

Structural and excited-state properties of oligoacene crystals from first principlesTonatíuh Rangel,^{1,2,*} Kristian Berland,³ Sahar Sharifzadeh,⁴ Florian Brown-Altvater,^{1,5} Kyuho Lee,¹ Per Hyldgaard,^{6,7} Leeor Kronik,^{8,†} and Jeffrey B. Neaton^{1,2,9,‡}¹*Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*²*Department of Physics, University of California, Berkeley, California 94720-7300, USA*³*Centre for Material Science and Nanotechnology, University of Oslo, NO-0316 Oslo, Norway*⁴*Department of Electrical and Computer Engineering and Division of Materials Science and Engineering, Boston University, Boston, Massachusetts 02215, USA*⁵*Department of Chemistry, University of California, Berkeley, California 94720-7300, USA*⁶*Department of Microtechnology and Nanoscience, MC2, Chalmers University of Technology, SE-41296 Göteborg, Sweden*⁷*Materials Science and Applied Mathematics, Malmö University, Malmö SE-205 06, Sweden*⁸*Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel*⁹*Kavli Energy NanoSciences Institute at Berkeley, Berkeley, California 94720-7300, USA*

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Molecular crystals are a prototypical class of van der Waals (vdW) bound organic materials with excited-state properties relevant for optoelectronics applications. Predicting the structure and excited-state properties of molecular crystals presents a challenge for electronic structure theory, as standard approximations to density functional theory (DFT) do not capture long-range vdW dispersion interactions and do not yield excited-state properties. In this work, we use a combination of DFT including vdW forces, using both nonlocal correlation functionals and pairwise correction methods, together with many-body perturbation theory (MBPT) to study the geometry and excited states, respectively, of the entire series of oligoacene crystals, from benzene to hexacene. We find that vdW methods can predict lattice constants within 1% of the experimental measurements, on par with the previously reported accuracy of pairwise approximations for the same systems. We further find that excitation energies are sensitive to geometry, but if optimized geometries are used MBPT can yield excited-state properties within a few tenths of an eV from experiment. We elucidate trends in MBPT-computed charged and neutral excitation energies across the acene series and discuss the role of common approximations used in MBPT.

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Organic solids are promising candidates for optoelectronics applications due to their strong absorption, chemical tunability, flexibility, and relatively inexpensive processing costs, among other reasons. The acene crystals, a specific class of organic semiconductors, are well characterized, known to possess relatively high carrier mobilities [1], and exhibit a propensity for unique excited-state transport phenomena, notably singlet fission (SF) [2–7]. The larger acenes in particular have received recent attention because SF was reported to be exothermic, or nearly so, for tetracene, pentacene, and hexacene [8–12].

The interesting optoelectronic properties of acene crystals, combined with the potential for materials design via functionalization at the monomer level, have generated significant fundamental theoretical interest in these systems. Theoretical studies of excited-state properties of acene crystals have often been performed with small molecular clusters, using wave-function-based methods [7,13–18], or with extended systems, using density functional theory (DFT) and many-body perturbation theory (MBPT) [19–26]. These calculations have often yielded excellent agreement with experiment and new insights into excited-state properties of acene crystals.

As shown in Fig. 1, acene crystals consist of aromatic monomers packed in ordered arrangements. Their constituent monomers possess strong intramolecular covalent bonds, but

weak intermolecular dispersive interactions govern the crystal structure. Because the approximate exchange-correlation functionals most commonly used in DFT calculations do not account for dispersive interactions, the above-mentioned theoretical calculations have nearly always made use of experimental data for intermolecular distances and orientation. This limits predictive power because experimental lattice parameters can be scarce or conflicting. In particular, different polymorphs of the same material may exist, sometimes even coexisting in the same sample [22,26–33].

Fortunately, the last decade has seen rapid development of DFT-based methods that can capture dispersive interactions and several studies have demonstrated that addressing these interactions allows for predicting accurate geometries and cohesive energies of molecular solids in general and acenes in particular (see, e.g., Refs. [22,34–46]). Specifically, Ambrosch-Draxl *et al.* [22] have suggested that a combination of dispersion-inclusive DFT methods, which they found to predict lattice parameters in agreement with experiments for acene crystals, followed by MBPT calculations can be used to explore quantitative differences in optical properties of pentacene polymorphs. Their work suggests that a broader study of the entire acene family with MBPT methods, especially their recent refinements, would be highly desirable.

In this paper, we combine dispersion-inclusive DFT and MBPT to study the geometry and excited states of the entire series of acene crystals, from benzene to hexacene. In each case, we compare the computed geometry, electronic structure, and optical excitations with experiment, for both the gas phase and solid state. To account for long-range van

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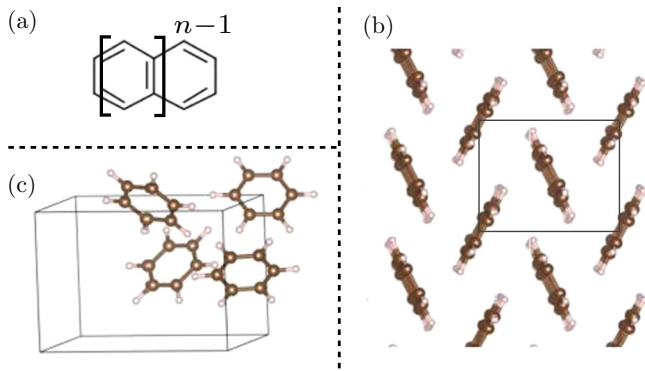


FIG. 1. The acene family. (a) General formula. (b) Herringbone structure, taken up by most acenes in the solid state, with space group $P21/a$ for naphthalene and anthracene and $P1$ for larger acenes. (c) Benzene crystallizes in an orthorhombic unit cell with four molecules per unit cell, with space group $Pbca$.

der Waals (vdW) dispersive interactions, we use primarily nonlocal vdW density functionals (vdW-DFs), but also employ Grimme “D2” pairwise corrections [47] and compare our results where possible with previously reported data computed with the Tkatchenko-Scheffler (TS) [48] pairwise correction approach [37,49]. We find that the new consistent-exchange (cx) vdW density functional (vdW-DF-cx) [50,51] can predict acene lattice parameters within 1% of low-temperature measurements, as can the TS method. For optimized acene crystal structures, our MBPT calculations within the GW approximation and using the Bethe-Salpeter equation approach lead to gas-phase ionization potential energies, solid-state electronic band structures, and low-lying singlet and triplet excitations in good quantitative agreement with experiments. For larger acene crystals, we demonstrate that a standard G_0W_0 approach based on a semilocal DFT starting point is insufficient, and that eigenvalue-self-consistent GW calculations are required. Interestingly, we find that low-lying excited states are sensitive to crystal geometry, particularly so for singlets, which are significantly more delocalized than triplets. This work constitutes a comprehensive survey and validation study of both crystal structure and excited-state electronic structure for this important class of molecular crystals. Furthermore, it suggests strategies for accurate predictive modeling and design of excited states in less-explored molecular systems, using current state-of-the-art methods.

The paper is organized as follows. First, we summarize the computational methods used in this work in Sec. II. Next, in Sec. III A we provide a detailed account of our calculations for the structural properties of the acene crystals, demonstrating and reviewing the accuracy of several different vdW-corrected DFT methods. We then turn to presenting MBPT results for charged and neutral excitations. We start with charged and neutral excitations in gas-phase acene molecules, given in Sec. III B, followed by similar results for the solid state in Secs. III C and III D, where we provide calculations for charged and neutral excitations, respectively, at the experimental geometry. In Sec. III E, we critically examine the sensitivity of GW and GW -BSE calculations to structures optimized with different DFT-based approaches. Finally, we present conclusions in Sec. IV.

II. COMPUTATIONAL METHODS

A. Treatment of dispersive interactions

As mentioned above, great strides have been made over the past decade in the treatment of dispersive interactions within DFT (see, e.g., Refs. [52,53] for overviews). Of the many approaches suggested, one commonly used method is the augmentation of existing (typically semilocal or hybrid) exchange-correlation (xc) functionals by pairwise corrections to the internuclear energy expression, which are damped at short range but provide the desired long-range asymptotic behavior [47,48,54–59]. The most widely used examples of this idea are the D2 [47] and D3 [57] corrections due to Grimme and the Tkatchenko-Scheffler (TS) [48] correction scheme. A different commonly used approach, known as vdW-DF, includes dispersion interactions via an explicit nonlocal correlation functional [60–62]. Several vdW-DF versions are in use, starting with the original vdW-DF1 [63] functional. These include, e.g., an improved version, vdW-DF2 [64], making use of a more accurate semilocal exchange functional and an updated vdW kernel; the simplified yet accurate form of Vydrov and van Voorhis, VV10 [65]; and the more recently developed vdW-DF-cx [50] functional, an update with improved performance for lattice constants and bulk moduli of layered materials and dense solids. In the following, we abbreviate vdW-DF1 as DF1, etc., for functionals in the vdW-DF class.

