The universal and fundamental criteria for charge separation at interfaces involving nanoscale materials are investigated. In addition to the single-quasiparticle excitation, all the two-quasiparticle effects including exciton binding, Coulomb stabilization, and exciton transfer are considered, which play critical roles on nanoscale interfaces for optoelectronic applications. We propose a scheme allowing adding these two-quasiparticle interactions on top of the single-quasiparticle energy level alignment for determining and illuminating charge separation at nanoscale interfaces. Employing the many-body perturbation theory based on Green’s functions, we quantitatively demonstrate that neglecting or simplifying these crucial two-quasiparticle interactions using less accurate methods is likely to predict qualitatively incorrect charge separation behaviors at nanoscale interfaces where quantum confinement dominates. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4898155]

I. INTRODUCTION

Nanomaterials, in particular, those within the quantum confinement regime, are promising for the next-generation photovoltaic (PV) cells because their electronic and optical properties can be tuned by controlling their sizes, shapes, and surface chemistry, as well as the potential benefit from collecting hot charge carriers and multiple exciton generation by a single photon. In PV cells based on nanomaterials, the exciton binding energy ($E_b$) can be 1–2 orders higher than that in the corresponding bulk materials, leading to much more tightly bound excitons, so the fast dissociation of bound excitons into relatively free electrons and holes, i.e., the charge separation process, is critical to efficient energy conversion. Charge separation in these excitonic PV cells occurs at interfaces between nanomaterials and/or molecules, and understanding the underlying mechanisms and the ability of quantitatively assessing charge separation at nanoscale interfaces are central to rational design of excellent nanoPV.

During the past decade, considerable progress has been made experimentally to construct nanoscale interfaces that facilitate efficient charge separation. However, due to the ensemble nature of the measurements on nanostructures, experiment alone is extremely challenging in interpreting data and accurately characterizing interfacial properties. On the other hand, extensive theoretical efforts have been spent on investigating a variety of nanoscale interfaces for PV applications. The simplest model for interfacial charge carrier dynamics is the quasiparticle (QP) energy level alignment, in which a staggered type-II junction enables charge transfer. Many theoretical analyses adopted this straightforward approach; however, the excitonic effects in quantum-confined nanomaterials and molecules play a major role in determining the electronic excitation dynamics, which might be completely different from the behavior predicted by the simple QP energy level alignment.

Only a handful previous theoretical works have considered such effects, e.g., Bittner et al. computed exciton binding energies and band offsets to explain the different charge separation characters using the configuration interaction method. Similarly, the semiempirical intermediate neglect of differential overlap Hamiltonian coupled to a single configuration interaction scheme and the Hartree-Fock Austin model gave reasonable results for charge transfer in organic-organic interfaces. Besides, the time-dependent density functional theory (TDDFT) and the unrestricted DFT calculations have been applied to obtain accurate excitonic energies in nanoscale interfacial systems and excellent agreement between theoretical excitation energies for donor/acceptor complexes and experimental data was achieved by employing the perturbative many-body GW method and the Bethe-Salpeter-Equation (BSE) approach.

However, no systematic theoretical work has ever been published to fully address the role of all excitonic effects including exciton binding, Coulomb stabilization and exciton transfer on charge separation at nanoscale interfaces. Furthermore, it is not clear how to include the two-QP interactions in the manifesting single-QP energy level alignment, which has been widely adopted to describe interface characteristics for bulk materials.

