

Gap renormalization of molecular crystals from density-functional theory

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Fundamental gap renormalization due to electronic polarization is a basic phenomenon in molecular crystals. Despite its ubiquity and importance, all conventional approaches within density-functional theory completely fail to capture it, even qualitatively. Here, we present a new screened range-separated hybrid functional, which, through judicious introduction of the scalar dielectric constant, quantitatively captures polarization-induced gap renormalization, as demonstrated on the prototypical organic molecular crystals of benzene, pentacene, and C₆₀. This functional is predictive, as it contains system-specific adjustable parameters that are determined from first principles, rather than from empirical considerations.

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An important phenomenon in molecular crystals is the renormalization of the fundamental energy gap of the gas-phase molecule owing to polarization effects.¹ The energy associated with creation of a quasihole is reduced, with respect to that of the gas-phase molecule, because the polarization of the surrounding dielectric medium results in an effective negative image charge that repels the ejected electron. Similarly, the energy associated with creation of a quasielectron is increased, because an effective positive image charge attracts the added electron. Therefore, the fundamental gap, defined as the difference between the ionization potential (IP) and the electron affinity (EA),^{2,3} is smaller in the solid than in the molecule. This effect is crucial in, e.g., small-molecule-based organic electronic materials, for which the gas-phase fundamental gap of the small molecule is typically several eV too large for practical applications, but the renormalized, solid-state gap is suitable for electronics and/or photovoltaics.

Experimentally, accurate fundamental gap measurements are difficult, as they are affected by material quality, surface effects, measurement approach and analysis, etc.^{4–6} Many-body perturbation theory, in which quasiparticle excitations are deduced from solutions of Dyson's equation (typically in the *GW* approximation⁷), have been very successful in predicting a strong renormalization of the electronic gap, as demonstrated for benzene,⁸ pentacene, and 3,4,9,10-perylene-dicarboxylic-dianhydride (PTCDA).⁹ However, *GW* is computationally demanding and it is very desirable to obtain the same physics from density-functional theory (DFT),^{10,11} the method of choice for fully quantum-mechanical calculations at a relatively moderate computational cost. Unfortunately, all standard exchange-correlation functionals used in present-day DFT calculations, namely, semilocal and hybrid functionals, fail to capture the gap renormalization,¹² as they are unable to treat long-range correlation effects.

In this Rapid Communication, we propose a new density functional, the screened range-separated hybrid (SRSH) functional. It provides a quantitative description of the fundamental gap of prototypical conjugated molecules—benzene, pentacene, and C₆₀—in both gas and crystal phase, by accounting for dielectric screening. Furthermore, our proposed approach is capable of predicting an outer-valence

quasiparticle band structure of similar quality to a *GW* calculation. SRSH therefore emerges as a quantitatively useful, low-cost alternative to *GW* for studies of the electronic structure of molecular solids.

Our starting point is the generalized partition of the Coulomb interaction into long- and short-range contributions using the error function:^{13,14}

$$\frac{1}{r} = \frac{\alpha + \beta \text{erf}(\gamma r)}{r} + \frac{1 - [\alpha + \beta \text{erf}(\gamma r)]}{r}. \quad (1)$$

Here, r is the interelectron coordinate and α , β , and γ are adjustable parameters. In the range-separated hybrid (RSH) approach,¹⁵ the two terms on the right-hand side of Eq. (1) are treated differently. The first, long-range (LR) term is treated in a Fock-like manner; the second, short-range (SR) term is treated in the generalized gradient approximation (GGA). α and β control the limiting behavior of the LR term, which tends to α/r for $r \rightarrow 0$ and to $(\alpha + \beta)/r$ for $r \rightarrow \infty$. γ is the range-separation parameter; i.e., it controls the range at which each of the two terms dominates. We emphasize that this treatment is well within the rigorous framework of DFT¹⁶ based on the generalized Kohn-Sham scheme of Seidl *et al.*¹⁷

We have previously shown^{16,18–20} that the gas-phase fundamental gap can be quantitatively obtained from the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap of an RSH calculation, if one enforces two nonempirical conditions.²¹ The first is that the Fock-like term be asymptotically correct, i.e., $\alpha + \beta = 1$, resulting in the following expression for the RSH exchange-correlation energy:

$$E_{xc}^{\text{RSH}} = (1 - \alpha)E_{\text{GGAx}}^{\text{SR}} + \alpha E_{xx}^{\text{SR}} + E_{xx}^{\text{LR}} + E_{\text{GGAc}}, \quad (2)$$

where E_{xx} , E_{GGAx} , and E_{GGAc} denote Fock-like exchange and GGA semilocal exchange and correlation, respectively. The second condition is that the range-separation parameter, γ , is optimally tuned so as to obey the ionization-potential theorem;²² i.e., the IP computed from total energy differences is the same as that obtained from the HOMO eigenvalue E_H for both neutral (n) and anionic (a) species (the latter if bound).

