Organic/Inorganic Hybrid Materials: Challenges for *ab Initio* Methodology

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S **Supporting Information**

CONSPECTUS: Organic/inorganic hybrid structures are most exciting since one can expect new properties that are absent in either of their building blocks. They open new perspectives toward the design and tailoring of materials with desired features and functions. Prerequisite for real progress is, however, the in-depth understanding of what happens on the atomic and electronic scale. In this respect, hybrid materials pose a challenge for electronic-structure theory. Methods that proved useful for describing one side may not be applicable for the other one, and they are likely to fail for the interfaces.

In this Account, we address the question to what extent we can quantitatively describe hybrid materials and where we even miss a qualitative description. We note that we are dealing with extended systems and thus adopt a solid-state approach. Therefore, density-functional theory (DFT) and many-body perturbation theory (MBPT), the *GW* approach for charged and the Bethe–Salpeter equation for neutral excitations, are our methods of choice. We give a brief summary of the used methodology, focusing on those aspects where problems can be expected when materials of different character meet at an interface. These issues are then taken up when discussing hybrid materials. We argue when and why, for example, *standard* DFT may fall short when it comes to the electronic structure of organic/metal interfaces or where the framework of MBPT can or must take over.

Selected examples of organic/inorganic interfaces, structural properties, electronic bands, optical excitation spectra, and charge-transport properties as obtained from DFT and MBPT highlight which properties can be reliably computed for such materials. The crucial role of van der Waals forces is shown for sexiphenyl films, where the subtle interplay between intermolecular and molecule–substrate interactions is decisive for growth and morphologies. With a PTCDA monolayer on metal surfaces we discuss the performance of DFT in terms of interfacial electronic structure. We face the problem of a so far *hidden variable*, namely, electron-vibrational coupling, regarding level alignment at interfaces between organic and inorganic semiconductors. Poly(*para*-phenylene) adsorbed on graphene and encapsulated in carbon nanotubes represent case studies to demonstrate the impact of polarization effects and exciton delocalization in optoelectronic excitations, respectively. Polaron-induced band narrowing and its consequences for charge transport in organic crystals is exemplified for the HOMO bandwidth in naphthalene crystals. On the basis of these prototypical systems, we discuss what is missing to reach predictive power on a quantitative level for organic/inorganic hybrid materials and, thus, open a perspective toward the computational discovery of new materials for optoelectronic applications.
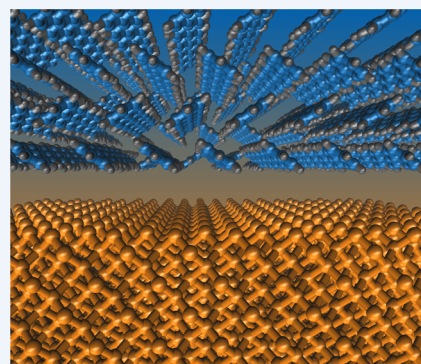
INTRODUCTION

Steady progress in finding new materials with tailored functions and performance governs nearly all aspects of our lifestyle. Thanks to the highly developed level of concepts and computational tools, first-principles theory can nowadays significantly contribute to advancing the materials design process, even independently from or parallel to experimental studies. State-of-the-art methods within and beyond density-functional theory (DFT) can pretty well describe certain properties and classes of materials. But unfortunately, they also fail badly for others. Special attention is required for hybrid structures, which consist of two or more components with distinctively different properties. Such materials are most promising since one can expect exciting physics through new features arising at the interface that are absent in either of the building blocks.

Plastic electronics is currently entering the market of mobile phones, TV sets, solar cells, and other optoelectronic devices. The breakthrough of flexible all-organic electronics, however, is still missing. Organic materials alone are even not likely to do a good job because their charge-carrier mobilities are notoriously low, and (a drawback, e.g., for photovoltaics) photoexcited electron–hole pairs may easily recombine before being exploited. Inorganic semiconductors, on the other hand, are appealing for their high charge-carrier mobilities and weak electron–hole binding but suffer from inefficient coupling to light. Thus, heterojunctions making use of these two different material classes allow for not only combining the best of the

two worlds but above all going beyond the characteristics of their constituents. As a matter of fact, organic/inorganic hybrids represent an up-and-coming basis for future applications, be it lighting devices, field-effect transistors, solar cells, photoswitches, or novel devices that would not be possible with inorganic or organic materials alone.

