

Polarons in materials

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Abstract | Polarons are quasiparticles that easily form in polarizable materials due to the coupling of excess electrons or holes with ionic vibrations. These quasiparticles manifest themselves in many different ways and have a profound impact on materials properties and functionalities. Polarons have been the testing ground for the development of numerous theories, and their manifestations have been studied by many different experimental probes. This Review provides a map of the enormous amount of data and knowledge accumulated on polaron effects in materials, ranging from early studies and standard treatments to emerging experimental techniques and novel theoretical and computational approaches.

Polarons are among the most studied and cross-disciplinary research subjects in physics, chemistry and materials science^{1–3}. The term ‘polaron’ was coined by Solomon Pekar in 1946 to define the unit formed by an excess charge carrier (electron or hole) localized within a potential well, self-generated by displacing the surrounding ions^{4,5}. The resulting composite quantum object can be identified as a quasiparticle consisting of an electron or a hole dressed by a cloud of virtual phonons: an excess charge injected into a polarizable solid displaces the ions in its neighbourhood and creates a polarization cloud that follows the charge carrier as it propagates through the crystal (FIG. 1a). Depending on the spatial extent of this polarization cloud, a general classification into small and large polarons can be introduced; the different nature and properties of small and large polarons originate from the range of action of the electron–phonon interaction. The distinct physical properties of small and large polarons are summarized in BOX 1.

The concept of auto-localization in an ideally perfect crystal caused by lattice deformation was initially conceptualized by Lev Landau in 1933 (REF.⁶). Since then, several groundbreaking theories and experimental observations have gradually disclosed and described the importance of polaron formation in an exceptionally wide spectrum of systems, including solids, liquids, polymers and cold gases¹. The development of polaron theories has its roots in the seminal works of Herbert Fröhlich^{7,8} and Theodore Holstein^{9,10}, who formalized the dichotomy between large-radius and small-radius polaronic states by establishing rigorous quantum-field Hamiltonians, which became the standard theoretical groundwork for successive advancements^{11–13} (TABLE 1).

In parallel with continued theoretical progress, experimental evidence is rapidly accumulating that shows the pervasiveness of polarons in materials and their key role in many different phenomena¹⁴. Polaron hallmarks have been measured in transition-metal oxides^{3,15,16},

amorphous compounds¹⁷, organic semiconductors^{18,19}, conducting polymers^{20–22}, diluted magnetic semiconductors²³, manganites^{24–27}, cuprates²⁸, hybrid perovskites^{29,30} and 2D materials^{31–33}. Polaron-mediated effects have been identified as the key factor in physical phenomena such as charge transport^{18,34–36}, surface reactivity^{37–41}, colossal magnetoresistance^{24,42}, thermoelectricity⁴³, photoemission^{29,30,44} and (multi)ferroism^{30,45}, to name just the most relevant ones.

These achievements were made possible through innovations and improvements of experimental probes and computational approaches. Today, the presence of polarons in materials can be detected by a variety of experimental techniques, including scanning tunnelling microscopy and spectroscopy (STM and STS, respectively)⁴⁶ and atomic force microscopy (AFM)⁴⁷, angle-resolved photoemission spectroscopy (ARPES)⁴⁸, various core-level spectroscopies⁴⁹, electron paramagnetic resonance (EPR)^{50,51}, Raman scattering⁵², muon spin relaxation⁵³, neutron scattering²⁷, luminescence⁵⁴, infrared spectroscopy⁵⁵, time-resolved optical Kerr effect (TR-OKE) spectroscopy³⁰, transport measurements¹⁶ and many more (TABLE 2).

Concurrently, the efficient implementation of polaron theories in computational codes has allowed the calculation of polaron-specific properties (including polaron energy, polaron dispersion and effective mass, polaron wavefunction and polaron mobility) (FIG. 1) using a variety of approaches, including analytical schemes^{56,57}, quantum Monte Carlo^{58–60}, first-principles density functional theory (DFT)^{3,61–64}, dynamical mean-field theory (DMFT)^{65–67} and multiscale modelling^{68,69}. A recent, rigorous, ab initio computational theory of polarons was developed by Feliciano Giustino and colleagues combining the Landau–Pekar model with DFT^{13,70}.

After almost 90 years of polaron research, work on polarons continues to thrive and expand into new fundamental and applied areas^{30,32,34,40,44,45,47,57,64,71–84}.

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With this Review, we aim to provide a survey of the historical milestones and a selection of the rapid contemporary developments from a joint theoretical and experimental perspective. We provide a comprehensive map of the theoretical models and experimental techniques, and present several paradigmatic examples of the different types of polarons and polaron-driven phenomena that can develop in materials. The primary focus is on small and large polarons, but we widen the context by including also other types of polarons, such as bipolarons, magnetic polarons, Jahn–Teller/ferroelectric polarons and Zener polarons. Among the many materials discussed in this Review, a special emphasis is placed on TiO_2 and halide perovskites. For TiO_2 , a vast amount of data are available spanning roughly the last two decades, from the seminal first-principles and EPR works of Gianfranco Pacchioni and Elio Giamello^{50,61} to the most recent advances. Halide perovskites represent the most rapidly developing research area in which polarons play an essential role,

and many (even fundamental) aspects are the source of animated debates. To conclude, we discuss how to further improve the characterization and modelling of polarons, and suggest research directions to investigate novel polaronic effects in realistic systems.

Theoretical account of polaron properties

This section provides a brief overview of the theoretical constructs and computational models developed in the past 90 years to describe, interpret and compute the properties of polarons (TABLE 1).

Landau–Pekar model

Inspired by the seminal elaboration of Landau on an electronic carrier slowly moving through an ionic solid⁶, the first quantitative description of a single electron immersed in a dielectric medium was developed by Pekar⁴. The resulting Landau–Pekar model relies on the continuum approximation, in which the ionic

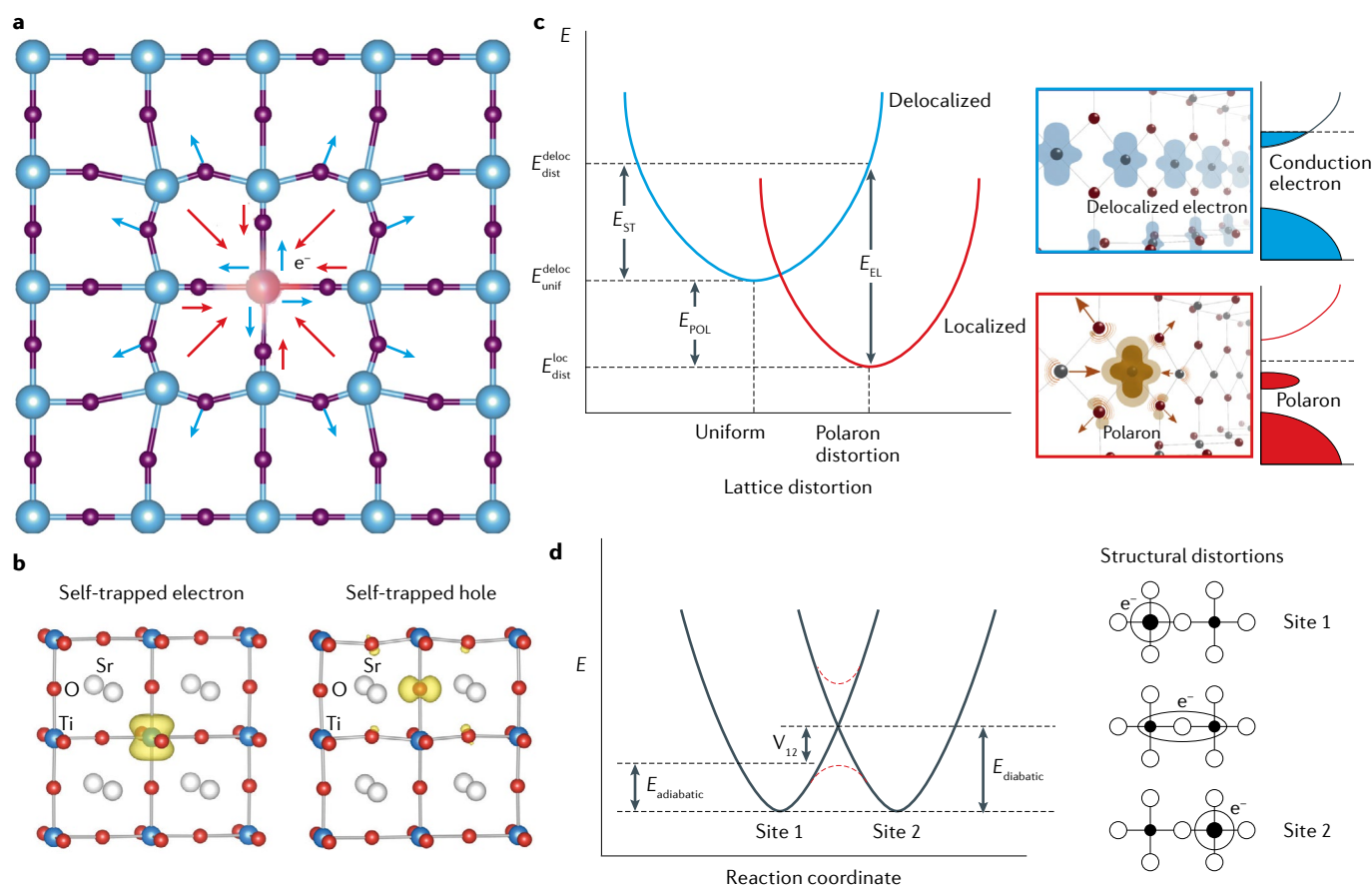


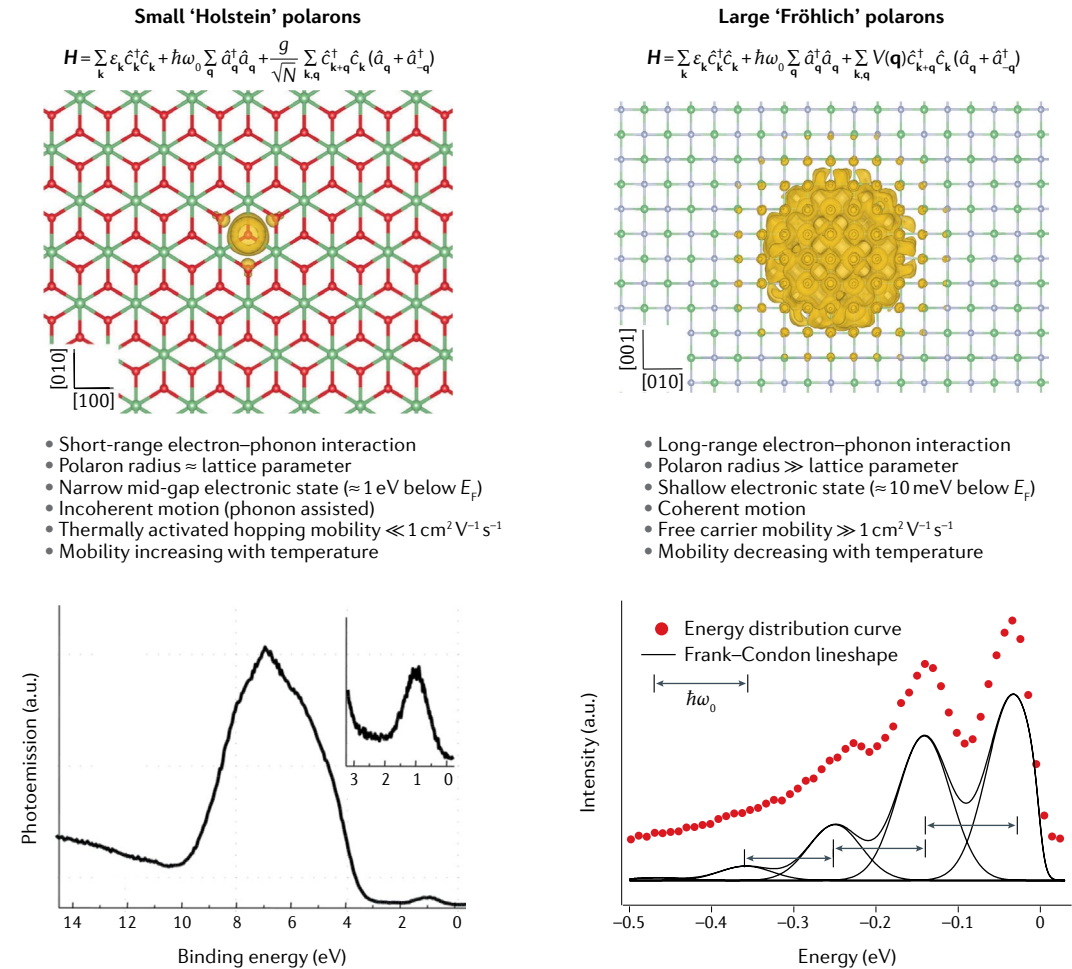
Fig. 1 | Basic properties of polarons. **a** | Schematic illustration of the polarization caused by the self-trapping of an electron at a lattice site and formation of a (small) polaron. Arrows represent attractive (red) and repulsive (blue) forces. **b** | Electron and hole polaron charge isosurfaces in SrTiO_3 . **c** | Configuration coordinate diagram depicting the energy balance as a function of lattice distortion for a conduction (delocalized) electron and for a localized polaron. E_{ST} is the structural energy, E_{POL} the polaron binding energy and E_{EL} is the electronic energy. The right side of the panel shows charge density isosurfaces and the corresponding schematic band structure of a delocalized conduction electron (upper panel) and a small polaron with the polaron peak localized below the Fermi energy (lower panel). **d** | General scheme of the Marcus–Emin–Holstein–Austin–Mott small-polaron hopping theory showing

the transfer of an electron from site 1 to site 2 in the diabatic (finite electronic coupling strength V_{12}) or adiabatic (quantum tunnelling) regime. Black and red lines indicate the typical energy profile obtained for diabatic and adiabatic regimes, respectively. The schematic plot on the right shows the hopping of an electron (large filled circle) from site 1 (top) to site 2 (bottom) through an intermediate transition state, where the electron is delocalized over both adjacent sites. The hopping is accompanied by a progressive breathing-in/ breathing-out structural distortion of the atoms surrounding the trapping centres (small empty circles). Panel **a** reprinted with permission from REF.³⁴, Wiley. Panel **b** reprinted with permission from REF.³⁴⁵, APS. Panel **c** adapted from REF.³, Springer Nature. Panel **d** (left) adapted with permission from REF.¹²³, ACS. Panel **d** (right) reprinted with permission from REF.¹²¹, APS.

Box 1 | Basic characteristics of small and large polarons

The effective Holstein and Fröhlich Hamiltonians, which describe small and large polarons, respectively, are presented at the top of the figure. Here, c_k and a_q are annihilation operators for a particle with wave vector k and a phonon with wave vector q , respectively, ϵ_k represents the band energies, N is the total number of unit cells, and g and $V(q) = (\frac{2\sqrt{2}\pi\alpha}{V})^{\frac{1}{2}} \frac{1}{q} (\frac{\hbar^2\omega_0^3}{m})^{\frac{1}{4}}$ are the short-range and long-range electron–phonon coupling terms, respectively, the latter given in terms of the volume of the system V and of the electron–phonon parameter α (Eq. 2). The charge isosurface of a small polaron in Li_2O and of a large polaron in LiF are shown under the Hamiltonians, accompanied by a list of characteristic features and properties of small and large polarons. A valence-band photoemission spectrum of a small polaron in reduced rutile TiO_2 and an energy distribution curve of a large polaron in n -doped anatase TiO_2 (REF.⁴⁸) are shown at the bottom of the figure: note the different energy scales.

