

REVIEW ARTICLE

Small polarons in real crystals: concepts and problems

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Abstract. Much of small polaron theory is based on highly idealized models, often essentially a continuum description with a single vibrational frequency. These models ignore much of the wealth of experimental data, which find interpretation in many atomistic simulations. We review here a range of properties of small polarons in real, rather than model, systems. The phenomena fall into three main classes: (i) the mechanisms and dynamics of self-trapping of polarons; (ii) static properties—the relative energies of large and small polarons, the optical transitions expected, their effect on positions of other ions and on lattice vibrations, their population in thermal equilibrium, and so on; (iii) small polaron hopping and diffusion. We discuss the key concepts and methods of calculation of polarons, and explore the properties of self-trapped holes and excitons in ionic crystals, and those of an excess electron in liquid water.

1. Introduction

In 1932 a short note by Landau [1] set the stage for small polaron studies with classic brevity and clarity. He observed that there were two quite distinct cases for an electron coupled to an otherwise perfect (but deformable) lattice. In one, the electron moved ‘freely’; in the other, the electron would be trapped at a strongly distorted region. Landau even noted that the electron could be trapped in the second case only by excitation over a barrier. The stimulus for this work was the further conjecture that this ‘small polaron’ might explain colouration in NaCl. This last point was not verified, at least as proposed, although the alkali metal halides did provide the first clear examples of small polarons when Kanzig discovered the V_K centre in 1955 [2]. The possibility of the exciton immobilization or self-trapping at low temperatures was suggested by Frenkel in 1926 [3], and Kabler [4] and Lushchik [5] showed the existence of the self-trapped excitons in KI in 1967.

Landau’s remarks on the barrier to self-trapping were verified for the excitons in alkali metal halides, though not until much later. However, the existence of the barrier between the free and the self-trapped exciton states was further developed theoretically by Rashba in 1957 [6], when he pointed out the importance of the short-range interactions. The coexistence of free and self-trapped excitons in alkali halides was first observed experimentally by Lushchik and co-workers in 1976 [7] and interpreted theoretically in several papers in terms of a potential barrier between these states (see [8] for a review).

The conditions Landau envisaged would clearly affect transport properties too. The strong electron–phonon coupling would lead to very short mean-free paths; indeed, as shown by Yamashita and Kurosawa [9] and by Holstein [10], one would expect an incoherent ‘hopping’ transport mechanism in many cases of interest. Instead of the traditional behaviour of metals, where the phonon scattering becomes stronger as vibrational amplitudes increase,

so the carrier mobility decreases when the solid grows hotter, one might expect the small polaron mobility to increase with temperature as incoherent hopping from one site to another becomes easier.

Landau's ideas were taken up by many later workers. Some generalized the picture phenomenologically, whereas others studied the particular properties of some hypothetical polaron state. Most of the present theories may be roughly classified in three categories: (i) developing the *criteria* for self-trapping and the phenomenological theory of polarons and excitons; (ii) simulating the *process* of self-trapping from delocalized states; (iii) studying the microscopic *structure* and properties of localized polarons.

Phenomenological approaches based on the theory of electrons (excitons) in phonon fields [11] focus on the studies of how the stability of different types of polarons depends on the strength of the coupling between electron (exciton) and lattice, the dimension of the lattice and other parameters. Much of this field has been reviewed recently by Gerlach and Lowen [12]. In particular, Emin and Holstein [13] gave a very clear analysis using an adiabatic approximation and a continuum model for the lattice. Their scaling argument pointed out that, depending on the nature of the electron-phonon coupling (e.g. deformation potential against Frohlich coupling), there were several different categories of behaviour (see figure 1): some systems might have large polarons only, others small polarons only, still others could be of either type, with a barrier between the configurations, etc. In particular, for a three-dimensional continuum, a purely short-range electron-continuum interaction always yields two distinct cases: a small polaron state and a non-polaronic free state; the addition of a long-range component to the electron-continuum interaction can convert a non-polaronic state into a finite-radius polaron state. Another result of this work and that of Toyozawa [14] concerns the dependence on the dimension of the lattice. In one dimension only a single stable state is predicted, corresponding to the localized polaron. This contrasts with the three-dimensional case, where two minima of the adiabatic potential are always predicted, corresponding to delocalized and strongly localized situations.