B. Many-body perturbation theory

As mentioned above, our first-principles MBPT calculations are based on the GW approach for charged excitations and on the GW -BSE approach for neutral ones. GW calculations proceed perturbatively based on a DFT starting point, which for solids is usually computed using the Kohn-Sham equation within the local density approximation (LDA) or the generalized gradient approximation (GGA). The Kohn-Sham eigenvalues and eigenfunctions are used to evaluate approximately the self-energy operator Σ as iGW , where G is the one-electron Green function of the system and $W = \epsilon^{-1}v$ is the dynamically screened Coulomb interaction; v is the Coulomb potential and ϵ is the wave-vector- and frequency-dependent dielectric function [66,67]. The DFT eigenvalues are then updated via first-order perturbation theory. This approach is known as the G_0W_0 approximation. This method is often very successful, but nevertheless it is somewhat dependent on the DFT starting point. GW can be evaluated, in principle, self-consistently by different approaches [68,68–74], mitigating the starting-point dependence by iterating over eigenvalues and wavefunctions. Given the computational demands associated with acene crystals, in the following we limit our study to the diagonal part of Σ and, if going beyond G_0W_0 , we only update the eigenvalues in G and W , retaining the original DFT wave functions under the assumption that they are close to the true QP wave functions [66,75–77]. We denote this sort of partial self-consistency as $evGW$, where “ev” emphasizes that self-consistency is achieved only with respect to the eigenvalues.

Given the GW -computed quasiparticle energies, as well as the static inverse dielectric function computed within the ran-

dom phase approximation, we compute neutral excitation energies by solving the Bethe-Salpeter equation (BSE) [78–80]. We use an approximate form of the BSE, developed within a first-principles framework by Rohlfing and Louie [80], which involves solving a new eigenvalue problem obtained from an electron-hole interaction matrix. We generate solutions within the Tamm-Dancoff approximation (TDA) and limit our calculations to low-lying singlet and triplet excitations.

C. Computational details

Our DFT calculations are performed with the QUANTUM ESPRESSO (QE) package [81], unless otherwise indicated. Γ -centered Monkhorst-Pack \mathbf{k} -point grids are used for all calculations [82]. For geometry optimizations, where Hellmann-Feynman forces and stress tensor components are minimized, we use a number of \mathbf{k} points along each crystallographic direction corresponding to a spacing of ~ 3.3 bohrs⁻¹ between neighboring points in reciprocal space. All Hellmann-Feynman forces are converged to 10^{-5} Ry/bohrs and total energies are converged to 10^{-5} Ry. We use a plane-wave basis kinetic energy cutoff of 55 Ry. Taken together, these choices lead to total energies converged to 1 meV per atom.

For calculations with vdW-DF functionals, we use the ultrasoft pseudopotentials (USPPs) given in Ref. [50]; for vdW approaches based on interatomic pairwise potentials, we use Fritz-Haber-Institut (FHI) norm-conserving (NC) pseudopotentials (PPs) [83] because these corrections are not compatible with USPPs in the present version of QE. Following a prior successful approach with vdW density functionals [84], we use Perdew-Burke-Ernzerhof (PBE) [85] PPs for DF2 and DF and PBEsol [86] PPs for DF-cx [62]. In principle, native vdW-PPs have begun to be explored with vdW-DFs, and we relegate the evaluation of such pseudopotentials for acenes to future work [87]. The latter choice is based on the fact that the exchange functional of DF-cx is much closer in form to PBEsol than to PBE. A test study reveals that the results are not significantly affected by this choice: for naphthalene, the lattice parameters (and volume) obtained using DF-cx with PBE PPs differ by no more than 1.2% (0.2%) from standard DF-cx calculations.

To test the reliability of our PP choice, we benchmarked our calculations of solid naphthalene (see Sec. III A for details) against other codes and pseudopotentials. The lattice parameters obtained with our USPPs, the FHI NC-PPs available at the QE site [88] and Garrity-Bennett-Rabe-Vanderbilt (GBRV) [89] USPPs agree within 0.3%. Additionally, we relaxed the structure of benzene with the VASP code, using projector-augmented waves [90] with vdW-DF2, obtaining lattice parameters in agreement with those obtained from QUANTUM ESPRESSO to within 0.4%. Note that a higher, 110-Ry cutoff was used for the FHI-NC-PPs calculations. The GBRV-USPPs were constructed to be exceptionally hard and required a plane-wave cutoff of 350 Ry to achieve a convergence threshold of 1 meV/atom.

For each acene crystal, using any of the DFT approximations mentioned above, following geometry optimization we compute cohesive energies (E_{coh}) via the standard relation

$$E_{\text{coh}} = E^{\text{gas}} - \frac{1}{N} E^{\text{solid}}, \quad (1)$$

where E^{gas} is the total energy of an isolated monomer, E^{solid} is the total energy of the solid phase unit cell, and N is the number of molecules per unit cell in the solid.

Our MBPT calculations are performed with the BERKELEY GW package [91]. Capitalizing on its efficient and highly parallel diagonalization techniques, Kohn-Sham starting-point wave functions and eigenenergies for input into MBPT are generated with the ABINIT software suite [92].

In some of the calculations given below, we deliberately use experimental lattice constants to study the accuracy of the GW -BSE approach independent of geometry. For consistency, we use room-temperature experimental data for all acenes [93–97] except for hexacene, where crystallographic data are only available at $T = 123$ K [98]. For pentacene, we consider the thin-film polymorph (denoted below as P_3) because it is the one most commonly measured in experiment (see Sec. III A). In other calculations, where we explore the impact of the geometry, we use the optimized geometry obtained from the DFT calculation.

We note that BERKELEY GW requires NC-PPs as input, but we use USPPs for lattice optimizations. Prior to the MBPT calculations, we relaxed the internal coordinates using NC-PPs within PBE, with the lattice parameters held fixed at their optimized value. This was found to result in negligible differences for both geometry and excited-state properties. We followed the same internal relaxation procedure when using experimental lattice vectors, following Ref. [23].

Our GW calculations involve a number of convergence parameters, which are set to assure that quasiparticle gaps, highest-occupied molecular orbital (HOMO) energies, and band-edge energies for crystals and gas-phase molecules are converged to ~ 0.1 eV. Our dielectric function is extended to finite frequency using the generalized plasmon-pole (GPP) model of Hybertsen and Louie [66], modified to handle noncentrosymmetric systems by Zhang *et al.* [99]. For solids, we use an energy cutoff of 10 Ry to truncate the sums in \mathbf{G} space used for the calculation of the polarizability. We sum over a number of unoccupied bands equivalent to an energy range of 30 eV. Response functions and Σ are evaluated on \mathbf{k} -point meshes selected to lead to a spacing of ~ 1.6 bohrs⁻¹ in reciprocal space. For gas-phase molecules, we use an energy cutoff of 25 Ry for the polarizability and sum over a number of unoccupied bands equivalent to 52 eV above the lowest unoccupied molecular orbital (LUMO) energy. Molecules are modeled in a large supercell with dimensions chosen to contain 99% of the HOMO (see Supplemental Material [100] for details), with the internal coordinates relaxed using PBE. We use the static-remainder technique to accelerate the convergence with number of bands [101], using the version of Deslippe *et al.* [102]. A Wigner-Seitz Coulomb truncation scheme is used to eliminate interactions between molecules of neighboring cells in the periodic lattice [91]. These convergence criteria and parameters have been tested and used, in part, in Ref. [103].

For our BSE calculations, the BSE coupling matrix is constructed with 8 valence \times 8 conduction bands, sufficient to converge the transition energies involving the lowest states, as shown explicitly in the Supplemental Material [100]. Two \mathbf{k} -point meshes are used: a coarse \mathbf{k} -point mesh for the BSE kernel and a fine \mathbf{k} -point mesh to calculate the low-lying

excited states. Coarse \mathbf{k} meshes are chosen to be the same as those used in the GW step, while fine meshes are the same as in the geometry optimization. These \mathbf{k} meshes are explicitly provided in the Supplemental Material [100].