Charge isosurfaces reprinted with permission from REF.⁷⁰, APS; photoemission spectra adapted with permission from REF.³⁴⁶, Annual Reviews; energy distribution curve reprinted with permission from REF.⁴⁸, APS.



crystal is treated as a polarizable dielectric continuum, and the electron–electron interaction is treated within the effective-mass approximation. The main (Schrödinger-type) equation of the Landau–Pekar model is derived by minimizing the total Landau–Pekar energy functional $E(\psi)$ with respect to the polaron wavefunction $\psi(r)$ (REF.¹):

$$\left(-\frac{\nabla^2}{2m} - e^2 \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \int dr' \frac{|\psi(r')|^2}{|r' - r|} \right) \psi(r) = E_0 \psi(r), \quad (1)$$

where m is the band mass, ϵ_0 and ϵ_∞ are the static (electronic and ionic) and high-frequency (electronic,

ion-clamped) dielectric constants, and E_0 is the polaron ground-state energy. Despite its simplicity, this model provides a ready-to-use formula to estimate the polaron ground-state energy, radius (the spatial extension of the polaron wavefunction) and effective mass; the model is also representable in terms of the dimensionless electron–phonon interaction α :

$$\alpha = e^2 \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \sqrt{\frac{m}{2\omega_0}}, \quad (2)$$

where ω_0 is the characteristic longitudinal optical phonon frequency (acoustic phonons are not considered). However, an intrinsic contradiction restricts the applicability of the Landau–Pekar model: the model is

designed to treat continuum Fröhlich polarons, but formally justified results can only be obtained in the strong electron–phonon coupling regime, where the polaron radius is small, a situation hardly realizable in realistic materials^{1,13}. Also, for a bound polaron solution, the electron–phonon coupling α must be positive. This implies $\epsilon_0 > \epsilon_\infty$. The Landau–Pekar model is, thus, only applicable to polar crystals, but polarons also exist in nonpolar crystals. In this respect, the term ‘polaron’ is a misnomer and does not reflect the exact nature of this quasiparticle.

In 2019, Giustino and colleagues recasted the Landau–Pekar equations in a DFT formalism using a Bethe–Salpeter formalism^{13,70} and showed that the resulting (variational)

first-principles theory of polarons overcomes the limitations of the original Landau–Pekar model. It allows for a material-specific description of both small and large polarons within a unified formalism, taking into account the coupling with both acoustic and optical phonons¹³, and treating both short-range and long-range electron–phonon interactions (an example of the calculated small and large polaron wavefunction is given in BOX 1).

Historically, the models describing polarons are usually divided into two classes, based on the original theories of Fröhlich^{7,85,86} (continuum large polarons) and Holstein^{9,10} (lattice small polarons), which are succinctly reviewed in the next section.

Table 1 | Compendium of theoretical and computational models for studying polarons

Year	Theoretical and computational models	Polaron properties
1933 (REF. ⁶)	Dielectric theory: charge moving in a dielectric crystal	Auto-localization due to lattice deformation
1946–1948 (REFS ^{4,306–308})	Self-consistent theory of a large polaron	Enhancement of effective mass
	Landau–Pekar model	Localization of the wavefunction
1950s ^{7,8,85,86}	Quantum-mechanical variational theory of large polarons	Effective mass, energy, mobility
	Fröhlich large polaron Hamiltonian (continuum approximation)	Intermediate electron–phonon interaction
1955–2017 (REFS ^{11,12,93,161,162})	All-coupling continuum polaron theory	Energy, effective mass, mobility (large polaron)
	Feynman variational path-integral formalism	
1956 (REF. ⁹⁵), 1980s ^{94,96}	Monte Carlo calculations	Large polaron ground-state energy
1958 (REFS ^{309,310}), 1959 (REFS ^{9,10})	Holstein small polaron theory	Small polaron conduction mechanism
	Holstein small polaron Hamiltonian (lattice approximation)	Effective mass, energy
1963–2000s ^{87–89,311}	Exact solution of the two-site Holstein polaron	Dynamical characteristics
1969 (REF. ¹⁴⁸), 2000 (REFS ^{149,150})	Emin–Holstein–Austin–Mott theory	Small polaron hopping
1980 (REF. ¹⁴⁶), 1985 (REFS ^{119,147})	Marcus theory	Polaron hopping
1994 (REF. ¹⁰¹)	Exact diagonalization	Small polaron frequencies
1997 (REF. ³¹²)	Hartree–Fock	Small polaron density of states
1998–2000 (REFS ^{58,59})	Diagrammatic Monte Carlo	Energy, effective mass, phonon distribution, spectral density
1999 (REF. ¹⁵⁷)	Random walk Monte Carlo	Dispersive transport and recombination
2001 (REF. ¹⁰⁴), 2010 (REF. ⁵⁶)	Analytical variational approach (variational LDB many-polaron wavefunction) ¹⁰³	Many-polaron (large) optical conductivity
2001 (REF. ⁶⁰)	Path-integral Monte Carlo	Large polaron energy (2D and 3D)
1995 (REF. ⁶⁵), 1997 (REF. ⁶⁶), 2003 (REF. ⁶⁷)	Dynamical mean-field theory	Small polaron energy, mass, spectral and transport properties
2010 (REF. ¹⁵⁴), 2018 (REF. ¹⁵⁵)	First-principles molecular dynamics of small polarons	Polaron configurations
2002 (REF. ⁶¹), 2006 (REF. ¹⁶⁶)	Hybrid functionals	Small polaron spin density
2006 (REF. ⁹²)	Analytical approximation for the Green’s function	Energy, mass, dispersion, spectral weight
2006 (REFS ^{117,118}), 2009 (REF. ³¹³)	DFT+U	Small polaron migration, DOS, bipolaron
2007–2010 (REFS ^{68,69})	Multiscale modelling and kinetic Monte Carlo	Charge transport
2014 (REF. ¹⁵¹)	Random phase approximation	Small energy and hopping
2009 (REF. ⁶²), 2011 (REF. ¹³²)	Generalized Koopmans’ density functional	Small polarons states
2015 (REF. ⁶⁴)	Density-functional perturbation theory	Fröhlich electron–phonon vertex
2016 (REF. ¹⁰²)	Renormalization group (large polaron)	Energy, effective mass
2019 (REFS ^{13,70})	Ab initio theory of polarons	Formation and excitation energies wavefunction (small and large polarons)

DFT, density functional theory; DOS, density of states; LDB, Lemmens, Brosens and Devreese; U, on-site Hubbard energy.

Table 2 | Overview of the experimental works reviewed in the main text

Year	Material	Polaron source	Technique	Detected polaron
1963 (REF. ¹⁵)	UO ₂	Oxidation	Conductivity measurements	Small
1964 (REF. ³¹⁴)	SrTiO ₃	O vacancies, Nb	Conductivity and Seebeck	Large
1970 (REF. ²⁰⁶)	ZnS, ZnSe	Photoexcitation	Raman spectroscopy	Large
1976 (REF. ³¹⁵)	EuO	O vacancies	Optical absorption	Small
1977 (REF. ²⁰²)	CeO ₂	O vacancies	Conductivity and Seebeck	Small
1987 (REF. ³¹⁶)	Conjugated polymers	Photoexcitation	Photoluminescence	Small
1994 (REF. ²²²)	BaTiO ₃	Nb doping	EPR	Small
1996 (REF. ²⁷)	LaMnO ₃	Sr doping	Neutron scattering	Small
2001 (REF. ²²⁵)	LaMnO ₃	Ca doping	NMR and muon spin rotation	Small
2005 (REF. ²²⁷)	CeO ₂	O vacancies	STM	Small
2007 (REF. ²²⁶)	PrMnO ₃	Ca doping	TEM	Small (Zener)
2007 (REF. ²⁰⁰)	a-TiO ₂ and r-TiO ₂	Nb doping	Conductivity and optical measurements	Large (a), small (r)
2008 (REF. ¹⁹⁶)	r-TiO ₂	O vacancies	Resonant photoelectron diffraction	Small
2010 (REF. ⁵⁶)	SrTiO ₃	Nb doping	Optical conductivity	Large
2013 (REF. ⁵¹)	r-TiO ₂	O vacancies	EPR	Small
2013 (REF. ⁴⁸)	a-TiO ₂	O vacancies	ARPES	Large
2014 (REF. ⁴⁶)	r-TiO ₂	O vacancies	STM and STS	Small
2015 (REF. ⁵⁵)	r-TiO ₂	UV/H adatom	Infrared spectroscopy	Small
2016 (REF. ³¹⁷)	LiNbO ₃	Photoexcited	Infrared spectroscopy	Small
2017 (REF. ³⁰)	CH ₃ NH ₃ PbBr ₃ and CsPbBr ₃	Photoexcited	TR-OKE	Large
2017 (REF. ²¹⁹)	a-TiO ₂	Photoexcited	TR-XAS	Large
2020 (REF. ⁸³)	Fe ₂ O ₃	Photoexcitation	RIXS	Small

UV/H indicates that polarons were generated either by ultraviolet light or by adsorption of H atoms. a, anatase; ARPES, angle-resolved photoemission spectroscopy; EPR, electron paramagnetic resonance; NMR, nuclear magnetic resonance; r, rutile; RIXS, resonant inelastic X-ray scattering; STM, scanning tunnelling microscopy; STS, scanning tunnelling spectroscopy; TEM, transmission electron microscopy; TR-OKE, time-resolved optical Kerr effect; TR-XAS, time-resolved X-ray absorption spectroscopy.

Fröhlich and Holstein Hamiltonians

The Fröhlich and Holstein models constitute the historical backbone of polaron theory. The Fröhlich approach follows the continuum approximation and neglects the discreteness of the crystal lattice. It allows the description of large polarons in ionic, polar and ferroelectric materials, caused by the long-range component of the electron–phonon interaction. In these materials, the static dielectric constant ϵ_0 is necessarily larger than the high-frequency (optical) ϵ_∞ , implying that the Fröhlich model is not formally applicable to nonpolar systems, similarly to the Landau–Pekar model. By contrast, the Holstein theory considers short-range electron–phonon interactions resulting from the coupling between a carrier and the strain where it resides. This model explicitly takes into account the discreteness of the lattice. In principle, it can describe polarons with different spatial extensions if explicit forms of the electron–phonon coupling are provided; as such, it is suitable to describe strongly coupled small and large polarons. The Fröhlich and Holstein theories are formalized in terms of the fundamental effective Hamiltonians given in BOX 1, where the various terms (electronic bands, phonons and electron–phonon coupling) are typically treated by means of approximate parametric expressions (that is, non-*ab initio*).

All attempts to find exact solutions for the Fröhlich model have been fruitless, and the Holstein model can be solved exactly only in the two-sites case^{87–89}; analytical and numerical solutions are unavoidable. Extensive studies have been devoted to solving and understanding the properties of small and large polarons at all coupling strengths (weak, intermediate and strong)^{1,90}. These are summarized in TABLE 1 and briefly recapped below. The first groundbreaking and influential approach was the Feynman variational path-integral formalism for large polarons introduced in 1955 (REF.¹¹). Among the various many-body propositions, the diagrammatic Monte Carlo⁵⁸ method turned out to be an efficient and accurate scheme to solve both the Holstein and the Fröhlich Hamiltonians^{59,91,92}.

Feynman's path-integral approach

In analogy with quantum electrodynamics, Feynman reformulated the polaron problem into a variational path integration for a system composed of an excess charge carrier coupled with a cloud of independent phonons through a harmonic interaction.

Starting from a polaron Lagrangian, Feynman integrated the phonon field to obtain an effective Euclidean polaron action $S[\mathbf{r}(t)]$, which includes retardation effects

(it is non-local in time) arising from the interaction of the electron with the phonon disturbance it has created while travelling through the lattice (which exponentially dies out in time). Within this model, the free energy F of the polaron system at finite temperature $k_B T = 1/\beta$ (where k_B is the Boltzmann constant) can be expressed as a path integral of the form:

$$e^{-\beta F} = \int \mathcal{D}\mathbf{r}(t) e^S, \quad (3)$$

where $\mathcal{D}$ denotes integration overall paths. To solve this electron path integral analytically, Feynman employed an original variational principle, in which the exact polaron action is replaced by an approximate, but exactly solvable, quadratic action dependent on two model parameters. These parameters are then varied to minimize the ground-state energy for a given α and phonon frequency¹¹.

This path-integrated harmonic model provides one of the most accurate analytical approximations for the ground-state energy and effective mass of Fröhlich

polarons for all coupling strengths α (REFS^{1,93}). The integral cannot be performed in closed form, but it is possible to obtain approximate expressions in the weak and strong coupling limit, which for the ground-state energy E_0 and effective mass m^* take the forms:

$$\frac{E_0}{\omega_0} = \begin{cases} -\alpha - 0.0123\alpha^2 + O(\alpha^3) & \alpha \rightarrow 0 \\ -0.106\alpha^2 + O(1) & \alpha \rightarrow \infty \end{cases} \quad (4)$$

$$\frac{m^*}{m} = \begin{cases} 2 + \frac{\alpha}{6} + O(\alpha^2) & \alpha \rightarrow 0 \\ 0.106\alpha^4 + \dots & \alpha \rightarrow \infty \end{cases} \quad (5)$$

An accurate solution of the Feynman integral requires numerical integration, which can be executed by means of Monte Carlo techniques^{50,94–96}. FIGURE 2a shows the Monte Carlo-derived evolution of the polaron ground-state energy and effective mass as a function of α for a large Fröhlich polaron, and is compared with data obtained using the diagrammatic Monte Carlo (DiagMC) scheme⁵⁸, one of the most successful schemes

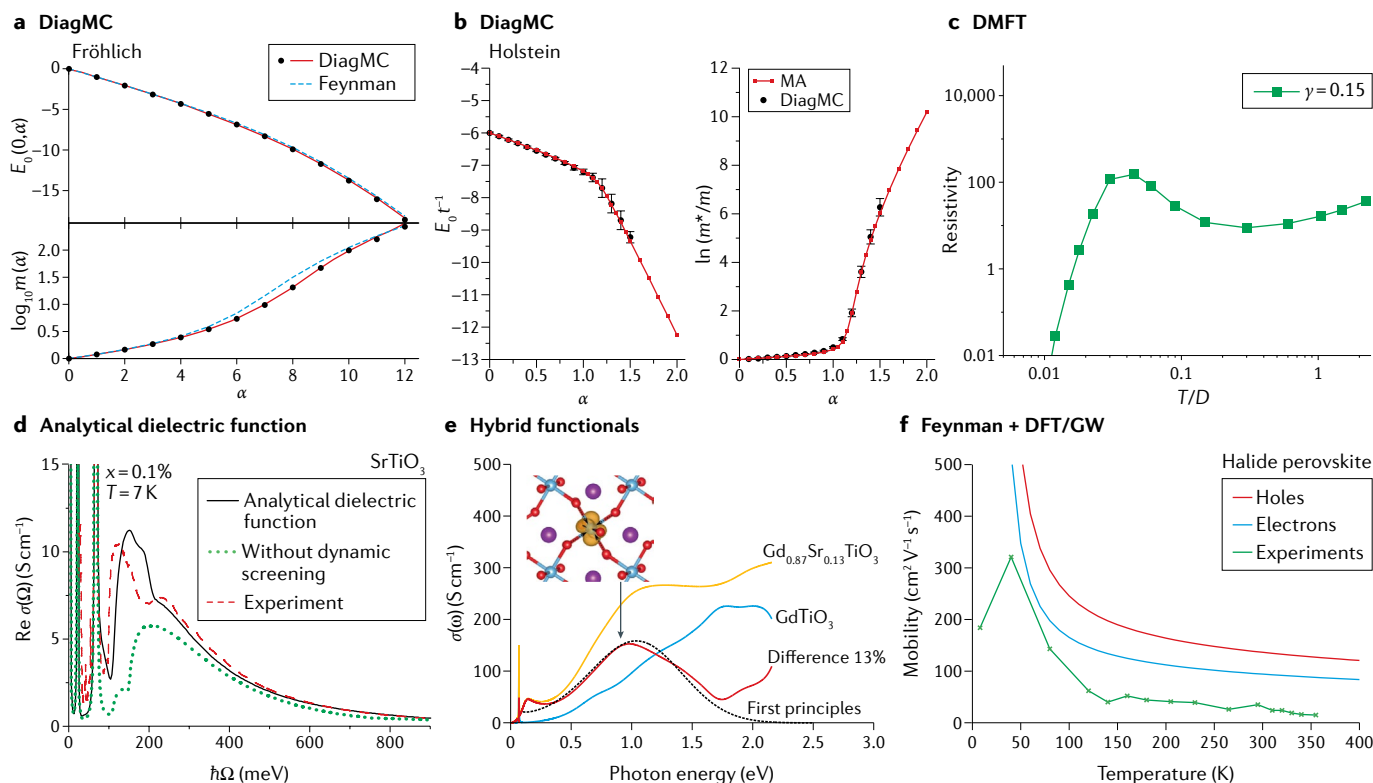


Fig. 2 | Polaron properties predicted by different theoretical and computational models. a,b | Diagrammatic Monte Carlo (DiagMC): effective mass, m^* , and ground-state energy, E_0 , for a large, Fröhlich 3D polaron (panel **a**, compared with analytical approximations based on Feynman's path-integral treatment⁹³ and a small, Holstein polaron (panel **b**). α is the electron–phonon coupling strength. Data for the Holstein polaron are compared with momentum average (MA) approximation results⁹². **c** | Dynamical mean-field theory (DMFT): temperature-dependent resistivity showing the crossover from coherent metallic-like motion (low temperature) to phonon-assisted hopping (exponential decrease) for the Holstein polaron in the adiabatic regime; at high temperature, residual scattering leads to an increase of the resistivity. D is the unrenormalized half bandwidth. **d** | Analytical dielectric function approach: comparison between measured and calculated optical conductivity, σ , of n -doped SrTiO₃. **e** | First principles

(hybrid functionals): effects of a hole small polaron on the optical conductivity of Gd_{1-x}Sr_xTiO₃, showing the onset of a polaron peak as x increases from 0 to 0.13. The curve obtained with first-principles methods for the difference between the spectra at $x=0$, blue, and $x=0.13$, yellow, is shown in black and compared with the experimental curve (red: difference between the spectra at $x=0$ and $x=0.13$). **f** | Feynman variational method (parameter-free, inputs obtained by GW and density functional theory (DFT) calculations): temperature-dependent large polaron mobility (red for holes and blue for electrons) in a methylammonium lead iodide perovskite; experimental results are shown by the green line. Panel **a** adapted with permission from REF.⁹¹, APS. Panel **b** reprinted with permission from REF.⁹², APS. Panel **c** reprinted with permission from REF.⁶⁷, APS. Panel **d** adapted from REF.⁵⁷, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Panel **e** reprinted with permission from REF.¹³¹, AIP. Panel **f** reprinted with permission from REF.¹⁶², APS.

to solve different types of (single and multiple) polaron problems^{59,81,91,97}. The basic ideas behind DiagMC are discussed below.