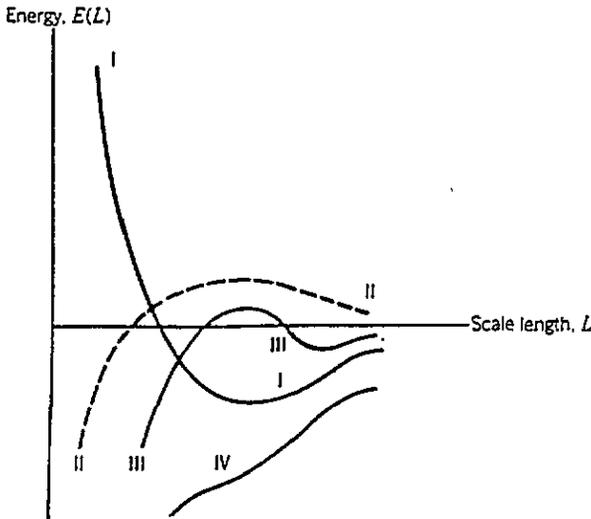


Figure 1. Regimes of behaviour for an electron coupled to lattice distortion. The total energy is given as a function of scale length L characterizing a localized normalized electron wavefunction $(L/L_0)^{-3/2}\psi(\mathbf{r}/L)$. I: no short-range potential deformation-potential interaction. Only a large polaron forms. II: pure short-range coupling to dilatation. Note that there are only small polaron ($L \rightarrow 0$) and free polaronic ($L = \infty$) minima. III, IV: general cases showing only small polarons (IV) or both small and large polarons separated by a barrier (III). After Emin and Holstein [13].

Toyozawa and co-workers [11, 15] also looked at the effect of electron correlation, in an 'STU' model (where S is a measure of the electron-phonon coupling, T is a measure of the bandwidth of a bare electron in the absence of such coupling, and U is the Hubbard U , measuring the electron-electron interaction and including electron correlation). Other

workers made extensive formal calculations, especially based on the Frohlich model. These theories and the results of extensive experimental studies revealed a much richer picture of possible polaron and exciton states, which we attempt to summarize in table 1. The distinction between small and large polarons has very clear observable consequences. For example, the large polaron mobility decreases with rising temperature through phonon scattering, whereas small polaron mobilities rise with temperature, as shown in figure 2. As was pointed out by Ueta and co-workers [11] this small/large polaron nomenclature, although convenient, should be used with some caution. It may give a wrong impression that the 'small' polaron is simply the strong-coupling limit of the electron-polarization (optical phonon) interaction. The short-range interaction with acoustic phonons can trigger a self-trapped state, which can coexist with the large-radius or delocalized state [6, 11, 16]. It is this short-range interaction that makes the self-trapping a kind of critical phenomenon, which may be characterized by the abrupt change of parameters like the effective mass as a function of electron-phonon coupling constant. In contrast, although optical phonons do make a major contribution to nature of the polaron state, interaction with them alone leads only to a smooth change of the effective mass. The issues here point to one of the problems of the phenomenological theories, namely the emphasis on behaviour as a function of coupling constant. Experimentally, it is very difficult to alter the coupling constant, so that is hard to validate the phenomenological theories.

Table 1. Types of polaron. This table gives examples of some of the polaron systems observed experimentally.

Large polaron	e in alkali halides; e, h in II-V and group-IV semiconductors.
Small polaron	(i) One species only (e small or h small, not both) on one ion: h in AgCl, solvated e in water and alcoholic systems. (ii) Both electrons and holes small; one ion only: e, h on cation for certain transition metal oxides. (iii) One species on two sites: h in halides (V_K centre). (iv) One species on many sites: 'Polaron' in <i>trans</i> -polyacetylene. (v) Exciton: excitons in alkali halides, SiO ₂ .
Trapped polaron	(i) Trapped onto impurity site: transition metal ion impurity. (ii) Trapped onto impurity/defect sublattice V_K next to Br in KCl. (iii) Trapped onto another sublattice V_K next to Na in KCl; h near Li in MgO. (iv) Both large and small polarons trapped by the same defect: (a) Bistability: CdF ₂ :In (b) CsI: Na; (e large, h small).
Bipolaron	(i) Electrochromics WO ₃ etc. (ii) Oxide superconductors.