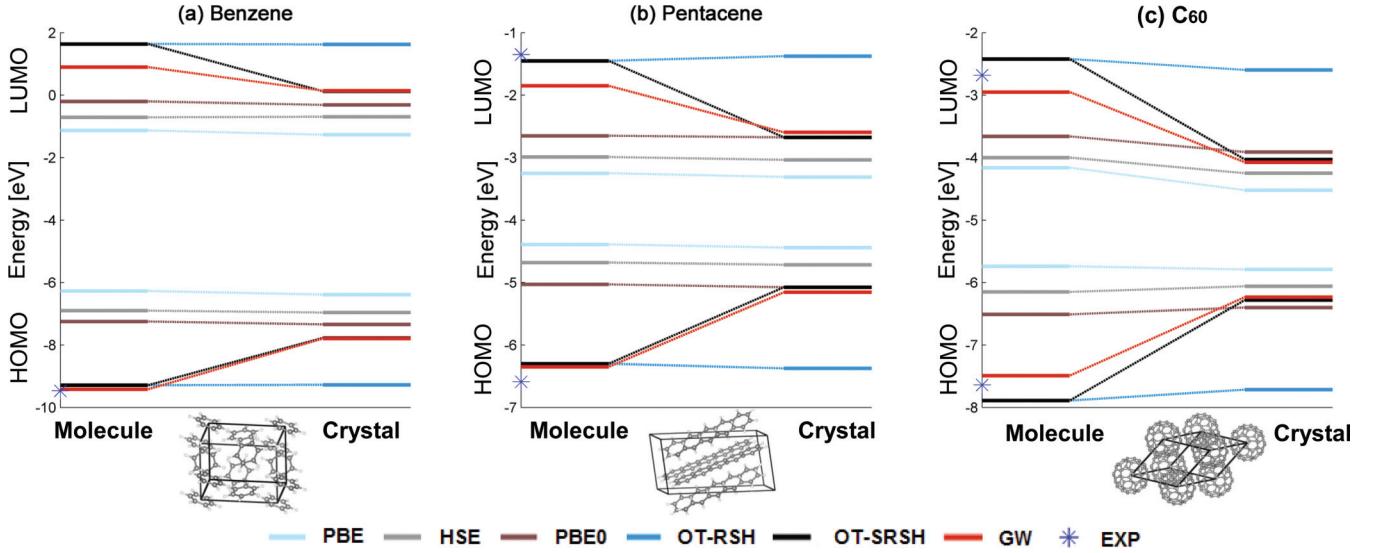


FIG. 1. (Color online) Fundamental gaps of (a) benzene, (b) pentacene, and (c) C_{60} for the gas-phase molecule (left) and the molecular crystal (right), calculated with the PBE, HSE, PBE0, OT-RSH, and OT-SRSH functionals, and compared to GW . Bulk gaps were aligned to the middle of the gas-phase gap. Gas-phase HOMO and LUMO levels are additionally compared to experimental IP and EA values, taken from Ref. 25. GW values for gas-phase pentacene and benzene were taken from Refs. 20 and 26, respectively.

Explicitly, γ is obtained from minimizing the target function

$$J^2(\gamma; \alpha) = (E_{Hn}^{\gamma; \alpha} + IP_n^{\gamma; \alpha})^2 + (E_{Ha}^{\gamma; \alpha} + IP_a^{\gamma; \alpha})^2. \quad (3)$$

In prior work, the gas-phase fundamental gap was found to be a very weak function of α , the fraction of Fock exchange in Eq. (2). However, this fraction affects the ordering of deeper lying states owing to the mitigation of short-range self-interaction errors.²⁰ Although α can be determined from first principles in some cases,^{20,23} a value of $\alpha = 0.2$ appears to be universally useful for small organic molecules.^{20,24} Therefore, we make no attempt to optimize it here.