Let us take the example of photovoltaics to get an overall picture of the quantities and processes involved. As outlined above, hybrid systems can make concurrent use of the efficient organic absorbers and the efficient dielectric screening provided by the inorganic components.[1] Consequently, the electron–hole interaction is weakened at the hybrid interface compared with that in the organic material. In other words, an exciton created at or diffusing to the interface may adopt Wannier-type character, where, for instance, the hole resides in the organic part, while the electron may spread out into the inorganic region. This, in turn, facilitates dissociation into free charge carriers at the respective side and transport to the respective electrode. The complexity of a theoretical description becomes ultimately clear: key quantities are the hybrids' interface structures, the corresponding optoelectronic properties and excitation lifetimes, and charge-carrier transport properties. We need to know the binding strength of electron–hole pairs together with their spatial extension, the nature of exciton diffusion, and the time scales of their formation and recombination. Besides all that, the temperature-dependent charge-carrier mobilities of either side are of outermost importance. Only knowing all these quantities provides the urgently needed insight into phenomena of hybrid materials.

In this Account, we want to address where we are on our way toward a quantitative description and detailed understanding of organic/inorganic hybrid materials and their functions. We stress that while the molecular properties predetermine those of their condensed phases to some extent, the interplay between intermolecular and molecule–substrate interaction is most decisive for the properties and functions of the interfaces. We will thus focus on the latter and discuss the current status of *ab initio* methodology, comprising DFT and many-body perturbation theory (MBPT), in the light of this. Due to the complex topic paired with length restrictions, we could only include representative examples out of a vast amount of literature. For further reading, we refer to the Supporting Information.

■ METHODOLOGY: STATE-OF-THE-ART AND THE NEED TO GO BEYOND

The performance of DFT and methods beyond has been the subject of intensive investigation during many years. In fact, the foundations of both DFT and MBPT have been laid half a century ago. Thus, success stories and drawbacks are well documented in its full breadth in literature. In the following, we shortly summarize a few aspects in view of possible problems for situations where materials of different character meet at an interface. We will then take up these issues when discussing hybrid materials further below.

Structure

While gradient-corrected exchange-correlation (xc) functionals have pushed the accuracy of lattice parameters toward the 1% range in the 1990s, the reliable determination of geometries of organic materials remained a severe bottleneck, lacking a DFT description of the long-range dispersion forces. Earlier calculations for crystalline organic materials done for fixed lattice parameters at the level of semilocal xc functionals revealed remarkably good internal geometries,[2,3] well capturing the strong intramolecular bonds and the weak hydrostatic intermolecular interactions. However, only the advent of van der Waals (vDW) density functionals[4] gave access to rather reliable cohesive properties of organic π-conjugated molecular crystals. Thanks to efficient implementations,[5] its application was feasible even for large systems and enabled the prediction of surface energies.[6] Concerning metals, one should keep in mind that although PBE, for example, gives their lattice parameters very close to experiment, this is not the case for cohesive energies. Higher level of accuracy has been reached by the random phase approximation for correlation (together with exact exchange), successfully applied to crystalline solids,[7,8] and the adsorption of molecules on inorganic substrates.[9,10] An efficient alternative to the latter is provided by a method recently developed by Tkatchenko and co-workers.[11] For a review on vdW interactions in organic systems and at organic/inorganic interfaces, see ref 12.

Electronic Bands

The *GW* approach of many-body perturbation theory[14] can today be considered the state of the art to describe electronic band structures. Nevertheless, as long as correlation effects are relatively weak, Kohn–Sham bands often provide a good zeroth approximation, in particular for metals but also for many band gap materials. For the latter, in many cases, the self-energy correction can be mimicked by a rigid shift of the conduction bands. Thus, what is known as the *band gap problem*[15,16] often only becomes relevant when energy levels are needed on an absolute energy scale, or when the individual self-interaction errors of different states lead to a wrong ordering of bands.[13,17] In such cases, *GW* results, when obtained non-self-consistently (termed G_0W_0) are likely to depend on the underlying DFT density. A solution to this starting-point dependence is found in hybrid functionals, which are closer to the final result and thus render the perturbational treatment of G_0W_0 applicable.[18–20] Hybrid functionals alone are often successfully used as a compromise between accuracy and computational efficiency.[21] As will be discussed below, the situation is far more complicated at interfaces, where small quantitative errors bear the risk of leading to qualitatively wrong results. In fact, the level alignment at interfaces appears as one of the most crucial problems of electronic-structure theory.

