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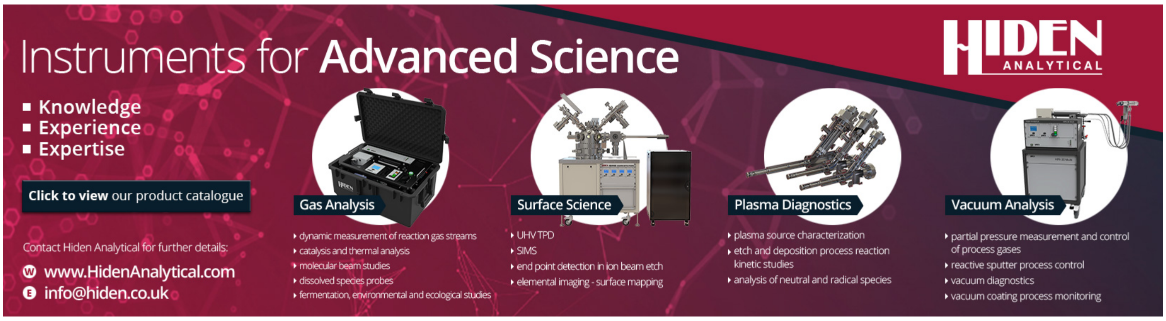
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ABSTRACT

Charge localization is an important phenomenon that influences various material properties, including excited-state energetics, charge transport, catalytic activity, and recombination. As such, it has significant implications for optoelectronic and photocatalytic applications. In this Perspective, we begin by addressing the methodological challenges associated with modeling localized charges, highlighting their complexity and the need for accurate computational approaches. We then discuss how charge localization impacts the performance of solar cells and photocatalysts, providing specific examples to illustrate these effects. Connections between theoretical predictions and experimental observations are explored to underline the importance of integrating modeling and experiments. Finally, we outline future research directions, emphasizing the development of advanced methods to better capture localized charge behavior and its role in materials design.

I. INTRODUCTION

Semiconductors are essential for many modern technologies. Their behavior depends on the presence of excess charges, electrons, and holes, introduced by doping, photon excitation, or electric current. In some semiconductors, especially when they are relatively soft structurally and easily polarized, excess charges can localize in potential wells, self-generated by displacing the surrounding ions (see Fig. 1). Charge localization in materials is related to the formation of quasiparticles such as polarons and self-trapped excitons.[1] Excess charges in polarizable solids form polarization clouds, which travel with the charge carrier. The extent of this polarization cloud gives rise to two distinct classifications: large and small polarons. The effects of both large and small polarons on materials are substantial. Large Fröhlich polarons, which extend over multiple unit cells, interact relatively weakly with lattice vibrations.[2,3] Their impact can manifest itself in altered charge transport properties, phonon coupling, and slight structural modifications within the material. On the other hand, small Holstein polarons, localized at a single or few atomic sites, can strongly alter the local atomic structure and act similarly to structural defects.[4,5] They can influence electronic band structures, charge mobility, and optical properties.[6–8] While both types of polarons significantly affect material properties, this Perspective explores the role of small polarons, highlighting key aspects of charge localization in semiconductors from the authors' viewpoint.

II. CHALLENGES IN MODELING CHARGE LOCALIZATION

Despite significant advances in computational techniques, accurately modeling charge localization remains a challenging task because of the complex interplay between electronic and lattice degrees of freedom. There are two main ways to describe polarons in periodic systems from first principles: the supercell approach and the use of unit cells with model electron–phonon Hamiltonians (e.g., Refs. 9–12). In this Perspective, we focus on the supercell approach, although many of the challenges discussed also apply to other methods. The supercell technique involves adding charges to atomistic models containing tens to hundreds of atoms, often accompanied by an initial guess for distortions linked to polaron formation. Despite its usually higher computational cost, this method is widely used due to its simplicity and adaptability to surfaces, interfaces,[13,14] and defective materials,[15–17] which are central to real devices. However, its application requires addressing key challenges, including the self-interaction error (SIE),