Diagrammatic Monte Carlo

The DiagMC method is a type of quantum Monte Carlo method for strongly correlated systems based on the stochastic sampling of Feynman diagrams^{58,98}. Feynman diagrams are a powerful tool in many-body physics that appear in perturbative expansions of quantum statistical averages. From a mathematical point of view, the diagrammatic expansion of a function of interest $Q(\{y\})$ (typically a Green's function) is a series of integrals of the type:

$$Q(\{y\}) = \sum_{n=0}^{\infty} \sum_{\xi_n} \int \cdots \int \mathcal{D}_{n,\xi_n}(\{y\}; x_1, \dots, x_n) dx_1 \dots dx_n, \quad (6)$$

where n labels the order of the perturbation (potentially infinite), $\{y\}$ are external parameters, ξ_n indexes different diagrams of the same order n and the x s are the integration variables.

The overall idea behind the DiagMC method is to represent the functions $\mathcal{D}$ by Feynman graphs and interpret $Q(\{y\})$ as a distribution function for the external variables $\{y\}$ (REF.⁵⁸). The whole space of Feynman diagrams is generated stochastically using a standard Markov chain Monte Carlo and a Metropolis–Hastings update scheme^{58,59,99}.

To solve the polaron problem, the DiagMC procedure is applied to the perturbative expansion of the one-electron– N -phonons Green's function used to solve a general polaron Hamiltonian by mapping the function $Q(\{y\})$ into the polaron Green's function $G^{(N)}$:

$$G^{(N)}(\mathbf{k}, \tau, \{\tilde{\mathbf{q}}_i\}) = \sum_{n=0}^{\infty} \sum_{\xi_n} \int \cdots \int \mathcal{D}_{n,\xi_n}(\mathbf{k}, \tau, \{\tilde{\mathbf{q}}_i\}; \mathbf{x}) d\mathbf{x}, \quad (7)$$

where $\mathbf{k}$ is the wave vector and $\mathbf{x} = (\tau_1, \dots, \tau_n, \mathbf{q}_1, \dots, \mathbf{q}_n)$ is a vector of integration variables (times of interaction vertices and internal phonon wave vectors). The integrands $\mathcal{D}_{n,\xi_n}$ are given as a product of free electron Green's functions, free phonon Green's functions and squared electron–phonon interaction vertices, and are clearly representable by a series of Feynman diagrams.

Equation 7 represents, therefore, a conventional diagrammatic expansion for the polaron Green's function, which can be efficiently calculated by DiagMC. In the original formulation, the lowest-energy eigenvalues $E_0(k, \alpha)$ (polaron spectrum) are obtained through an exponential fit of the asymptotic behaviour of the Green's function at long imaginary times:

$$G^{(N)}(\mathbf{k}, \tau \rightarrow \infty, \{\tilde{\mathbf{q}}_i\}) \propto e^{-E_0(\mathbf{k})\tau}. \quad (8)$$

Other polaron quantities of interest can be calculated in the framework of quantum DiagMC, including effective mass, self-energy, mobility⁸¹ and spectral function¹⁰⁰. An example of the application of DiagMC to the Fröhlich and Holstein polaron is provided in FIG. 2a,b, which show

the polaron dispersion and effective mass as a function of the electron–phonon coupling strength and provides a direct comparison with the Feynman path-integral approach and a few other analytical approximations.

From model Hamiltonians to first principles

Besides DiagMC, other sophisticated approaches have been adopted to solve the Fröhlich and Holstein Hamiltonians. Noteworthy are the fundamental studies by Sergio Ciuchi and colleagues using DMFT^{60,65–67} — an example of DMFT-derived results is the temperature-dependent resistivity for a small polaron displayed in FIG. 2c, showing the crossover from classical activated motion at high temperatures to coherent motion at low temperatures — but also exact diagonalization¹⁰¹, renormalization group¹⁰² and many analytical studies that, apart from those mentioned in relation to FIG. 2b, also include models such as those inspired by the variation method of Lemmens, Devreese and Brosens for many-polaron systems^{56,57,103,104}. A representative illustration of the predictive power of (semi)analytical methods is shown in FIG. 2d, where the measured optical conductivity for n -doped SrTiO₃ is compared with memory-function results⁵⁷ (here, combined with first-principles inputs).

Numerical and analytical solvers are powerful and versatile approaches and can allow for the inclusion of many-body effects. However, a direct comparison with material-specific experimental data is often hindered by the intrinsic limitations of effective Hamiltonian approaches, namely, the parametric or phenomenological treatment of the individual physical terms of the Hamiltonian: the single-particle band structure, the full phonon dispersion and the electron–phonon interaction. The Fröhlich and Holstein model Hamiltonians are simplifications of the more general electron–phonon Hamiltonian, and these terms are treated in an approximate way. In the Fröhlich model, the one-particle band energies are replaced by a model parabolic dispersion, and the phonon terms involve a single dispersion-free phonon mode, which is coupled with the wave-vector-dependent coupling term $V(\mathbf{q})$ (dependent on the coupling parameter α). Similarly, the Holstein model involves a single local mode and the local displacement couples (through the trivial coupling term q) to the electronic bands, typically described within a tight-binding picture. A natural improvement (albeit of great complexity) would be the extension to many electron and phonon bands and a realistic account of all terms, including the short-range and the long-range electron–phonon interaction. From a numerical perspective, all these contributions can be calculated by first-principles methods: the energy bands can be computed accurately within the GW approximation^{105,106} (a reasonable compromise are also hybrid functionals^{107,108} or the DFT+ U method^{109,110}), whereas phonon properties, including electron–phonon interactions, can be estimated by density functional perturbation theory^{111,112}, including the Fröhlich term⁶⁴. Also, properties such as the spectral function, a natural output of DiagMC⁵⁹, can be mapped to first-principles techniques, as shown in REF.⁷⁶ using cumulant expansion.

The time is ripe to develop new techniques and numerical procedures to combine first-principles methods with quantum-field phonon Hamiltonians, merging the benefits of each approach into a general realistic many-body quantum framework allowing for truly complete first-principles calculations of polarons.

To complete the overview of the theoretical approaches, we summarize a few aspects of first-principles methods for polarons in the next section.

First principles: DFT and beyond

Most electronic structure schemes used to study polaron properties in real materials have their roots in Kohn–Sham DFT, in which the many-body interactions are embedded into an approximated exchange–correlation (xc) functional in a mean-field fashion¹¹³, resulting in a system of single-particle Schrödinger equations:

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{c}}(\mathbf{r}) + V_{\text{x}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad (9)$$

where the Hamiltonian is split into kinetic, Hartree (V_{H}), external (V_{ext}) and exchange–correlation (V_{x} and V_{c}) terms, $\phi_i(\mathbf{r})$ are the single-particle Kohn–Sham orbitals and ε_i the corresponding eigenvalues.

Despite its great success^{114,115}, DFT within the simplest local (LDA) and semi-local (GGA) functionals exhibits systematic failures owing to self-interactions errors, manifested by the wrong variation of the energy functional E as a function of the orbital occupation n ($d^2E/dn_i^2 > 0$ instead of the correct $d^2E/dn_i^2 = 0$ behaviour). These shortcomings are particularly substantial for the description of localized states and band gaps, two crucial quantities in polaron physics. To attenuate these difficulties, different improvements have been proposed, involving an orbital-selective inclusion of additional electronic correlations or incorporating non-local terms in the xc functionals. The most widely used extensions of DFT, successfully used in the study of polaron properties, are the renowned DFT+ U method¹⁰⁹ and generalized Kohn–Sham (GKS) schemes¹¹⁶.

In DFT+ U , the DFT energy functional is corrected in the target correlated orbital space (typically the $l=2$ manifold) by adding an on-site Hubbard, U . The polaron formation energy can be computed as the difference between the localized (polaronic) and delocalized solution³, as sketched in FIG. 1c. The first applications of DFT+ U to the polaron problem dates back to the mid 2000s, to study the formation of hole localization in Al-doped SiO_2 (REF.¹¹⁷) and the migration of small polarons in olivine Li_xFePO_4 (REF.¹¹⁸). In these early studies, polaron hopping was described within the Marcus theory^{119,120}, in which charge transfer occurs via tunnelling from two independent Born–Oppenheimer surfaces around the initial and the final polaron site (FIG. 1d). Alternative models to account for polaron mobility are briefly reviewed in the next section.

Since then, DFT+ U has been adopted in many polaron studies, yielding generally good agreement with observations^{46,121}. It should be noted, however, that the results (polaron energy, degree of localization,

hopping barrier, energy levels and so on) are typically highly sensitive on the choice of the U parameter^{46,122–125}, which is generally chosen by means of a fitting protocol (for example, good match with the measured band gap). This degree of arbitrariness on the choice of U limits the predictive power of DFT+ U , and validation with experimental data is vital for achieving a proper account of polaron properties. To cure the parametric nature of this scheme, a few prescriptions have been proposed to compute U values entirely ab initio, such as the Cococcioni scheme¹²⁶ or the constrained random phase approximation^{46,127}. These solutions lead to a parameter-free framework, but it should be considered that a single (orbital-selective) U correction is, in some cases, not sufficient to account simultaneously for all ground-state properties of a system (band gap, vacancy formation energy, volume and so on). This limitation can be rectified by consistently acting on all orbitals with orbital-dependent single-particle corrections, as in the self-interaction correction method¹²⁸ or, more commonly, by adopting the GKS theory¹¹⁶.

In the GKS theory, the original interacting system is mapped into a partially interacting system. Hybrid functionals are arguably the most popular GKS scheme and involve the replacement of a fraction of local density approximations (LDA) and generalized gradient approximations (GGA) with the exact Hartree–Fock form:

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{c}}(\mathbf{r})\right)\phi_i(\mathbf{r}) + \int V_{\text{x}}^{\text{Hybrid}}(\mathbf{r}, \mathbf{r}')\phi_i(\mathbf{r}')d\mathbf{r}' = \varepsilon_i \phi_i(\mathbf{r}) \quad (10)$$

where $V_{\text{x}}^{\text{Hybrid}}(\mathbf{r}, \mathbf{r}')$ represents the non-local Hartree–Fock exchange, which assumes different forms, depending on the specific hybrid recipe¹²⁹. Commonly used prescriptions are the PBE0/HSE and B3LYP hybrids, which have been applied for a wide range of polaron properties, ranging from early works on defective TiO_2 (REFS^{50,61}) and doped quartz¹³⁰ to the interpretation of the optical conductivity of doped $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_3$ in terms of hole–polaron-induced features¹³¹ (FIG. 2e). Alternative GKS schemes rely on a formal recovery of the correct $d^2E/dn_i^2 = 0$ linear behaviour by means of on-site potential perturbations that remove the (de)localization bias intrinsic to DFT approximations, as done in the Lany–Zunger model^{62,132–135}.

An additional critical issue in DFT calculations using periodic boundary conditions (PBCs) is the spurious self-interaction of a localized charge (polaron and, in general, point charge defects) with its periodic image. These finite-size effects can be prevented by adopting large unit cells, typically with several hundreds of atoms, with large distance between point defects and images, at the cost of performing very demanding calculations. To alleviate the computational cost of this supercell approach, one can use progressively larger cells and extrapolate to the dilute limit, or implement a posteriori corrections¹³⁶, such as the one recently proposed by Sebastian Kokott and colleagues, based on a proper account of long-range polarization effects⁶³. Alternatively, polaron formation has been successfully

studied by solid-state embedding approaches, in which a small cluster of atoms around the polaronic site is described at the quantum-mechanical level and embedded in a molecular mechanics or polarizable continuum environment tuned to reproduce the long-range interactions of the crystal^{137–140}. This approach has the advantage of reducing the computational cost (as the quantum-mechanical clusters are typically smaller than the supercells in PBCs) and removing the spurious interactions of the PBC technique; however, the results are very sensitive to the cluster size and shape, which dramatically influence the prediction of polaron properties^{141,142}.

It is important to note that, also, the already mentioned *ab initio* theory of polarons, combining the Pekar–Landau ansatz with DFT, does not require supercells, addressing, instead, the self-interaction problem by including a suitable self-interaction correction term in the standard DFT functional^{13,70}.

We complete this theoretical overview by addressing polaron transport and mobility.

Polaron mobility

In polaronic materials, charge transport is largely affected by polaron diffusion, which is of great fundamental and technological interest^{34,143}. Several diffusion mechanisms have been identified for both large and small polarons, with distinct regimes depending on temperature, strength of the electron–phonon coupling, electronic bandwidth and characteristic phonon frequency^{67,81,144}. Despite this complex scenario, a simplified picture can be drawn to highlight the general tendencies of small and large polarons¹⁴⁵. Small polarons are likely to undergo phonon-assisted hopping, as the charge carrier localization is destabilized by the thermally induced atomic distortions around the trapping site, resulting in occasional hops. This incoherent motion results in a mobility μ typically much smaller than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which increases upon raising the temperature, owing to the enhanced thermal distortions. Conversely, large polarons tend to sustain a free-carrier-like coherent motion: the large effective mass of the large polarons determines a high mobility, as it preserves the polaron motion from occasional scattering with the phonon field; the mobility decreases by raising the temperature, because the scattering becomes more effective (BOX 1).

Small polarons. Hopping mobility is typically studied in the framework of the Marcus theory^{119,146,147}. The conceptual basis of this theory was settled in the 1980s and was further developed by Emin, Holstein, Austin and Mott (EHAM)^{148–150}. Both theories represent the initial and final polaron states with (parabolic) potential-energy surfaces¹²¹ (FIG. 1d). The associated electrical conductivity σ is expressed by the general form:

$$\sigma = \kappa e^{-\beta E_{\text{act}}}, \quad (11)$$

where the prefactor κ and the activation energy E_{act} assume different forms in the adiabatic and non-adiabatic (diabatic) regimes. In the adiabatic regime, polarons move much faster than the phonon

field, hence, their propagation time is much smaller than that of the local lattice distortions; polarons hop via tunnelling from site to site. Conversely, in the non-adiabatic regime, polarons move much more slowly than the lattice polarization, with a hopping frequency smaller than the corresponding phonon one. The activation energies and, to some extent, also the prefactor can be calculated directly from first-principles schemes defining specific polaron transfer pathways within nudged elastic band methods or linear interpolation schemes^{121,151}. A concise but detailed discussion of the Marcus and EHAM models can be found in REFS^{34,121,152,153}.

