

## Quantum Monte Carlo calculations of the energy-level alignment at hybrid interfaces: Role of many-body effects

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An approach is presented for obtaining a highly accurate description of the energy-level alignment at hybrid interfaces, using quantum Monte Carlo calculations to include many-body effects as a correction to the standard single-particle picture. For a representative interface between an organic molecule and an inorganic slab, we illustrate the crucial role of many-body effects for correctly describing the energy-level alignment, leading to qualitatively different optoelectronic properties from the prediction within the single-particle description. Further, the heterojunction behavior as a function of quantum confinement in the slab is predicted to be qualitatively different upon inclusion of many-body effects.

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Understanding organic-inorganic interface properties at the molecular level is of critical importance for fostering advances in a range of fields from organic optoelectronics to molecular electronics. In particular, the electronic energy-level alignment (energetic offsets of occupied and unoccupied states at the interface) is a fundamental property for designing interfaces with desirable optoelectronic behaviors. Although considerable progress has been made experimentally,<sup>1–8</sup> accurate characterization of interfacial properties remains a formidable challenge due to the difficulty in measuring properties across a single junction at the atomistic scale. This challenge makes theory an indispensable tool for understanding and predicting interfacial optoelectronic properties.

Density functional theory (DFT) has become a leading method for investigating ground-state properties of materials due to its balance between accuracy and applicability. However, it is well known that DFT within most exchange-correlation (XC) approximations underestimates the band gap severely due to an insufficient description of many-body effects for describing the excited *quasiparticle* (QP) states. Although DFT often provides single-particle Kohn-Sham (KS) states that are quite similar to the QP states, the energies of these states differ considerably from the QP energies within the true many-body description.<sup>9</sup> For many semiconductor interfaces,<sup>10</sup> DFT has predicted fairly accurate band offsets due to error cancellation on both sides of the interface.<sup>11,12</sup> However, a hybrid structure composed of two distinct materials, such as the organic-inorganic interface, poses a much greater challenge for DFT and traditional mean-field methods in general because of the dissimilar electronic environment across the interface.

To overcome the shortcoming of DFT, many-body perturbation theory within the *GW* approximation<sup>9,13</sup> has been employed and shown to correct the single-particle eigenvalues, with band gaps comparable to experiment. Recently *GW* calculations have also been successfully applied to compute the band offsets at semiconductor-insulator interfaces<sup>14</sup> and the energy-level alignment at organic-inorganic interfaces.<sup>15</sup> However, the application of the *GW* calculations is somewhat limited by its scaling ( $N^{4-5}$  where  $N$  is the number of electrons in the system), and also different levels of approxi-

mation in the self-energy appear to make rather substantial differences.<sup>14</sup> Computationally less demanding approaches based on DFT using hybrid functionals and the Hubbard  $U$  method have also been employed for the semiconductor-oxide<sup>16</sup> and  $C_{60}$ -metal<sup>17</sup> interfaces, respectively; however, the accuracy of these methods relies heavily on adjustable empirical parameters.

Here we present a scheme based on the quantum Monte Carlo (QMC) method<sup>18</sup> to obtain accurate energy-level alignment at hybrid interfaces. This approach allows one to include many-body effects as a correction to the DFT single-particle picture within a framework that scales as  $N^3$ , typically recovers more than 90% of the correlation energy, and provides a uniform level of accuracy for a range of different systems. Applying this scheme to a representative interface between the Si(001) slab and an organic molecule, we show that the inclusion of many-body effects qualitatively changes the standard DFT single-particle description. Furthermore, quantum confinement effects lead to the prediction of an incorrect transition in the heterojunction behavior unless many-body effects are properly taken into account.