In this work, we analyze the conditions for charge separation when the excitonic effects are important, by expanding and generalizing the QP energy level alignment model. We propose the effective energy level combining the single-QP energy and the two-QP excitonic binding as well as the Coulomb interaction of the separated electron and hole. For a nanomaterial, its effective QP energy levels barely change when interfacing with other materials whose sizes are similar. Efficient charge transfer across nanoscale interfaces can take place only if the associated effective and original QP energy levels form a type-II junction. In addition, exciton...
transfer is found to only suppress charge separation. Applying the present theory to four representative model inorganic-organic nanoscale interfaces between silicon quantum dots (Si QDs) and small organic molecules by carrying out the GW/BSE computations,\textsuperscript{20, 35–39} we show that incorrect charge (Si QDs) and small organic molecules by carrying out the present theory to four representative model inorganic-

III. RESULTS AND DISCUSSION

Our DFT calculations employed a finite-difference approach in real space using the Parsec code,\textsuperscript{40} with the norm-conserving pseudopotentials and the local density approximation (LDA) for the exchange-correlation functional. The grid spacings are set to be 0.2 Å for small molecules and 0.25 Å for small SiQDs, while the radii of the relevant sphere domains are set to be 10 Å and 12 Å, respectively, so that wavefunctions vanish outside the boundary and eigenvalues reach convergence. The \( T_d \) symmetry has been enforced on all SiQDs. The interface geometries are optimized until all atomic forces are less than 0.002 hartree/Å. The GW/BSE calculations are carried out using the RG-WBS package.\textsuperscript{39} Specifically, the self-energies are computed within the non-self-consistent \( G_0W \) approximation, wherein \( G \) is estimated by the Kohn-Sham Green’s function and \( W \) is obtained within the time-dependent adiabatic LDA along with the vertex correction. To ensure good convergence, 300 single-particle eigenfunctions are used to construct the two-QP exciton wavefunctions.

The Coulomb interaction energy is calculated by\textsuperscript{17}

\[
E_c = \sum \frac{Q_D Q_A}{\epsilon R_{DA}},
\]

where \( Q_D \) and \( Q_A \) are the partial charges on donor and acceptor, respectively, \( R_{DA} \) is the effective distance between them, and \( \epsilon = 3 \) is the dielectric constant taken to be typical value of organic systems.\textsuperscript{32} Estimating the Coulomb interaction using a fixed dielectric constant could only be safely applied to systems consisting of donor and acceptor with similar and known dielectric constants. The partial charges are obtained by Mulliken analysis implemented in Dmol package.\textsuperscript{41} The Conductor-like Screening Model (COSMO)\textsuperscript{42} was used to account for the dielectric effect of the solvent. In Dmol calculations an all-electron approach was employed with the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE).\textsuperscript{43} A real-space, double numeric plus polarization (DNP) basis was used along with an octupole expansion to specify the maximum angular momentum function.\textsuperscript{41}

A. Effective energy levels

The most general condition for interfacial charge separation derives from the fact that the total electronic energy before charge separation \( (E_f) \) should be higher than that \( (E_i) \) after the transfer happens, i.e., the driving force \( \Delta G \) is positive:

\[
\Delta G = E_i - E_f > 0.
\]

This is because if \( E_i < E_f \), the phonon-assisted charge transfer can still take place, but its rate is extremely low at room temperature if \( E_f - E_i > k_B T \approx 24 \text{ meV} \), where \( k_B \) is the Boltzmann constant and \( T = 300 \text{ K} \). In the following discussions, we thus neglect the possible charge or exciton transfer with negative driving forces.

For an interface between materials \( A \) and \( B \), without losing generality we assume an exciton is generated in \( A \). The initial total electronic energy is

\[
E_i = E_{gs}^A + E_{gs}^B + E_{gs}^c + E_{gs}^f,
\]

where \( E_{gs}^A \) and \( E_{gs}^B \) are the ground-state energies for \( A \) and \( B \), respectively, \( E_{gs}^c \) is the optical gap for \( A \), and \( E_{gs}^f \) is the initial Coulomb interaction between \( A \) and \( B \). The final total electronic energy can be one of the following:

\[
E_f = E_{gs}^A - E_{HOMO}^A + E_{gs}^B + E_{LUMO}^A + E_{c,f},
\]

\[
E_f = E_{gs}^A + E_{LUMO}^A + E_{gs}^B - E_{HOMO}^B + E_{c,f},
\]

depending on whether the electron [Eq. (4)] or hole [Eq. (5)] transfers from \( A \) to \( B \). Here HOMO and LUMO denote the highest occupied and the lowest unoccupied molecular orbitals, and \( E_{c,f} \) is the final interfacial Coulomb energy.