Complementary insights on the motion of small polarons can be achieved by first-principles molecular dynamics (FPMD)^{41,46,154,155}. FPMD enables the study of the hopping dynamics of single and multiple small-polaron systems at different temperatures and the extraction of the most favourable spatial polaron configurations¹⁵⁵. The analysis of the FPMD energy landscape with statistical tools allows us to interpret the energy balance and work out the driving mechanisms favouring specific polaron configurations. The energy contributions essential in self-trapping processes are summarized in FIG. 1c and involve the energy cost to locally deform the lattice to accommodate an excess charge (so-called structural energy (E_{ST})) and the energy gain arising from the electron–phonon-assisted charge localization and formation of occupied mid-gap states (so-called electronic energy (E_{EL})). For multipolaron systems, the situation is complicated by the polaron–polaron interaction, which involves two effects: the direct Coulomb repulsion between like-charged quasiparticles and the interference of their atomic deformation patterns¹⁵⁶. To understand the interaction between two adjacent polaron distortions, let us consider the case of two like-charged polarons (FIG. 3, left). The polarons exert counteracting forces on the atoms between them, and, at large separation, their mutual interaction is repulsive. At short separation (approximately one lattice constant), the interaction may become attractive, as both polarons co-act to displace the surrounding ions into the same direction; if this attractive interaction is larger than the Coulomb repulsion of the two like-charged quasiparticles, the pair of small polarons may bind together, forming a bipolaron. Applying a similar rationale to the case of oppositely charged polarons leads to the process schematized in the right part of FIG. 3; here, increased short-range repulsion opposes electron–hole recombination.

We have already mentioned that small-polaron hopping can be described within DMFT (FIG. 2c), which allows the treatment of local many-body effects and the quantum nature of phonons, and nicely describes the loss of coherence at high temperature⁶⁷. The full identification of the different regimes for the dynamic and static small-polaron mobility as a function of α and T (band-like, incoherent metallic, hopping and high-temperature saturation region) has been only recently achieved for the 1D Holstein model in the framework of DiagMC¹⁴⁴.

Another approach for modelling polaron transfer and transport is continuous-time random walk combined

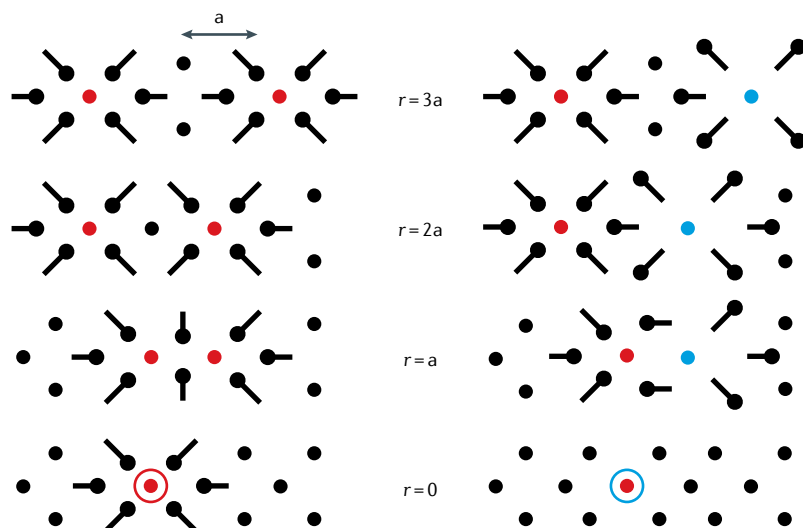


Fig. 3 | Interaction between two small polarons. Interaction between like-charged polarons (left). By progressively reducing the inter-polaron distance r , the interaction between overlapping polaron deformation patterns transforms from repulsive to attracting. If this interference energy gain is larger than the Coulomb repulsion between like-charged polarons, the two polarons glue together, forming a bipolaron. Interaction between hole and electron polarons (right). In this case, the short-range, repulsive overlap between the deformation patterns can strongly affect the recombinative properties. Reproduced from Emin, D. et al. Small polarons. *Physics Today* **35**, 34 (1982), with the permission of the American Institute of Physics.

with Monte Carlo simulations¹⁵⁷, particularly useful to describe dispersive transport and recombination effects in nanocrystalline materials, as it can consider both energetic and configurational disorder.

Large polarons. Large-polaron (coherent) transport can, to some extent, be likened to that of free carriers with two important differences: large polarons have a large effective mass and a generally big thermal momentum¹⁴⁵; and they move slowly and are only weakly scattered by phonons. The study of large-polaron mobility and the calculation of materials-specific transport properties are typically conducted following the Boltzmann equation^{158,159} or the Feynman, Hellwarth, Iddings and Platzman (FHIP) approach^{160–162}.

In a recent article, Jarvist Frost has instructively summarized the most widely used formulas to compute large-polaron mobilities and developed a versatile computer code for the variational solution of the Feynman polaron model at finite temperatures¹⁶².

The originally proposed low- T approximation for the FHIP mobility μ_{FHIP} is given by:

$$\mu_{\text{FHIP}} = \left(\frac{w}{v}\right)^3 \frac{3e}{4m} \frac{\exp(\beta')}{\Omega \alpha \beta'} \exp\left(\frac{v^2 - w^2}{w^2 v}\right), \quad (12)$$

where w and v are Feynman variational parameters, m represents the band effective mass, Ω is the phonon frequency, α the coupling constant and $\beta' = \hbar\Omega/k_B T$.

A first attempt to extend the validity of this formula to higher temperatures was introduced by Leo Kadanoff, who derived a similar equation using the Boltzmann formalism extended to all coupling strengths α within the relaxation-time approximation¹⁵⁸, showing the intrinsic

compatibility of the Feynman and Boltzmann language. This approach has been recently used in conjunction with kinetic Monte Carlo simulations to estimate the mobility in lead-halide perovskites⁶⁹.

A more recent improvement has been proposed by Robert Hellwarth and Ivan Biaggio¹⁶¹, who extended the FHIP formalism beyond the low- T limit and derived the following expression:

$$\mu_H = \left(\frac{w}{v}\right)^3 \frac{3e}{m} \frac{\sqrt{\pi} \sinh(\beta'/2)}{\Omega \alpha \beta'^{5/2}} K^{-1}, \quad (13)$$

where K is an integral providing the polaron response to a first-order change in the driving force. The first complete numerical evaluation of this integral was achieved¹⁶² for the calculation of the large-polaron mobility in a methylammonium lead iodide perovskite using a first-principles extension of the Feynman variational expression within Ōsaka's finite-temperature variational solution¹². A representative result of this study is displayed in FIG. 2f, which shows a comparison between the calculated μ_H and single-crystal terahertz conductivity measurements. A good quantitative agreement is obtained at room temperature. We briefly discuss the polaron properties in halide perovskites in a later section.

Finally, we would like to spend a few words on charge transport beyond the quasiparticle scattering regime, in which the inelastic scattering rate exceeds the thermal energy of quasiparticles and the kinetic equation (suitable for the coherent regime) can no longer be applied⁸¹. Also in this case, DiagMC appears to be a superior method, capable of revealing the main beyond-quasiparticle features and providing the fundamental basis for the interpretation of mobility data in materials with strong electron–phonon coupling⁸¹. From a first-principles perspective, Jin-Jian Zhou and Marco Bernardi⁸⁰ have proposed a finite-temperature retarded cumulant diagram-resummation technique (including higher-order electron–phonon interactions) that delivers an overall good picture of beyond-quasiparticle mobility in SrTiO₃ in the range 150–300 K.

Types of polarons

The previous sections have introduced general types of polarons: small and large polarons (BOX 1), hole and electron polarons (FIG. 1b), and single polarons and bipolarons (FIG. 3). This section extends the classification of polarons by discussing the most notable types that can form in materials and their origin and role, and provides selected examples of their manifestations.

The focus is on dielectric polarons, namely, self-trapping of an excess charge arising from the coupling of an electron or hole with the (self-induced) polarization field developed in a polarizable medium. For the sake of completeness, we mention that, in the context of molecular solids, biological materials and polymers, the commonly used jargon is molecular polarons, to designate polarons whose self-trapped electronic charge carrier is primarily confined within a single molecule¹⁴⁵. The embedding medium can contain displaceable ions and polar molecules, causing a strong interaction between the excess charge carrier and molecular

vibrations (which makes the formal difference between dielectric and molecular forms disputable). A relevant manifestation in this context is the so-called charge carrier solvation, in which a polaron formed in a semiconducting unit immersed in a polar solvent interacts with the solvent and modifies its polarization, leading to a modification of the optical absorption spectra and carrier mobility^{163,164}.

The main types of polarons reported in the literature are listed in TABLE 3, which also includes a basic description of each, and illustrated in FIG. 4. In addition to differences arising from the size (small and large) or the charge (positive or negative), the main distinction among the various polaron types originates from the characteristic coupling with the surrounding environment, alternative to the standard short-range or long-range electron–phonon coupling. These interactions include:

Specific types of structural/electronic distortions, such as static and dynamic Jahn–Teller effect, or ferroelectric instabilities (FIG. 4a,b). For instance, the lattice polarization around a Jahn–Teller centre is enhanced by the spontaneous breaking of the local point symmetry caused by the lifting of a carrier’s orbital degeneracy.

- Entanglement with a cloud of magnetic (or antiferromagnetic) excitations (FIG. 4c); namely, the intrinsic spin of the extra electron or hole can couple with the surrounding spin lattice and induce a magnetic polarization through a variety of spin–spin interactions (a peculiar type of magnetic polaron arises from the coupling between two spin-polarons by double exchange, known as a Zener polaron) (FIG. 4d).

- Dimensionality: the strength and intensity of the electron–phonon coupling can be confined in two dimensions, giving rise to 2D, surface or interface polarons.
- Interaction with defects or dopants. In this case, polaron formation is driven (or enhanced) by the interaction with chemical defects (a common case is oxygen vacancies)⁴⁶, dopants (for example, Li and H)¹⁶, structural defects (steps or domains)¹⁶⁵ or muons⁴⁷ (FIG. 4e). The interaction of polarons with water can also be grouped in this category^{166–168}.
- Polaron–polaron bound states. The most notable examples are bipolarons (FIG. 4f) and polaron excitons (schematically introduced in FIG. 3). Bipolarons are similar to Cooper pairs in the Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity, but the two electrons (or holes) are bound by the exchange of a virtual phonon in real space (and not in *k*-space as in BCS)^{1,169,170}. A polaron exciton is, instead, a bound state formed by the combination of an electron and a hole polaron. In this case, the properties of the excitonic bound pair are affected by the lattice deformations accompanying the (re)combination process. Self-trapped excitons¹⁷¹ are attracting a great deal of attention, owing to their relevance in light–electric interconversion and photoluminescence. Ubiquitous in organic molecular crystals, self-trapped excitons have been recently observed and characterized in halide perovskites^{172,173} and van der Waals interfaces formed by transition-metal dichalcogenides¹⁷⁴. The theoretical account of excitonic properties requires

Table 3 | Types of polarons in materials

Polaron type	Description	References
Electron or hole polaron	Self-trapped electron or hole coupled with phonons	Reviews ^{1,137,145,156,318,319}
Large Fröhlich polaron	Long-range electron–phonon interaction, spatially extended	Theory ^{7,8,85,86} , experiments (<i>n</i> -doped a-TiO ₂) ¹⁴⁸
Small Holstein polaron	Short-range electron–phonon interaction, spatially confined	Theory ^{9,10,309,310} , experiments (UO _{2+x}) ¹⁵
Bipolaron	Bound pair of two polarons (Holstein or Fröhlich), similar to a superconducting Cooper pair ¹⁶⁹	Theory ^{28,320–322} (manganites, cuprates), experiments and DFT (BaK _x Bi _{1-x} O ₃) ^{313,323,324}
Magnetic (spin) polaron	Small polaron coupled with localized spins	Theory ^{325,326} , experiments and DFT (EuO (REFS ^{315,327}), Fe ₃ O ₄ (REF. ⁷⁹), (La _{1-x} A _x) _{2/3} Ca _{1/3} MnO ₃ (REFS ^{24,328}))
Jahn–Teller polaron	Polaron stabilized by Jahn–Teller effects	Experiments (La _{1-x} Sr _x MnO ₃ (REF. ²⁷), cuprates ²⁸), experiments and DFT (ABO ₃) ^{329,330} , theory ^{331,332}
Ferroelectric polaron	Polaron stabilized by ferroelectric distortions	Experiments and DFT (halide perovskites) ^{30,45} , DFT (SrTiO ₃ (REFS ^{333,334}), strained BaTiO ₃ (REF. ¹⁷⁶))
Zener polaron	Two spin polarons coupled by double exchange (FM polaron dimer)	Theory (doped manganites) ²⁵ , experiments ^{25,26} , HF ³³⁵ , DFT ^{177,336}
2D polaron	Polaronic self-trapping confined in 2D	Theory ^{318,337} , experiments (MoS ₂) ³² , DFT (Hf/ZrO ₂) ³³
Polaron exciton (self-trapped exciton)	Bound pair consisting of an electron polaron and a hole polaron	Theory ^{338–340} , experiments (ZnO (REF. ³⁴¹), C60 (REF. ⁵⁴)), review ¹⁷¹ (conjugated polymers) ³⁴²
Dopant/defect polarons	(Small) polarons bound to dopants and defects	Experiments and theory (TiO ₂) ⁴⁶ , book ¹⁴⁵
Molecular polaron	Self-trapping caused by short-range chemical bond formation	Theory ³⁴³ , experiments (DEH molecule) ³⁴⁴ , review (conducting polymers) ²

a, anatase; DEH, *p*-diethylaminobenzaldehyde diphenylhydrazone; DFT, density functional theory; FM, ferromagnetic; HF, Hartree–Fock.

further extensions of the polaron theories reviewed above. In the context of *ab initio* methods, one of the most accurate schemes is non-equilibrium many-body perturbation theory, which can describe processes activated by ultrashort laser pulses, including coherent and non-coherent dynamics of excitons¹⁷⁵.