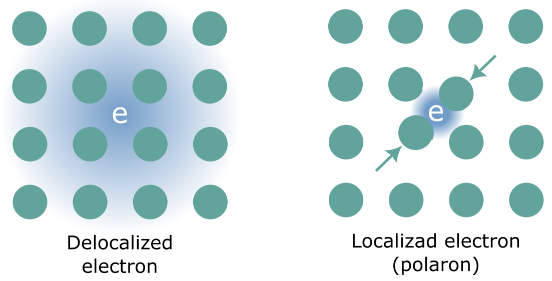

FIG. 1. Schematic illustration of the formation of a small electron polaron and associated lattice distortion.

finite-size corrections, configurational space sampling, and dynamical effects, as represented in Fig. 2 and detailed later.

A. Self-interaction error

One of the main challenges related to modeling charge localization is due to SIE inherent in density functional theory (DFT).[18,19] This error arises because standard DFT approximations, such as semi-local functionals, fail to fully cancel out the electron's interaction with itself. This leads to destabilization of the polaronic state and often to charge delocalization. This error can be corrected by using hybrid functionals, in which a fraction of exact exchange from the Hartree–Fock theory is included.[20–23] This fraction can be a fixed global value, as done in the widely adopted PBE0(α)[24] and B3LYP[25] functionals, or depend on the distance, as done in range-separated hybrid functionals, such as HSE06[26] and CAM-B3LYP.[27] It is worth noting that the amount of exact exchange needed to correct SIE is material-specific, and an accurate description of polarons should not generally be expected from standard hybrid functionals such as PBE0 and HSE06.

To remove SIE exactly, the fraction of Fock exchange in the hybrid functional should be optimized for the given material. Two non-empirical methods for parametrizing a hybrid functional include satisfying the generalized Koopmans' theorem[18,22,28–30] and basing the parameterization on the dielectric function.[30–37] The Koopmans' condition enforces that single-particle energy levels remain unchanged upon occupation, thereby addressing many-body self-interaction errors (see Fig. 3). The combination of global hybrid functionals with the Koopmans' condition has been shown to capture both the polaronic states and band gaps of a series of materials.[22] It is worth noting that to correctly predict the formation energy of a polaron, accurate descriptions of distortions, polaronic level, and the band edges are necessary. Doubly screened hybrids have also been shown to predict band gaps in good agreement with experiment and higher levels of theory,[30,32,36,38,39] and their applicability to polaronic states should be further tested.[40,41]

In addition to the use of relatively computationally expensive hybrid functionals, more efficient methods to overcome SIE have been proposed. First, DFT+U can be used to introduce an additional on-site potential to specific orbitals, where charge localization is anticipated. This method has been employed to localize charges not only on elements typically associated with strongly correlated d- and f-orbitals[42–45] but also on oxygen orbitals to stabilize hole polarons.[46,47] Alternatively, Falletta and Pasquarello developed a method based on the application of a weak local potential in the Kohn–Sham Hamiltonian.[48] This technique enforces the piecewise linearity of the total energy upon partial electron occupation and has been shown to yield good agreement with hybrid functionals in several test cases. While schemes to ensure piecewise linearity in bulk materials are becoming well established, their applicability to interfaces, surfaces, and low-dimensional systems remains an open question, particularly in environments with varying screening effects. For example, a study by Chen *et al.*[49] demonstrated that in 2D materials, the optimal fraction of Fock exchange is not unique, as band edges and localized defect states experience different screening behaviors. This suggests that functionals optimized for bulk may not be directly transferable to surfaces and interfaces, where similar challenges may arise.

B. Finite-size effects and corrections

In the supercell approach, modeling charge localization in a periodic system generates finite-size effects that can introduce spurious terms in the total energy.[50–52] These arise because localized states in a finite supercell can interact with their periodic images as well as with the neutralizing background charge, leading to incorrect total energies and Kohn–Sham energy levels. While these artifacts become vanishingly small when the supercell size is increased, reaching a desired convergence could, in some cases, require supercells too large for feasible calculations.