Combining Eqs. (2)–(5), one finds the charge separation conditions for electron or hole transfer, respectively,

\[
E_{LUMO}^A - E_{HOMO}^A > 0,
\]

\[
E_{HOMO}^A + E_{LUMO}^B > 0.
\]

where the Coulomb stabilization energy \( \Delta E_c = E_{c,f} - E_{c,i} \), and \( E_{c,i} = E_{gs} - E_{gs}^c = E_{LUMO}^A - E_{HOMO}^A - E_{gs}^c \). It is convenient to define the effective LUMO and HOMO energy levels,

\[
E_{eff,LUMO}^A = E_{LUMO}^A - E_{LUMO}^c - \Delta E_c,
\]

\[
E_{eff,HOMO}^A = E_{HOMO}^A + E_{HOMO}^c + \Delta E_c.
\]
so that the intuitive picture of interfacial level alignment can still be used to determine if charge transfer can occur, as schematically illustrated in Fig. 1.

If both the effective LUMO and the HOMO of A are higher than the LUMO and HOMO of B, respectively, as shown in Fig. 1(a), the electron will transfer from A to B; whereas when both the LUMO and effective HOMO of A are lower than the LUMO and HOMO of B, respectively, as shown in Fig. 1(b), the hole will transfer from A to B. In both cases, an effective type-II junction is formed, ensuring charge separation at the nanoscale interface, with the driving force

\[
\Delta G_{A\rightarrow B}^\text{el} = E_{\text{LUMO}}^\text{eff} - E_{\text{LUMO}}^B, \quad (10)
\]

and

\[
\Delta G_{A\rightarrow B}^\text{h} = E_{\text{HOMO}}^B - E_{\text{HOMO}}^\text{eff}, \quad (11)
\]

for electron or hole transfer, respectively.

In a bulk interface, both \(E_b\) and \(\Delta E_c\) are negligible, hence \(E_{\text{LUMO}}^\text{eff} \approx E_{\text{LUMO}}\) and \(E_{\text{HOMO}}^\text{eff} \approx E_{\text{HOMO}}\), and its junction type can be safely determined by the frontier QP energy levels. This is the reason why the bulk heterojunction type is normally defined by QP energy levels. But in a nanoscale interface, \(E_b\) and \(\Delta E_c\) are remarkably enhanced, and a full analysis is necessary. Here \(E_b > 0\), indicating that the strength of Coulomb interaction between electron and hole before the exciton is dissociated; while \(\Delta E_c < 0\), whose magnitude is the strength of Coulomb interaction between electron and hole after the exciton is dissociated. Consequently, \(E_b > |\Delta E_c|\), and then \(E_b + \Delta E_c > 0\); as a result, based on Eqs. (8) and (9), \(E_{\text{LUMO}}^\text{eff} < E_{\text{LUMO}}\) and \(E_{\text{HOMO}}^\text{eff} > E_{\text{HOMO}}\), suggesting that for an effective type-II junction facilitating either electron transfer [Fig. 1(a)] or hole transfer [Fig. 1(b)], its corresponding QP energy level alignment is also of type-II. Therefore, a staggered type-II QP energy level alignment is only a necessary condition for charge separation, but not sufficient. Note that if there is partial charge transfer between the donor and the acceptor, one has to calculate the D/A interface directly.