We note in passing that, although the effective mass is one of the main characteristics of a large polaron, it should be treated with caution at $T \neq 0$. As was pointed out recently by

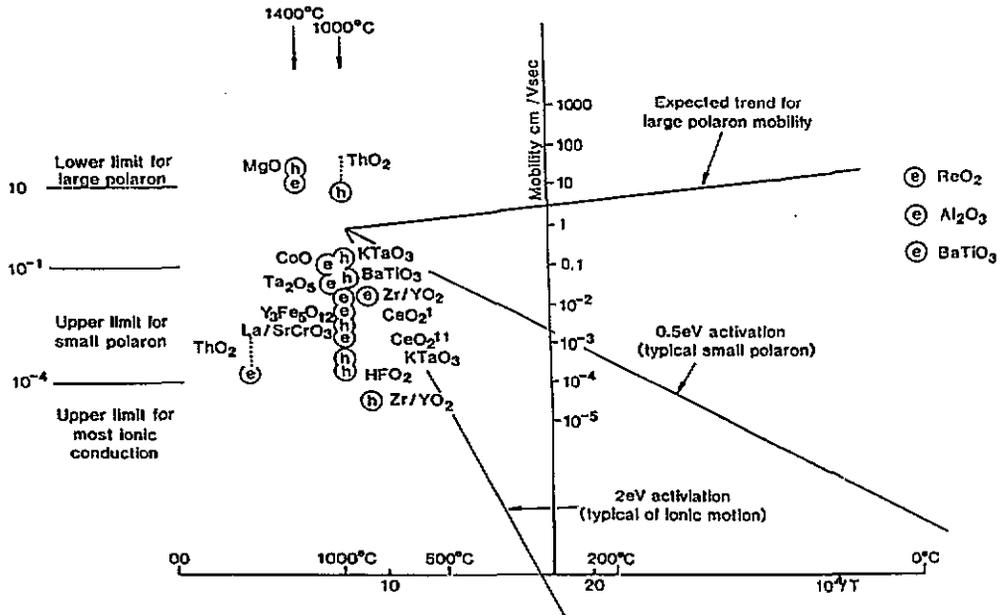


Figure 2. Observed electron (e) and hole (h) mobilities in oxides. The lower limit for large polarons corresponds to a mean-free path equal to the interatomic distance. The upper limit for small polarons corresponds to one hop every lattice vibration period. Note the opposite trends with temperature: for small polarons and ions, thermal activation is needed, so higher temperatures raise the rate; for large polarons, phonon scattering reduces the mobility at higher temperatures.

Smilga [17], a comparison of the experimental shift of the cyclotron line maximum with the temperature dependence of the 'inertial mass' of a polaron is not always straightforward.

The enhancement of the effective mass at the transition from the free to the self-trapped polaron state proves to be of the order of $\exp(\gamma^{-1})$, where γ is defined as the ratio of the phonon energy to the halfwidth of the bare electron band. Since this parameter characterizes the relative rapidity of an excess electron and atoms in the lattice, γ is sometimes referred to as a non-adiabaticity parameter. As shown by Emin and Holstein and by Toyozawa and co-workers [13, 14] (see also [18] for a review), in the adiabatic limit ($\gamma \rightarrow 0$) the transition between the free and the self-trapped states corresponds to a change in the relative stability of two minima in the adiabatic potential, and these minima are separated by an energy barrier (see figure 1). We emphasize that these theories do not take into account a finite speed of the lattice relaxation (the so-called 'cooling transitions', cf. Stoneham [19]). In particular, as was noted by Wagner and Koenigter [20], on the transition between free and localized states of an exciton there could be a 'phonon bottleneck' which does not allow the lattice modes coupled to the exciton to get rid of their energy by means of phonon transport. The speed of the lattice relaxation plays a crucial role in all dynamic processes, including the polaron(exciton) localization and transport [21]. In particular, it is one of the main factors that determine the characteristics of the 'hot' luminescence of excitons in alkali halides, which is emitted in the course of their self-trapping [22].

Although the phenomenological theory is reasonably satisfactory, as reviewed by Ueta and co-workers [11], a few workers looked more closely at what might be expected in real solids. Among those was Mott, whose early work in this field is summarized in [23]. These studies led the way to the systematic use of Mott-Littleton methods [24] in serious

quantitative studies of polarons. The methods suggested first by Mott [23], Gilbert [25], Toyozawa [16], Tolpygo [26] and Fowler [27] then were developed by many other workers. However, numerical studies of the microscopic structure and properties of self-trapped holes and excitons are still difficult problems (see, for example, [28]).