The problem of finite-size errors is well known in the context of modeling defects in semiconductors, and various correction

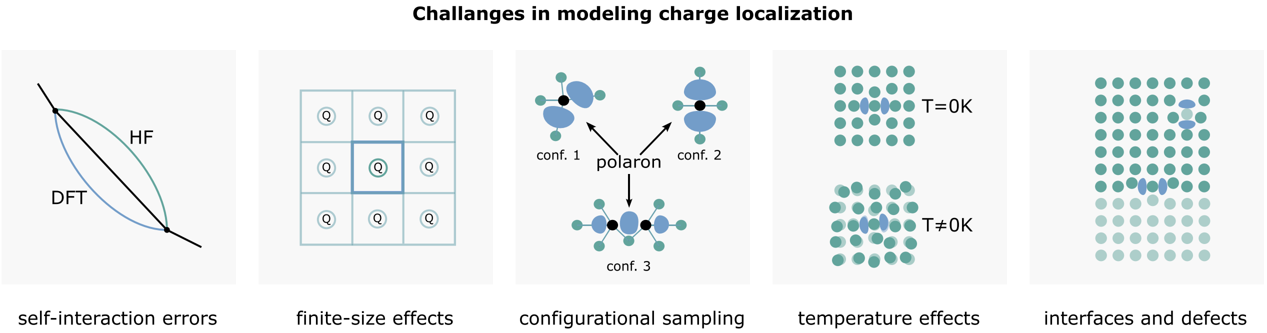

FIG. 2. Illustration of five key challenges in modeling charge localization described in this Perspective: (1) self-interaction errors, (2) finite-size effects, (3) multiple competing configurations, (4) thermal effects, and (5) interactions with defects and interfaces.

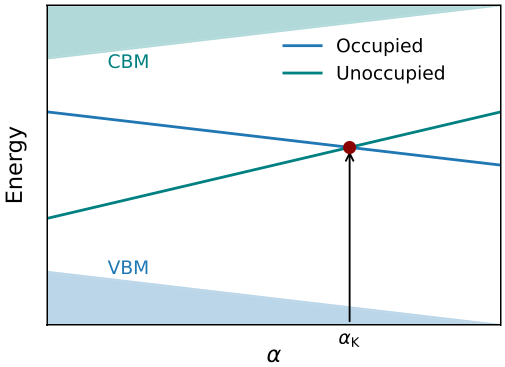

FIG. 3. Scheme for construction of a hybrid functional based on the Koopmans' condition. The optimal α_K is found by identifying where the occupied and unoccupied single-particle energy levels cross.

schemes have been developed, both for bulk and surfaces.[53–56] These errors arise due to spurious interactions between periodic images of localized charges and the neutralizing background charge, leading to incorrect total energies and Kohn–Sham energy levels. The same methods need to be applied when modeling small polarons with periodic boundary conditions. The most commonly used schemes introduce two key corrections: (i) an electrostatic correction accounting for the interaction of the monopole charge with its periodic images and the neutralizing background, and (ii) a potential alignment term to address the offset in the electrostatic potential caused by the supercell boundaries. In addition, corrections to the Kohn–Sham energy levels can be derived directly from the total energy corrections, as outlined in Ref. 57.

One particular aspect related to finite-size corrections and modeling polarons is their application when constructing a functional through the generalized Koopmans' theory. This approach can be based on verifying whether the positions of the filled and empty levels related to the polaron coincide for a given parametrization. While the empty state corresponds to a neutral simulation cell, it has been shown that ionic distortions lead to polarization charges, which, in turn, cause finite-size errors that need correction.[58–60]

C. Configurational space sampling

Charge localization is often accompanied by significant structural distortions, as the local lattice relaxes around the trapped charge. When modeling polarons, an initial guess of distortions is commonly applied, before the structure can relax freely. In simple and symmetric systems, there might be a unique way in which the atoms can distort, and different guesses would lead to the same final energy minimum. However, in complex materials, multiple localization modes can coexist.[23,61–64] In such cases, different initial guesses can lead to metastable polaronic states, making it important to consider all potential localization modes and assess their relative stabilities. This can be done by examining the local symmetries and orbitals expected to be involved in the formation of a polaron in the material. Randomized initial distortions applied systematically, as shown for defects with possible metastable configurations,[65] could also address this issue. It is worth noting that metastable states in the bulk at 0 K may become the most stable configurations in the presence of defects, interfaces, or at finite temperatures, highlighting the need to account for all possible states.