Optical Excitations

While the time-dependent version of DFT (TDDFT) has been most favorable for molecules, its success for extended systems is pretty limited to metals or other systems where excitonic effects are very weak. Apart from such cases, the Bethe–Salpeter (BSE) equation is the method of choice for studying optical excitations.[22] It is able to capture the features of strongly bound electron–hole pairs in core-level excitations and molecular materials, as well as the Wannier-type excitons in inorganic semiconductors. On a quantitative scale, the optical spectra may be affected by the starting-point dependence of the underlying *GW* band structure. A direct dependence on the DFT quantities that enter the BSE should also be expected but has not been addressed in literature so far.

Charge Transport

The description of charge transport from first-principles has advanced considerably during the past decade, but using very different approaches for the different material classes and applications. For inorganic semiconductors, the combination of

DFT with Boltzmann-type transport equations has been proven successful to calculate bulk transport coefficients.[23,24] For molecular electronics (e.g., metal−molecule−metal geometries), the current flow is commonly described as quantum transport using (nonequilibrium) Landauer−Büttiker theory.[25,26] For purely organic single crystals, the two most widely used concepts are the quantum-chemical Marcus theory of electron hopping and polaron theories based on Holstein-type models.[27,28] They allow for quantitative calculations of carrier mobilities,[29−32] including their full 3D anisotropy and temperature dependence.[33−35] Nevertheless, we note that so far these methods are not fully *ab initio* but rather theoretical models combined with *ab initio* material parameters.

Open Problems

In most of the theoretical frameworks outlined above, we are still missing a basically unexplored variable. As a matter of fact, in the context of DFT and beyond, electron-vibrational coupling (EVC) has so far been largely ignored. Besides the well-known effect of zero-point vibrations (ZPVs) on structural properties, it is hardly accounted for in standard DFT calculations. A quantitative estimation of its impact on structure, electronic structure, and optical excitations for a broad range of materials is difficult due to the interplay of band-narrowing and polaron binding. Only very few studies have highlighted ZPV and temperature effects on band gaps,[36] electronic stucture,[37] and optical spectra.[38] In the case of charge transport, the situation is different because EVC as an elementary scattering process is already included in most transport concepts, typically however on different levels of theory and not on a fully *ab initio* basis. This situation is obviously unsatisfying and intolerable for hybrid materials. For a complete and quantitative understanding of materials in general and hybrid materials in particular, we are missing a new level of electronic-structure theory where electrons, vibrations, and their coupling are treated on the same footing.

■ HYBRID MATERIALS: WHERE WE ARE AND WHERE TO GO

Hybrid Structures

Detailed knowledge of the interface geometry is a crucial prerequisite for determining and understanding the materials' properties and functions. The growth of organic molecules on inorganic substrates remains challenging for both experiment and theory. Bringing together two different types of materials, strong covalent bonding at one side and weakly interacting molecules at the other side, gives rise to a new level of complexity in the description of crystal-growth phenomena. Currently, the interpretation of organic thin-film growth relies on the models developed for their inorganic counterparts. In contrast, on the molecular side also kinetic processes related to their structure and *shape* matter. Likewise, the pronounced anisotropy of molecule−molecule and molecule−substrate interactions have to be considered.[39,40] The subtle interplay between these quantities plays a decisive role in the morphology of organic/inorganic interfaces, since both are weak and comparable in magnitude. This is demonstrated in Figure 1 morphologies where three films of sexiphenyl (6P) grown on different substrates are depicted exemplarily.