B. Applications to four nanoscale interfaces

Four model inorganic-organic nanoscale interfaces between weakly bonded Si QDs and small molecules, including Si\(_{35}\)H\(_{36}\)–C\(_3\)H\(_8\)N, Si\(_{35}\)H\(_{36}\)–anthracene, Si\(_{35}\)(CH\(_3\))\(_{36}\)–C\(_{14}\)H\(_{24}\)N\(_2\)O\(_4\), and Si\(_{35}\)(CH\(_3\))\(_{36}\)–anthracene are studied to show that the QP energy level alignment might predict wrong charge separation behaviors. Table I summarizes calculated ionization potential (IP), electron affinity (EA), and optical gap (\(E_g^*\)) for anthracene and Si\(_{35}\)H\(_{36}\), and these data demonstrate that our present results agree very well with available experimental data and previous theoretical results. Fig. 2 plots

![Image](333x144 to 376x177)

FIG. 1. Schematic illustrations of interfacial charge separation criteria. A type-II junction is formed using the effective LUMO for electron transfer (a) or using the effective HOMO for hole transfer (b). Here \(E_{\text{LUMO}}^A\), \(E_{\text{LUMO}}^B\), \(\Delta E_{\text{LUMO}}\), and \(\Delta G\) are exciton binding energy, optical gap, Coulomb stabilization energy, and charge transfer driving force, respectively.

![Image](401x139 to 471x183)

![Image](141, 154701 (2014))

Table I. Calculated ionization potential (IP), electron affinity (EA), and optical gap (\(E_g^*\)) in unit of eV for anthracene and Si\(_{35}\)H\(_{36}\), in comparison with available previous theoretical results and experimental data.

<table>
<thead>
<tr>
<th></th>
<th>Present theory</th>
<th>Previous theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP</td>
<td>7.23</td>
<td>7.06(^b)</td>
<td>7.44(^b)</td>
</tr>
<tr>
<td>EA</td>
<td>1.05</td>
<td>0.91(^a)</td>
<td>0.53(^c)</td>
</tr>
<tr>
<td>(E_g^*)</td>
<td>3.03</td>
<td>3.11(^d)</td>
<td>3.11(^e)</td>
</tr>
<tr>
<td>IP</td>
<td>8.20</td>
<td>8.0(^f)</td>
<td></td>
</tr>
<tr>
<td>(E_g^*)</td>
<td>4.23</td>
<td>4.1(^g)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Reference 34.
\(^b\)Reference 45.
\(^c\)Reference 46.
\(^d\)Reference 47.
\(^e\)Reference 48.
\(^f\)Reference 39.
\(^g\)Reference 49.

![Image](141, 154701 (2014))

FIG. 2. Energy level alignment for interfaces (a) Si\(_{35}\)H\(_{36}\)–C\(_3\)H\(_8\)N, (b) Si\(_{35}\)H\(_{36}\)–anthracene, (c) Si\(_{35}\)(CH\(_3\))\(_{36}\)–C\(_{14}\)H\(_{24}\)N\(_2\)O\(_4\), and (d) Si\(_{35}\)(CH\(_3\))\(_{36}\)–anthracene. The notations here follow those in Fig. 1, with energy in eV.

For each interface, on the left is plotted the effective LUMO or HOMO for exciton being generated in the Si QD, whereas on the right is plotted the effective LUMO or HOMO if exciton has transferred to or been generated in the organic molecule. (e) Structures of the organic molecules. Here the white, gray, dark blue, and red spheres represent H, C, N, and O atoms, respectively.
their energy level alignment, while Fig. 3 illustrates the first interface in details. The frontier HOMO/LUMO orbitals in the interfacial system (not shown) well resemble those corresponding QP orbitals in the isolated QD and organic molecule [Fig. 3(b)], because of the weak Van de Waals interaction between them. For simplicity, we assume excitons are generated in QDs. The frontier QP energy levels for the first two interfaces [Figs. 2(a) and 2(b)] form type-II junctions with both HOMO and LUMO in QDs lower than those in molecules, respectively; therefore, only hole transfer might be possible. Since the effective HOMO in Si$_{35}$H$_{36}$ is lower than the HOMO in C$_3$H$_8$N, while the effective HOMO in Si$_{35}$H$_{36}$ is higher than the HOMO in anthracene, efficient hole transfer from Si QD to molecule can occur in the former interface, as shown in Fig. 3(c), but not in the latter case, although in both cases the QP energy levels form a staggered alignment.