D. Dynamical effects and electron–phonon coupling

Most computational studies on polarons are conducted at 0 K. Nevertheless, temperature can impact their behavior, with high temperatures often leading to charge delocalization due to thermal fluctuations. However, thermal effects might also, in principle, stabilize polarons, particularly in materials where the dielectric properties, phonon dynamics, and anharmonicity exhibit complex temperature dependencies.[66]

A notable example is the halide perovskite methylammonium lead iodide ($MAPbI_3$), a material with applications in solar cell. Standard approaches fail to identify charge localization at 0 K in this material. However, hybrid functional molecular dynamics (MD) simulations of excess charges reveal the formation of polaronic states for both holes and electrons within just a few femtoseconds of simulation.[67] This finding prompted a reassessment of the nature of polarons in $MAPbI_3$, which were initially thought to be stabilized primarily by the reorganization of MA cations around the charges. However, the experimentally and computationally observed time scales for charge localization,[67,68] which are incompatible with the slower rotation of MA molecules,[69] suggest a different mechanism. Specifically, thermal

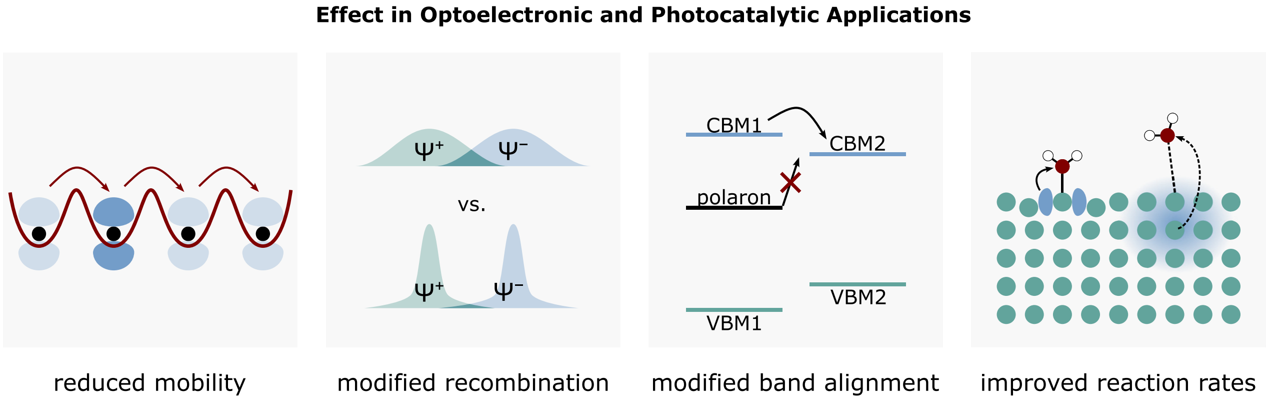

FIG. 4. Illustration of the effects of charge localization described in this Perspective: (1) reduced charge carrier mobility, (2) modified recombination rates, (3) modification of band alignment at interfaces and with reaction levels, and (4) enhancement of reaction rates.

disorder in the dipolar MA cations induces charge localization, while the distortions in the inorganic sublattice effectively stabilize the polaronic states.[70,71]

In another halide perovskite, $CsPbBr_3$, the electron polaron can be found computationally at 0 K but is marginally less stable than the delocalized electron.[23] Thermodynamic integration simulations showed that temperature can stabilize the polaronic state by 0.21 eV. Similarly, in $BiVO_4$, a material used for photoelectrochemical water splitting, charge transition levels related to both hole and electron polarons are influenced by temperature. At room temperature, these levels get stabilized on the absolute energy scale, although the overall stability is challenging to assess because the band edge positions also shift significantly with temperature.[72]