DFT calculations are performed using the SIESTA code<sup>19</sup> with numerical atomic orbitals optimized at the triple valence plus double polarization level.<sup>20</sup> Core-valence electron interactions are described using norm-conserving pseudopotentials.<sup>21</sup> The Perdew-Burke-Ernzerhof<sup>22</sup> generalized-gradient approximation (GGA) is used for the XC functional. QMC calculations are performed with the diffusion Monte Carlo (DMC) method,<sup>18</sup> using the QWALK code.<sup>23</sup> The antisymmetric fermionic nodes are given by the Slater-Jastrow trial wave function. The DFT single-particle states are used to construct the Slater determinant; the variational parameters, including electron-electron, electron-nucleus, and electron-electron-nucleus terms, are optimized by variance minimization. DMC time steps of 0.04 and 0.01 a.u. are used for Si slabs and organic molecules, respectively.

Organic-silicon interfaces have been investigated<sup>2,4,5</sup> because of the potential for integrating Si-based microelectronics with novel functional components stemming from the organic adlayers. In addition to the extensive research on functionalization mechanisms, the interfacial electronic structure is of great interest for understanding transport char-

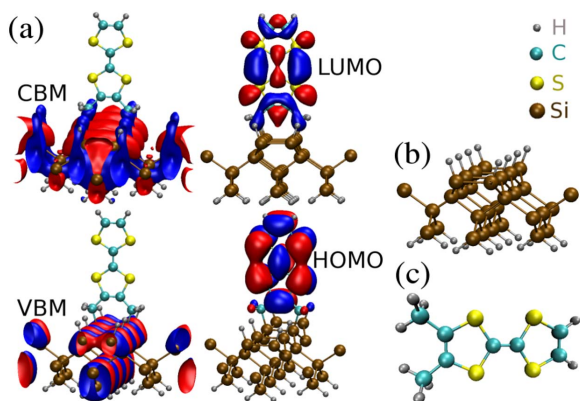


FIG. 1. (Color online) (a) The isosurfaces of the single-particle states characterizing the energy-level alignments at the organic-inorganic interface. (b) Si(001) slab. (c)  $C_8S_4H_8$  molecule.

acteristics. Figure 1(a) shows the hybrid interface we used as a representative case to develop and apply our QMC-based approach. The interface structure is composed of a fully H-saturated Si(001)  $2 \times 1$  reconstructed surface and a molecular derivative of tetrathiafulvalene (TTF), which is widely studied for optoelectronic applications. The surface is represented by a four-layer slab with a  $p(2\sqrt{2} \times 2\sqrt{2})R45^\circ$  surface supercell.

In order to illustrate the extent of the many-body correction recoverable in our approach, we first discuss QMC results for several related systems for which well-established experimental or other accurate theoretical values are available, specifically benzene ( $C_6H_6$ ) and thiophene ( $C_4H_4S$ ). These QMC results are summarized in Table I. The QMC IP values are in excellent agreement with experiment, and the QMC QP gap also agrees well with the *GW* calculation. As expected, DFT predicts a much smaller gap between the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) due to an underestimate of the IP and overestimate of the EA within the single-particle description.

In a solid, the QMC band gap can be estimated by promoting an electron from the valence-band maximum (VBM) to the conduction band minimum (CBM) since the exciton binding energy ( $E_{Xb}$ ) is often negligible [ $\sim 0.02$  eV for Si (Ref. 24)], and therefore the optical gap does not differ ap-

preciably from the QP gap. Our QMC result of 1.37(9) eV for the  $\Gamma_{25'} \rightarrow X_{1c}$  excitation in Si is close to the *GW* result of 1.43 eV,<sup>25</sup> compared with the experimental value of 1.25 eV,<sup>26</sup> while DFT predicts a substantially smaller excitation energy of 0.64 eV. When  $E_{Xb}$  is much larger (e.g., due to quantum confinement), the QP gap differs significantly from the optical gap. In such cases, the QP gap needs to be computed as  $E_g^{QP} = E(N+1) + E(N-1) - 2E(N)$  when QMC is employed.