The success of the above approach for the gas phase is demonstrated in Fig. 1 for the three prototypical organic molecular crystals studied in this work. In the figure, we compare HOMO-LUMO gaps obtained from the Perdew-Burke-Ernzerhof (PBE) nonempirical GGA functional,²⁷ its corresponding nonempirical hybrid functional, PBE0;²⁸ the Heyd-Scuseria-Ernzerhof (HSE) short-range PBE-based hybrid functional²⁹ and the above-defined optimally tuned RSH (OT-RSH) functional, with PBE ingredients for the semilocal exchange and correlation; a many-body perturbation theory within the GW approximation; and experimental IP and EA.^{25,30,31} Of all representative density functionals studied, only the optimally tuned RSH yields gas-phase gaps in excellent agreement with experiment. Note that GW gaps were obtained in the G_0W_0 approximation with a PBE starting point, which can somewhat underestimate gas-phase gaps.^{9,32} The same is observed here.

Figure 1 also shows the HOMO-LUMO gaps³³ obtained from the above functionals, compared to the GW gaps, for the corresponding molecular solids.³⁰ As expected, none of these functionals, including RSH, yields the gap renormalization captured by GW . This is because the GW self-energy is sensitive to environmental effects while none of the DFT functionals in their present form is.³⁴ Thus, for a given functional, the computed solid-state gap is similar to the

gas-phase value. Small remaining differences reflect minor geometrical effects and/or residual hybridization, rather than dielectric phenomena. In other words, nonlocal polarization effects are clearly unaccounted for.

Among all functionals studied, the RSH stands out as the only one leading to a correct description of the $1/r$ asymptotic potential in the gas phase.¹⁶ A more general asymptotic potential should be $1/(\varepsilon r)$, where ε is the scalar dielectric constant.³⁵ The gas phase limit is obtained as a special case with $\varepsilon = 1$. We can easily generalize our adjustable parameters accordingly by choosing $\alpha + \beta = 1/\varepsilon$, instead of the above $\alpha + \beta = 1$. The resulting exchange-correlation expression, which we name screened RSH (SRSH), is

$$E_{xc}^{\text{SRSH}} = (1 - \alpha)E_{\text{GGAx}}^{\text{SR}} + \alpha E_{xx}^{\text{SR}} + \left(1 - \frac{1}{\varepsilon}\right)E_{\text{GGAx}}^{\text{LR}} + \frac{1}{\varepsilon}E_{xx}^{\text{LR}} + E_{\text{GGAx}}. \quad (4)$$

This immediately leads to parameters appropriate for the solid state: As α and γ determine the balance of SR exchange and correlation necessary for describing the molecule, they must remain unaltered as long as the intermolecular hybridization is weak, as expected for molecular crystals.³⁶ But β changes from $1 - \alpha$ [Eq. (2)] to $1/\varepsilon - \alpha$ [Eq. (4)], and therefore the LR Fock exchange is screened as appropriate for incorporating the dielectric response. ε , then, is an adaptive nonempirical parameter, reflecting the specific dielectric properties of the solid and chosen to be 1 for the gas phase.

To test this idea, we calculated the bulk scalar dielectric constant using the random phase approximation (RPA).³⁰ The results are shown graphically in Fig. 1 (and in full in the Supplemental Material³⁰). Clearly, the new SRSH functional fully captures the gap renormalization, thereby accounting for nonlocal polarization, a feat beyond the scope of all other functionals, including the standard RSH.

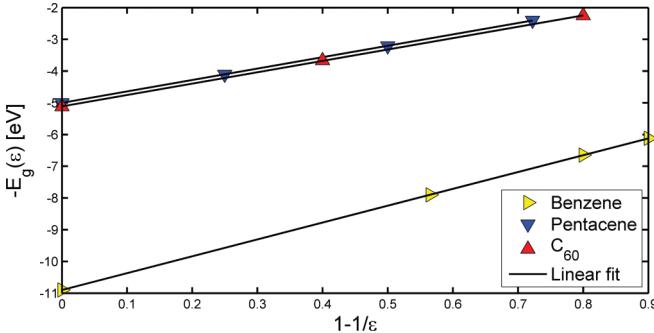


FIG. 2. (Color online) SRSRH-computed HOMO-LUMO gaps [eV] (Ref. 33) of benzene, pentacene, and C_{60} solids, as a function of $1 - 1/\varepsilon$, with ε being the asymptotic potential decay parameter in the SRSRH functional. Straight lines are a linear fit.