III. RESULTS AND DISCUSSION

A. Lattice geometry and cohesive energy

We begin our discussion by considering the effect of the chosen DFT approximation on the crystal geometry and cohesive energy. Experimental unit-cell volumes for the acene crystals are compared in Fig. 2(a) with volumes calculated using the LDA, PBE, PBE-D2, PBE-TS (from Refs. [37,49]), DF1, DF2, and DF-cx approaches. A similar comparison for cohesive energies is given in Fig. 2(b). A complete set of structural data, along with error estimates, is given in Appendix A. For tetracene, its polymorph 1 (P_1) also called the high-temperature polymorph [97,107], referred to as TETCEN in the Cambridge Structural Database (CSD) [108], is considered. This crystal is known to undergo a pressure-assisted transition to a different high-pressure or low-temperature polymorph (P_2) [29,109–113], the study of which is beyond the scope of this work. This low-temperature polymorph has been successfully described within the TS method in Ref. [49]. For pentacene, three well-known polymorphs are considered, using experimental structures available in the CSD [108]. These are as follows:

(i) P_1 : the Campbell structure, referred to as PENCEN in the CSD. It is also known as the high-temperature polymorph. Found first by Campbell in 1962 [97], it had been lost until reported again in 2007 [114].

(ii) P_2 : a common bulk-phase polymorph, referred to as PENCEN04 in the CSD [28,115].

(iii) P_3 : a common thin-film polymorph, referred to as PENCEN10 in the CSD [94,115]. Most experimental data correspond to this polymorph.

Figure 2 shows, as expected, that standard (semi)local functionals do not result in good agreement with experimental results. PBE significantly overestimates lattice constants and underestimates cohesive energies. This can be attributed directly to the lack of treatment of dispersive interactions in PBE [40]. LDA lattice constants are underestimated by $\sim 3\%$, but this binding is spurious, rather than reflecting a successful treatment of dispersive interactions [40]. The spurious binding is attributable to the insufficient treatment of exchange [116,117].

Turning to explicit vdW functionals, Fig. 2(a) clearly shows that DF1 overestimates lattice constants essentially as much as LDA underestimates them. This is because DF1 is based on the exchange of revPBE [118], a variant of PBE with exchange that is too repulsive for the systems studied here. At the same time, Fig. 2(b) shows that it still overestimates binding energies. We note that cohesive energies of acene crystals have been calculated with DF1 prior to this work [22,34,37], with differing conclusions. While DF1 results for E_{coh} are in agreement with experiment to better than 5% in Refs. [22,34], Ref. [37] reports DF1 results that deviate from experiment by as much as $\sim 17\%$. These differences can be partially explained by the different choices these studies made for the experimental reference data. Some differences remain even if we use the experimental values of Ref. [41], in which the contributions due to vibrations are carefully taken into account, throughout. Despite having carefully ruled out lack of convergence in our calculations, the average percentage error (see Table VI in the Appendix) in E_{coh} is then somewhat larger in this study, being 16%, 10%, and 9% in the data of our work, Ref. [37], and Ref. [22], respectively. For the lattice parameters, however, we find good agreement (within 2%) with those reported previously.

Figure 2(a) clearly shows that DF2 improves geometries with respect to DF1, in agreement with the findings in Ref. [37], with further improvement gained from DF-cx. Specifically, lattice constants are within 2% and 1%,

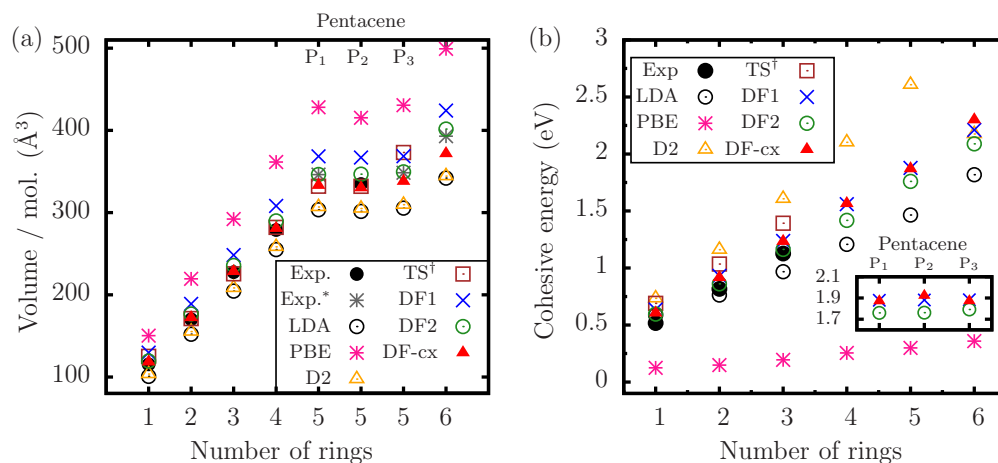


FIG. 2. (a) Volume per molecule for the acene crystals, calculated using different approximations within DFT: LDA (black empty circles), PBE (pink stars), DF1 (blue crosses), DF2 (green empty circles), DF-cx (red filled triangles), PBE-D2 (orange empty triangles), and PBE-TS (brown squares). These are compared to low-temperature experimental data, for $T \leq 16$ K from Refs. [95,104,105] and extrapolated to 0 K as indicated in Appendix A (in black filled circles). For two pentacene polymorphs and hexacene, only experimental data at $T \geq 90$ K is available [94,97,98] (in dark gray stars). (b) Cohesive energies E_{coh} for the acene series, obtained with the same set of approximations as in (a). Experimental E_{coh} (black filled circles) are obtained from enthalpies of sublimation (Ref. [106], see text). Inset: calculated E_{coh} for three pentacene polymorphs. † PBE-TS cohesive energies are taken from Ref. [41] and PBE-TS volumes from Refs. [37,49].

respectively, of experiment. Fortuitously, DF2 values for the lattice parameters are similar to the thermally expanded lattice parameters obtained at room temperature. This is attributable to a cancellation of errors, as we model the structure at 0 K. Recent work [45] reported that a DF2 variant, called rev-vdW-DF2 [119], predicts lattice constants for benzene, naphthalene, and anthracene that are in remarkable agreement with low-temperature experiments (within 0.5%). For tetracene and P₂ pentacene, good agreement with room-temperature experiments is found [45], but the reported volumes overestimate structures extrapolated to 0 K by $\sim 2\%$ for pentacene P₂ and 8% for tetracene.

For cohesive energies, Fig. 2(b) shows that neither DF2 nor DF-cx improve meaningfully upon DF1 cohesive energies. Specifically, the values obtained for DF2 are in excellent agreement (within 0.05 eV) with those reported in Ref. [37], as is the conclusion regarding lack of improvement over DF1. Interestingly, rev-vdW-DF2 reduces the error in cohesive energies with respect to experiments by half [45].

Turning to pairwise correction methods, Fig. 2(a) shows that lattice vectors calculated with D2 and TS corrections, added to underlying PBE calculations, are within 3% and 1% of experimental data, respectively, whereas cohesive energies are within 30% to 40% of experiment. Thus, they perform as well as DF methods in terms for geometries prediction but somewhat worse for cohesive energies.

To summarize, both the latest pairwise approaches and the latest DF methods can provide lattice parameters in outstanding agreement with experimental data (within $\sim 1\%$) across the acene series, illustrating the predictive power of vdW methods and allowing for an excellent geometrical starting point for MBPT calculations. However, errors in cohesive energy are still on the order of 10% to 30%. In future work, it would be interesting to examine whether techniques which add nonlocality beyond pairwise interactions, particularly the many-body dispersion method [41,43], can reduce the error in the cohesive energy. It would also be interesting to examine Grimme's "D3" method [57], which also attempts to mimic many-body terms and other features that may improve calculated lattice constants and energies with respect to the "D2" approach [120].

B. Charged and neutral excitations of gas-phase molecules

Before discussing excitations in acene solids, it is instructive to consider charged and neutral excitations in the constituent gas-phase molecules. Computed results for the ionization potential (IP) and electron affinity (EA), computed with the GW approach, as well as lowest-energy singlet (S_1) and triplet (T_1) excitation energies, computed within the GW -BSE approach, of gas-phase acene molecules, are given in Fig. 3. The same data are presented in Table I.