Beyond their formation and stability, an important aspect of polaron behavior is their mobility, which can be accessed already from calculations at 0 K. Several computational approaches have been developed to study polaron hopping, including the use of kinetic Monte Carlo simulations combined with the Landau–Zener theory, as demonstrated by Wu and Ping in $BiVO_4$.[73] More recently, piecewise linear functionals were used to investigate the hopping properties of small polarons, offering a computationally efficient approach to studying mobilities of localized charges.[74,75]

While these studies provide insights into charge transport at 0 K, modeling polaron dynamics at finite temperatures remains computationally demanding. Hybrid functional molecular dynamics can capture temperature-dependent effects but is often too expensive for long timescale simulations. This challenge can be solved by the development of alternative approaches. One strategy would be to use more affordable methods for correcting self-interaction errors, such as DFT+U or local potentials.[48] Another promising approach relies on techniques based on machine learning (ML) to model polaron dynamics efficiently, as recently demonstrated by Birschitzky *et al.*[76]

E. Adapting to surfaces, interfaces, and defects

The supercell approach is particularly useful for modeling localized states near surfaces, interfaces, and defects, which are critical for the performance of optoelectronic and photocatalytic devices. In these environments, the local structure deviates from the bulk, due to the asymmetry of interatomic interactions, potentially influencing polaronic distortions and associated charge localization. These effects, in turn, can significantly impact the properties of defects and surfaces.

For instance, the presence of defects has an important effect on charge localization in $BiVO_4$, where oxygen dimerization was found in connection with acceptor defects.[16] It has been shown that accounting for charge localization and its impact on the formation energies of intrinsic defects is necessary to accurately predict Fermi-level pinning in agreement with experiments. Polaron–vacancy interactions have also been highlighted at the surfaces of $BiVO_4$, TiO_2, and CeO_2.[76–78]

In halide perovskites, charge localization can reduce charge recombination at defects. For example, our study on hole trapping at the negatively charged iodine interstitial showed that at room temperature, charge trapping by the defect is energetically unfavorable, with the hole instead remaining as a polaron hopping in the material.[79]

Surfaces also play a critical role in the stability and nature of polarons. In $BiVO_4$, surfaces have been shown to alter the localization mode of hole polarons while simultaneously lowering their energy.[14,80] In contrast, electron polarons were found to be less stable in the outermost surface layer, preferring to localize deeper within the material. This behavior facilitates effective charge separation at the surface.[14,78] Similarly, electron polarons on the TiO_2 surface are also more stable in the subsurface layers.[81]

Charge localization determines recombination at interfaces and grain boundaries in perovskite-based devices.[82,83] Charge localization on $MAPbI_3$ surfaces has received considerable attention because of their interesting dichotomy stemming from a different alignment of energy levels.[84,85] While passivated MAI-terminated surfaces do not favor polaron formation, PbI_2-terminated surfaces not only enhance the stability of hole polarons but are also highly sensitive to surface defects.[86]

Defects on PbI_2-terminated surfaces exhibit strongly augmented trapping activity, potentially acting as recombination centers, inhibiting charge transfer across interfaces, and compromising the long-term stability of the material. In particular, polaronic localization of holes on unpassivated PbI_2 surfaces has been linked to the loss of iodine observed in $MAPbI_3$ under operating conditions. Specifically, a double hole polaron is formed on the surface of the perovskite in the form of an iodine vacancy/I_3^- trimer Frenkel defect, which eventually leads to the dissociation of molecular I_2 from the system. However, this degradation mechanism is effectively suppressed when the surface is properly passivated.[87]