The left side shows the scanning tunneling microscopy (STM) picture of a 6P monolayer on Cu(110),[41] which shows perfectly ordered flat-lying molecules. For the same molecules deposited on muscovite mica, nanoneedle growth is found. The
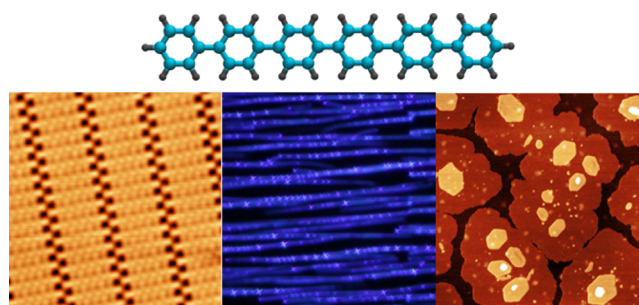

Figure 1. One molecule, three different morphologies: an indication of the subtle interplay between intermolecular and molecule−substrate interactions. From left to right, sexiphenyl (6P) monolayer on Cu(110),[41] nanoneedle growth on muscovite mica,[42] and terrace-shaped mounds of nearly upright standing molecules on disordered mica.[43]

symmetry of the molecule correlated with the directions of surface corrugations turned out to be decisive for the needle orientation, together with some adjustments related to the molecular packing.[42] In contrast, terrace-shaped mounds of nearly upright standing molecules form on disordered mica. Combining atomic-force microscopy with theoretical approaches, the morphology could be explained by the presence of an appreciable step-edge barrier.[43]

The variance of possible structural conformations is additionally enriched by the tendency of molecular solids toward formation of several polymorphic structures, depending on the details of the growth procedure as well as film thickness. Like in the examples above,[42,43] the corresponding structures only could be resolved by combined experimental−theoretical studies.[3,44]

The decisive contribution of long-range dispersion forces has been demonstrated for molecules physisorbed on metal surfaces.[9,45,46] They are also important for obtaining correct adsorption geometries of chemisorbed systems. Even if interactions between molecules and substrate are well described by (semi)local or hybrid xc functionals, molecular distortions or tilting angels are governed by vdW interactions.[12,47]

We stress that such investigations are computationally extremely demanding due to the large unit cells that often render pure *ab initio* calculations impossible. Therefore, in many cases one has to resort to classical force-field methods whose accuracy is difficult to control. Their success for simulating organic crystals is mainly due to the existence of well tuned force-field libraries. However, the transferability of such force parameters to hybrid interfaces is highly questionable, since polarization effects and charge redistribution represent serious problems for force-field methods to be applied to inorganic solids. Thus, also but not only in view of this situation, xc functionals reliably and efficiently describing vdW forces within DFT in any bonding situation are essential.

Electronic Properties of Hybrid Interfaces

Let us focus on organic−metal interfaces first. A potential drawback of semilocal DFT functionals in capturing the qualitatively correct interface electronic structure is sketched in Figure 2. It depicts the situation for a PTCDA monolayer on coinage metal (111) surfaces (left panel). From the electronic structure of the individual materials, we can get a first idea what to expect for the combined system. The middle panel shows the measured Fermi level of bulk Au, Cu, and Ag on the left and the HOMO and LUMO of the PTCDA molecule on the right.
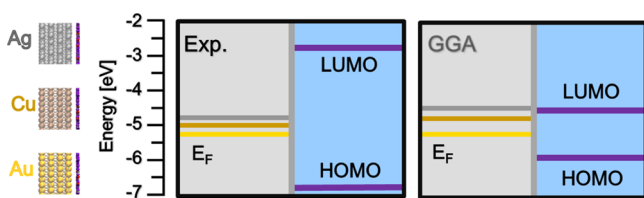
Figure 2. Level alignment in organic/metal interfaces. (left) Side view of a PTCDA monolayer on Me(111) (Me = Ag, Cu, and Au). (middle) Experimental Fermi levels of bulk Ag, Cu, and Au (left side) vs HOMO and LUMO of the PTCDA molecule (right side).[48] (right) Fermi levels of bulk Ag, Cu, and Au (left side) vs HOMO and LUMO of the PTCDA molecule (right side) from GGA-PBE calculations.[46] Alignment wrt vacuum level.

Figure 3. Level alignment at an interface between an organic (blue) and an inorganic (orange) semiconductor. In the *real* case (middle), the HOMO (LUMO) resides in the organic (inorganic) side. To the left and to the right, we see what can be expected from a *GW* calculation, while the outermost panels mimic the GGA behavior. The dotted lines are guides to the eye showing that, in this scenario, i.e., ignoring ZPV, both GGA and *GW* would find HOMO and LUMO in the inorganic side.