We find that calculated G_0W_0 -computed IPs and EAs are within 0.4 eV of experiment, with an average error of only 0.2 eV. The agreement is particularly good for the smallest acenes [103], for reasons that have to do with our use of the PPM, as elaborated in Ref. [124]. For the largest acenes, the deviations of the IP and EA values from experiment possess opposite signs, leading to a larger error (up to 0.7 eV) in the fundamental gap, i.e., the difference between the IP and

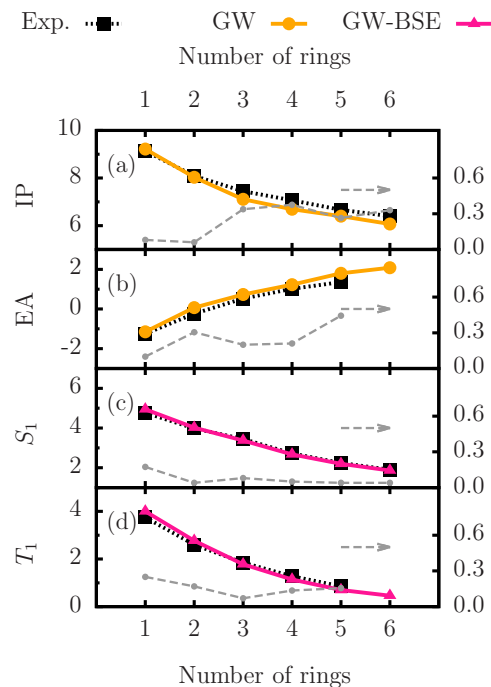


FIG. 3. Excited-state energetics, in eV, of the gas-phase acene molecules. (a) Ionization potentials (IPs) and (b) electron affinities (EAs) calculated within GW [solid orange (light gray) lines (circles)], as well as the (c) lowest singlet (S_1) and (d) lowest triplet (T_1) excitation energies calculated within GW -BSE [solid pink (gray) lines (triangles)]. All results are compared with experimental data [dashed black lines (squares)] [121–123]. The absolute deviation from experiment is given in eV in gray dashed lines (right axis). As discussed in the text, G_0W_0 based on a PBE starting point and the GPP approximation is used throughout.

the EA. Many recent studies (see, e.g., Refs. [68,77,125–130]) indicate that a different starting point for the G_0W_0 calculation, or use of self-consistent GW scheme, will improve agreement with experiment. Based on the results of, e.g., Refs. [23,68,131] for some of the acenes, we expect the same here, but do not pursue this point further as we wish to facilitate the comparison to the solid-state data given below.

The neutral singlet and triplet excitation energies, S_1 and T_1 , computed with G_0W_0 -BSE, are close to experimental values, deviating by 0.3 eV at most across the entire series. Given that, as mentioned above, the fundamental gap exhibits larger discrepancies between theory and experiment, the accuracy of the neutral excitation energies is likely to be partly due to a cancellation of errors between the G_0W_0 gaps and BSE binding energies.

C. Charged excitations in acene crystals

We begin our MBPT analysis of the acene series by intentionally using the experimental geometries [93–98] as our starting point. This is done to isolate errors associated with the particular flavor of the GW -BSE method used here from errors related to structural deviations (the latter are analyzed in Sec. III E).

GW results for the fundamental gap, compared wherever possible to experiment, are summarized in Table II. GW band

TABLE I. Charged and neutral excitation energies for gas-phase acene molecules. Theoretical and experimental ionization potential (IP), electron affinity (EA), lowest singlet (S_1), and lowest triplet (T_1) energies are tabulated, in eV. IP and EA are calculated within G_0W_0 , as described in the text. S_1 and T_1 are calculated within the G_0W_0 -BSE approach. Experimental data are taken from Refs. [121–123].

		Number of rings					
		1	2	3	4	5	6
IP	GW	9.2	8.0	7.1	6.6	6.4	6.1
	Expt.	9.0–9.3	8.0–8.2	7.4	7.0–7.2	6.6	6.4
EA	GW	–1.2	0.1	0.7	1.2	1.8	2.1
	Expt.	–1.4 to –1.2	–0.2	0.5	1.0	1.3	
S_1	GW -BSE	4.9	4.0	3.4	2.7	2.2	1.9
	Expt.	4.8	4.0	3.5	2.7	2.2	1.9
T_1	GW -BSE	4.0	2.8	1.8	1.1	0.7	0.5
	Expt.	3.7	2.6	1.9	1.3	0.9	

structures are provided in the Supplemental Material [100]. Table II shows that the G_0W_0 results fully capture the quantum-size effect, i.e., the reduction of the fundamental gap value with increasing acene size. Furthermore, for most acenes G_0W_0 yields fundamental gaps in good agreement with experimental data. The computed data somewhat underestimate experimental values for $n = 3$ to 5, an effect partly compensated for by gap reduction owing to thermal expansion in the experimental data, which was taken at higher temperatures, mostly room temperature. However, our G_0W_0 values decrease too rapidly with size. Thus, for naphthalene the fundamental gap is somewhat overestimated, but for pentacene it is somewhat underestimated. For hexacene, G_0W_0 is no longer acceptable. While we are not aware of an experimental fundamental gap value, the G_0W_0 value we compute is smaller than the singlet excitation energy (see Sec. III D) and therefore certainly underestimates the fundamental gap.

As in the gas-phase data, we attribute the discrepancy in hexacene to a starting-point effect. We note that for pentacene, it was shown in Ref. [23] that the QP gaps obtained with the plasmon-pole model and with a full-frequency integration are essentially identical. Therefore, we do not believe that use of the plasmon-pole approximation plays a major role here. The $evGW$ method partly compensates for starting-point effects. However, as also shown in Table II, $evGW$ tends to overestimate the experimental gaps. For hexacene, however, we are more confident in the $evGW$ value as it compensates

TABLE II. Fundamental gaps of the acene crystal series, computed within the G_0W_0 and $evGW$ approximations, compared to experimental data, taken from Refs. [132–141]. Experimental lattice constants are used. All quantities are in eV.

No. of rings	Δ_g		
	G_0W_0	$evGW$	Expt.
1	7.3	8.2	7.6–8.0
2	5.5	6.1	5.0–5.5
3	4.0	4.5	3.9–4.2
4	2.9	3.5	2.9–3.4
5	2.2	2.8	2.2–2.4
6	1.3	1.8	

for the underestimate of the G_0W_0 -computed value (an issue confirmed by optical data presented in Sec. III D).

Beyond band-gap values, it is very instructive to compare the GW -calculated electronic density of states (DOS) to measured photoemission and inverse photoemission spectroscopy (PES and IPES, respectively) data. Such a comparison is not straightforward. Experimentally, it is challenging to pinpoint absolute conduction and valence band energies [142,143]. As discussed in detail in Ref. [23], agreement between theory and experiment is often observed only after a rigid shift (of valence and conduction bands separately). This rigid shift has been attributed to a combination of several physical effects, including surface polarization, vibrational contributions, and a dynamical lattice, and to some extent also to residual errors of both theory and experiment. We therefore employ the same rigid shift procedure here, as follows. First, because absolute potentials are never defined in periodic boundary calculations, we align the top of the GW -computed valence band with experimental values from Refs. [144,145]. To compare with experiment, each photoemission and inverse photoemission curve is aligned with the GW valence and conduction band DOS, respectively. Based on the results of Table II, this procedure is performed using G_0W_0 values for benzene to pentacene and $evGW$ values for hexacene. The resulting comparison, across the entire acene series, is shown in Fig. 4, with the rigid shift employed indicated on the figure. In agreement with the findings of Ref. [23], the rigid shift is significant, with a combined PES and IPES shift of ~ 1 eV. But after employing it, we find excellent agreement, in both energy position and line shape, for all theoretical and experimental spectra across the entire acene series in a region up to ~ 6 eV from the Fermi level.

D. Neutral excitations in acene crystals

Having discussed charged excitations, we now turn to analyzing lowest-energy singlet and triplet excitation energies in the acene crystals. As in the previous sub-section, we use experimental lattice parameters in order to avoid errors associated with geometry.

Lowest neutral excitation energies, computed with both G_0W_0 -BSE and $evGW$ -BSE, are compared with experimental data in Fig. 5. The same comparison is also summarized in Table III. Importantly, no significant temperature