While the formation of hole polarons at the $MAPbI_3$ surface is intimately related to iodine chemistry, a strikingly different behavior is observed when substituting Pb with Sn, i.e., in $MASnI_3$. In fact, due to the toxicity of lead, $MAPbI_3$ is not considered an eco-friendly or commercially viable alternative to silicon. Consequently, there has been a surge in the development of lead-free perovskites aimed at replicating the promising performance of $MAPbI_3$.[88] However, the electronic properties and charge localization in tin-halide perovskites are dominated by tin chemistry.[89–91] On unpassivated SnI_2-terminated surfaces, two holes are captured by undercoordinated surface tin, prompting the oxidation of Sn(II) to Sn(IV), which comes with a double polaron localized on a surface SnI_4 unit.[92,93] On the other hand, in this case, plain passivation of the surface is not really effective as the MAI-covered surface now features double electron polarons, in the form of Sn–Sn dimers. For this reason, additives such as SnF_2 should be included in the synthetic process; in fact, strongly electronegative fluorine bonding tin atoms on the surface hinders charge transfer to tin atoms, leading to the emergence of a double polaron.[94]

Another strategy to destabilize both hole and electron double polarons at the surface of metal halide perovskites is alloying Sn and Pb in the material. In fact, $MAPb_{0.5}Sn_{0.5}I_3$ is found to feature electronic properties, which are intermediate between those of the lead and tin counterparts. This translates into a competition between iodine and tin chemistry at the surfaces of the material, resulting in a general decrease in trapping activity for both holes and electrons.[89,93]

III. CHARGE LOCALIZATION IN SOLAR CELLS

Charge localization can play an important role in the performance of solar cells, affecting charge transport, recombination rates, and overall efficiency (see Fig. 4). In particular, small polarons can influence the mobility of charge carriers, reducing the effective conductivity of materials. Moreover, polarons may also help reduce charge recombination by localizing states with opposite charges in spatially different regions of materials, as shown in $MAPbI_3$.[67,70,79] At the same time, strong localization, especially in the case of small polarons, may also enhance non-radiative recombination. However, the impact of polaron size on recombination depends on the host material and the shape of the potential energy surface of the excited state.

Charge localization has been found to be stable in several lead- and tin-halide perovskites, ranging from larger polarons in $MAPbI_3$ to strongly trapped ones in tin-halide perovskites, especially when two electrons are localized at the same time within Sn–Sn dimers.[23,67,70] Strong trapping of charges in the form of double polarons has also been demonstrated in antimony sulfide (Sb_2S_3).[95] Self-trapping, along with strong electron–phonon coupling, has been identified as potentially placing a fundamental limit on its open-circuit voltage.

At surfaces or at undercoordinated sites, charge carriers are even more prone to localization, generating deeper mid-gap levels that impede smooth conduction and band alignment with transport layers.[86] Furthermore, surfaces and grain boundaries in lead halide perovskites are primary sources of instability, where self-trapping of charge carriers is significantly stabilized compared to the bulk, potentially leading to defect formation, such as iodine vacancies and color centers.[87] As discussed in the previous section, in mixed tin/lead perovskites, surface chemistry plays a crucial role in determining electronic properties, where a competition between tin and iodine oxidation hinders tin oxidation under Sn-rich conditions, improving long-term stability and optoelectronic performance, but low tin content exacerbates hole trapping and poor electronic properties.[89,90,93]

These findings highlight a trade-off related to charge localization in solar cell materials. On the one hand, polaron formation slows recombination and boosts carrier lifetimes; on the other hand, it diminishes mobility and can yield deep trap states.

IV. CHARGE LOCALIZATION IN PHOTOCATALYSIS

Charge localization is increasingly recognized as a pivotal factor influencing catalytic redox processes at semiconductor–electrolyte interfaces. In $BiVO_4$, for instance, double hole polarons in the form of O–O dimers have been shown to open alternative water-oxidation routes, lowering overpotentials and circumventing standard scaling constraints.[80] A similar phenomenon occurs in rutile TiO_2, where hole polarons on the (110) surface significantly reduce the predicted overpotential for oxygen evolution, bringing theoretical models into closer agreement with experimental values.[96] Tin-halide perovskites present a related scenario; in $DMASnBr_3$, a recently synthesized water-stable perovskite,[97,98] double electron polarons appear at the interface through Sn–Sn dimers, enabling a direct proton-to-hydride route and sidestepping more convoluted radical-hydrogen pathways.[99,100] This polaron-driven mechanism often leads to lower activation energies and improved reaction kinetics.