Unlike many-body perturbation approaches, QMC requires a separate calculation for each QP energy. In addition, although one would normally compute the electron density for the interface system to determine the spatial location of the QP, such a density calculation within QMC is computationally very expensive. Hence it is advantageous to pursue an approximate but efficient scheme to include many-body effects from QMC for correcting the single-particle description of the energy-level alignments, as is similarly done in *GW* calculations.<sup>27</sup> We exploit the fact that the eigenvalue of the highest occupied KS single-particle state formally corresponds to IP,<sup>28</sup> which can also be obtained using QMC; by reproducing the interfacial states that form the energy-level alignment in *auxiliary* systems as the frontier orbitals, we are able to compute the many-body corrections using QMC: for the occupied states, we approximate  $\delta E_i = E_i^{QP} - E_i^{DFT} \approx -IP - E_{HOMO}^{DFT} = [E(N) - E(N-1)] - E_{HOMO}^{DFT}$  and for the unoccupied states,  $\delta E_j = E_j^{QP} - E_j^{DFT} \approx [-IP + E_g] - E_{LUMO}^{DFT} = [E(N+1) - E(N)] - E_{LUMO}^{DFT}$ .

It is rather straightforward to construct such auxiliary systems for the purpose of computing many-body corrections by separating the interface. Figures 1(b) and 1(c) show the separated systems with additional hydrogen atoms to remove the unwanted unpaired electrons due to the chemical bond cleavage between the slab and the molecule. While such a straightforward decomposition is possible for the interface structure where the energy-level alignment is meaningful, the applicability of this scheme relies on how well the original KS states are reproduced in the separated auxiliary systems. The overlap of the original KS states in the interface and these newly created KS states as the frontier orbitals in the separated auxiliary systems is greater than 93%. Within DFT, we compute the difference in energy levels between the separated and interface systems to be less than 0.1 eV, far smaller than the many-body effects described below. Consequently,

TABLE I. Calculated electron affinity (EA), ionization potential (IP), and the HOMO-LUMO gap  $E_g$  of benzene ( $C_6H_6$ ) and thiophene ( $C_4H_4S$ ), comparing with *GW* results and experimental data. All energies are in unit of eV.

	$C_6H_6$			$C_4H_4S$		
	EA	IP	$E_g$	EA	IP	$E_g$
DFT-KS	1.13	6.25	5.12	1.17	5.68	4.51
<i>GW</i>			10.51 <sup>a</sup>			
QMC	-1.61(3)	9.26(3)	10.87(6)	-1.55(4)	8.99(4)	10.54(8)
Expt.	<0.0	9.244 <sup>b</sup>		<0.0	8.86 <sup>b</sup>	

<sup>a</sup>Reference 15.

<sup>b</sup>Reference 30.

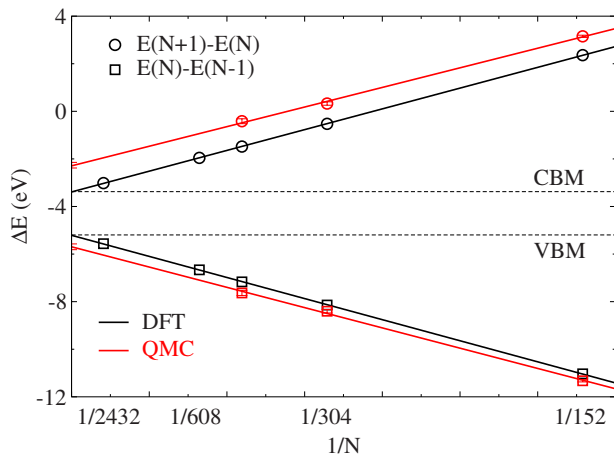


FIG. 2. (Color online) The energy differences,  $E(N+1)-E(N)$  and  $E(N)-E(N-1)$ , as functions of  $1/N$ , where  $N$  is the number of electrons per supercell of the Si slab shown in Fig. 1(b). The solid lines are linear fits to the DFT and QMC values, and the dashed lines indicate the single-particle eigenenergies of VBM and CBM states.

this approximation amounts to neglecting the part of the many-body correction stemming from the electron correlation across the interface; however, the magnitude of such a long-range correlation energy is substantially smaller than the majority of the many-body correction recoverable in our approach.