Figs. 2(c) and 2(d) show that the QP energy level alignments in these two interfaces are of type-II as well, with both HOMO and LUMO in QDs lower than those in molecules, respectively, so that only electron transfer is possible if excitons are located in Si QDs. Comparing the effective LUMO of Si QDs with the LUMO of C$_{14}$H$_{12}$O$_4$ and anthracene, we conclude that electron can transfer from Si$_{35}$(CH$_3$)$_{36}$ to C$_{14}$H$_{12}$N$_2$O$_4$, but not to anthracene.

Note that interface dipole will significantly affect level alignment; however, in these semiconducting interfaces studied in our work, there is almost no interfacial dipole formed, as verified by our DFT calculations for isolated donor and acceptor and for the D/A complex. Fig. 4 shows that energy level alignment obtained from isolated donor and acceptor [left and right sides of panel (a)] is very close to that obtained from the D/A complex [center of panel (a)], and the wave functions of corresponding frontier orbitals are also nearly identical, suggesting that there is barely any interface dipole formed.

The absence of the surface polarization response in DFT calculations prevent them from capturing the variation in the electronic correlation energy. In general, the effects of surrounding environment on interfacial energy alignment are complicated because of the induced polarization, charge redistribution, etc. However, for the interfacial systems studied in this work, these effects are expected to be mostly negligible, since both silicon quantum dots and these organic molecules have very small polarizabilities. At such semiconducting interfaces normally there are barely any interfacial polarization and charge redistribution, in contrast to metal-organic interfaces where significant charge transfer across interface and surface polarization can occur.

Another assumption made in our model is that the charge distribution of the surrounding molecules does not play a critical role. To verify this, we calculated the DFT energy levels for various numbers of organic molecules interfacing with the same Si QD. As shown in Fig. 5 for the Si$_{35}$H$_{36}$/C$_3$H$_8$N interface, adding three more C$_3$H$_8$N molecules barely affects the interfacial level offsets. We also find that frontier orbital wave functions for the interface with 4 C$_3$H$_8$N molecules are essentially the same as those for the interface with only one C$_3$H$_8$N molecule. For the interface with 4 C$_3$H$_8$N molecules the nearly degenerate frontier orbitals of these molecules split slightly. We also calculated the energy levels for the frontier orbitals of the Si$_{35}$H$_{36}$/C$_3$H$_8$N complex with the environmental dielectric constant (ε) varying from 1 (vacuum) to 78.5 (water) using the COSMO, and the data summarized in Table II confirm that polar solvents such as water can shift
TABLE II. Calculated HOMO/LUMO energies (in eV) for the Si\textsubscript{35}H\textsubscript{36}/C\textsubscript{14}H\textsubscript{4}N complex with two very different values of dielectric constant (ε).

<table>
<thead>
<tr>
<th></th>
<th>ε = 1</th>
<th>ε = 78.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO (C\textsubscript{3}H\textsubscript{8}N)</td>
<td>−1.43</td>
<td>−1.64</td>
</tr>
<tr>
<td>LUMO (Si\textsubscript{35}H\textsubscript{36})</td>
<td>−2.51</td>
<td>−2.56</td>
</tr>
<tr>
<td>HOMO (C\textsubscript{3}H\textsubscript{8}N)</td>
<td>−2.79</td>
<td>−2.85</td>
</tr>
<tr>
<td>HOMO (Si\textsubscript{35}H\textsubscript{36})</td>
<td>−6.13</td>
<td>−6.18</td>
</tr>
</tbody>
</table>

these energy levels in semiconducting interfaces only by negligible amounts. We also note that due to presence of electron and hole in the charge transfer (CT) state, the neighboring molecules will be polarized, which in turn will further stabilize the CT state. It could make our estimation of the energy of the CT state less accurate, though the above calculations suggest that this effect is not expected to be significant.

