exchange-correlation functionals) and with the DMC method. According to the mean-field approximation of DFT, the probability of finding both electrons in the same atom is always 1/2, regardless of the bond
length. This is a good approximation when the atoms are near their equilibrium bond length (∼1.4 bohr), but it fails in the dissociation limit where each H atom has a half spin-up electron and a half spin-down electron.

The reason behind the good accuracy of HSE in the description of (SiV) might be explained by the fact that in this case there are two electrons with parallel spins occupying the e_g orbital. Furthermore, it was demonstrated that this many-body state can always be represented by a single Slater determinant. In contrast, the (SiV)^− center has two electrons of opposite spins occupying the e_g orbital. Thus, the electron correlation error would be significantly higher in this case and the mean-field approximation seems to be inaccurate.

**B. Small polarons in 3C-SiC**

It was recently pointed out that the inclusion of a fraction of Hartree-Fock interaction in hybrid functionals may introduce a spurious exchange splitting between occupied and unoccupied states. In spin-polarized calculations, this effect could lead to unusually large magnetic moments, wrong magnetic ground-states, and a slow convergence of the total energy of the system with respect to the supercell size.

In the following, we investigate the effects of the inclusion of Hartree-Fock interaction in the HSE functional by considering the negatively charged 3C-SiC. The excess electron may: (1) self-localize by coupling to a lattice distortion, forming a polaron, or (b) retain its free-carrier character. For TiO_2, Janotti et al. found that the solution crucially depends on the fraction of the Hartree-Fock exchange included in the exchange-correlation functional.

We performed spin-polarized calculations to determine the ground state of the negatively charged 3C-SiC system. We added an extra electron to the conduction band and then allowed the system to relax. Our calculations were performed in a 64-atom supercell, using the HSE functional (α = 25%) for structural relaxations. In Figure 4, we compare the spin-density of the system obtained by HSE and DMC calculations. We observe that both approximations give qualitative different results. According to HSE, the negatively charged 3C-SiC is an electride-like compound, which is characterized by charge localization at interstitial regions; on the other hand, DMC predicts the formation of a small polaron. The HSE wave function has large magnetic moments on the Si atoms near the local maxima of the spin-density and exhibits negative values on the nearby C atoms. We found that the unusual HSE result is due to a finite size effect, a direct consequence of the long-range nature of the Hartree-Fock exchange that converges extremely slowly with respect to the supercell size. If we decrease the fraction of the Hartree-Fock exchange to 10% or use a fine k-point mesh, we find that the spin-density is in close agreement with the DMC result. Therefore, we strongly recommend the use of large simulation cells and a careful choice of the screening parameter (μ) which defines the extent of the Hartree-Fock exchange in real space.

**C. Localized defect levels in the band gap**

In the simulation of point defects in semiconductors and insulators, a correct description of the band gap as well as the absolute position of the band edges is of critical importance. The severe underestimation of the band gap in standard DFT has lead to large discrepancies and conflicting results among theoretical calculations. Hybrid functionals can give reliable band gaps for most semiconductors when an optimum system-
dependent fraction of Hartree-Fock exchange energy is used. Moreover, it is commonly assumed that they can give a reliable description of defects states, although the use of the same parameters to describe orbitals with a distinct degree of localization seems questionable. In the following, we assess the accuracy of the HSE functional in the not uncommon case when a localized defect state merges with one of the band edges of the host. We consider the Cd vacancy in CdTe, which is among the most important native defects.

The Cd vacancy in CdTe has been extensively investigated both theoretically and experimentally, still several aspects remain unclear. In the neutral charge state, the Cd vacancy undergoes a structural distortion from $T_d$ to $C_{2v}$ symmetry. The situation is similar to the well-known AX distortion, where two Te atoms move toward each other to form a new bond. The net result is the loss of one bond (as each Te atom breaks one bond with a Cd atom) and the creation of an empty anti-bonding orbital. At DFT-PBE level, this anti-bonding state is strongly hybridized with the conduction-band minimum (CBM), as shown in Figure 5. However, this effect is likely to be an artifact of DFT due the fact that the CdTe band gap is too small such that the anti-bonding level erroneously lies above the CBM at the $\Gamma$ point. This can be seen by considering the isoelectronic case of the neutral Zn vacancy in ZnTe, where the anti-bonding state appears isolated in the gap.

In Figure 5, we compare the DFT-PBE band structure and the squared wave function corresponding to the anti-bonding level (labeled as A) of the neutral cation vacancy in CdTe and ZnTe. In contrast to CdTe, in the latter case the unoccupied anti-bonding level lies isolated in the band gap of the host, as the CBM is higher in energy. To accurately obtain the position of this anti-bonding level introduced by the Cd vacancy in CdTe, we performed many-body GW calculations that can give accurate band structures of solids. We used DFT-PBE wave functions as a starting point for a subsequent COHSEX+$G_0W_0$ perturbative calculation. We performed the calculations in a 64-atom supercell, using the ABINIT code. We found that the unoccupied anti-bonding state lies in the upper half of the band gap, below the CBM.

Taking the $G_0W_0$ result as a reference, the natural question arise: is the HSE hybrid functional able to correctly describe the position of the anti-bonding orbital associated with the neutral Cd vacancy in CdTe? According to our results, the HSE functional opens the band gap, however, it keeps the PBE result by placing the anti-bonding orbital above the CBM. A similar behaviour was previously reported for ZnO:Co, where DFT results are incorrect for optical absorption and the Co $d-d$ splitting is overestimated in the order of 300% when the fraction of Hartree-Fock exchange corresponds to the one necessary to reproduce the experimental band gap of ZnO. Another example is the carbon vacancy in 3C-SiC, where the position of the localized defect state erroneously appears above the CBM.

The failure of the HSE to describe the position of the anti-bonding orbital in the neutral Cd vacancy in CdTe is an example of the drawback of the uniform treatment of electronic states with distinct degrees of localization. Fortunately, this issue may be corrected through the addition of empirical nonlocal external potentials or by using the orbital dependent exact exchange extension of hybrid functionals proposed by Ivády et al.

IV. SUMMARY

We have investigated the accuracy of the HSE hybrid-exchange-correlation functional to describe three systems, which represent different levels of complexity: the negatively charged and the neutral silicon-vacancy center in diamond, 3C-SiC with an extra electron, and the neutral Cd vacancy in CdTe.

In contrast to that commonly assumed, our results show that the HSE functional is unable to describe many-electron interactions in systems with moderate correlation, such as the negatively charged silicon-vacancy center in diamond. Moreover, the application of the HSE functional to systems with different degrees of localization shows systematic errors: (1) Due to the slow convergence of the Hartree-Fock exchange with respect to the supercell size, HSE could predict an incorrect ground state for the negatively charged 3C-SiC. (2) When localized defect states artificially merge with delocalized (Bloch-like) conduction-band states at DFT-PBE level, as in the case of the neutral Cd vacancy in CdTe, HSE corrects the band gap but keeps the spurious hybridization given by PBE, predicting an incorrect position of the localized level with respect to the CBM.

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* mflores@next-solar.net

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