The recent development of new femtosecond scale pulse optical spectroscopic experimental techniques [29] set a new stage for experimental studies of the mechanisms of dynamical processes in the condensed phase after electronic excitation. Valuable results have already been obtained on the dynamics of the relaxation processes of the excited states of the triplet self-trapped exciton in NaCl [30]. A similar technique has been applied to the study of the hole polaron self-trapping in KBr [31], KI and RbI [32] and relaxation of solvated electron in water [33,34] and alcoholic systems [35]. Studies of the dynamics of the early stages of self-trapping of polarons and excitons in real systems have created a new class of very fascinating problems.

In the later parts of this review we shall be concerned with a range of properties of small polarons, focusing primarily on the concepts and methods of their atomistic computer modelling and simulation. These fall into three main classes: (i) mechanisms and dynamics of self-trapping of polarons; (ii) static properties—the relative energies of large and small polarons, the optical transitions expected, their effect on positions of other ions and on lattice vibrations, their population in thermal equilibrium, and so on; (iii) small polaron hopping and diffusion. One cannot separate the computational modelling entirely from the analytic theory. We will therefore discuss some aspects of the analytic theories which provide a background for computational studies. A number of recent reviews have concentrated on these general concepts and phenomenological theories of polarons. These are by Stoneham [36], Gerlach and Lowen [12], Fisher, Hayes and Wallace [37], Stoneham and Smith [38]. To keep this review to a reasonable length, we shall omit several important problems: polarons and solitons in polymeric materials like *trans*-polyacetylene, magnetic polarons in magnetically disordered materials, bipolarons in superconductors, and negative- U systems.

The range of practical implications is itself quite formidable, even if one ignores the applications to amorphous and disordered systems and to some of the newer systems (like borides or fullerene C_{60} [39]) which may have some small polaron characteristics too. The self-trapping of excitons has been observed in a wide variety of insulating solids with strong exciton-lattice coupling, like alkali metal halides, alkali earth fluorides and some oxides [21,40,41]. It is responsible for various photochemical- and radiation-induced processes, including defect formation and optically-induced desorption [21,42]. Small-radius hole polarons and self-trapped holes are well studied in alkali metal, alkaline earth and silver halide, and other crystals [11,43]. The fact that the carrier is localized has important consequences: first, electron-electron interactions are more important; second, reactions involving localized carriers lead to local release of energy so that polarons participate in photo-induced processes.

It is clear that polaron studies lead to several particular technical difficulties, which will become increasingly clear with specific examples. First, localized carriers mean ions in non-standard charge states. Some, like the $3+$ states of Co or Ni or the $1-$ state of O, are seen in Nature, whereas others, like the $-1/2$ state of Cl, are known only in molecular ions. Estimates of the polarizabilities and short-range forces involving the non-standard charge states are problematic. Therefore they have to be treated using many-electron quantum mechanical techniques. Second, we shall combine (and sometimes compare) energies from two quite distinct calculations: those from band structure for a rigid perfect lattice, and lattice distortion and polarization from cluster-type calculations. Real caution is needed to avoid double-counting of energies; there are also problems in the determination of the

correct bandwidth of the polaron band and in the appropriate value for the crystal electron affinity. Third, we shall consider very small energies, often 0.1 eV or so, where useful accuracy is easier to claim than to demonstrate, except in very favourable circumstances.

2. Localization process

After Kanzig's initial spin resonance observation of the V_K centre in KCl [2], there was one general point which caused special concern, especially among those theorists whose background was band theory. This is based on Bloch's proof that, for a perfectly periodic solid, the eigenstates must also have periodicity: surely one should not find apparently localized states? In fact, one should consider the whole system (i.e. electrons and phonons) and should recognize that the small polaron might be found on any translationally equivalent site with equal probability. The Bloch-like wavefunction of the polaron in both free and localized states has a general form:

$$\Phi_{jk}(\mathbf{r}, \mathbf{Q}) \sim \sum_L \exp(-ikL) \Psi_{jL}(\mathbf{r}, \mathbf{Q}) \quad (1)$$