To further explore the physics behind the gap renormalization, consider a simple electrostatic model of polarization associated with charging a sphere contained within a dielectric.^{1,4,9} In this model, gap renormalization is given by $E_g(\text{molecule}) - E_g(\text{crystal}) = 2P = \frac{e^2}{R}(1 - \frac{1}{\varepsilon})$, where P is the lattice polarization, e is the electron charge, and $R = (\frac{3\Omega}{4\pi n})^{1/3}$ is an effective molecular radius, with Ω the volume of the primitive unit cell and n the number of molecules within it. If our DFT-based approach indeed captures electrostatic polarization, the degree of gap renormalization should be linear in $1 - \frac{1}{\varepsilon}$ for any ε . Figure 2 shows the solid-state gap computed for various values of ε . The relation is indeed linear for all three systems. Furthermore, Table I compares the effective radii and the electronic polarization resulting from this model when only accounting for the primitive cell volume per molecule, and the same properties when extracted from a linear fit to the SRSRH data of Fig. 2 and from the gas- and crystalline-phase fundamental gaps of GW . All results are in qualitative agreement. Quantitative differences mostly reflect differences in the obtained gas-phase gaps, i.e., reflect our choice of α and γ and of G_0W_0 , as well as model limitations, rather than our incorporation of dielectric phenomena.

Beyond gap determination, we examine the outer-valence band structure of the three prototypical molecular crystals. Following Hybertsen and Louie,³⁷ we consider the energy difference between GW quasiparticle energies and PBE energies, as a function of the quasiparticle energy, for bound states in the range of several eV from the valence and conduction band edges. We then do the same for the SRSRH energies. The comparison, given in Fig. 3, suggests that the accurate solid-state gaps obtained from SRSRH are not coincidental: The

TABLE I. Effective cell radius and electrostatic polarization as calculated from the electrostatic model of polarization, compared to SRSRH and GW results extracted from gap renormalization.

	Method	Benzene	Pentacene	C_{60}
Effective radius (atomic units)	Model	5.82	8.23	10.37
	SRSRH	5.12	7.57	7.59
	GW	6.40	10.07	8.44
Polarization (eV)	Model	1.32	1.19	1.05
	SRSRH	1.50	1.30	1.43
	GW	1.20	0.97	1.29

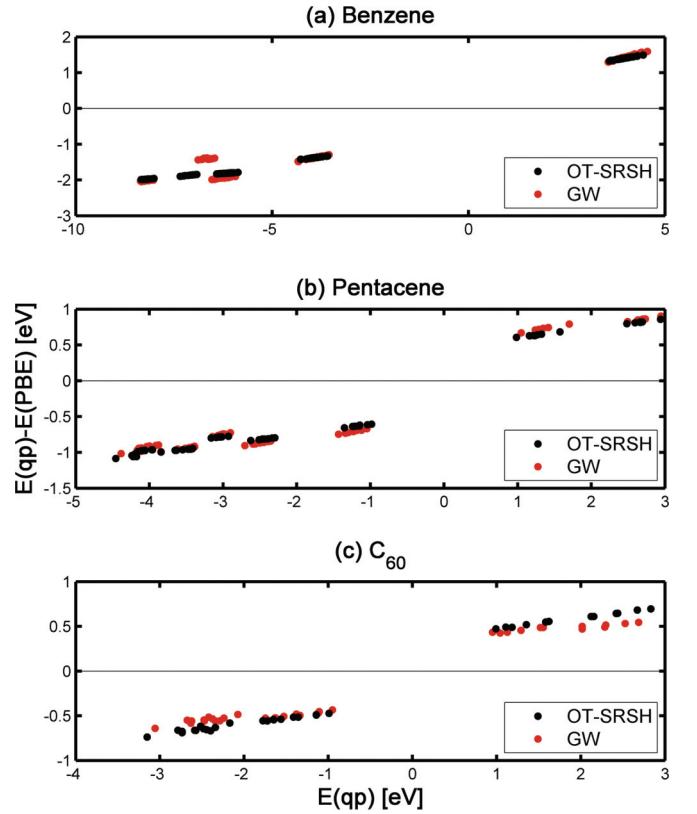


FIG. 3. (Color online) Energy differences between OT-SRSRH/ GW and PBE eigenvalues, as a function of OT-SRSRH/ GW energies, for the benzene, pentacene, and C_{60} solids. All eigenvalues are shifted to the middle of the HOMO-LUMO gap for each method.