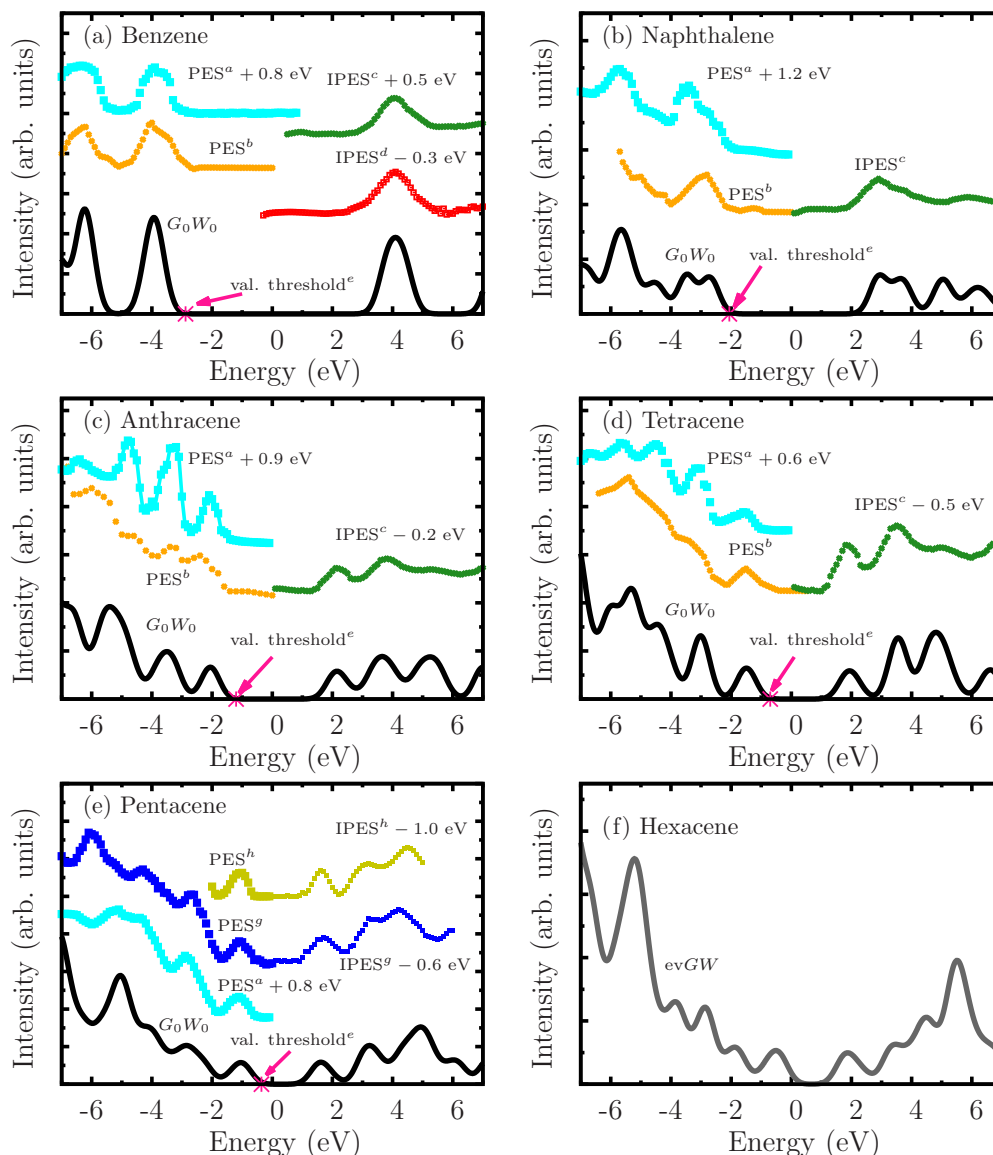


FIG. 4. Quasiparticle DOS, calculated using GW , compared with experimental photoemission (PES) and inverse photoemission (IPES) spectra. Two different GW approximations are used: G_0W_0 for benzene through pentacene and $evGW$ for hexacene (see text for details). The calculations are based on experimental lattice parameters [93–98] to avoid errors related to geometry. In each case, the DOS is interpolated on a dense mesh of \mathbf{k} points using maximally localized Wannier functions [146] and broadened by convolution with a 0.4-eV Gaussian. Band structures and DOS with lower broadening are given in the Supplemental Material [100]. Experimental PES data have been rigidly shifted, by an amount indicated in the figure, so as to match reference ionization potential data of Refs. [144,145] (pink stars) and PES data of Ref. [147] (orange points). The GW valence band edge has been set to the same position. IPES data have then been shifted to match the GW -computed position of the conduction band edge. See text for full details. ^a Reference [148]. ^b Reference [147]. ^c Reference [121]. ^d Reference [149]. ^e References [144,145].

dependence of low-lying excitation energies is observed experimentally [152,153], allowing for comparison to experiments performed at higher temperatures. Both calculations correctly predict the experimental quantum-size-effect trend, i.e., the decrease of S_1 and T_1 excitation energies with increasing acene size. However, for the S_1 excitations the computed slope is somewhat too large. Thus, the G_0W_0 -BSE calculation overestimates experiment by 0.25 eV for benzene, agrees perfectly with experiment for tetracene, and underestimates experiment by 0.4 eV for hexacene. Once again, we view this primarily as a starting-point issue. For the larger acenes, the

PBE gap is very small (only 0.2 eV for hexacene). Likely, this results in increasingly worse overscreening, as in a simple model the dielectric constant is inversely proportional to the square of the quasiparticle gap [154]. This assertion is supported by the fact that for hexacene, a G_0W_0 approach [71,101], in which self-consistency in G alone is performed, results in a singlet energy of $S_1 = 1.06$ eV, which is almost equivalent to the G_0W_0 -BSE value of 1.00 eV. A starting point with a larger gap, as in $evGW$ -BSE, leads to reduced screening and may therefore yield better neutral excited states for this system. In particular, the $evGW$ -BSE value for hexacene is

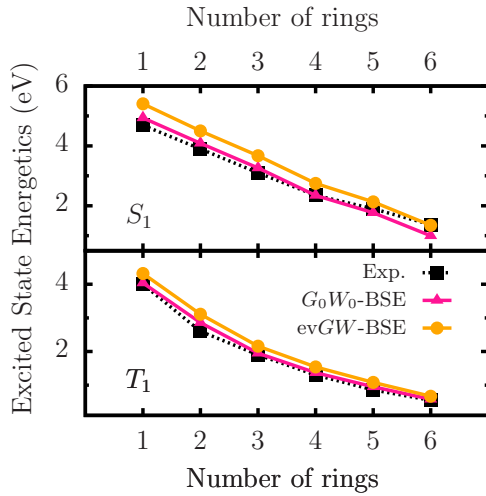


FIG. 5. Lowest-lying excitation energies of acene the crystals, computed within the G_0W_0 [pink (medium gray) lines (triangles)] and $evGW$ -BSE orange [(gray) lines (circles)] approximations, compared to experimental data [black dotted lines (squares)], taken from Refs. [123,150,151] and references therein. Experimental lattice constants have been used throughout. Lowest singlet (S_1) and triplet (T_1) energies are shown at the top and bottom panels, respectively.

in perfect agreement with experiment. However, as with the charged excitations, $evGW$ -BSE is not a panacea [71,155]; it shifts the G_0W_0 -BSE results by an almost uniform 0.3–0.4 eV, leading to an overestimate of S_1 for the smaller acenes.

The lowest triplet excitation energies T_1 obtained from G_0W_0 -BSE show a generally similar trend, but agree well with experiment for hexacene and show a modest overestimate for the smaller acenes, up to 0.3 eV for benzene and naphthalene. As with the singlet excitations, $evGW$ -BSE calculations predict T_1 values in good agreement with experiments (within 0.2 eV) for pentacene and hexacene, but overestimate T_1 for the smaller systems, by as much as 0.5 eV for benzene.

As mentioned above, all BSE calculations we have presented use the Tamm-Dancoff approximation (TDA). The TDA was found to be accurate in describing the lowest-lying excitations of molecules and small silicon clusters [129,156,157], although this does not necessarily hold

TABLE III. Lowest singlet S_1 and triplet T_1 excitation energies of the acene crystals, computed within the G_0W_0 and $evGW$ -BSE approximations, compared to experimental data, taken from Refs. [123,150,151] and references therein. Experimental lattice constants have been used in the calculations throughout. All quantities are in eV.

No. of rings	T_1			S_1		
	G_0W_0	$evGW$	Expt.	G_0W_0	$evGW$	Expt.
1	4.1	4.3	3.8	5.0	5.4	4.7
2	2.9	3.1	2.6	4.2	4.5	3.9
3	2.0	2.2	1.9	3.3	3.7	3.1
4	1.4	1.5	1.3	2.4	2.8	2.4
5	1.0	1.1	0.9	1.8	2.1	1.9
6	0.6	0.7	0.6	1.0	1.4	1.4

for in general [158,159]. The applicability of the TDA in three-dimensional solids has not been explored as much. Nevertheless, as an example we find for the tetracene crystal that the S_1 value obtained within G_0W_0 -BSE is negligibly affected (by only 0.02 eV) upon relaxing the TDA.

To summarize, within our other assumptions, i.e., a PBE starting point, the GPP model, and the Tamm-Dancoff approximation, G_0W_0 -BSE is the optimal choice for the smaller acenes, up to tetracene, but $evGW$ is better for the largest acenes: hexacene and perhaps pentacene.

E. Effects of structure on charged and neutral excitations

Having discussed the need for adequate treatment of vdW interactions for predicting geometry and independently the accuracy of approximations within the GW and BSE schemes, we now turn to question of the sensitivity of the calculated excitations to structural parameters.

We start by considering charged excitations obtained within the GW approximations and assessing their dependence on the geometry obtained from LDA, GGA, the three van der Waals functionals (DF1, DF2, and DF-cx) used in Sec. III A, and experiment. The calculated k -point averaged G_0W_0 -calculated fundamental gap Δ_g , along with the valence band width (vbw) and the conduction band width (cbw), for each of the geometries, is given in Table IV. (Here, the bandwidth is defined as

TABLE IV. Effect of structure on the k -point averaged fundamental gap Δ_g , along with the valence bandwidth (vbw) and the conduction bandwidth (cbw), all calculated in the G_0W_0 approximation. All values were obtained from lattice parameters fully relaxed within the LDA, PBE, DF1, DF2, and DF-cx functionals, as well as from experimental parameters [93–95,105,107]. All energies are in eV.