Clearly, the Fermi level is inside the HOMO−LUMO gap in all cases. For the DFT counterpart (right panel), the potential *band gap problem* becomes apparent. While the PTCDA LUMO is slightly above E_F for copper and gold, this is not the case for silver. Such situation bears the risk of spurious charge transfer from the metal to the molecule, even at *infinite* distance. In the adsorbate system, experiment finds the former LUMO somewhat below E_F,[48] in remarkably good agreement with GGA-PBE results.[46] Whether this is just a serendipitous situation is not straightforward to answer, since bonding at organic/inorganic interfaces results from an interplay of hybridization of wave functions, vdW interaction, Pauli repulsion, and electron-transfer processes. In fact, the most widely used exchange-correlation functionals suffer from delocalization and static-correlation errors[49] that lead to systematic problems for the description of electron transfer. Consequently, we cannot rely on such functionals to give the correct ground-state density, which in turn is a prerequisite for G_0W_0 to provide meaningful results. Such scenario clearly asks for some self-consistent *GW*. Standard global or range-separated hybrid functionals are not the solution here, since the extremely different nature of the individual components cannot be reconciled with a fixed amount of exact exchange and fixed screening parameter as used in range-separated hybrids.

Another important aspect concerns image-charge effects that arise when a molecular system is brought into contact with a metal. Due to enhanced ionization potential and lowered electron affinity, the band gap of the molecular side is considerably lowered and depends on the adsorption distance. This correlation effect is well captured by G_0W_0[50,51] (see example below).

Now we may ask the question whether semilocal DFT can predict the correct level alignment at an interface between an organic and an inorganic semiconductor. Let us perform a gedankenexperiment considering a hybrid material for solar cells. It exhibits type-II level alignment with the HOMO residing in the organic and the LUMO in the inorganic part, thus allowing for charge separation at the interface upon illumination by sunlight. Such scenario is depicted in Figure 3.

Semilocal DFT (just labeled GGA, since the particular flavor would not make any difference) could, through underestimation of both band gaps, lead to type I level alignment with both HOMO and LUMO sitting in the inorganic part. *GW* should generally do much better, widening the gaps on both sides. However, analogous to the metal/organic interface, non-self-consistent G_0W_0 still bears the risk of spurious charge transfer introduced by the underlying DFT level. Leaving this aside for a moment, there is another uncertainty coming into
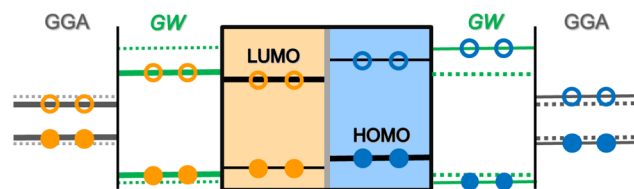
play here, namely, ZPV effects. They typically lower the band gap (as much as 400 meV in diamond[36]), and we can arguably expect this to be more pronounced in the organic side.[53] Thus, ignoring ZPV, even *GW* would give a *qualitatively* wrong picture, since it should *overestimate* the HOMO−LUMO distance. This *worst-case scenario* is sketched in the figure.

Optical Excitations in Hybrid Materials

Given the proper hybrid electronic structure, the solution of the BSE is expected to provide the right answer for the nature of optical excitations. These may be strongly bound Frenkel excitons as found for small molecules, Wannier-like excitons, typical for inorganic semiconductors, charge-transfer excitations, as realized in condensed molecular phases, or hybrid excitons as expected for organic/inorganic interfaces. In fact, such excitations have been observed already in peapods, consisting of organic π-conjugated molecules encapsulated in (semiconducting) carbon nanotubes (CNTs).[54,55]

Let us stay with this example, which is a prototype of weakly bound hybrid systems. It is less demanding than other materials for two reasons. First, the band gap is determined by the CNT, being substantially smaller than that of the molecule. Second, it is purely van-der-Waals bound, that is, no charge is transferred between the subsystems. In such case, one could at first anticipate the band structure to be a superposition of the constituent electronic structures and correspondingly for the optical excitations. Indeed, it was found that the alignment of the electronic levels is basically governed by the CNT curvature, which determines the ionization potential of the molecule inside the tube.[52] Nevertheless, the peapod's band structure is more complicated due to image-charge effects. Exciting an electron from the molecule polarizes the nearby surface, and the Coulomb interaction stabilizes the added hole, resulting in a decreased transport gap. This fact is depicted at the left side of Figure 4 for poly(*para*-phenylene) (PPP) physisorbed on graphene. It shows the polymer's HOMO and LUMO level as calculated from LDA and G_0W_0 on top of LDA, respectively, as a function of the adsorption distance *d*. The LDA band gap is basically constant, except for very small *d*, where the charges of the two subsystems start to overlap and thus rearrange. In contrast, the G_0W_0 band gap strongly depends on the distance, reaching the value of the pristine system only far away from the graphene surface.