An essential technical point involves the calculation of a charged slab. Computing  $E(N+1)$  and  $E(N-1)$  of an extended periodic electronic system requires a uniform neutralizing background charge to prevent energy divergence. This background charge introduces fictitious interactions, which for a partially periodic system, such as a slab or a wire, vary with the vacuum thickness  $L_{\text{vac}}$ . Directly removing the fictitious energy ( $E_{\text{fic}}$  per  $N$  electron) within QMC would require a rather time-consuming calculation of the electron density. Instead, we employ an extrapolation approach<sup>29</sup> to obtain  $E_{\text{CBM}}$  and  $E_{\text{VBM}}$  for the Si slab using the linear dependence of  $E_{\text{fic}} \propto 1/N$ , which can be understood from the fact that  $E_{\text{fic}}$  is proportional to the square of the background charge density ( $\rho_b \propto 1/N$ ) and to the unit-cell volume ( $\Omega \propto N$ ). A similar procedure is often needed in QMC calculations for removing finite-size errors due to periodic boundary conditions.

We calculated  $E(N+1)-E(N)$  and  $E(N)-E(N-1)$  by varying surface supercells with  $L_{\text{vac}}=10$  nm, which ensures negligible slab-slab interactions and applicability of the extrapolation scheme. The energy differences are plotted as a function of  $1/N$  and extrapolated to the  $N \rightarrow \infty$  limit by linear fitting, as shown in Fig. 2. The DFT results demonstrate the essentially perfect linear dependence of  $E_{\text{fic}}$  on  $1/N$ , and the calculated  $E_{\text{CBM/VBM}}$  from extrapolation agree very well with the corresponding single-particle eigenvalues, which indicates the validity of the extrapolation as a consequence of the theorem of Janak.<sup>28</sup> The extrapolated QMC results of  $E(N+1)-E(N)$  and  $E(N)-E(N-1)$  yield  $1.13 \pm 0.11$  and  $-0.51 \pm 0.10$  eV for the many-body corrections to  $E_{\text{CBM}}^{\text{DFT}}$  and  $E_{\text{VBM}}^{\text{DFT}}$ , respectively, increasing the band gap of the four-layer Si slab from the DFT value from 1.79 to  $3.4 \pm 0.2$  eV. In the

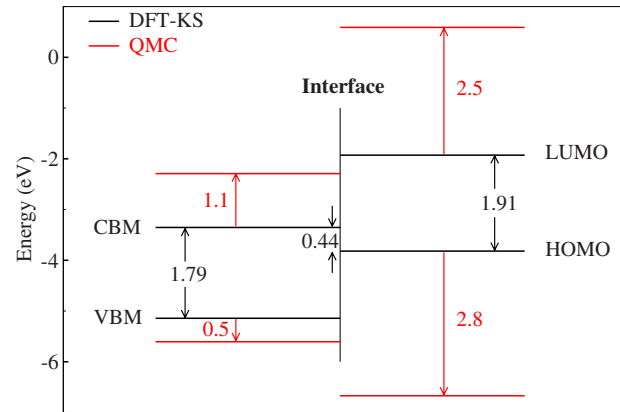


FIG. 3. (Color online) The calculated energy-level alignments of the interface from DFT single-particle energies and with many-body effects from QMC. The CBM, VBM, LUMO, and HOMO states correspond to those shown in Fig. 1(c).