The nomenclature proposed here is a general classification guided by the observations and idioms reported in the literature, but should not be taken too rigidly. Other mixed states composed by different types of polarons can form and are encountered in materials. For instance, Jahn–Teller effects in a magnetically active background give rise to Jahn–Teller magnetic polarons (FIG. 4g), as

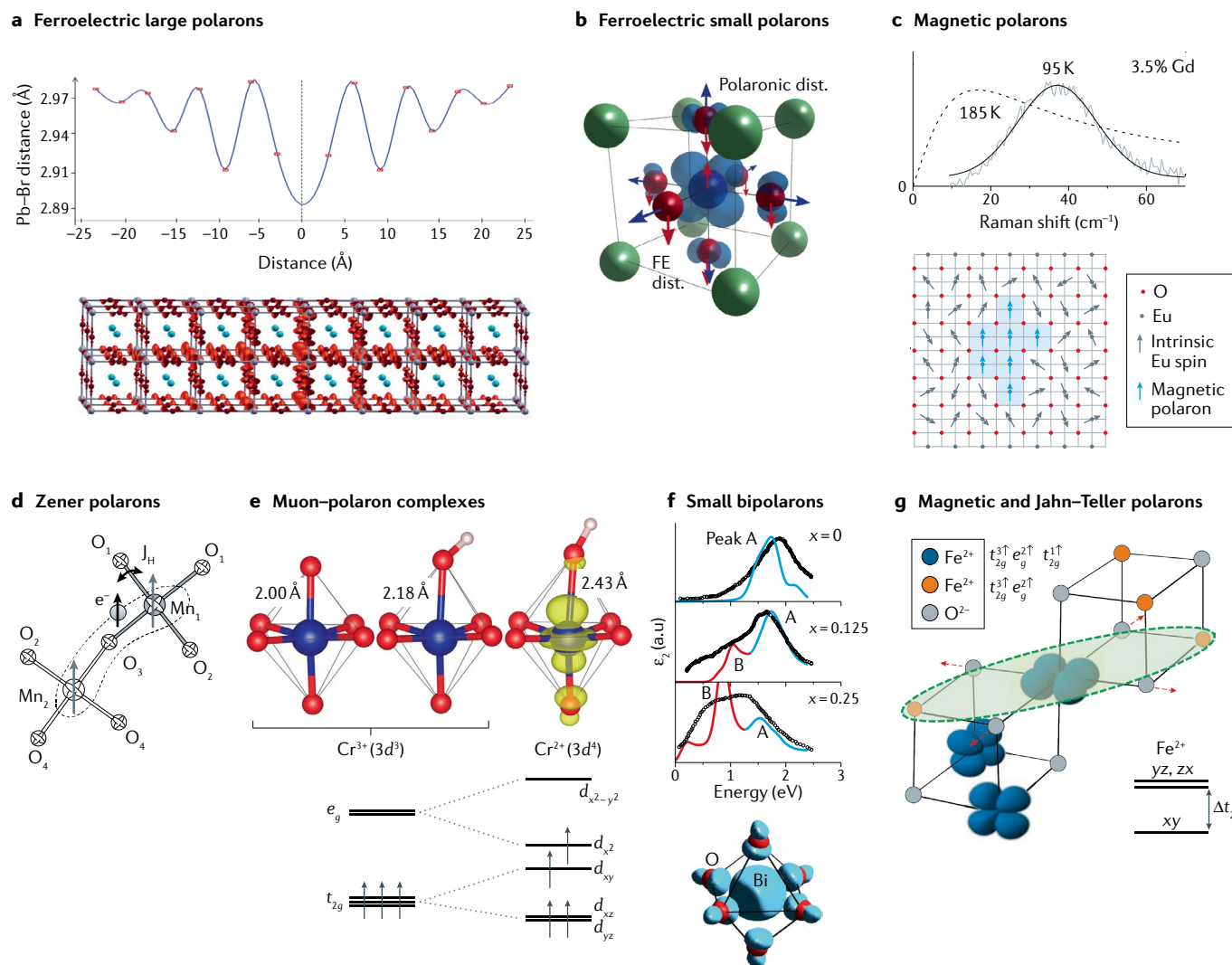


Fig. 4 | Theoretical and experimental visualizations of different types of polarons. **a** | Ferroelectric large polarons in halide perovskites³⁰. Calculated spatial extension of Pb–Br distances in CsPbBr₃ (top), connected with modes in polaron stabilization, correlate with the decay of large hole–polaron density (red charge isosurface, bottom). **b** | Schematic view of a ferroelectric polaron, in which ferroelectric and polaron structural distortions coexist. **c** | Formation of a magnetic polaron cluster in Eu_{1-x}Gd_xO (REF.⁵²): at temperatures higher than the Curie temperature, Raman scattering reveals the change from a carrier scattering regime dominated by spin fluctuations (dashed line, 185 K) to a magnetic polaron regime, in which polaron spins form a ferromagnetic cluster (95 K, inelastic response well described by a Gaussian profile). At low temperature, the polaron charge delocalizes and the system evolves into a ferromagnetic metal state. **d** | Zener polaron in a half-doped manganite²⁶. **e** | Octahedrally coordinated Cr atom in antiferromagnetic Cr₂O₃ without the muon (left), with the positive muon (middle) and forming a neutral-charge muon–polaron complex⁴⁷ (right). **f** | Insulator-to-metal transition mediated by small bipolarons in BaBi_{1-x}K_xO₃ (REF.³¹³). The positive charge donated by K forms small bipolarons (blue

isosurface) that give rise to an additional peak (peak B) in the optical spectra (comparison between measurements, circles and calculations, solid lines). For $x > 0.25$, K-doped BaBiO₃ undergoes an insulator-to-metal transition. **g** | Jahn–Teller magnetic polarons in magnetite⁷⁹. The spin-polarized t_{2g} electrons at the Fe²⁺ sites are locally coupled with the Jahn–Teller distortions (red arrows, causing a splitting of the t_{2g} manifold); the t_{2g} Fe²⁺ electrons are partially delocalized in the neighbouring Fe³⁺ ions (Jahn–Teller inactive), forming the so-called trimeron (dashed oval). Panel **a** reprinted with permission of AAAS from REF.³⁰, © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) <http://creativecommons.org/licenses/by-nc/4.0/>. Panel **b** adapted from REF.¹⁷⁶, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Panel **c** reprinted with permission from REF.⁵², APS. Panel **d** reprinted with permission from REF.²⁶, APS. Panel **e** reprinted from REF.⁴⁷, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Panel **f** adapted with permission from REF.³¹³, APS. Panel **g** adapted from REF.⁷⁹, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

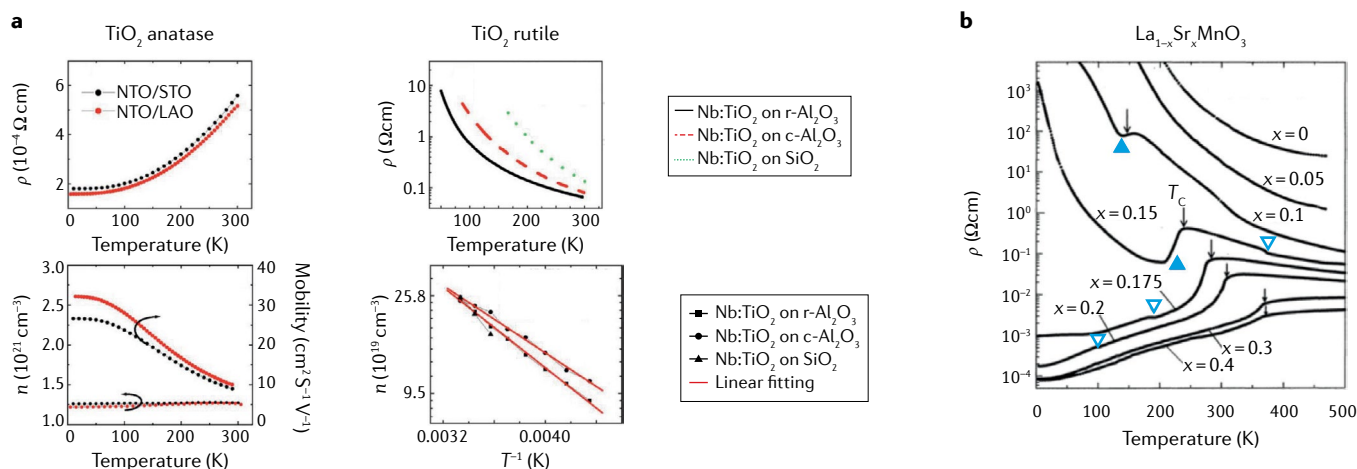


Fig. 5 | Transport measurements. **a** | Transport measurements in anatase and rutile TiO_2 thin films doped with 5% Nb. The resistivities, ρ , of the two polymorphs show opposite behaviour as a function of temperature, T . Hall measurements show that the carrier concentration, n , is constant in anatase, whereas it appears to be thermally activated in rutile. The behaviour observed in anatase is typical of large polarons, and that in rutile of small polarons. **b** | Hole polarons, introduced by doping Sr into the perovskite manganite LaMnO_3 , have a dramatic effect on resistivity (the level of doping increases from top to bottom). The arrows indicate the Curie temperature, T_C , which increases for increasing doping, and open and filled triangles indicate structural phase transitions and polaron ordering, respectively. Panel **a** reprinted with permission from REF.²⁰⁰, AIP. Panel **b** reprinted with permission from REF.²⁰¹, APS.

was recently observed in magnetite⁷⁹. Similarly, it is natural to extend the concept of ferroelectric polarons to multiferroics^{176,177}. Also, any of the polaron types listed in TABLE 3 can be related to a defect or can be confined in 2D¹⁷⁸.

Many materials (in particular, transition-metal oxides) exhibit polaron formation, and their properties are affected by the formation and mobility of polarons. These materials include manganites, cuprates, titanates, bismuthates and iron oxides (TABLE 3). Apart from TiO_2 and halide perovskites, which constitute the focus of this Review, recent advances have been reported for metal peroxides⁷⁴, BiVO_4 (REFS^{179,180}), WO_3 (REF.⁷⁵), CeO_2 (REFS^{72,123,181}), BaCeO_3 (REF.¹⁸²), GdTiO_3 (REF.¹⁸³), SrTiO_3 (REFS^{184,185}), YTiO_3 (REF.¹⁸⁶), KTaO_3 (REF.¹⁸⁷), BaSnO_3 (REF.¹⁸⁸), BiFeO_3 (REF.¹⁸⁹), iron oxides^{84,190,191}, ZnO (REF.⁷⁸), Co_3O_4 (REF.¹⁹²), BiVO_4 (REF.¹⁹³), Ga_2O_3 (REF.¹⁹⁴) and layered compounds¹⁹⁵.

Experimental characterization of polarons

Polarons manifest themselves in many different ways and can be probed with a large array of experimental techniques; a partial overview is given in TABLE 3. This section briefly discusses the most common methods as well as emerging techniques, using examples of prototypical polaronic systems, and illustrates the impact of polarons on materials properties. Each method has its own strengths, and obtaining a complete picture of polaron behaviour in a specific material typically requires a combination of complementary techniques and, when possible, a direct comparison with simulations.

Transport measurements

Polarons dictate the transport properties of materials, and electrical resistivity measurements provided the first direct proof for polaron formation¹⁵. FIGURE 5a illustrates typical transport signatures of small and large polarons,

which arise in the rutile and anatase TiO_2 polymorphs, respectively, upon doping with Nb (REF.⁴⁶). The dopant, Nb^{5+} , replaces a Ti^{4+} ion and donates a single electron. It causes negligible lattice distortions that would otherwise lead to additional electron trapping. The resistivity of TiO_2 anatase (FIG. 5a, top left) decreases at lower temperatures, and the material remains conducting; large polarons are predominant⁴⁶ and coherently propagate through the lattice⁴⁸. By contrast, the resistivity of TiO_2 rutile (FIG. 5a, top right) increases with cooling, as self-trapped electrons require an activation energy for hopping.

Hall measurements provide complementary information about mobility and carrier concentration, n (FIG. 5a, bottom). In anatase, n is temperature-independent; all dopants are ionized and the electrons contribute to electrical conduction. The electron mobility shows a metal-like behaviour, increasing at low temperature when scattering at phonons is suppressed. In rutile, n shows Arrhenius behaviour, and the activation energy can be estimated (here, it is 75 and 88 meV for two different samples). This activation energy is not related to donor ionization but to polaron hopping to neighbouring sites. Other techniques (such as X-ray photoemission spectroscopy (XPS), STM or DFT) can prove that the electron polarons leave the dopant^{46,196} and reside on lattice Ti sites (creating the characteristic Ti^{3+} state), and that the attractive coupling to the original donor is small^{155,197}.

The different behaviours of rutile and anatase affect applications. For example, n -doped anatase is a transparent conductive oxide¹⁹⁸, whereas rutile becomes opaque upon doping. Anatase is the preferred electrode in dye-sensitized solar cells¹⁹⁹ because of its favourable transport behaviour. A general consensus on the polaron behaviour in anatase and rutile has only been achieved during the past decade, using a combination

of transport measurements²⁰⁰, ARPES results⁴⁸ and DFT calculations⁴⁶. Previous literature mostly assumed that the anatase polymorph had higher polaron formation energies, which was a misinterpretation of the strong coupling between large polarons and optical phonons visible in optical spectroscopies.

A more complex polaronic behaviour is observed in FIG. 5b, showing data for a perovskite-based manganite. Here, Sr is used as a *p*-dopant, introducing hole polarons into the material and inducing mixed Mn⁴⁺/Mn³⁺ valence. The high magnetic moment of Mn and its interaction with the lattice result in a rich variety of competing ground states. For instance, for a Sr doping level of 15%, the material undergoes a successive transition from a polaron liquid (insulator) to a Fermi liquid ('metal') and, finally, to a polaron lattice^{27,201}. Pressure-dependent transport and magnetization experiments²⁵ were instrumental in mapping out the role of orbital ordering and Zener polarons.

Like electronic transport, thermal transport is also affected by polaronic behaviour. The relation between the Seebeck coefficient and electrical conductivity can distinguish band-like conduction from small-polaron hopping²⁰², and identify the major scattering mechanisms of charge carriers²⁰³. Seebeck measurements are especially useful in materials with low conductivity, for which Hall measurements are not possible.

Optical spectroscopies

Optical reflectivity and photoconductivity. Optical measurements are well suited to explore the role of electron–phonon coupling. Such measurements are best performed over a wide span of photon energies, ranging from the THz regime to the visible. An instructive example is given in FIG. 6a, which shows the optical conductivity derived from reflectivity and transmission measurements on SrTiO₃ single crystals doped with different levels of Nb (REF.²⁰⁴). The conductivity, derived from the inversion of the Fresnel equation and Kramers–Kronig analysis, shows several features: when going from high to low photon energies, one observes absorption across the optical band gap, sub-band gap excitation at 2.4 eV from dopant electrons occupying the *t*_{2g} states and optically active phonons. The softest phonon experiences a significant hardening with doping. The narrow Drude peak (dots in the left panel of FIG. 6a) is due to the coherent part of the polaronic conduction, and the mid-infrared band spreading from 0.1 to 1 eV is due to a multi-phonon side band of the Drude response, here assigned to the 'incoherent' contribution²⁰⁴. A detailed analysis of these spectra, based on Fröhlich many-body large-polaron theory, is given in REF.⁵⁶.

Raman spectroscopy. Inelastic or Raman scattering is an ideal complement to photoconductivity measurements. The Raman spectra in FIG. 6b were taken on a doped manganite sample that experiences a phase transition from a high-temperature, semiconducting paramagnetic state to a ferromagnetic metallic state at 145 K (REF.²⁰⁵). Above the transition temperature, the spectrum shows three phonon bands on a low-frequency background (dashed line) that disappears below the critical temperature.

The background is attributed to collision-dominated scattering from incoherent hopping of carriers, that is, to small polarons. More detailed analysis indicated a coexistence of large and small polarons in the low-temperature metallic state²⁰⁵. In semiconductors, the Raman scattering cross section is dramatically enhanced when the exciting wavelength is in resonance with the band gap. This enhancement is clearly seen in FIG. 6c, where the fifth longitudinal optical phonon mode is observed for ZnS at resonant conditions. In pioneering work, James Scott and colleagues²⁰⁶ reported an empirical relationship between the number of excited optical phonons and the coupling constant α under such conditions. This relationship can be used, for example, to evaluate the anisotropy of α in solids²⁰⁷.

Resonant inelastic X-ray scattering. In recent years, advancements in synchrotron-based measurements (high brilliance of sources and detector resolution) have led to analogous experiments being possible with X-rays as the excitation source. Resonant inelastic X-ray scattering (RIXS)²⁰⁸ is a powerful emerging technique. The X-rays are tuned to resonantly excite an electron from a specific core level to an unoccupied state; as the excited state decays, it emits X-rays that are measured. During the lifetime of the intermediate state, the lattice responds to the additional electron with itinerant distortions. The impressive energy resolution achievable with modern spectrometers allows an analysis of the resulting phonon contribution, and an evaluation of the electron–phonon coupling in an element-resolved and momentum-resolved fashion²⁰⁹.

Photoabsorption. The presence of polaron-induced gap states is reflected in photoabsorption. The example in FIG. 6d is drawn from the instructive paper by Jean Luc Bredas and G. Bryan Street², which lays out the comparison between the radical states in ionized polymers (which are distorted as compared with a neutral molecule) and polaron physics. The polymer polypyrrole becomes conducting upon doping (or, in chemical language, oxidation) with ClO₄⁻. For low doping levels, polaronic states form at the band edges (energy diagrams in FIG. 6d). These give rise to the three absorption peaks in the lowest trace in FIG. 6d, with excitation from the valence band to the lower and upper polaronic levels, and transitions in between these states. As the doping level is increased, bipolarons become energetically favourable and, eventually, form bands. These bipolaron bands dominate the transport behaviour of the conducting polymer, an assignment strengthened by EPR²¹⁰, in which the signal of the unpaired spin in the polaronic state disappears when bipolarons with paired spins form.

Photoluminescence. Photoluminescence is widely applied to powder materials synthesized for photocatalysis²¹¹, and organic molecules and polymers with applications in optoelectronics^{2,212}. Full interpretation of photoluminescence data is often difficult: both electrons and holes can form a polaron, providing photoluminescence signals at longer wavelength than the excitation photons. The many configurations include polarons, bipolarons and solitons (in organic terminology, radical ions, divalent

ions and ions, respectively)²¹³; additionally, charges may trap at defects. On single crystals at low temperatures, the hyperfine structure can be resolved and the type of polarons²¹⁴ can be identified, but, often, photoluminescence is used for a quick comparison of samples that have been prepared or treated in different ways.