This fact plays an important role for the optical excitations. Here we have to consider, however, also delocalization of the electron−hole wave function due to the formation of a hybrid exciton.[54] The impact of both effects can be seen in the right panel of Figure 4. On top, the imaginary part of the dielectric
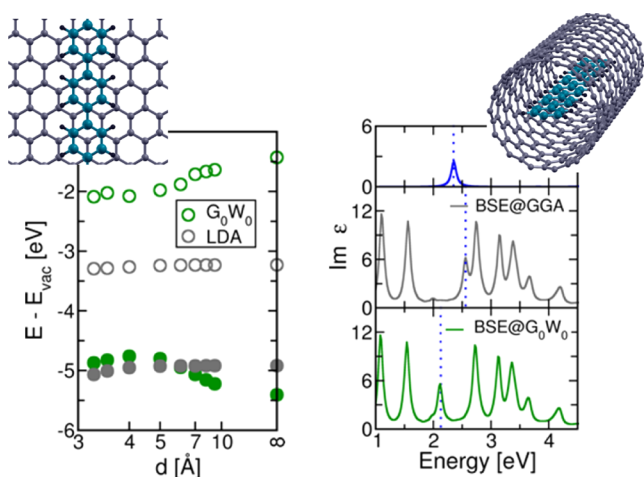
Figure 4. (left) HOMO and LUMO (at Γ) of PPP on graphene, obtained from LDA (gray) and G_0W_0 (green), respectively. Data from ref 51. (right) Dielectric function for isolated PPP (top) and a peapod, where PPP is encapsulated in a (14,0) CNT, obtained from BSE on top of scissors-corrected GGA (middle) and on top of G_0W_0 (bottom). The dotted lines mark the position of the exciton originating from PPP that gives rise to blue-light emission. Data from ref 54.

function is depicted for an isolated PPP chain as calculated by solving the BSE. The underlying electronic structure is obtained from PBE-GGA and corrected by a scissors shift. The middle panel shows the excitonic spectrum for the case when PPP is encapsulated in a (14,0) CNT, again obtained from the BSE based on scissors-corrected GGA bands. Compared with the situation above, we clearly observe a blue shift of the respective peak (dotted line) indicating a reduced exciton binding energy because the electron is now partially residing on the CNT. Including, however, the upward (downward) shift of the molecular valence (conduction) bands by polarization effects by computing the optical spectra on top of G_0W_0 gives rise to a red-shift counteracting the exciton delocalization. Both effects together can well explain the experimentally observed hardly altered frequency of light emission in the case of encapsulation compared with the molecule in solution (or gas phase).[54,55]

Charge Transport in Hybrid Materials

Because the charge-carrier transport through inorganic materials is very efficient, the overall current flow in hybrid systems is mostly determined either by the hybrid interface itself (e.g., in molecular transistors) or by the lower mobility in the organic material (e.g., after charge separation in hybrid solar cells). Due to the different nature of the charge transport in these two cases, ballistic quantum transport through single molecules vs diffusive transport through bulk organic semiconductors, the respective theoretical concepts are also different.

For molecular transport, the Landauer–Büttiker theory for electron transmission has become the de facto standard and can nowadays be applied within an *ab initio* framework. However, since the quantum transport through a molecular junction is extremely sensitive to the alignment of the HOMO/LUMO levels of the molecule with respect to the Fermi level of the metal electrodes, the theoretical challenges presented in the above sections directly apply also here.[56]

In the case of diffusive transport through bulk organic materials (focusing on highly ordered crystals) the DFT *band*

gap problem is less important, because the electron (hole) transport can be understood already in terms of intraband LUMO (HOMO) scattering processes. Thereby, the knowledge of bandwidths and carrier masses is most essential. However, here, we face a different problem because these properties are not solely determined by the purely electronic band structure but are modified due to the strong EVC in organic materials. This gives rise to polaronic effects that require a nonperturbative inclusion of EVC into the theoretical framework.[57]