where $\Psi_{jL}(\mathbf{r}, \mathbf{Q})$ is a normalized wavefunction of the polaron on site L , j enumerates branches of the corresponding polaron bands, \mathbf{r} and \mathbf{Q} are the electron and the phonon coordinates, respectively. There are several points to note here: the point symmetry of the free and the localized polaron states (e.g. the one-centre hole or the V_K centre) are different, therefore k , L , \mathbf{Q} and even j are generally not the same; for the localized state the transition matrix elements of the Hamiltonian between different sites, $|H_{LL'}|$, although they are much less than the corresponding diagonal matrix elements, determine the transport properties of the polaron; special attention should be paid to the timescale on which experiments are done relative to the timescale of polaron relaxation from a free state and its transitions from site to site.

2.1. Electronic polaron

The electrons respond more rapidly than the ions to the creation of a carrier, and the electronic polarization of the host lattice ions affects the way the localization process evolves. The response to a free carrier can be described in terms of an electronic polaron, a quasi-particle which consists of an electron or hole together with its associated electronic polarization [45]. The nature of the electronic polaron state has been discussed by many workers in the context of the interpretation of interband transitions, in particular, optical properties of insulators, photoelectron emission spectra, x-ray photoemission spectra (XPS) and x-ray absorption spectra (XAS), electron spectroscopy for chemical analysis (ESCA), and other spectroscopic experiments (see, for example, [46] and references therein). This state is also relevant to many electrochemical processes that are concerned with thermalization and solvation of electrons. There are two basic questions to address here. First, what is the *wavefunction* of the electronic polaron? This determines the matrix elements of the electronic excitations in spectroscopic experiments, and the localization rate in the polaron studies. Second, what is the *energy* of the electronic polaron with respect to the ground state of the system before excitation? This determines the ionization and excitation spectra, and the relaxation energy into a final polaron state.

We must emphasize a distinction between two models. For polar systems, it is clear that the dynamical effects of electronic relaxation and correlation may strongly affect the extent of localization and the energy of the quasi-particle in both crystals and liquids. This was

recently recognized also for the hydrated electron [47]. Another common approach, which might be adequate for electrons in liquid helium and similar systems, adopts a one-particle cavity model; it is claimed that the effects of electronic relaxation of the atoms caused by the polaron can be neglected and its localization is sensibly described within a one-electron model in terms of a classical polarization of the media or more refined approaches [48].

This point can be illustrated in the example of core-level spectroscopy, where, in the final state of x-ray photoemission or absorption spectra, a core hole is left behind, and in some cases it couples with valence electrons. Qualitatively, a very similar situation exists for excitations from different states in the valence band of crystals with mixed bands, such as AgCl. In the systems with incompletely filled f or d electrons, the coupling between the core hole and the d or f electrons is strong enough to bring about characteristic spectral splitting in XPS and XAS (see [49] for review).

The energy of electronic relaxation following localized excitations or ionization from core states is comparable with, or even larger than, the interactions between valence electrons which determine the valence band width. These many-electron effects are often treated using quantum chemical calculation techniques and embedded molecular cluster model. Although the wavefunction of the polaron state should be periodic, the localized cluster description can give reasonable ionization and excitation energies. There are several technical points to note here. (i) Most of the many-electron calculations use the one-electron approximation, in particular the Hartree-Fock (HF) method. Within this method the eigenfunction of the Fock operator is not necessarily the eigenfunction of the point group operator representing the total group of the system. What Bagus and Schaefer pointed out [50] was that symmetry-unrestricted or 'broken symmetry' HF solutions will provide a better first-order description in such a situation. The instability of HF symmetry breaking solutions in different types of systems has been discussed by many workers (see, for example, [51] and references therein). (ii) A simple model analysis shows [52] that the occurrence of broken symmetry solutions for hole states depends on the relative magnitudes of orbital energy splitting and the relaxation energy connected with the electron ionization from these orbitals. If local relaxation effects accompanying ionization are large compared to the delocalizing interactions that determine the orbital energy splitting, the lowest energy is obtained with a wavefunction corresponding to the lower symmetry so that the hole can localize on one of the geometrically equivalent atoms. (iii) Since all atoms are in their sites, both point and translational symmetry should be preserved in the exact wavefunction of the electronic polaron. This can be achieved if we use the more rigorous treatment discussed below.