In these four model systems, tiny Si QDs have strong exciton binding ($E_\text{b} > 2$ eV) and large Coulomb stabilization energy ($\Delta E_c \approx 1.1$ eV), and our calculations have demonstrated that the excitonic effects play a substantial role on charge separation at nanoscale interfaces. Our proposed effective HOMO/LUMO levels provide a simple and illuminating physics picture to reveal the complex exci- tonic dynamics of charge separation at these interfaces.

C. Influence of exciton transfer on charge separation

An additional complexity originates from exciton transfer across interface, which has been observed in organic and inorganic systems, but whose impact on charge transfer remains unclear, i.e., can exciton transfer induce an originally forbidden interfacial charge separation?

Starting from the same initial conditions as expressed in Eq. (3), the final electronic total energy after exciton transfer is

$$E_f = E_{g_1}^A + E_{g_2}^B + E_{g_2}^B + E_{c,f}.$$  (12)

Apparently, here $E_{c,i} \approx E_{c,f}$, and $E_c > E_f$ leads to the condition for meaningful exciton transfer from A to B:

$$E_{g_2}^B > E_{g_2}^B.$$  (13)

The conditions for charge transfer from B to A can be described in Eqs. (6) and (7), if A and B are swapped, with driving force $\Delta G_{B \rightarrow A}^\text{coul} = E_{\text{LUMO}}^B - E_{\text{LUMO}}^A$ or $\Delta G_{B \rightarrow A}^\text{coul} = E_{\text{HOMO}}^B - E_{\text{HOMO}}^A$, for electron or hole transfer, respectively. An interface facilitating electron transfer from A to B could only enable hole transfer from B to A, and it is easy to verify that $\Delta G_{B \rightarrow A}^\text{coul} < \Delta G_{A \rightarrow B}^\text{coul}$ because $E_{g_2}^B > E_{g_2}^B$. Similarly, an interface for hole transfer from A to B could only induce electron transfer from B to A, with the driving force $\Delta G_{B \rightarrow A}^\text{coul} < \Delta G_{A \rightarrow B}^\text{coul}$.

Therefore, we draw an important conclusion that exciton transfer only reduces or completely suppresses charge transfer: (1) if the interface before exciton transfer favors charge transfer, then it can either still separate charges with a reduced driving force or can not induce charge transfer any more after exciton transfer; (2) if the interface before exciton transfer does not favor charge separation, then after exciton transfer it still can not separate charges with appreciable rate.

The four interfaces shown previously in Fig. 2 are re-investigated to explicitly elucidate the effect of exciton transfer on charge separation, and we still assume that the exciton is initially generated in Si QDs. Exciton can transfer from Si\textsubscript{35}H\textsubscript{36} to C\textsubscript{3}H\textsubscript{8}N because the optical gap in the former (4.2 eV) is larger than the latter (2.7 eV); however, charge separation is forbidden from the molecule to the QD since the effective LUMO of the molecule is lower than the LUMO of the QD, as illustrated in Fig. 2(a). This exemplifies that exciton transfer could completely suppress charge separation. Another example is the Si\textsubscript{35}(CH\textsubscript{3})\textsubscript{36}–C\textsubscript{14}H\textsubscript{4}N\textsubscript{2}O\textsubscript{4} interface [Fig. 2(c)], on which exciton can transfer as well. After exciton transfer, charge separation condition is still satisfied; however, the driving force is reduced to 0.7 eV from 0.9 eV. The interface plotted in Fig. 2(b) does not favor charge transfer from the QD to the molecule; although exciton transfer can occur, the reverse charge transfer from the molecule to QD is still forbidden, with an even more negative driving force (−1.1 eV) than before (−0.5 eV). Finally, exciton transfer is forbidden in the last nanoscale interface [Fig. 2(d)]; and if exciton is generated in anthracene, charge separation cannot occur as well.

