



Orbital gap predictions for rational design of organic photovoltaic materials



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ABSTRACT

Ionization potentials (IP) and electron affinities (EA) of organic molecules with applications in photovoltaic devices are calculated using modern density functional theory (DFT). Calculated frontier orbital energies are compared to experimentally determined IPs and EAs at gas phase and thin film environments. Gas phase frontier orbital energies calculated with widely-used DFT functionals accidentally coincide with thin film measurements, reproducing condensed phase results for the wrong reasons. Recently developed range separated hybrid (RSH) functionals, on the other hand, provide gas phase frontier orbital energies that correspond properly to measured IPs and EAs. We also employ a polarizable continuum model to address the effects of the electrostatic environment in the solid state. We find that the environmentally-corrected RSH orbital energies compare well with thin film experimental measurements.

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1. Introduction

Significant computational efforts have been recently focused on developing design principles for organic photovoltaics (OPV) and organic light emitting diodes (OLED) [1–31]. An important aspect of device design is understanding how fundamental properties of organic semiconducting (OSC) molecules are affected by the environment. For example, the ionization potential (IP) and electron affinity (EA) of OSCs play a vital role in electron transfer and transport processes, and these values have been shown to depend on the molecular environment in which they are measured [1,2,32]. Several studies investigating such environmental effects compare gas phase, solution, and thin film experiments, thereby addressing the confusion in the literature related to the different types of IP and EA measurements [1,2]. Unfortunately discrepancies still remain

in the comparison between experimental and calculated properties, a particularly notable example of which is the accidental agreement between gas phase calculated orbital energies and condensed phase measured IPs and EAs [1–4,6,7,26,33,27].

Computational modeling intended to contribute effectively to rational design of optoelectronic applications (e.g., of OPV and OLED devices) must be explanatory and predictive. However, theoretical insights are unreliable when the underlying computational method succeeds due to an uncontrolled cancellation of errors [3,4,6]. Density functional theory (DFT) provides a cost-effective computational method for calculating optoelectronic properties of relatively large molecular systems. Despite these benefits, widely-used implementations of DFT have been shown to systematically under/overestimate the IP/EA obtained from calculated molecular orbital energies [34–40]. In fact, these values calculated at the gas phase erroneously compare quite well with condensed phase IP and EA measurements, rendering the resulting molecular level insights uncertain [2–4,6,7,26]. For example, Djurovich

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et al. pointed out the correlation between inverse photoelectron spectroscopy EA measurements performed on thin films and calculated lowest unoccupied molecular orbital (LUMO) energies (ε_L) of single molecules in the gas phase [2].

Clearly, gas phase calculations should not account for solid state effects, which are expected to vary across the wide range of OSC molecules. Instead, environmental effects should be carefully taken into account. Indeed, properly considering these effects in conventional DFT calculations reveals the specious agreement between gas phase orbital energies and condensed phase IP and EA measurements.

In this work, we demonstrate the previously observed discrepancies in conventional DFT methods for predicting (gas phase) IP and EA energies of relevant OSC molecules [41,26,34]. Optimally-tuned range-separated hybrid (OT-RSH) DFT approaches offer improvements to gas phase IP and EA energies compared to conventional approaches [41,26,34,37,38,42]. In particular, this study shows the improved modeling for condensed phase IP and EA properties of OSC molecules afforded by an OT-RSH DFT based approach. Specifically, we show that

1. Orbital energies calculated at the gas phase using OT-RSH functionals compare well to gas phase measured IPs and EAs, thereby improving the notoriously underestimated band gap associated with conventional functionals.
2. Orbital energies corrected for solid state effects using a polarizable continuum model (PCM) compare well to experimentally measured thin film IP and EA, thereby achieving reliable modeling of electron transport properties.

Thus, this study demonstrates that the OT-RSH approach achieves a predictive quality in modeling IP and EA properties and therefore can provide a theoretical foundation for developing design principles in organic optoelectronic devices.

2. Theoretical background

In this section, we provide a brief formal discussion on the relationship between DFT orbital energies and the IP and EA properties. For an N -electron system, the IP is equal to the energy required to remove an electron from the system, and the EA is equal to the energy gained when an electron is added to the system as follows:

$$\text{IP}(N) = E(N-1) - E(N) \quad (1)$$

$$\text{EA}(N) = E(N) - E(N+1), \quad (2)$$

where $E(x)$ refers to the ground state energy of the x electron system. Accordingly, $\text{IP}(N+1) = \text{EA}(N)$. The fundamental gap, E_g , is then given by

$$E_g(N) = \text{IP}(N) - \text{EA}(N). \quad (3)$$

The fundamental gap is measured experimentally, as discussed in Dandrade et al. and Djurovich et al. [1,2], and

can also be calculated from ground state energy differences as in Eq. (3). To relate these values to DFT orbital energies, we briefly introduce the DFT formalism with further details in Appendix A and Ref. [43].

DFT is based on the Hohenberg Kohn (HK) theorem [44], which asserts that the ground state energy can be expressed in terms of the electron density of a system, $\rho(r)$. The Kohn–Sham (KS) formalism provides a practical implementation of DFT via solving for one-electron orbitals [45]. In the KS method, the total energy $E[\rho]$ can be written as a functional of the density,

$$E[\rho] = T_s[\rho] + E_H[\rho] + E_{xc}[\rho] + \int dr \rho(r)v(r), \quad (4)$$

where $v(r)$ is the external potential, $T_s[\rho]$ is the non-interacting kinetic energy, and $E_H[\rho]$ is the classical Coulomb electron repulsion energy. The exchange–correlation energy, $E_{xc}[\rho]$, accounts for non-classical electron interactions and must be approximated in practice since the exact form of the functional is unknown. The self-consistent KS equations provide a practical procedure for finding the ground state energy in terms of the one-electron spin orbitals $\{\psi_i(r,s)\}$. The approach requires defining an effective one-electron Hamiltonian

$$\hat{h}_{\text{eff}}\psi_i = \left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(r) \right] \psi_i = \varepsilon_i\psi_i, \quad (5)$$

where ε_i are the orbital energies, and the electron density is given by

$$\rho(r) = \sum_i^N \sum_s |\psi_i(r,s)|^2. \quad (6)$$

The effective KS potential is the functional derivative of the energy with respect to the density, and is given in terms of the exchange–correlation functional E_{xc} :

$$\begin{aligned} v_{\text{eff}}(r) &= v(r) + \frac{\delta E_H[\rho]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \\ &= v(r) + \int dr' \frac{\rho(r')}{|r-r'|} + v_{xc}(r). \end{aligned} \quad (7)$$

The physical significance of orbital energies in DFT derives from two important relations to the chemical potential, Janak's theorem and the piecewise-linearity property [46,47,41,48–52]. According to Janak's theorem, the orbital energy is equal to the change in total energy with respect to occupation of that orbital [46],

$$\frac{\partial E[\rho]}{\partial n_i} = \varepsilon_i \quad (8)$$

where n_i is the fractional occupation number ($0 \leq n_i \leq 1$) of orbital ψ_i , and $\rho(r) = \sum_i^N n_i \sum_s |\psi_i(r,s)|^2$. The orbital energy therefore corresponds to the chemical potential (μ) that is understood to depend on the overall electron number. However, the energy required for removing an electron from the highest occupied molecular orbital (HOMO) of the x electron system is also expressed in Eq. (1), resulting in correspondence between the HOMO energy, ε_H^x , and the IP energy known as the IP theorem [41]:

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