Transient absorption spectroscopy. Performing optical measurements in a time-resolved manner provides information about polaron dynamics and polaron formation time. In transient absorption spectroscopy, the system is pumped with a femtosecond pulse, and the optical absorbance in the ultraviolet–visible region is monitored as a function of time delay. The difference

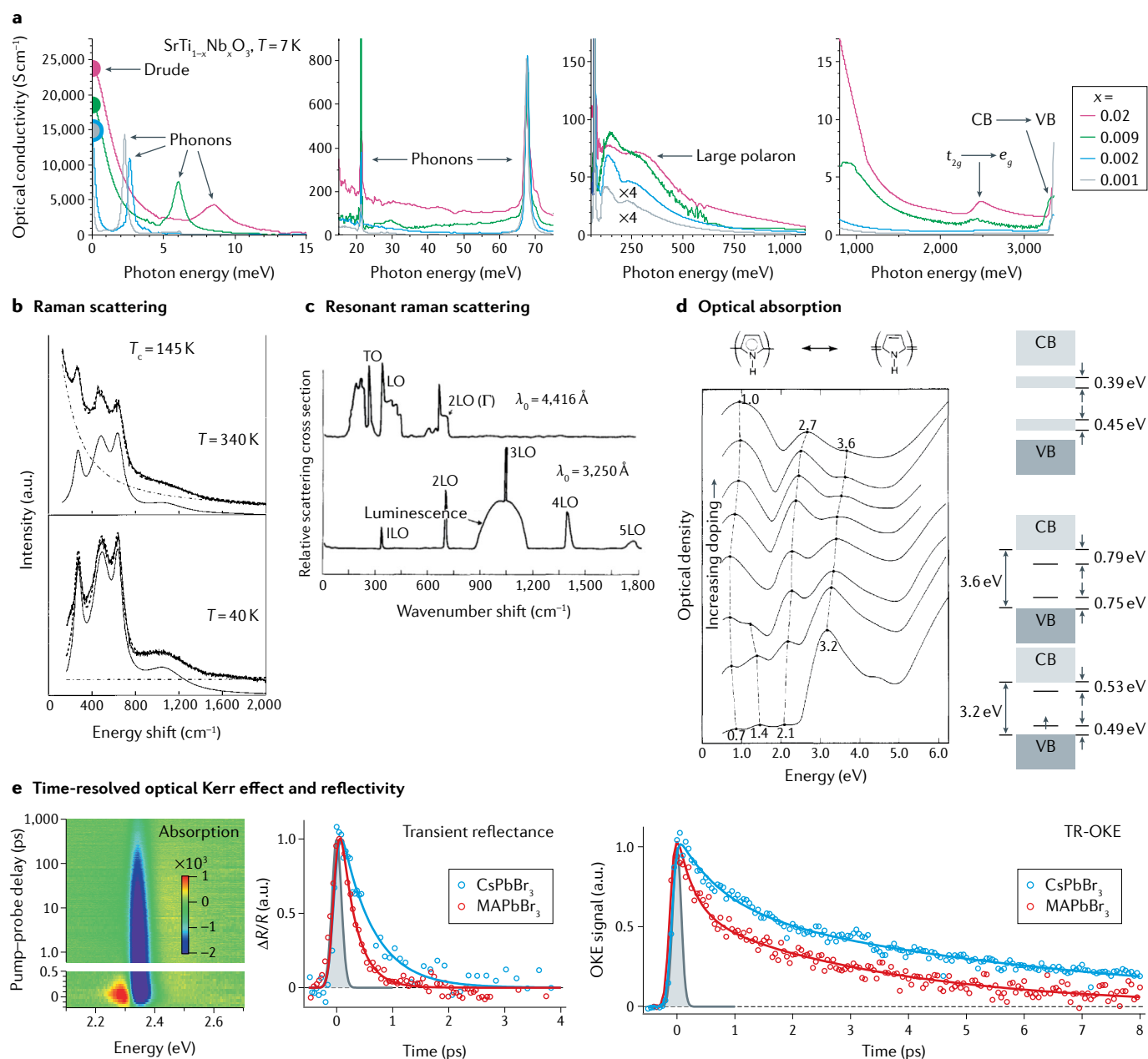


Fig. 6 | Optical spectroscopies. **a** | Photoconductivity measurements on SrTiO_3 with various Nb doping levels. The arrows highlight features due to various excitations. **b** | Raman scattering of a $\text{Pr}_{0.7}\text{Pb}_{0.21}\text{Ca}_{0.09}\text{MnO}_3$ single crystal. The diffusive electronic response (dashed curve) in the high-temperature paramagnetic phase disappears below the transition temperature, T_c , to the metallic, ferromagnetic phase; the lighter curve was obtained after subtracting this as a background. **c** | Raman spectra from ZnS taken with optical radiation tuned to energies on (bottom) and off (top) resonance. **d** | Optical absorption in the conducting polymer polypyrrole, which forms bands of bipolarons with increased doping, as shown by the energy diagrams. **e** | Time-resolved optical spectroscopy measurements on two lead halide perovskites. The fast decay

time of the transient absorption (left), reflectivity (middle) and transient optical Kerr effect (OKE) signal (right) are interpreted as the formation time for large polarons. CB, conduction band; LO, longitudinal optical; TO, transverse optical; TR-OKE, time-resolved optical Kerr effect; VB, valence band. Panel **a** reprinted with permission from REF.²⁰⁴, APS. Panel **b** reprinted with permission from REF.²⁰⁵, APS. Panel **c** adapted with permission from REF.²⁰⁶, Elsevier. Panel **d** adapted with permission from REF.², ACS. Panel **e** reprinted with permission of AAAS from REF.³⁰, © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) <http://creativecommons.org/licenses/by-nc/4.0/>.

spectra reflect the time evolution of different ground and final states after photoexcitation. FIGURE 6e shows an example from lead halide perovskites (MAPbBr₃ and CsPbBr₃)³⁰. Here, electrons, pumped from the valence band to the conduction band, form large polarons. The right panel shows the TR-OKE signals as a function of time delay from the probe pulse (the OKE signal is due to the rotation of the polarization of the infrared probe pulse, caused by the transient non-linearity introduced by the pump pulse). From a fast Fourier transform of such transients, the phonons involved in lattice distortions become apparent; for example, for sub-band gap excitations, the Raman active modes are clearly visible. The left and middle panels in FIG. 6e show the transient absorption/reflectivity of a white probe pulse, again as a function of time delay to the same pump pulse. All types of signals show an initial decay with similar time constants, 0.3 and 0.7 ps for MAPbBr₃ and CsPbBr₃, respectively, which is interpreted as the polaron formation time, in agreement with the DFT analysis of the displacement frequencies (although a correct localization of large polarons in these materials is technically hard to achieve). For the TR-OKE, the fast initial decay is followed by a longer-lived anisotropy, attributed to polaron motion³⁰.

Valence-band photoemission

Photoelectron spectroscopy. Photoelectron spectroscopy (PES) of the valence band is a well-established technique for the analysis of the electronic structure of materials in general, and for polaronic effects in particular²¹⁵. The emission of photoelectrons is fast compared with the motion of atoms, which means that the lattice does not relax while the electron is removed. Thus, the apparent binding energy E_{EL} measured by photoemission corresponds to the sum of the polaronic energy E_{POL} and the lattice strain E_{ST} :

$$E_{\text{EL}} = E_{\text{POL}} + E_{\text{ST}} = h\nu - E_{\text{K}} - \Phi, \quad (14)$$

where $h\nu$ is the incident photon energy, E_{K} is the kinetic energy of the emitted electron and Φ is the work function of the spectrometer.

Representative spectra are shown in BOX 1 for the prototypical examples of rutile and anatase TiO₂. Small polarons (rutile) manifest themselves as deep states (with an $E_{\text{EL}} \approx 1$ eV below the Fermi level), reflecting the larger energy stored in lattice distortions. Large polarons (anatase) typically appear as a shallow sharp peak, some tens of meV below the Fermi level, with a tail with a characteristic peak-dip-hump structure²¹⁵.

ARPES. It is instructive to consider angle-resolved photoemission measurements for small and large polarons. FIGURE 7a shows results on the large-polaron material anatase⁴⁸. As the parallel component of the momentum of the emitted photoelectron is preserved, the k -dispersion is directly measured. The polaronic band is located 40 meV below the Fermi level and has multiple images at higher binding energies, see also BOX 1. These image bands originate from the strong coupling to longitudinal optical (LO) phonons, that is, the electron is emitted and one or multiple LO phonons

are excited during the photoemission process. Strong coupling with LO phonons is typical for large polarons and is often used to identify the presence of polaronic effects²¹⁵ in shallow bands and distinguish polarons from other phenomena (this behaviour was confirmed by DFT for anatase TiO₂)⁴⁴.

Small polarons are localized at a single lattice site. The momentum k is not a good quantum number, and small-polaron features appear flat in k -space in ARPES. Nevertheless, angle-resolved photoemission can provide information about the preferential location of such small polarons.

X-ray photoelectron diffraction. When photoelectrons have an energy of several hundred eV, interference effects lead to ‘forward focusing’ and an enhanced intensity behind a scatterer. In X-ray photoelectron diffraction (XPD), the intensity is strongly increased along the direction from the emitter to its nearest neighbour. If the emitter is at the top surface, then the intensity is uniform in space. If the emitter sits in subsurface layers, its position can be triangulated from the maxima in polar plots.

FIGURE 7b shows the results for such an XPD measurement¹⁹⁶ on rutile TiO₂ (110); plotted is the intensity of the gap state at 1 eV (BOX 1). To increase the cross section for this state, resonance effects were exploited: the photoemission data were taken with a photon energy of 462 eV at the Ti2p–3d transition. Bright spots in the polar plot correspond with directions between different atom pairs, and the atom labelling is explained in the structural model. This work¹⁹⁶ provided the first direct experimental evidence that polarons in rutile (110) are preferentially located at subsurface sites, and even provided a quantitative estimate for the occupancy of the different Ti atoms.

Core-level spectroscopies

Core-level spectroscopies probe the electronic structure in an element-specific way. Various combinations of incoming and outgoing radiation are possible, leading to an array of techniques that can be used to characterize polarons⁴⁹.

X-ray photoemission spectroscopy. XPS is a well-established method to determine the oxidation state (or valence) of atoms. In a highly simplified, initial-state picture, the binding energy of a core-level electron shifts to smaller values when the Coulomb attraction of the positive nucleus is screened by adding valence electrons. Because small electron/hole polarons are essentially local centres with increased/reduced valence, their presence causes a downshift/upshift in the XPS binding energies. However, electron–phonon interactions lead only to a broadening of XPS peaks²¹⁶.

X-ray absorption spectroscopy. In X-ray absorption spectroscopy (XAS), a core electron is promoted to an excited state in the conduction band; this technique gives more information about polaronic states than XPS and, increasingly, also about the polaron dynamics when ultrafast pump–probe set-ups are used. The position of an absorption edge shifts with the oxidation

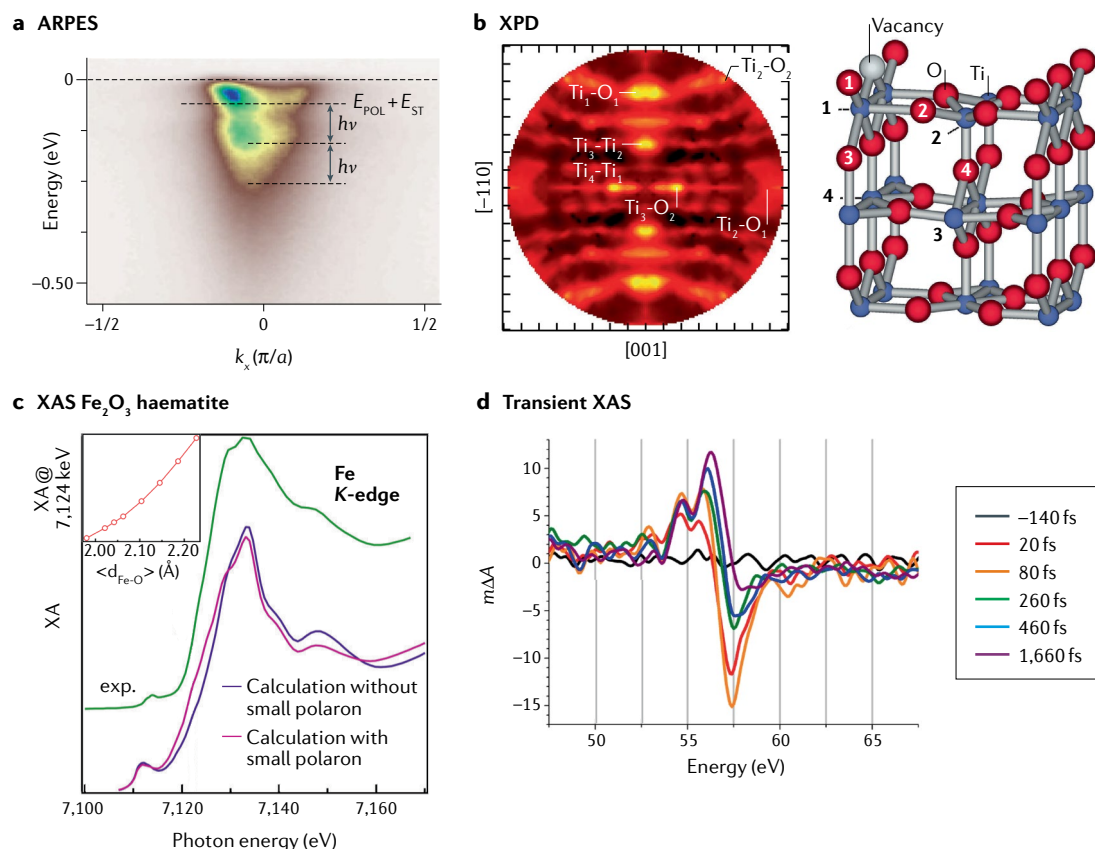


Fig. 7 | ARPES, XPD and XAS measurements of large and small polarons. **a** | Dispersion as a function of momentum k of large polarons measured on the anatase TiO_2 (101) surface by angle-resolved photoemission spectroscopy (ARPES, $h\nu = 84$ eV). $h\nu$ is the photon energy, E_{ST} the structural energy and E_{POL} the polaron binding energy. **b** | X-ray photoelectron diffraction (XPD) data for the small-polaron state on the rutile TiO_2 (110) surface ($h\nu = 462$ eV). The plot shows the intensity of the gap state with a binding energy of 1 eV, taken along different crystallographic directions. Interference leads to 'forward focusing', and the spots marked in the plot correspond to directions along pairs of atoms, as labelled on the cluster. Note that the experiments in panels **a** and **b** were conducted with different photon energies. **c** | X-ray absorption spectroscopy (XAS) measurements of haematite Fe_2O_3 at the Fe K-edge. The experimental curve is shown in green; purple spectra were calculated with a full multiple scattering code without (dark purple) and with (light purple) the inclusion of small polaron formation. The intensity at the onset is sensitive to the average Fe–O bond length ($<d_{Fe-O}>$, inset), which is elongated by the presence of small electron polarons. **d** | Transient XAS measurements at the $M_{2,3}$ Fe edge after the excitation of an electron–hole pair across the band gap. Plotted are the difference spectra after excitation with different time delays. From these measurements, a polaron formation time of 240 fs was extracted. Panel **a** reprinted with permission from REF.⁴⁸, APS. Panel **b** reprinted with permission from REF.¹⁹⁶, APS. Panel **c** reprinted with permission from REF.²¹⁷, AAAS. Panel **d** reprinted with permission from REF.²¹⁸, ACS.

state of an atom, and the fine structure reflects the signatures of its environment, as in the case of the crystal field splitting caused by the surrounding ligands in ionic compounds⁴⁹. The shape of an XAS peak is, thus, sensitive to local distortion. FIGURE 7c shows the Fe K-edge of Fe_2O_3 haematite²¹⁷. The purple spectra were calculated considering increased Fe–O bond lengths induced by a small electron polaron (see inset) and show good agreement with the experimental data. Fe_2O_3 would be a promising material for photoelectrochemical water splitting, but the sluggish charge transport and trap states induced by polaronic effects are a severe limitation. The formation of the polarons introduced by direct photoexcitation across the Fe_2O_3 band gap is followed in FIG. 7d. In this case, the Fe $M_{2,3}$ edge was probed in transient XAS measurements²¹⁸. The initial excitation involves charge transfer from the O ligand to the Fe 3d states, then the excited Fe^{2+} state decays to a long-lived

trap state in 240 fs. In addition to monitoring absorption, one can analyse the X-rays emitted when the core hole is filled (in X-ray emission spectroscopy) or the energy loss in the scattered X-ray beam in the normal state and after charge injection (in RIXS)^{49,83}.