That a broken symmetry HF wavefunction corresponding to the hole localization at one site in a small cluster has a lower energy is partly due to an increase of the electronic relaxation energy (the relaxation energy decreases as the charge is spread out), and partly due to electronic polarization of surrounding atoms (see, for example, [53] and p 35 of [54]). However, the correlation between electrons, which was only partly taken into account in the broken symmetry HF state, promotes the delocalization of the hole and restoration of the symmetry of the wavefunction. This effect can be treated by projecting proper symmetry states out of broken symmetry wavefunctions and using different configuration interaction techniques [55-57]. In particular, the wavefunction of the system may be constructed as a linear combination of wavefunctions corresponding to the hole localized onto different equivalent sites. The non-diagonal elements of the Hamiltonian between these states are the many-electron transfer integrals. If these matrix elements are large the total energy may be greatly reduced and the electronic density distribution may appear quite different from that corresponding to the broken symmetry solution. As has been demonstrated in [55], within an accuracy of several tenths of one eV, the broken symmetry solution already gives quite

a reasonable description of the photoionization and optical absorption spectra. However, this accuracy is not enough for the calculation of the barriers for self-trapping of polarons and excitons, which should be treated with proper account taken of electron correlation.

Because the electronic polarization of the lattice accompanying the electronic polaron is largely 'inertialess' it affects transport properties but little. For a slowly moving quasi-particle we will consider the electronic polaron as a 'free' state. In simple cases, such as alkali halides where the electronic polaron state for the valence hole may be sensibly treated as localized on one of the p orbitals of the anion, the dispersion of the free hole band coincides with that for the valence band. As was demonstrated by Fowler [27] it is acceptable to calculate electronic polarization effects in these crystals using the classical approach of Mott and Littleton. In the next sections we will examine the effect of the 'inertial' coordinates on the localization process and polaron structure.

2.2. Localization rate

The phenomenological theory for the three-dimensional case in the adiabatic limit qualitatively demonstrated that a purely short-range polaron-continuum interaction always yields two distinct states: a small polaron-like state and a free state separated by an adiabatic potential barrier [13]. The addition of long-range component to the polaron-continuum interaction can convert a free state into a large-radius polaronic state, still with a barrier between the two states. If a long-range component is 'sufficiently strong', the large-radius state may collapse into the small-radius polaronic state suppressing the barrier. Therefore if the system is first produced in a free state, and if self-trapping is to occur, it may have to pass through a potential barrier (see figure 3). The height of this barrier depends on the nature (one-centre, two-centre, etc.) and the degree of localization of the final state of this transition. If the localization process happens after the polaron has thermalized and at low temperatures the system should tunnel from the bottom of the band of free states (or from the large polaron state), and in order to calculate the tunnelling rate one needs to know the wavefunction of the localized state (the so-called state of nucleation [58]) at the tunnelling energy (see figure 3). A state of nucleation with appreciable lattice distortion but less localized than the final self-trapped state is formed by quantum mechanical tunnelling, and then relaxes in order to stabilize itself. In this case a self-trapping rate is a rate with which the most probable nucleation state is formed [58]. The initial nucleation state in some cases can relax into a transient metastable localized state and subsequently transfer into a final stable state. Model calculations suggest that in some other cases the adiabatic picture may fail and the localization process may be driven by the speed of lattice relaxation [20].

We should stress that these arguments are valid not only for the crystal case but also for localization of an excess electron in water and other polar solutions [59], as well as in liquid helium and neon [60]. However, current understanding of the dynamics of localization of polaron in crystals and polar solvents differs. Generally speaking, the non-radiative decay rate for the transition from the free polaron state to the localized state is determined by an electron matrix element of the non-radiative coupling between these two states and a Franck-Condon vibrational overlap factor. The latter is determined by the configurational changes between the initial and the final states, so both short-range structural modifications and long-range polarization (i.e. optical modes) are involved, as was described in the previous paragraph. These appreciable configurational changes are provided both in crystals and in the polar liquid by short-range structural fluctuations. However, in liquids, pre-existing configurational order may also contribute to the localization process. In particular, a quantum molecular dynamics simulation [61] of the electronic states accessible to an excess electron in pure liquid water prior to any induced liquid configurational relaxation