	G_0W_0 using lattice-parameters from					Expt.
	LDA	PBE	DF1	DF2	DF-cx	
Benzene						
Δ_g	6.6	7.9	7.3	7.1	7.1	7.3
vbw	0.7	0.2	0.4	0.5	0.5	0.4
cbw	0.7	0.4	0.5	0.5	0.5	0.5
Naphthalene						
Δ_g	4.9	6.0	5.6	5.5	5.3	5.5
vbw	0.7	0.2	0.4	0.5	0.5	0.5
cbw	0.7	0.2	0.3	0.3	0.4	0.3
Anthracene						
Δ_g	3.6	4.5	4.3	4.1	4.0	4.0
vbw	0.6	0.2	0.3	0.4	0.4	0.3
cbw	1.0	0.3	0.5	0.6	0.7	0.6
Tetracene						
Δ_g	2.4	3.6	3.1	2.9	2.7	2.9
vbw	0.7	0.1	0.3	0.4	0.6	0.4
cbw	0.9	0.3	0.5	0.7	0.8	0.7
Pentacene P3						
Δ_g	1.5	2.9	2.3	2.1	1.8	2.2
vbw	1.2	0.3	0.6	0.7	0.9	0.7
cbw	1.1	0.3	0.6	0.7	0.9	0.7

the width in eV of the lowest π^* or highest π manifold of bands.) Hexacene is excluded here and below so that we can restrict our attention to G_0W_0 and avoid additional differences arising from comparison between G_0W_0 and $evGW$.

As shown in Sec. III A, and in more detail in Appendix A, lattice parameters increase with functional in the following sequence: LDA/DF-cx/DF2/DF1/PBE. Interestingly, Table IV shows that Δ_g follows the same trend, while vbw and cbw follow the opposite trend. These trends can be rationalized as follows: the larger the lattice parameters, the smaller the intermolecular hybridization and the smaller the bandwidth. Naturally, the smaller the hybridization, the larger the band gap. However, quantitatively the change in bandwidths explains only part of the gap increase with increasing lattice parameters. A second effect is that the solid-state gap is renormalized from the much larger molecular gap (compare with the molecular gaps [IP-EA] given in Table I of Sec. III B) because the neighboring molecules serve as a dielectric medium whose response creates a polarization field that reduces the gap [160]. As discussed in detail in Refs. [21,23,25], this phenomenon, which is well captured by GW calculations, itself depends on the unit-cell volume. This is because a larger intermolecular separation reduces the polarization field and therefore the renormalization, thereby increasing the gap.

Finally, we note that the although GW gaps calculated from the experimental geometries are within 0.1 eV (0.2 eV for benzene) of those obtained with DF2 lattice parameters, it should be taken into account that this is due to the accidental agreement of zero-temperature DF2 volumes with room-temperature experimental values (see Sec. III A).

We now turn to the discussion of structure on neutral excitations. G_0W_0 -BSE calculated low-lying excitations, based on the same geometries used in Table IV above, are

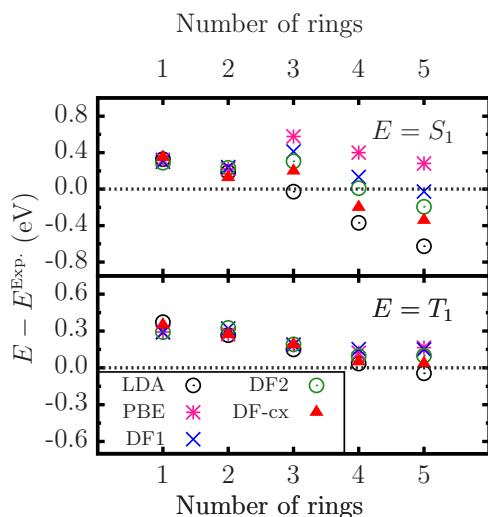


FIG. 6. Effect of structure on the lowest singlet (S_1) and triplet (T_1) excitation energies, calculated in the G_0W_0 -BSE approximation, given as deviation from experimental data (see references cited in Table III). All computed values were obtained from lattice parameters fully relaxed within the LDA (black empty circles), PBE (pink stars), DF1 (blue crosses), DF2 (green empty squares), and DF-cx (red triangles) functionals, and are given as differences from experimental values. All energies are in eV.

given in Fig. 6 and in Table V. For comparison, Table V also reports neutral excitations calculated using experimental lattice parameters and shown above to be in good agreement with experimental excitation energies (see Sec. III D). As discussed above, no significant temperature dependence of low-lying excitation energies is observed [152,153], which facilitates the comparison to experimental excitation energies measured at higher temperatures.

Clearly, the dependence of T_1 excitation energies on geometry is quite minimal (± 0.1 eV at most across the entire acene series). The same is true for the S_1 excitations in the smaller acenes (benzene and naphthalene), but the dependence on geometry increases with acene size. For pentacene, it is already quite significant, with the S_1 excitation values changing by 0.9 eV by switching from the LDA to the PBE geometry. As before, agreement with experiment is much improved by using DF-based geometry, with best results obtained using DF2 and DF-cx (with differences between the two being too small to be physically meaningful), based on which S_1 energies are found to be within 4%–5% of experimental values. The remaining

TABLE V. Effect of structure on the lowest singlet (S_1) and triplet (T_1) excitation energies, calculated in the G_0W_0 -BSE approximation. All computed values were obtained from lattice parameters fully relaxed within the LDA, PBE, DF1, DF2, and DF-cx functionals, as well as from experimental values. All energies are in eV. For comparison, experimental values, taken from Refs. [123,150,151] and references therein, are also given. Also given are the mean absolute error (MAE), defined as $\sum_i^{N_m} |X_i - X_i^{\text{Expt.}}|/N_m$, with X being the excitation energy, the maximum absolute error (MAXE), and the mean absolute percentage error (MA%E), defined as $\text{MA}\%E = \sum_i^{N_m} |X_i - X_i^{\text{Expt.}}|/X_i^{\text{Expt.}}/N_m \times 100$.

		G_0W_0 -BSE						
		using lattice parameters from						
		LDA	PBE	DF1	DF2	DF-cx	Expt.	Expt.
Benzene								
	S_1	5.1	5.0	5.0	5.0	5.0	5.0	4.7
	T_1	4.2	4.0	4.1	4.0	4.1	4.1	3.7
Naphthalene								
	S_1	4.1	4.2	4.2	4.2	4.1	4.2	3.9
	T_1	2.9	2.9	2.9	2.9	2.9	2.9	2.6
Anthracene								
	S_1	3.1	3.6	3.5	3.4	3.3	3.4	3.1
	T_1	2.0	2.0	2.1	2.0	2.0	2.0	1.9
Tetracene								
	S_1	2.0	2.9	2.5	2.4	2.2	2.4	2.4
	T_1	1.3	1.4	1.4	1.4	1.3	1.4	1.3
Pentacene P3								
	S_1	1.3	2.1	1.9	1.7	1.5	1.7	1.9
	T_1	0.8	0.9	0.9	0.9	0.8	0.9	0.9
S_1	MAE	0.3	0.4	0.2	0.2	0.3	0.2	
	MA%E	12	12	7	7	10	7	
	MAXE	0.6	0.5	0.4	0.3	0.4	0.4	
T_1	MAE	0.2	0.2	0.2	0.2	0.2	0.2	
	MA%E	8	9	10	7	6	8	
	MAXE	0.5	0.4	0.4	0.3	0.4	0.4	

TABLE VI. Cohesive energies of the acenes. Calculated (E_{coh}) and experimental ($E_{\text{coh}}^{\text{Expt.}}$) cohesive energies are tabulated. Experimental cohesive energies are taken from Ref. [41]. MAE and MA%E are shown for all functionals: $\text{MAE} = \sum_i^{N_m} |E_{\text{coh},i}^{\text{Expt.}} - E_{\text{coh},i}|/N_m$ and $\text{MA}\%E = \sum_i^{N_m} |E_{\text{coh},i}^{\text{Expt.}} - E_{\text{coh},i}|/E_{\text{coh},i}/N_m \times 100$, where N_m is the total number of crystals. The asterisk indicates that TS data are taken from Ref. [41].