X-ray free-electron lasers. X-ray free-electron lasers (XFELs) bring a much higher brilliance, shorter time signature, and spatial and temporal coherence to such experiments; as more facilities come online, they promise a bright future for characterizing polarons in novel ways. One pertinent example is the time-resolved XAS experiment on TiO_2 anatase described in REF.²¹⁹, conducted with an XFEL. Here, the time signature of the photoexcited electron polaron could be followed; it would be very exciting to see similar insights for the hole polaron as well. An important feature is the high coherence of these sources: in X-ray photon correlation spectroscopy²²⁰,

the evolution of consecutive speckle patterns is measured and allows us to follow the dynamics of a disordered system as a function of wave vector transfer, q , and time. Together with diffuse X-ray scattering, this should allow us to map out and visualize the ultrafast dynamical processes that lead to polaron formation.

Spin-resonance techniques

Electron paramagnetic resonance. EPR detects unpaired spins (more specifically, their resonance when excited by microwave radiation while tuning an external magnetic field) and, through their g tensor, the coupling with their environment (these quantities can be obtained by computer simulations, which provide useful insights to interpret EPR signals)²²¹. Because the EPR signal intensity is a direct measure of the number of unpaired spins, it was useful in confirming the presence of bipolarons in conducting polymers, as the continuous-wave EPR signal did not scale with dopant density²¹⁰. Defects in ionic solids disturb the charge balance and result in localized charges or ‘trap states’: a prominent example is BaTiO_3 , where impurities that introduce paramagnetic centres were extensively characterized by EPR²²². Spurious Na^+ replacing lattice Ba^{+2} results in a polaronic hole on the neighbouring lattice O^{2-} ion. The natural isotope ^{23}Na has a nuclear moment $I = 3/2$, and the hyperfine interaction of the spin on the resulting O^- ion allows its identification; conversely, a Nb^{5+} donor atom in the lattice results in an additional spin at a Ti^{3+} site. EPR measurements can be easily combined with measurements based on other types of radiation. Once EPR signatures were established for BaTiO_3 , the electrons and holes that are induced by photoexcitation could be studied, and their trap sites and temporal behaviour followed²²². This approach is particularly interesting for photocatalytic materials. For TiO_2 , Chiesa et al.²²³ reviewed how EPR can be used to determine the degree of wavefunction localization, taking advantage of pulsed techniques and of material enrichment with ^{17}O (which has nuclear spin, unlike the naturally more abundant ^{16}O). This results in a rich lineshape, owing to the resulting hyperfine coupling.

A different type of isotope effect was used to establish Jahn–Teller polarons in the colossal magnetoresistance material $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{1+y}$ (REF.²²⁴) (TABLE 3). Comparative EPR measurements were conducted after replacement of ^{16}O with ^{18}O , which has the same nuclear spin $I = 0$, but higher mass. Doped manganites have mixed valency, Mn^{3+} and Mn^{4+} , and the electron couples via the O between two neighbouring Mn, so the mass of the O matters for charge transport. From the temperature dependence of the linewidth of the EPR signal, the exchange integral J could be determined quantitatively; the results were consistent with the Jahn–Teller polaron model.

Nuclear magnetic resonance. Nuclear magnetic resonance (NMR) spectroscopy is conceptually similar to EPR, but it excites the spins of nuclei, rather than of electrons. NMR was particularly useful for mapping out the complex behaviour of Jahn–Teller polarons in doped $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{1+y}$ manganites²²⁵. The most abundant isotope, ^{139}La , has a nuclear spin of $I = 7/2$ and is, thus, well suited for NMR studies. In the perovskite structure,

it couples to the magnetic moments of the eight neighbouring Mn ions, and their ferromagnetic alignment leads to a strong shift in the resonance frequency. In addition, the quadrupole moment of the La nucleus interacts with the local electric field gradient due to the surrounding ions, and is, thus, sensitive to local distortions indicative of polarons. In the ordered paramagnetic phase, the resulting field-induced Zeeman splitting leads to an angular-dependent fine structure in single crystals, and to a broad background in polycrystalline samples; the temperature dependence of this background reflects the transition from the high-temperature paramagnetic to the low-temperature ferromagnetic phase. Fast and inhomogeneous spin relaxations diminish the NMR signal, and, with appropriately pulsed fields (spin echo measurements), it was established that the wipeout of the NMR signal observed for lightly doped, insulating materials is due to diffusion of short-range charge excitations coupled to lattice distortions, that is, polarons²²⁵.

Muon spin relaxation. A complementary technique for investigating the local magnetic and electronic environment around a nucleus is muon spin relaxation (μSR). Here, a beam of low-energy (a few keV) positive muons with 100% spin polarization is directed on a sample. The muons preserve their spin polarization upon implantation into the material, and decay with a mean lifetime of 2 μs by emitting a positron. During this time, the spin interacts with its surroundings, and the angular correlation of the emitted positrons reflects the spin relaxation, providing information similar to that gained by pulsed NMR. Because μSR is very sensitive, it can be used to detect small magnetic polarons, localized electrons with their spin ferromagnetically aligned with the localization centres (TABLE 3). This was shown for Eu-based magnetic semiconductors: a fast relaxation of the muon in the paramagnetic materials was related to the local magnetic field of the magnetic polaron⁵³.

Diffraction techniques

As polarons, in particular, small polarons, induce sizeable structural distortions in the lattice, they are observable by diffraction with X-rays, electrons or neutrons. Long-range ordering of polarons results in superstructures, and structural refinements give bond lengths that reflect charge carrier localizations. Neutron diffraction, which is additionally sensitive to magnetic ordering, was instrumental in clarifying the behaviour of polarons in the rich phase diagrams of doped manganites. For example, the charge order transition from metallic to insulating $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (FIG. 5b) was attributed to the hole–polaron ordering²⁷ based on neutron diffraction data.

Transmission electron microscopy. As phases often condense into small, twinned domains, the local information afforded by high-resolution transmission electron microscopy (TEM) is helpful. As an example, FIG. 8a–c shows TEM results from $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (REF.²²⁶). Atomically resolved scanning transmission electron microscopy showed ordering (FIG. 8a), selected-area diffraction was used to resolve the superstructure (FIG. 8b)

and, together with column-resolved energy electron loss spectroscopy (which yields similar information to XAS, FIG. 8c), these measurements elucidated the ordering²⁶ of Zener polarons²⁵.

Scanning probe techniques

Scanning tunnelling microscopy. With the STM, spatially resolved information can be obtained at the atomic scale. Accessing the polaronic states is technically more challenging than the traditional imaging of ionic materials. STM is mostly used on *n*-doped materials, and STM images are typically acquired in empty states (tunnelling into the conduction band), whereas the electron polaron

states lie below the Fermi level. Filled-state imaging requires lower tunnelling currents, mainly due to low density of states, and the corresponding measurements are often performed in constant-height mode, because the local density of states can be too low for maintaining the feedback loop.

The following should be considered when interpreting STM images of polarons. First, the polarons have many equivalent positions in the crystal lattice. Second, the tunnelling currents used in STM are typically on the order of picoamps, $\approx 10^7$ electrons per second. STM, therefore, provides a weighted average of all possible polaronic configurations. This is illustrated in FIG. 8d–g.

Transmission electron microscopy

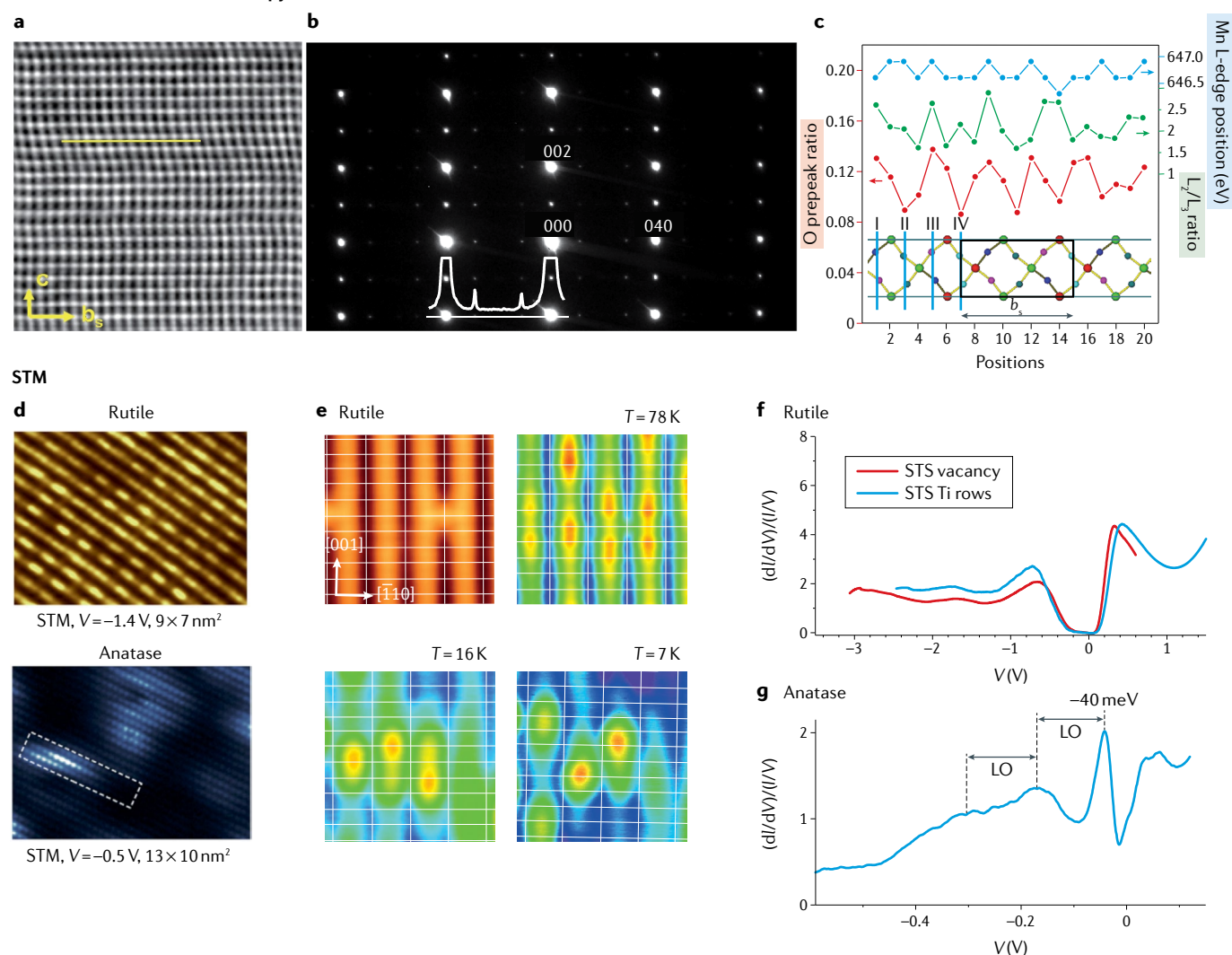


Fig. 8 | Real-space observations of polarons. **a–c** | Transmission electron microscopy results on $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_3$ with ordered Zener polarons. Scanning transmission electron microscopy measurements along the [001] direction showing pairing of Mn ions (panel a). Selected-area electron diffraction measurements that established the periodicity of the ordered phase (panel b). Site-resolved electron energy loss spectroscopy signatures across the yellow line in panel a, showing evidence for polaron ordering, as depicted in the sketch at the bottom of the panel (panel c). **d–g** | Scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS) of small and large polarons in TiO_2 . Filled-states STM images of rutile TiO_2 (110) measured at $T = 78$ K (top) and of anatase TiO_2 (101) measured at $T = 5$ K

(bottom) (panel d). STM images of a rutile TiO_2 surface taken in the vicinity of a single oxygen vacancy (top-left image, empty states); the spatial distribution of polaronic states around the vacancy at 78, 16, and 7 K can be observed in the filled-states images (panel e). STS spectra measured on the rutile surface, showing a deep state at ≈ -0.7 V (panel f). STS spectra measured on the anatase surface, showing a shallow peak at -40 meV and coupling to longitudinal optical (LO) phonons (panel g). *I*, current; *V*, voltage. Panels **a–c** reprinted with permission from REF.²²⁶, APS. Panel **d** (top) adapted from REF.⁴¹, Springer Nature. Panels **d** (bottom), **f** and **g** adapted with permission from REF.⁴⁶, APS. Panel **e** adapted from REF.¹⁹⁷, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

The top part of FIG. 8d shows a filled-state STM image of a strongly reduced rutile TiO_2 (110) surface¹⁹⁷. Rutile forms small polarons, but the density of states appears distributed over all surface Ti_{sc} sites due to the rapid polaron hopping at $T=78$ K. Spatial confinement of the small polarons can be observed upon cooling to lower temperatures near oxygen vacancies (FIG. 8e); at low temperature, the attractive coupling between the polaron and the vacancy becomes comparable to the thermal energy $k_{\text{B}}T$. The characteristic elongated spots observed at low temperature on rutile surfaces can be explained by comparing the experiments with STM images simulated by DFT for polarons localized on subsurface sites⁴¹ (FIG. 9). At higher temperatures, the spatially distributed character of the experimental STM signal can be recovered by averaging simulated images obtained for different localization sites¹⁵⁵. However, the comparison between experiment and theory is challenging when the interaction between sample and tip, typically neglected in DFT calculations, alters the measurement or induces additional polaron hopping^{39,41,197}.

The image in the upper part of FIG. 8d shows periodic modulations of the density of states. This was attributed to a tendency of polarons to arrange in a periodic pattern due to repulsive interactions⁴¹. Periodic patterns are often observed in systems with charge density waves²²⁷, which can be interpreted as ordered arrays of large polarons. STM can also identify specific places where polarons form, such as defects²²⁷ or step edges¹⁶⁵.

An example of a large-polaronic system is shown in the bottom part of FIG. 8d. Here, the occupied local density of states is enhanced in the vicinity of subsurface defects, and the shape and size of these regions match well with the size of large polarons estimated from theory⁴⁶ and photoemission⁴⁸. It took about a decade to find a consensus on the interpretation of STM images of small polarons in systems such as rutile TiO_2 (REF.²²⁸) or CeO_2 (REF.²²⁷), and images of large-polaronic systems are still debated.