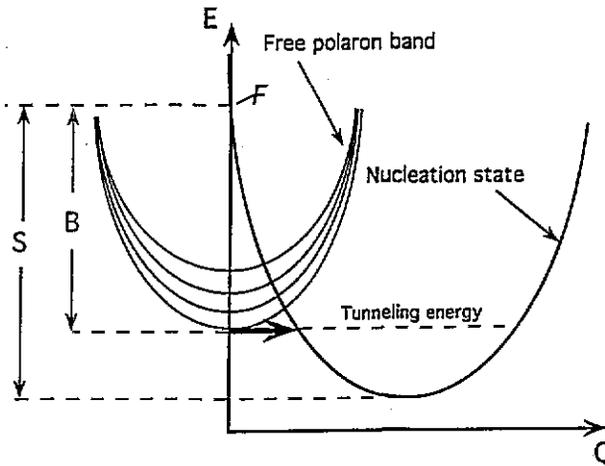


Figure 3. Adiabatic potentials associated with the free states and the nucleation state of the self-trapping exciton [58]. Q is the reaction coordinate for the nucleation of self-trapping.

has demonstrated the existence of many pre-existing fluctuations capable of trapping an electron into a shallow ground state. However, solvent configurations supporting deeply trapped states are relatively highly improbable in the pure liquid. Pre-existing shallow fluctuations may serve as initial traps for excess electrons in liquids, so that localization of at least a fraction of them may happen with barrierless pre-localization in already-existing potential wells. The other component may behave like electrons in crystals, and tunnel into nucleation states or localize adiabatically, as was numerically simulated in [62]. At present, it is very hard to determine which case actually occurs from experiment.

The calculation of the self-trapping rate for the adiabatic barrier scenario has been studied by several authors (see, for example, [8, 63]). The most comprehensive work relevant to real systems is that of Sumi [58]. In the study of the self-trapping of excitons in alkali halides he demonstrated that the nucleation state in these materials should have a scale of a lattice constant. In his work he considered the one- and two-centre-type nucleation states with different degrees of localization of the exciton wavefunction. Using a phenomenological approach, and the theory of non-radiative tunnelling transitions, he calculated the tunnelling rate between the free state and different nucleation states of the exciton as a function of the parameters of the Hamiltonian (the localization and relaxation energies in the nucleation state) and of temperature. The localization energy, B , is determined by an increase of the exciton kinetic energy due to its localization in the nucleation state, whereas the relaxation energy, S , is gained due to the relaxation of the lattice in this state. As has been shown by Sumi, both B and S strongly depend on the degree of localization of the exciton. At low temperatures the tunnelling rate from the free into the nucleation state is given approximately by [58]

$$W_0 = 4\pi^2 \nu B^2 e^{-S} S^{S-B} / \Gamma(S - B + 1) \quad \text{for } S \geq B \quad (2)$$

where ν is the characteristic frequency of the lattice vibrations that govern relaxation of the system, and Γ is the Gamma function. Sumi's theory gave a reasonable qualitative account of the mechanism of the self-trapping of excitons in alkali iodides, where the existence of the potential barrier between free and self-trapped states of the exciton was proved experimentally. In particular, the theory predicts that self-trapping of excitons in KI and RbI most probably takes place through the nucleation state of the one-centre type.

Intuitively, it is natural to believe that holes in alkali halides self-trap through a two-centre nucleation state (see figure 4(b)) which, in turn, relaxes directly into the well studied V_K configuration. However, recent femtosecond scale spectroscopic experiments suggest a different model for the early stages of this process in KI, RbI [32]. The two-photon excitation employed in these experiments, with an energy of about 8 eV first produces a free electron-hole pair in the bulk of these crystals. Very similar optical absorption spectra have been observed after the excitation pulse in pure samples of KI and in those doped with the electron-trapping impurity (NO_2^-) in the time domain 0.3–20 ps. An intense optical absorption spectrum is observed after only 0.3 ps. It differs strongly from that of the V_K centre, which appears only later after 3 ps, and rises during 10 ps. Similar behaviour of the transient optical absorption has been observed in RbI. However, in KBr a broad featureless optical absorption band was observed just after the pulse; this band transforms into the absorption spectrum of the V_K centre after about 10 ps. Since the behaviour of the transient optical absorption in both pure and doped samples of KI is the same, this suggests that the band may be attributed to some metastable state of the hole in these crystals. It is plausible to assume that the transient optical absorption observed 0.3 ps after the excitation of KI can be attributed to one-centre hole polarons (see figure 4(a)) which subsequently transform into the V_K centres.