	Cohesive energy (eV)							Expt.
	LDA	PBE	D2	TS*	DF1	DF2	DF-cx	
Benzene	0.59	0.12	0.73	0.69	0.64	0.60	0.61	0.52
Naphthalene	0.76	0.15	1.16	1.04	0.93	0.86	0.92	0.82
Anthracene	0.97	0.19	1.61	1.39	1.24	1.16	1.23	1.13
Tetracene	1.21	0.25	2.10		1.56	1.42	1.56	
Pentacene P ₁	1.46	0.30	2.61		1.88	1.76	1.87	
Pentacene P ₂	1.48	0.30	2.63		1.88	1.76	1.92	
Pentacene P ₃	1.42	0.31	2.61		1.88	1.79	1.87	
Hexacene	1.82	0.36	2.18		2.21	2.09	2.30	
MAE (Å)	0.09	0.66	0.35	0.22	0.11	0.05	0.10	
MA%E	11	80	42	28	16	8	13	

discrepancy may be due to terms not included in this work, such as zero-point and finite-temperature effects associated with lattice vibrations, as well as the remaining limitations of the GW -BSE approach in general and its approximations used here in particular.

The sensitivity of excitation energies to geometry, or lack thereof, is directly related to the degree of spatial localization of these states. For large acenes, notably pentacene, singlet states have been shown to extend over several molecules [19,24,150,161]. The degree of delocalization is larger for smaller unit-cell volumes, an effect related to the increased intermolecular hybridization [162]. Delocalization decreases the excitation energy, which is therefore larger the smaller the unit cell is. For short acenes, this is a much smaller effect and indeed no significant structure dependence is observed. Triplets, however, are always predominantly localized on a single monomer [161,162], explaining their weak dependence on the geometry. Owing to this negligible delocalization, triplet energies calculated in the gas and solid state are within 0.2 eV (compare with Table I), i.e., the triplet is largely independent of the solid-state environment.

Finally, we note that the calculated neutral excitation energies are not strongly affected by temperature, at least as reflected by the crystal structure used in our calculations. For benzene, naphthalene, and anthracene, the calculated singlet and triplet energies do not depend significantly on geometry. For the larger acenes, singlet energies change by at most 0.15 eV, while triplet energies change by even less, when varying the volume by $\sim 3\%$ (similar to thermal expansion at room temperature). This agrees with the experimentally observed absence of significant temperature dependence of low-lying excitation energies [152,153].

IV. CONCLUSIONS

In summary, we have studied the structure and excited-state properties of the series of acene-based crystals, from benzene

to hexacene, from first-principles using vdW-corrected DFT and MBPT. Both vdW-DF and pairwise correction methods were found to predict lattice parameters in excellent agreement with experimental data. We find that DF1 overestimates volumes but DF2 improves over DF1, consistent with the general trends for these functionals. DF-cx further improves lattice parameters, with a residual discrepancy of $< 1\%$. Furthermore, the relatively simple TS pairwise approach performs as well as the best DF methods.

For acenes in the solid state, charged excitations are generally well described by the G_0W_0 method, but partial self-consistency, in the form of the $evGW$ method, is needed for hexacene, likely owing to the PBE starting point employed in this study. The results are found to be sensitive to the geometry used owing to a combination of intermolecular hybridization and polarization-induced level renormalization. Neutral low-lying singlet and triplet excitation energies are generally well described using the G_0W_0 -BSE method. They are generally less sensitive to structure, except for the important case of singlet excitations in larger acenes. There, large structural sensitivity is found owing to significant delocalization of the singlet state.

Our study reveals the importance of an accurate account of dispersive interactions as a prerequisite to predictive calculations of excited-state properties in the acene crystals. Furthermore, it suggests routes for predictive calculations, in which both structures and excited states are calculated entirely from first principles, for broader classes of molecular solids.

ACKNOWLEDGMENTS

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APPENDIX: STRUCTURAL PROPERTIES: BENCHMARKING OF vdWs FUNCTIONALS

In this Appendix, we provide detailed information on the structural data obtained with different methods for the acene family of crystals. As in the main text, we consider standard DFT methods (LDA and PBE) and different vdW methods: D2, TS, DF1, DF2, and DF-cx.

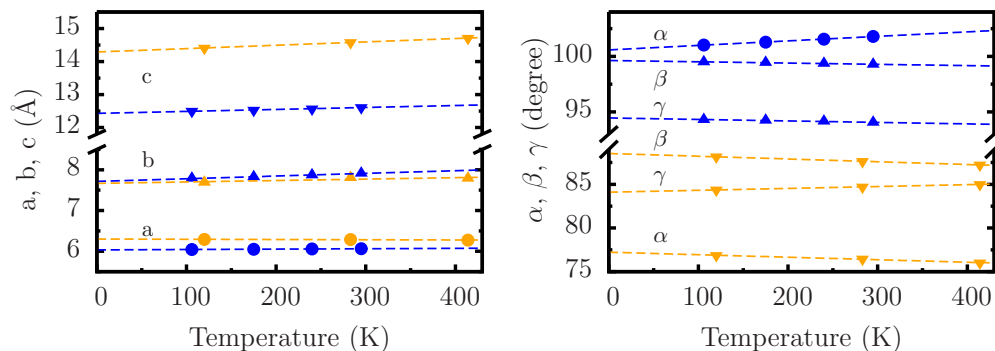


FIG. 7. Extrapolation of unit-cell geometry to 0 K: Experimental lattice parameters and angles of tetracene P_1 (blue) are extracted from Ref. [163] and those of pentacene P_2 (orange) are extracted from Ref. [114], also labeled as PENCEN06-PENCEN08 in the CSD. These are fitted to linear functions of the temperature (dashed lines). The fits possess an average root mean square of of 7×10^{-3} and 0.05 \AA and 0.02° and 0.05° for tetracene P_1 and pentacene P_2 , respectively.

TABLE VII. Structural parameters for the acene crystal series. Lattice parameters (using old conventions) a , b , and c (in \AA), lattice angles α , β , and γ (in degrees) and unit-cell volumes Ω (in \AA^3) are calculated from force and stress relaxation within different DFT approximations. Niggli lattice parameters (denoted by a prime) are also shown wherever they differ from old-convention ones. Experimental lattice parameters measured at low temperature T are also shown. For pentacene, three different polymorphs are considered, labeled as P_1 , P_2 , and P_3 . The asterisk denotes the following: where possible, lattice parameters are extrapolated to 0 K (see text for details). Mean absolute errors (MAE) and mean absolute percentage errors (MA%E) with respect to experimental lattice parameters are also shown: In the error evaluation, we only considered experimental data with $T \leq 16 \text{ K}$ or data extrapolated to 0 K. For brevity, symmetry-imposed angles are omitted. TS data taken from Ref. [37] for benzene and from Refs. [49,95,104,105] for longer acenes. Experimental data are taken from Refs. [94,95,97,98,104,105,163].

	LDA	PBE	D2	TS*	DF1	DF2	DF-cx	Expt.
Benzene								$T = 4 \text{ K}$
a	6.37	7.46	6.43	6.95	7.01	6.87	6.73	6.70
b	7.06	8.11	7.12	7.58	7.49	7.39	7.40	7.36
c	8.96	9.93	9.05	9.51	9.89	9.41	9.49	9.37
Ω	403.0	601.1	414.4	500.8	518.4	477.9	473.0	461.8
Naphthalene								$T = 5 \text{ K}$
a	7.74	8.99	7.79	8.12	8.48	8.22	8.06	8.08
b	5.76	6.31	5.79	5.90	6.06	5.97	5.91	5.93
c	8.37	9.13	8.44	8.65	8.79	8.57	8.75	8.63
β	125.5	122.1	125.3	124.2	123.3	122.9	124.4	124.7
Ω	304.0	438.9	310.4	342.2	377.9	353.3	344.4	340.4
a'	5.76	6.31	5.79	5.90	6.06	5.97	5.91	5.93
b'	7.40	8.77	7.47	7.85	8.21	8.03	7.87	7.78
c'	7.74	8.99	8.44	8.12	8.48	8.22	8.06	8.08
α'	112.9	118.1	121.7	114.5	116.4	116.4	113.4	114.1
Ω'	304.0	438.9	310.4	342.2	377.9	353.3	344.4	340.4
Anthracene								$T = 16 \text{ K}$
a	8.10	9.63	8.13	8.40	8.75	8.56	8.38	8.37
b	5.80	6.35	5.85	5.91	6.12	6.02	5.96	6.00
c	10.82	10.14	10.89	11.12	11.11	11.07	11.23	11.12
β	126.5	109.7	126.5	125.2	123.4	124.2	125.6	125.4
Ω	408.9	584.4	416.6	451.0	496.7	471.2	456.5	455.2
a'	5.80	6.35	5.85	5.91	6.12	6.02	5.96	6.00
b'	8.10	9.63	8.13	8.40	8.75	8.56	8.38	8.37
c'	8.86	10.14	8.91	9.31	9.65	9.44	9.32	9.26
α'	100.9	109.7	100.7	102.4	105.9	104.3	101.4	102.0
Ω'	408.9	584.4	416.6	451.0	496.7	471.2	456.5	455.2

TABLE VII. (*Continued.*)