D. Application to practical interfaces

While the effective HOMO/LUMO levels are proposed mainly to better illustrate the interfacial charge transfer dynamics by adopting the corresponding concepts used in bulk materials, they can also be regarded as inherent properties for a specific nanomaterial if its interfacing materials are similar in size so that the variation in Coulomb stabilization energy $\Delta E_c$ is small. In these four interfaces $\Delta E_c$ are within the range of 1.03–1.13 eV, and the effective HOMO/LUMO for one material barely change in various interfaces. But when interfacing materials are distinctively different, the effective HOMO/LUMO of a nanomaterial will depend on specific interface. However, this is also the case in bulk heterojunctions, where the band offsets could sensitively depend on surface orientation and termination, resulting in a variation in electron affinity $\gtrsim 1$ eV.

To further illustrate the application of the effective energy level alignment we proposed, we have performed calculations of the poly(3-hexylthiophene) (P3HT) and fullerene derivative phenyl-C61-butyric acid methyl ester (PCBM) interface, which is one of the most promising organic PV materials. Here the P3HT polymer is represented by the small molecule P3C\textsubscript{2}H\textsubscript{5}T, and the experimental value (1.9 eV) of optical gap in P3HT is adopted as suggested by previous literature.

In Table III we calculated IP, EA, and optical gap $E_{g}^*$ are compared with available experimental data and previous theoretical results. We note that (1) the rather large discrepancy between theory and experiment on IP and EA of P3C\textsubscript{2}H\textsubscript{5}T is probably due to the overly simplified molecular structure used in our calculations and (2) since the side chain of PCBM has negligible impact on its energy levels, the C60 molecule is used instead in our GW-BSE calculation. As shown in
TABLE III. Calculated ionization potential (IP), electron affinity (EA), and optical gap ($E_g$) in unit of eV for anthracene and P3C$_2$H$_5$T and C$_{60}$, in comparison with available previous theoretical results and experimental data.

<table>
<thead>
<tr>
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<th>Present theory</th>
<th>Previous theory</th>
<th>Experiment</th>
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<tbody>
<tr>
<td>P3C$_2$H$_5$T</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IP</td>
<td>5.76</td>
<td>5.89</td>
<td>5.1</td>
</tr>
<tr>
<td>EA</td>
<td>1.25</td>
<td>1.09</td>
<td>3.2</td>
</tr>
<tr>
<td>$E_g$</td>
<td>2.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_{60}$</td>
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<tr>
<td>IP</td>
<td>7.65</td>
<td>7.41</td>
<td>7.6</td>
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<tr>
<td>EA</td>
<td>3.12</td>
<td>2.31</td>
<td>2.65</td>
</tr>
<tr>
<td>$E_g$</td>
<td>2.12</td>
<td>2.24</td>
<td>1.94</td>
</tr>
</tbody>
</table>

*a*Reference 55.

*b*Reference 56.

*c*Reference 57.

*d*Reference 34.

*e*Reference 56.

*f*Reference 17.

In summary, to fully account of the significant two-QP excitonic effects at nanoscale interfaces, we have proposed the effective HOMO/LUMO on top of the traditional single-QP energy level alignment to determine junction type and the interfacial charge separation character. Our calculations clearly demonstrate that, due to strong quantum confinement, incorrect charge transfer behavior at nanoscale interfaces could be predicted without precisely considering exciton binding and Coulomb stabilization. Furthermore, exciton transfer is found to only suppress charge transfer. Since the QP energy level alignment is widely accepted and applied to determine the interfacial junction type, present results raise a grave caution. Instead, a universal theory for charge separation at any interfaces is presented, and an accurate and illuminating description is made by adding the two-QP excitonic effects to the single-QP energy levels, which shall be useful for designing and characterizing nanoscale interfaces for optoelectronic devices.

**ACKNOWLEDGMENTS**

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