Charge localization can also tune oxidation reactions in single-atom catalysts, where polaronic states affect the dynamic redox of Pt sites on CeO_2, thereby unlocking more efficient CO-oxidation mechanisms.[101] Additionally, TiO_2 surfaces bearing polarons can influence the adsorption and reactivity of CO molecules, with surface-localized polarons promoting different adsorption configurations compared to subsurface polarons.[102] This interplay modifies the binding energetics and shapes the subsequent reaction pathways involving adsorbed CO. Finally, electrochemical studies suggest that polaron formation in TiO_2 can strongly modulate its hydrogen evolution reaction (HER) kinetics, providing opportunities to rationally optimize semiconductor-based HER.[103]

These examples underline the crucial role of polaronic states in interfacial catalysis, while also highlighting the necessity of accurately modeling charge localization at surfaces and interfaces. Such an approach captures the nontrivial interplay between lattice distortions, defect states, and energetic alignment, offering perspectives on designing advanced photocatalysts and electrocatalysts.

V. CHARGE LOCALIZATION IN ORGANIC SEMICONDUCTORS

Organic semiconductors, with their intermediate polaronic behavior, low reorganization energies, and dependence on thermal disorder[104–108] bridge photovoltaics and photocatalytic applications. Unlike their inorganic counterparts, they exhibit (i) low reorganization energies from small dielectric constants and (ii) fluctuating charge localization influenced by thermal motions, modulating charge mobility.[104,109] Polaronic localization often occurs at molecular scales, with binding energy contributions from internal molecular rearrangement (internal reorganization energy) and stabilization from surrounding molecular motion (external reorganization energy).[108,110] These features complicate the predictions because neither band-like transport nor polaron hopping fully explains the observed charge transport.[107,109,111–115]

Most computational studies focus on single molecules or clusters, addressing internal reorganization energy or use extended model Hamiltonians.[112,116–118] Recently, large periodic supercells and Koopmans-compliant hybrid functionals have been applied to study charge localization in acenes and fullerene derivatives. In acenes, charge localization competes with delocalization, favoring molecular trapping in shorter acenes such as naphthalene and anthracene, while pentacene and tetracene show near-isoenergetic localized and semi-localized states.[108]

In fullerene derivatives, localized electron polarons are preserved across both 3D van der Waals crystals and the 2D covalently bonded graphullerene network.[119] Enhanced electron mobility in the 2D phase arises from shorter intermolecular distances in the covalently bonded network, enabling faster hopping despite intramolecular bonding constraints.

In this context, further studies are needed to include the effects of thermal disorder on polaron binding energy and the associated charge mobility within the supercell approach.

VI. BRIDGING MODELING AND EXPERIMENTS

Bridging the gap between computational modeling and experimental studies is essential to understand polarons and charge localization. Various experimental techniques for detecting polarons have been extensively reviewed in Ref. 120. Here, we highlight a few key methods and their interplay with computational approaches.

Photoluminescence (PL) spectroscopy can capture energy shifts associated with self-trapping and localized states and has been used to detect charge localization in halide perovskites and metal oxides.[121–126] Raman spectroscopy can reveal vibrational modes linked to polaronic distortions, which can be assigned to specific structural or electronic phenomena through simulations.[120,127,128] Dynamic aspects of polaron formation are accessible via transient absorption (TA) spectroscopy, which tracks localized states on ultrafast timescales.[127,129–131] Techniques such as x-ray photoelectron spectroscopy (XPS) and photoelectron spectroscopy (PES) probe shifts in core-level binding energies, offering insights into charge localization,[132,133] while electron paramagnetic resonance (EPR) detects unpaired spins, directly evidencing polarons in certain systems.[134] Recent advances in ultrafast electron diffuse scattering (UEDS) provide momentum-resolved views of polaron formation and phonon coupling dynamics,[131] and scanning probe techniques such as scanning tunneling microscopy (STM)[135] and atomic force microscopy (AFM)[136] enable spatial visualization of charge localization at surfaces or interfaces.