	LDA	PBE	D2	TS*	DF1	DF2	DF-cx	Expt.	
								$T = 0 \text{ K}^*$	$T = 106 \text{ K}$
Tetracene P_1									
a	5.89	6.35	5.93	6.05	6.15	6.05	6.05	6.03	6.04
b	7.43	9.26	7.43	7.71	8.21	7.92	7.69	7.71	7.79
c	12.45	13.60	12.55	13.03	13.34	13.16	12.93	12.88	12.95
α	78.4	72.6	78.7	77.7	75.1	75.6	78.0	77.6	77.3
β	72.8	71.5	72.5	71.9	71.2	72.0	72.6	72.1	72.1
γ	85.1	86.2	85.1	85.7	86.4	86.0	85.5	85.5	85.7
Ω	510.0	723.2	516.6	564.1	616.1	579.9	561.3	557.7	566.1
a'	5.89	6.35	5.93	6.05	6.15	6.05	6.05	6.03	6.04
b'	7.43	9.26	7.43	7.71	8.21	7.92	7.69	7.71	7.68
c'	12.09	13.06	12.16	12.53	12.76	12.67	12.53	12.43	12.50
α'	99.5	106.2	99.2	100.7	103.8	103.0	100.2	100.6	101.0
β'	100.5	99.0	100.2	99.2	98.3	99.0	100.1	99.6	99.5
γ'	94.9	93.8	94.9	94.3	93.6	94.0	94.5	94.5	94.3
Ω'	510.0	723.2	516.6	564.1	616.1	579.9	561.3	557.7	566.1
								$T = 295 \text{ K}$	
Pentacene P_1									
a	7.37	9.14	7.36	7.66	8.17	7.90	7.59	7.90	
b	5.97	6.33	6.00	6.04	6.16	6.08	6.07	6.06	
c	15.54	16.13	15.64	15.85	15.99	15.83	15.98	16.01	
α	103.8	101.6	103.5		100.7	101.1	102.0	101.9	
β	113.9	110.6	114.0		111.2	111.8	112.5	112.6	
γ	84.7	86.2	84.7		85.8	86.1	85.7	85.8	
Ω	607.0	856.1	613.5	664.1	736.8	692.7	666.0	692.4	
a'	5.97	6.33	6.00		6.16	6.08	6.07	6.06	
b'	7.37	9.14	7.36		8.17	7.90	7.59	7.90	
c'	14.23	15.49	14.33		15.09	14.84	14.84	14.88	
α'	83.5	102.9	94.0		99.1	97.9	95.7	96.7	
β'	78.1	99.8	102.0		99.0	99.7	100.7	100.5	
γ'	84.7	93.8	95.3		94.2	93.9	94.3	94.2	
Ω'	607.0	856.1	613.5	664.1	736.8	692.7	666.0	692.4	
								$T = 0 \text{ K}^*$	$T = 120 \text{ K}$
Pentacene P_2									
a	6.18	6.52	6.25	6.13	6.45	6.33	6.29	6.30	6.29
b	7.27	8.91	7.24	7.68	8.07	7.81	7.52	7.67	7.69
c	13.80	15.16	13.85	14.53	14.69	14.49	14.35	14.29	14.41
α	78.1	71.4	78.5	77.3	74.7	76.2	77.8	77.2	76.9
β	89.4	87.6	89.3	87.4	88.5	88.1	88.7	88.5	88.2
γ	83.7	84.9	83.5	84.7	84.8	84.6	84.1	84.1	84.4
Ω	603.0	830.7	609.8	663.9	734.0	693.5	660.3	669.4	674.7
								$T = 293 \text{ K}$	
Pentacene P_3									
a	5.71	6.16	5.78	6.65	6.04	5.88	5.92	5.96	
b	7.05	8.87	7.01	6.92	7.94	7.76	7.36	7.60	
c	15.29	15.95	15.41	16.27	15.54	15.53	15.68	15.61	
α	82.5	81.4	82.8		81.9	80.8	81.8	81.2	
β	89.8	87.7	90.0		87.4	87.9	87.2	86.6	
γ	90.0	90.0	90.0		89.4	89.7	89.7	89.8	
Ω	610.9	861.1	619.2	746.3	737.2	699.0	675.9	697.0	
								$T = 123 \text{ K}$	
Hexacene									
a	6.47	6.60	6.48		6.43	6.34	6.61	6.31	
b	6.85	9.10	6.85		8.04	7.84	7.05	7.70	
c	15.64	17.30	15.71		16.79	16.49	16.14	16.48	
α	95.2	75.1	95.1		101.1	99.9	95.8	98.8	
β	92.0	85.4	92.1		90.6	91.3	91.5	91.2	
γ	97.1	84.9	97.2		95.4	95.5	96.8	95.8	
Ω	684.0	998.4	688.8		848.3	803.3	743.3	785.9	
MAE (\AA)	0.29	0.76	0.25	0.09	0.28	0.11	0.06		
MA%E	3	9	3	1	3	1	1		

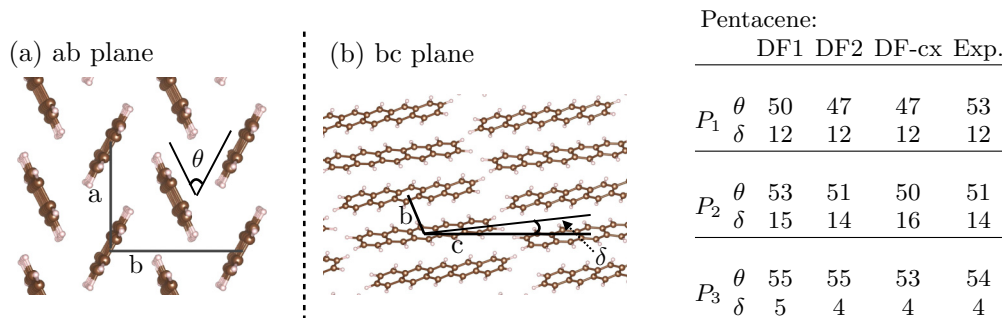


FIG. 8. Angles characterizing the pentacene herringbone structure: (a) Along the ab plane, the herringbone angle θ is the angle between the two distinct molecules. (b) Along the bc plane, δ is the angle between the c axis and the long axis of the molecule. (Right table) Angles calculated by different DF methods are compared to experimental data from Refs. [94,97,114], labeled as PENCEN, PENCEN06, and PENCEN10 in the CSD, and measured at 205, 120, and 293 K for pentacene P_1 , P_2 , and P_3 , respectively. While θ is almost constant for all polymorphs ($\theta \sim 50^\circ$ – 54°), δ is not. We use Niggli unit-cell conventions and all angles are in degrees.

Throughout, we make use of CSD [108] data to benchmark our results. For the smallest acenes, low-temperature data ($T \leq 14$ K) are available in the CSD under the entries BENZEN14, NAPHTA31, and ANTEN16, from Refs. [95,104,105]. Reference [164] also reports low-temperature data for benzene, consistent with the data of Ref. [104]. For tetracene-P1 and pentacene-P2, we extrapolate experimental data from Refs. [114,163] to 0 K, as shown in Fig. 7. Note that we assign the tetracene structures of Ref. [163] to its P1 polymorph.¹ For other pentacene polymorphs and hexacene, in the absence of sufficient low-temperature data that would

allow for extrapolation to 0 K, we compare to the lowest-temperature experimental data available from Refs. [94,97,98], also found in the CSD as PENCEN, PENCEN10, and ZZZDKE01. We emphasize that only by extrapolating experimental data to 0 K do we observe consistent trends in the comparison of our relaxed geometries for the various DFT methods used here. In the main text, we have also compared our data to experimental cohesive energies. These are taken from Ref. [41], in which temperature contributions have been removed. A complete set of experimental and calculated lattice parameters and cohesive energies is given in Tables VII and VI, respectively. Lattice parameters are usually found in literature following old conventions. However, recent data use the so-called Niggli [165] (or reduced-) lattice parameters. For completeness, we present both conventions in Table VII. Finally, in Fig. 8 we present a comparison of theory and experiment for the angles that characterize the herringbone structure in the three pentacene polymorphs. Here, all DF approximations predict angles in good agreement with experiment. At the experimental resolution and temperature, we cannot conclude definitively which DF version performs best for angle prediction, but see no reason for trends different from those reported in the main text.

¹The tetracene lattice parameters reported in the Ph.D. thesis of Haas [163] at 175 K almost perfectly match P_1 at 180 K as reported in Ref. [29] (the volumes agree within 0.5%). Further, by cooling the sample from 175 to 106 K, Haas reports a slight reduction in volume, as shown in Fig. 7 of our paper. Hence, we can assign Haas's structures to the P_1 polymorph. Note that the P_2 polymorph has an appreciably smaller c lattice vector (12.3 Å) than the P_1 phase (~ 12.5 Å).

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