For identifying polaronic behaviour, spectroscopy is an essential complement to imaging. Electron tunnelling follows similar rules as photoemission, so peaks in STS

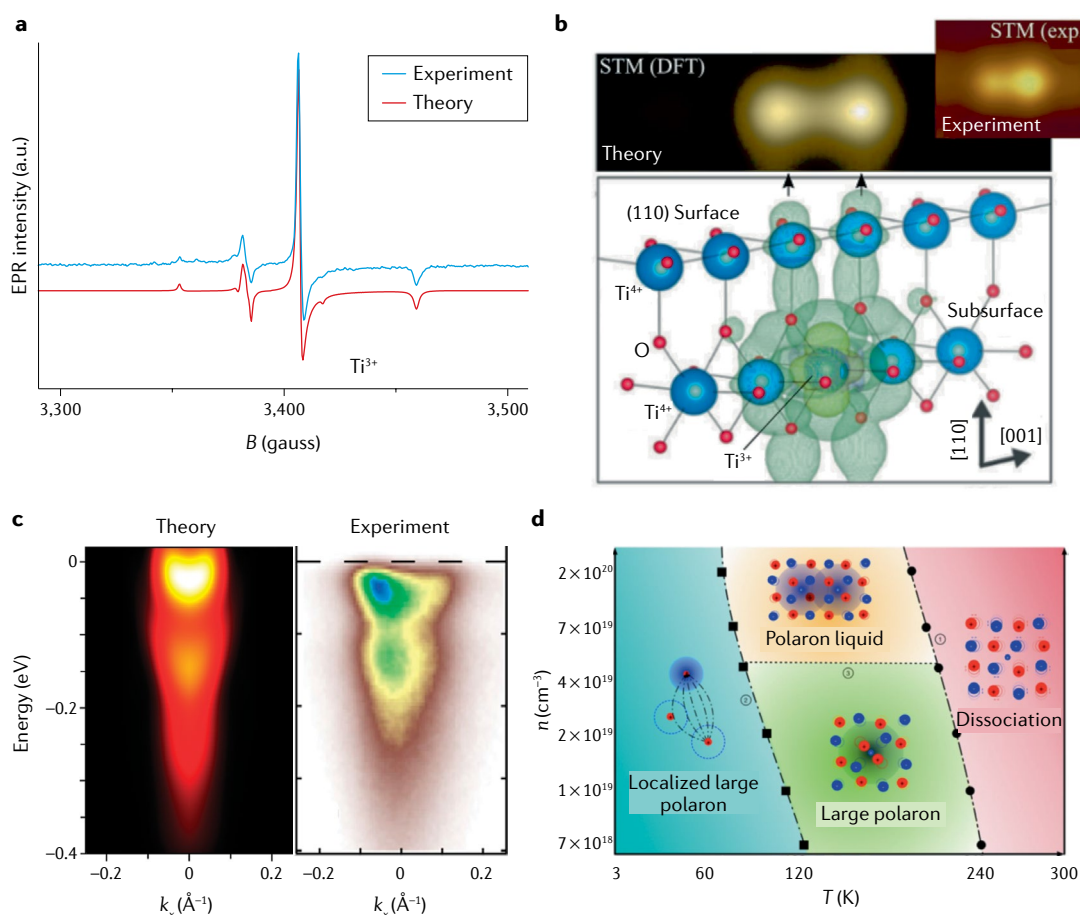


Fig. 9 | **Polarons in rutile and anatase TiO_2 .** **a** | Theoretical and experimental electron paramagnetic resonance (EPR) signal of a Ti^{3+} site hosting a small polaron in rutile. **b** | Charge density of a small polaron at the rutile TiO_2 (110) surface and its scanning tunnelling microscopy (STM) signature, both as obtained from density functional theory (DFT) calculations and as experimentally measured. **c** | Energy dispersion of large electron polarons in anatase, as obtained by first-principles calculations of electron–phonon coupling calculations (left) and angle-resolved photoemission spectroscopy measurements (right). **d** | Phase diagram of polarons in anatase, n is the concentration of excess charge, T the temperature and ρ the resistivity. Panel **a** reprinted with permission from REF.²²¹, ACS. Panel **b** adapted from REF.⁴¹, Springer Nature. Panel **c** (left) reprinted from REF.⁴⁴, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Panel **c** (right) reprinted from REF.⁴⁸, APS. Panel **d** adapted with permission from REF.²⁸⁵, ACS.

spectra typically match photoemission measurements: for example, compare the PES spectra in BOX 1 with the STS spectra for TiO_2 rutile and anatase in FIG. 8f,g.

Non-contact atomic force microscopy. A rapidly developing scanning probe technique is non-contact AFM (nc-AFM)²²⁹, especially in combination with the STM function. It allows investigation of highly insulating materials without the requirement for any tunnelling current, yet, keeps, or even surpasses, the excellent atomic resolution of STM. Combined AFM/STM can separate topographic from electronic structure effects, which is helpful to investigate complex materials²³⁰. The excellent force sensitivity allows the detection and manipulation of single electrons²³¹. In principle, with nc-AFM, it should be possible to directly address and manipulate single small polarons, although we are not aware of published work in this direction. Recent developments offer advanced approaches for investigating the electronic states of insulating materials²³² and measuring small electric fields with high precision and spatial resolution²³³. nc-AFM has high potential for addressing many of the open questions behind polarons, and interesting results are likely to be reported in the coming years.

Case studies: TiO_2 and halide perovskites

This section presents a compact survey of the most important polaron properties of TiO_2 , the historically most studied polaron material^{234–236}, and halide perovskites¹⁴³, the most rapidly emerging class of materials in the field of photovoltaic technologies and optoelectronics^{19f,173}.

Polarons in TiO_2

The two most common polymorphs of TiO_2 , rutile and anatase, show a broad range of different polaronic features, which impact their functionalities in electronic transport^{237,238}, energy conversion²³⁹, memristive devices^{197,240} and (photo)catalysis^{38,39,241–255}. Polarons in TiO_2 samples typically originate from defects and doping, or appear upon irradiation. As a pristine compound, TiO_2 is a semiconductor with nominal Ti^{4+} and O^{2-} valence states. EPR suggests the presence of additional Ti^{3+} species, due mostly to the presence of naturally occurring electron donors (interstitial Ti atoms, Ti_{int} , and oxygen vacancies, V_{O})^{51,221,256}. These additional species reveal electronic charge localization at single atoms, and may correspond to polaron formation, with an important distinction depending on the polymorph.

Rutile TiO_2 is prone to the formation of small electron polarons¹⁵⁰. In addition to EPR experiments (FIG. 9a), pioneering experiments based on optical absorption delivered one of the first strong indications of polaron formation^{257,258}. The polaron model has been invoked also to explain results obtained by charge transport experiments (FIG. 5), including the temperature dependence of the dielectric function²⁵⁹, the anisotropy of the conductivity²⁶⁰ and the dependence of conductivity on the oxidation state²⁶¹ and temperature²⁰⁰. Several independent DFT studies have characterized the properties of these small electron polarons in detail^{61,125,141,166,262–265}. Together with XPD and STM experiments, they

identified subsurface Ti atoms in the rutile TiO_2 (110) lattice as the most favourable trapping sites^{154,155,266–268}, with the polaronic charge spreading also on neighbouring Ti atoms on the surface⁴¹ (double spots measured by STM in FIG. 9b). The in-gap polaronic peak appears typically quite deep and sharp^{269,270}, although interactions with defects or other polarons may alter its properties^{55,155,266,270}. At high polaron density, the repulsive polaron–polaron interaction determines an instability of the lattice structure, which may drive the system to a structural reconstruction^{41,197}. The diffusion of polarons has been reported by FPMD simulations to occur via nearest-neighbour hopping and via temporary delocalization (random flight model)^{154,155,157,268,271–273}. Concerning nearest-neighbour hopping, two regimes have been reported, diabatic¹²¹ and adiabatic¹⁵³. Depending on the type of approximation used for the exchange and correlation functional, one or the other regime is favoured¹⁵¹, another critical example of the limits of numerical schemes to describe polaron properties¹²³.

In contrast to rutile, the formation of small polarons in anatase is debated^{270,274}. DFT suggests that strong electron localization on bulk Ti sites is quite unfavourable in anatase, and would occur only when using unrealistic values for U or exchange mixing parameter^{46,135,151}, or on surfaces near lattice defects and adsorbates^{133,168,262,263,275–277} or in nanoparticles²⁷⁸. The trapping of immobile electronic states at lattice defects is confirmed by ultraviolet photoelectron spectroscopy and energy loss spectroscopy²⁷⁹, and by surface-sensitive STM experiments¹⁶⁵, highlighting the difference with respect to the mobile behaviour of small polarons on rutile⁴⁶ (FIG. 8d). Finally, singly ionized O^- species appear in EPR experiments upon hole doping in anatase, but these states are strongly bound to the defects, rather than showing the mobility common to polarons²⁸⁰.

Interestingly, anatase seems to host, instead, large electron polarons, as suggested by the dispersed spatial extent of unpaired electron wavefunctions obtained by the EPR hyperfine signal²⁸¹, and by electrical conductivity²⁸² and dielectric function²⁸³ measurements (FIG. 5a). ARPES⁴⁸ and RIXS²⁸⁴ data reveal shallow states below the conduction band, which can be attributed to large polaron satellites, as recently confirmed by first-principles calculations accounting for the Fröhlich electron–phonon coupling⁴⁴ (FIG. 9c). STM experiments revealed a large-polaron-like dispersion of the electronic charge on the anatase surface if donors affect the lattice structure only slightly (as in the case of Nb substitutional doping, as opposed to the strongly localized states trapped at V_{O} sites)⁴⁶ (FIG. 8d). Moreover, magneto-transport experiments identified a phase transition from a Fröhlich polaron regime to a Fermi liquid, depending on the concentration of excess charge and temperature²⁸⁵ (FIG. 9d).

Polarons in halide perovskites

In the past decade, metal halide perovskites (MHPs) have emerged as a most appealing class of materials for optoelectronics, and have spurred intense research

activities²⁸⁶. Charge trapping and polaron formation have a large impact on carrier transport in MHPs. This section succinctly surveys the main results in this branch of research; for a more comprehensive discussion of MHPs, the interested reader is referred to recent reviews^{143,173}.

There is a general computational and experimental consensus that both small and large polarons can form in MHPs^{30,287–289} (FIGS 4a,6e), but how polarons affect carrier mobility is still a controversial issue. Small polarons are believed to have detrimental effects on MHPs, causing photodegradation and material degradation, as well as the formation of macroscopic charge domains, which hinder efficient charge extraction in solar cell devices¹⁴³. Conversely, long carrier lifetimes and diffusion lengths measured in MHPs have been associated with the formation of large polarons. In fact, with their large effective mass (10–300 m_e at room temperature, with m_e the mass of the free electron) and long coherence length, large polarons are believed to protect other carriers from scattering with longitudinal phonons²⁹⁰. Moreover, large polarons have been invoked as a possible explanation of the low recombination rate in MHPs²⁹¹: if the static dielectric constant is large enough, the interaction between oppositely charged large polarons at short distance can become repulsive, thereby, impeding electron–hole recombination (FIG. 3).

An interesting and still unresolved issue is the mechanism that favours either small or large polarons in MHPs. First-principles calculations on mixed lead–tin halide perovskites found that the modification of the metal halide bonds, correlated with the formation of small (short bonds) or large (long bonds) polarons, can be controlled by chemical doping, suggesting that increasing the Sn concentration should result in a progressive shift from a small to a large polaron scenario²⁹². Similar conclusions on the effect of cation alloying on the polaron binding energies has been obtained for Cs substitution in PbI_3 -based MHPs, which can be exploited to mitigate the formation of small polarons and, therefore, reduce their detrimental consequences on charge transport²⁹³.

This interaction between polarons and local structural distortions has also revealed that the binding energy of small electron polarons is significantly larger than that of hole polarons. It is also enhanced by the coupling with local Jahn–Teller distortions in the metal halide octahedra²⁹⁴, leading to the formation of Jahn–Teller polarons.

These are not the only type of polarons detected in MHPs not directly categorizable as conventional small/large polarons. Evidence for the onset of ferroelectric large polarons has been put forward^{30,45}, and even more attention has been devoted to the study of exciton polarons. Based on an effective exciton–phonon Hamiltonian, Ajay Ram Srimath Kandada and Carlos Silva found that strong exciton–phonon scattering processes should develop when the excitonic binding energy is close to the frequency of longitudinal optical phonons and the effective mass of electrons and holes are very different. Because these conditions are not fulfilled in 2D MHPs, in which exciton polarons form (manifested in the excitonic spectral structure), it was proposed that, in the 2D limit, the formation of exciton polarons is favoured

by the transformation of the electronic–vibrational landscape, in particular, related to the enhancement of short-range electron–phonon interactions¹⁷³. As a consequence, the resulting exciton polaron falls in an intermediate regime between the Fröhlich (long-range) and self-trapping (short-range) limits.

A final word before moving to the conclusive outlook. There have been many, sometimes contradictory, hypotheses on the nature and characteristics of polarons in MHPs, most of them derived from computational studies at ideal conditions or from approximated semi-empirical theories. We think that the time has come to filter this large amount of data and seek solid experimental verification and a complete theoretical treatment in order to achieve a rigorous description and understanding of the role of polarons in charge transport in these materials.

Outlook

As this Review has amply shown, the interest in polaron effects in materials is still increasing. It spans theoretical and numerical foundations, emerging experimental probes and functionalization for a variety of applications. A most interesting development is the growing effort to bridge and connect historically distant research communities in an effort to establish a common playground and a standard language to study and understand the multifaceted complexity of polarons. A prime example in this direction is the merger of Fröhlich and Pekar's formulations into a materials-specific first-principles DFT framework^{13,64,70}. A natural, albeit challenging, further development is joining quantum field theory and ab initio methods; this would lead to a genuinely ab initio many-body theory of polarons. One of the most promising routes to such a unified formalism is the connection between DFT and DiagMC, in which all terms of the general polaron Hamiltonian are calculated from first principles. As an added benefit, this combination would transcend the Holstein/Fröhlich (or lattice/continuum) dichotomy, as the electron–phonon coupling term would be treated entirely from first principles, simultaneously including both short-range and long-range interactions.

Another timely research line that will most likely be explored in coming years involves the extension to larger time and length scales in simulations of polaron properties. We expect that much effort will be devoted to the implementation of efficient, long-range electron–phonon coupling and electron–electron interaction terms in multiscale schemes. Even more attractive is the possibility to accelerate the calculation of polaron properties with machine learning techniques^{295,296}. For instance, machine learning could be employed to overtake the prohibitive limits of molecular dynamics to explore the polaronic configuration space (finding the most probable polaron sites), which would help tremendously in the study and prediction of transport effects²⁹⁷. Different data-driven approaches could be explored to tackle this problem, including atomistic neural networks potentials²⁹⁸, kernel ridge regression²⁹⁹ or machine-learned force fields³⁰⁰.

The rapid development in microscopic techniques affords the possibility to image polarons in real space,

and could provide a fertile area where innovations in theory and experiment complement each other in an ideal way. As recent examples show^{41,46,197}, imaging single electron polarons is well on its way; at this point, similar experiments on hole polarons have not yet been reported but could provide truly novel information. Considering that polaron effects are predominant at the surfaces of materials and manifest themselves with charge confinements detectable by STM and AFM, one could envisage using computer vision methods such as local-structural-state algorithms and agglomerative clustering algorithms³⁰¹ to interpret experimental images³⁰².

With shorter and shorter timescales accessible in experiments, the possibility to inspect and follow polaron dynamics opens up another exciting area of research. Ultrafast, X-ray-based spectroscopies will further evolve in coming years, and will provide powerful, novel ways to address pending issues in polaron physics, such as the clarification of the timescales in polaron-related excitations or the time needed for formation and recombination. In this context, the development of coherent and highly brilliant X-ray lasers promises exciting opportunities, as they enable experiments that address both extremely short timescales and, by taking advantage of core-hole resonance techniques, very small length scales.

Of extreme interest, for both theory and experiment, is the possibility to control and functionalize polarons. High-resolution nc-AFM emerges as a promising technique that is potentially capable to detect and manipulate the charge²³¹ and spin³⁰³ of single electrons. The application of an external electric or magnetic field could open additional channels to act on polaron charge and polaron spin, possibly resulting in a controlled tunability of static and dynamic properties (for example, coherent polaron motion, polaron clustering, polaron excitations or formation of spin-polaron lattices). The possibility to create a well-defined spin-polaron lattice, for instance, could be used to study the onset of spin-liquid states

(in this case, spin-polaron liquids) or, even more visionary, spin-polaron confinement could be engineered as an alternative to electron spins in semiconductor quantum dots for quantum information processing.

Regarding novel materials, hybrid perovskites, 2D materials and organic semiconductors represent one of the most exciting fronts where the role of polarons (in particular, dielectric and exciton polarons) is crucial to understand charge transport (and related energy-conversion applications).

On the applied side, there is currently a rapid search for efficient thermoelectric generators and Peltier elements³⁰⁴. Novel devices based on ionic crystals nowadays considerably supersede traditional metal-based generators³⁰⁴. Electron-phonon coupling and polarons contribute to all parameters relevant for thermoelectric generators, including the Seebeck effect, electrical conductivity and heat conduction. Generally, materials with high carrier mobility tend to be more efficient thermoelectrics, meaning that control over polaron formation and dynamics is surely beneficial to device performance.

Molecular functionalization is another possibility to modify polaron-related properties and, therefore, materials functionalities. For example, the polaron formation rate and polaron activation energy can be tuned by molecular absorption³⁰⁵. More generally, polaron-molecule interactions can dramatically change the chemical reactivity of materials, and it is foreseeable that future studies will explore the possibility to customize catalytic activity through direct control of polaron-related energetics.

The field of polaron physics commenced several decades ago, yet, it feels new and exciting. Despite massive research on these quasiparticles, we are only starting to fully understand their properties and exploit them for applications.

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Competing interests

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