In Figure 5, this is shown exemplarily for the HOMO band in a naphthalene crystal. The significance of EVC is strikingly
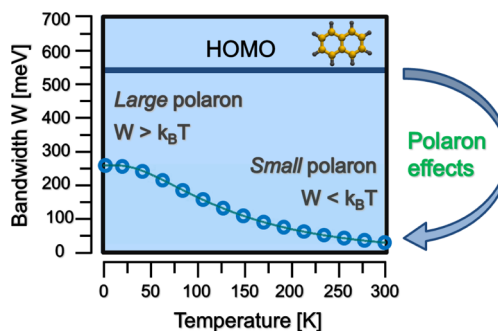

Figure 5. Polaron-induced band narrowing, exemplified for the HOMO bandwidth in naphthalene crystals. Results from DFT-LDA (blue line) and from polaron theory including ZPV and temperature effects (circles). Data from refs 28 and 57.

visible as a bandnarrowing (which, in turn, implies a hole-mass enhancement) already at $T = 0$ due to ZPV but even more pronounced at higher temperatures. This has important consequences for the resulting transport mechanism. At low T, even though the total bandwidth is only about 250 meV, it is quite large compared with the thermal energy k_BT, and the injected carriers can move like in a wide-band semiconductor (coherent band-like transport). In contrast, at room temperature, the bandwidth becomes comparable to k_BT, thermal disorder breaks the band picture, and incoherent phonon-assisted hopping motion dominates. Recent advances in polaron transport theories based on the Kubo formulism applied to Holstein-type models supplemented with DFT material parameters[33−35] have enabled a united description as reviewed in ref 28. Alternative concepts employing Marcus theory[27] or Schrödinger equations including semiclassical EVC[31] have also proved successful but are restricted to the high-T hopping regime.

While the above theories have been developed for organic crystals, they may be adapted to describe also charge transport at hybrid interfaces. For example, it is known from organic-transistor experiments that the carrier mobilities are strongly influenced by polarization effects at hybrid interfaces[58] Theoretically, this should be accounted for via inclusion of additional EVCs that cause the formation of interface polarons. Similarly, in single-molecule junctions the molecular vibrations also impact the transport characteristics (coherent vs incoherent tunneling, temperature dependence, power dissipation, etc.) thus requiring advanced novel concepts to include EVC into the respective quantum-transport theories.[59,60]

CONCLUSIONS AND OUTLOOK

In summary, modern *ab initio* electronic-structure theory going beyond DFT can already provide substantial insight into electronic structure and optical excitations of hybrid materials. Nevertheless, there are major challenges to be tackled. First, the role of vibrations needs to be clarified from first-principles on both the band structure and spectroscopy level. This will help to understand polaronic effects including the impact of temperature, which is crucial for any application. Even more important, the question whether a hybrid material is useful for some device requires consideration of excitation lifetimes and dynamics. We need to know not only the binding strength of electron−hole pairs and their spatial extension but also the time scale of their formation and recombination. Likewise, *ab initio* approaches to exciton diffusion are totally lacking. Moreover, present polaron-transport theories have to be extended toward a full *ab initio* description for a quantitative prediction of charge-carrier mobilities. In all these aspects, new ground needs to be broken.

In short, to fully understand hybrid materials and reach predictive power on a quantitative level, novel methodology on various levels is needed. A must for DFT and methods beyond is the ability to treat different interactions on the same footing. This includes urgent need for a systematic validation of *ab initio* methodology together with highly efficient and massively parallel computer codes. Only with this level of accuracy and understanding can we proceed to additional questions imposed by *real systems*, such as (un)intentional doping, band bending,[61] disorder, grain boundaries, and more.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Further reading concerning the different topics addressed in the manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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Karsten Hannewald received his Ph.D. in 2001 at the University of Jena (Germany), modeling the femtosecond dynamics of optically excited semiconductors. As a postdoctoral fellow at the University of Technology in Eindhoven (Netherlands), he started his research on organic crystals. After a brief stay as a guest researcher at the University of Arizona in Tucson (USA), he returned to Jena where he received his Habilitation in 2012. Currently, he is a senior researcher at the Humboldt-Universität Berlin, dealing with organic/hybrid electronics, as well as nanoelectronics with functional biological and organic materials.

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