While identifying polarons using some of the aforementioned techniques is rather straightforward, in other cases, comparison with modeling is necessary. This can be challenging, especially when modeling requires advanced techniques such as time-dependent density functional theory (TDDFT) or calculating Raman spectra. At the same time, simulations offer unique advantages, for example distinguishing between polarons, self-trapped excitons, and defect-related color centers in optical experiments, where experimental signals can be ambiguous.

VII. FUTURE DIRECTIONS

Advancing the understanding of charge localization and dynamics in materials requires the development of more efficient and accurate computational methods. Another goal is to create generalizable frameworks that encompass a broader range of material classes, enabling the prediction and optimization of material properties across diverse systems.

Machine learning approaches hold significant promise for addressing these challenges. By enabling the study of temperature effects and dynamics more effectively, these methods can provide insights into systems at interfaces and under realistic operating conditions. The integration of machine learning with traditional computational approaches could lead to significant efficiency gains and, therefore, to the possibility of studying charge localization in a more systematic way. One major advantage of ML-based methods is their ability to extend the accessible time and length scales of simulations, enabling better convergence of results and a more comprehensive exploration of polaronic configurations. This would allow for a direct assessment of polaron diffusion and hopping mechanisms, which are otherwise difficult to capture with conventional *ab initio* approaches. Furthermore, ML-based molecular dynamics could provide access to the thermodynamics of polaron formation, making it possible to compute free-energy landscapes and evaluate temperature-dependent stability over a wide range of conditions. However, several challenges remain in applying ML-based methods to polarons. In particular, machine learning interatomic potentials (MLIPs) based on local descriptors will not fully capture finite-size effects present in training data derived from periodic boundary conditions. Additionally, the dynamics of polarons obtained from ML-based simulations will be strongly influenced by small energy differences, such as those arising from the choice of functional. Since direct DFT-based MD at the required timescales is computationally prohibitive, it will be difficult to assess how reliably ML-based simulations capture polaron diffusion and other dynamical properties.

Establishing stronger connections with experimental results is another important goal. Enhanced validation of computational predictions through collaboration with experimental studies will ensure reliability and facilitate the design of materials with targeted properties. Particular emphasis should be placed on achieving accurate predictions of polaronic behavior and the related properties that can assist in their identification in experiments.

VIII. CONCLUSIONS

Charge localization profoundly influences the optoelectronic and photocatalytic properties of materials, playing a critical role in determining their performance in real-world applications. This phenomenon, manifesting through the formation of polarons and self-trapped excitons, can either hinder or enhance material functionalities, depending on the specific system and context. On the one hand, charge localization can reduce charge mobility and create deep trap states, negatively impacting transport properties. On the other hand, localized states can mitigate charge recombination and stabilize reactive intermediates, improving device efficiency and catalytic activity.

Despite significant advancements, accurately modeling charge localization remains a challenge due to the complex interplay of electronic, structural, and dynamic factors. Hybrid functionals, DFT+U, and emerging machine learning approaches have improved the description of localized states, yet capturing their dynamic behavior and interactions with experimental observables requires further refinement.

Future research should focus on developing more generalizable computational frameworks, incorporating temperature effects and realistic interface dynamics, and establishing robust links between theory and experiments. Special attention must also be given to the role of charge localization at surfaces, interfaces, and grain boundaries, as these environments often dictate the overall performance of optoelectronic and photocatalytic devices.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Francesco Ambrosio: Conceptualization (equal); Funding acquisition (equal); Writing – original draft (equal); Writing – review & editing (equal). **Julia Wiktor:** Conceptualization (equal); Funding acquisition (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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