SRSRH functional is capable of predicting an outer-valence band structure of a similar quality to GW .³⁸ As previously observed for the gas phase,²⁰ α , the short-range fraction of Fock exchange, plays a crucial role in achieving this. As shown in the Supplemental Material,³⁹ similar SRSRH results but with $\alpha = 0$ are not as accurate.

Having proven the utility and accuracy of our approach, we consider further attributes of it from the DFT point of view. First, we emphasize that attainment of gaps from DFT—in solids or molecules—is, in principle, generally possible only within a generalized Kohn-Sham approach.^{3,16,39} In the original Kohn-Sham framework, a usually nonnegligible derivative discontinuity, i.e., a finite “jump” in the exchange-correlation potential as the number of particles crosses an integer, hinders gap prediction.⁴⁰ This departure from the Kohn-Sham picture has been previously invoked as a prerequisite for the success of optimally tuned RSH functionals in predicting molecular gaps.^{16,18} The new SRSRH functional proposed here differs further and fundamentally from standard RSH formulations in the inclusion of a system-adjustable dielectric constant, incorporated such that it yields the correct system-specific asymptotic limit. This flexibility is *essential* to capturing the fundamental gap of *both* the gas-phase and solid-state environments³⁴ and, ergo, gap renormalization. Importantly, all other PBE-based functionals, used in Fig. 1, as well as the LC- ω PBE⁴¹ and LC- ω PBE0²⁴ RSH functionals, are special cases of the general SRSRH, with different, *rigid* choices for α , γ , and β . The specific parameters required for obtaining these special cases

are summarized in the Supplemental Material.³⁰ The non-RSH functionals and the HSE functional are asymptotically incorrect at both the molecular and solid-state limits. The traditional RSH functionals are asymptotically correct only in the molecular case, and still do not generally employ the optimal, system-dependent α and γ . Therefore, all these functionals are fundamentally incapable of describing gap renormalization due to polarization. One can then understand, for example, the excellent PBE0 prediction for the solid-state gap of pentacene as a direct consequence of the dielectric constant, $\epsilon = 3.6$, accidentally resembling $1/\alpha$ of PBE0. But this accidental success does not carry over to gas-phase pentacene, where the asymptotic limit is incorrect and the gap is much too small. Nor does it carry over to, e.g., solid-state benzene, where $\epsilon = 2.3$. There, the PBE0 functional overestimates the polarization and indeed the resulting gap is too small, as compared to GW or SRSH. The same logic explains why PBE and HSE, whose asymptotic potential is exponentially decaying rather than scaling as $1/r$, systematically underestimate even the solid-state gaps.

Several previous studies have attempted to use conventional RSH functionals towards the prediction of band gaps in (not necessarily molecular) solids. Generally, agreement with experiment has not been satisfactory whenever a rigid RSH form was used.⁴² Some very interesting attempts to adjust α and/or γ in either an RSH or a conventional hybrid functional have been reported,^{35,43–46} and some interesting connections between the choice of parameters and the dielectric constant have been pointed out. Our work differs substantially from these efforts, by retaining the *same* choice for α and γ in the molecule and the solid and accounting for the dielectric constant *only* through appropriate LR screening. This is essential to treating the molecule and the solid on the same footing in all but the dielectric screening—a prerequisite to describing polarization.

We mentioned above that polarization is inherently a phenomenon of nonlocal correlation. How, then, have we

described it without ever modifying the correlation expression from the standard semilocal one of the PBE functional? The answer is that we have screened the LR exchange. The difference between the screened exchange and the exact exchange is itself a form of correlation,⁴⁷ which is necessarily nonlocal owing to the nonlocal nature of the exchange operator. Finally, for the proof-of-principle computations given here we have obtained the scalar dielectric constant from an RPA calculation. However, the cost of this computational step can be brought down substantially by using other inexpensive yet effective methods for first-principles determination of scalar dielectric constants, e.g., those of Refs. 48–52.

In conclusion, we presented a new screened range-separated hybrid functional, which—to the best of our knowledge for the first time—is capable of capturing the effect of polarization on gap renormalization in molecular crystals in a way that is qualitatively correct and quantitatively accurate. This functional retains predictive power, as it contains adjustable parameters that are determined from first principles. We expect that this could pave the way towards nonempirical gap prediction from density functional theory in more general solid-state systems.

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