Si slab the many-body correction to the CBM level is much larger than that to the VBM level, consistent with previous *GW* calculations on Si nanowires.<sup>31</sup> Much larger many-body corrections of  $2.51 \pm 0.05 / -2.78 \pm 0.05$  eV to  $E_{\text{LUMO}}^{\text{DFT}} / E_{\text{HOMO}}^{\text{DFT}}$  are found for the organic molecule compared to the Si slab, increasing  $E_g$  from the DFT value from 1.91 to  $7.2 \pm 0.1$  eV in QMC. According to these calculations, we find that within DFT the present organic-inorganic interface is predicted to be of type-II (staggered) behavior with an energy gap of 0.44 eV, as seen in Fig. 3. In sharp contrast, the interface is predicted to be a type-I (straddling) alignment when many-body effects are accounted for, qualitatively changing the physical characteristics of this interface.

These results suggest important scientific implications as well as provide a note of caution as DFT is becoming increasingly popular for designing novel organic-inorganic materials for technological applications. Even for a rather simple interface, DFT predicts a type-II junction, which might make this system *appear to be* desirable, for example, as a photovoltaic heterojunction in excitonic solar cells. However, accurately accounting for many-body effects completely modifies not only the quantitative but also the qualitative interfacial energy-level alignment, revealing that this hybrid interface would actually be undesirable for such applications. Furthermore, increasing the slab thickness weakens the quantum confinement, leading to a decreasing band gap (increasing  $E_{\text{VBM}}$  and decreasing  $E_{\text{CBM}}$ ) until the bulk value is eventually reached. Within a DFT description, for a thickness of  $\geq 16$  layers,  $E_{\text{CBM}}$  is essentially equal to  $E_{\text{HOMO}}$ , and thus significant interfacial charge redistribution is expected due to chemical potential equilibration. However, when many-body effects are included, our results strongly suggest that the hybrid interface remains simply a type-I junction regardless of the layer thickness (Fig. 4).

In summary we presented a scheme for obtaining many-body corrections to a DFT single-particle description of the energy-level alignment at hybrid interfaces using the highly accurate QMC approach. We demonstrated our approach in the context of an interface between a Si(001) slab and a TTF molecular derivative, showing that inclusion of many-body

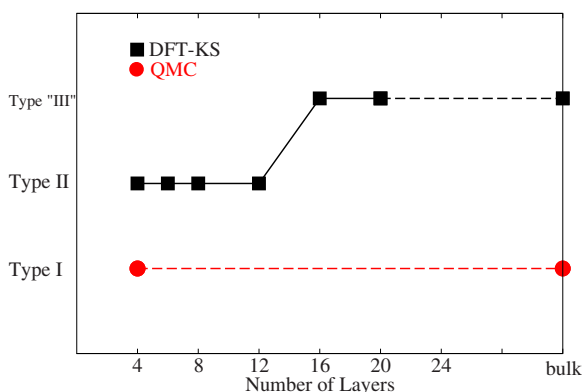


FIG. 4. (Color online) The junction behaviors of the interface as a function of Si-slab thickness, predicted by DFT and QMC. Type “III” refers to the case where the HOMO from the molecular part is essentially equal to or higher in energy than the CBM from the Si slab.

effects changes the junction character qualitatively. While this scheme is also applicable to other types of interfaces (e.g., organic-organic and semiconductor-semiconductor), we expect it to be most useful in cases where DFT does not

benefit from error cancellation due to similar electronic environments across the interface.

Compared with other methods such as *GW* for obtaining many-body corrections, our approach has both advantages and disadvantages. The most important advantage is that the full many-body Schrödinger equation is solved for all systems on roughly the same footing, while *GW* calculations involve a perturbative treatment of the self-energy and various models (e.g., plasmon-pole) to approximate the frequency-dependent inverse dielectric function. Although the energy gap correction  $\delta E_g$  is not very sensitive to the choices of these models or the ways to calculate the self-energy,  $\delta E_i$  has been shown to vary considerably.<sup>14</sup> On the other hand, the disadvantage of our approach is the computational cost compared to *GW* calculations for a periodic system because  $\lim_{N \rightarrow \infty} \partial E / \partial N$  must be evaluated from extrapolation, as shown in Fig. 2.

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