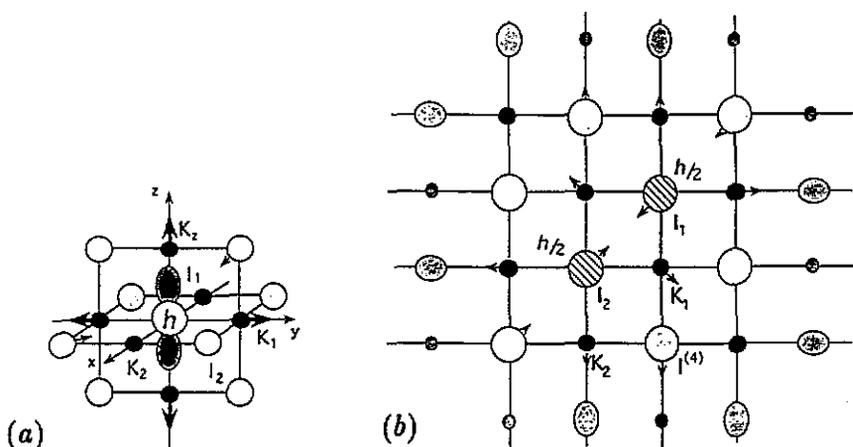


Figure 4. One-centre (a) and two-centre (b) types of hole self-trapping in cubic ionic crystals, which are shown schematically for KI. Arrows indicate the directions of non-equivalent displacements of the nearest-neighbour ions in both nucleation and relaxed states.

2.3. Quantum molecular dynamics approach

Another approach employed in several recent studies is based on the *adiabatic simulation* of the *dynamics* of electron excitation, localization and migration. It employs a quantum path-integral molecular dynamics technique, or a direct description of the electron in terms of wavefunctions, and has been successfully applied to the simulation of the excess electron localization and diffusion in molten ionic salts [64], liquid water [62], and small polar [65] and alkali halide [66] clusters. The path-integral technique is developed from the ideas of Feynman [67]; indeed, one of the first applications of his method was to the polaron problem [68]. Feynman's ideas exploit the equivalence between quantum systems and related (but different) classical systems; these ideas were taken up by many workers and developed into powerful simulation techniques [69, 70]. It is this quantum-classical

'isomorphism' that leads to a simple representation of quantum particles in computer simulations. In the case of the real wavefunction representation of an excess electron in polar media, efficient methods have been developed for evaluating the Born–Oppenheimer, or adiabatic, electronic states associated with a given molecular configuration [71, 72]. The excess electron–molecule interaction is usually treated in the pseudopotential approximation (see, for example, [48, 73]). The efficiency of the simulation of the propagation of the wavefunction in time is based on algorithms using only simple multiplicative operations and repeated fast Fourier transforms [71, 72].

Recent experiments have provided time-resolved femtosecond spectroscopy [34] of the electronic states of an excess electron in water at an early stage, well before the spectrum of the hydrated electron finally emerges. These experiments show that the electron transforms into a pre-localized state on a subpicosecond timescale and this manifests itself at the earliest times via a diffuse infrared spectrum. Even in the first experiments [33] it was noted that the relaxation process leading to initial infrared absorption is much shorter than the dielectric relaxation time of water (7.4 ps at 30°C). The evolution of the solvated electron absorption band (on the timescale ~ 4 ps) exhibits the solvent relaxation around the localized state initially formed. This process was simulated in [61, 62] by calculating the time evolution of the electronic ground state in the solution in the Born–Oppenheimer approximation. The time dependence of the electronic state arises solely from the time dependence of the nuclear coordinates. The new electronic state is evaluated by solving the time-independent one-electron problem for each new solvent configuration in the sequence of molecular dynamic timesteps. Although the results of the simulation seem to be reasonable, quantitative predictions are still not very reliable because of the oversimplified description of the electron–water and water–water interactions (see also discussions in [47]).

3. Stability and properties of small polarons

The basic strategy for the study of the polaron stability in most atomistic simulations concerns the *extrema* of the energy surface and the *energy differences* between such extrema, rather than the *process* of localization and the complete energy surface. The phenomenological theory of small-radius polarons predicts that the one-centre polaron state is always more stable than the two-centre state, whereas the energy difference between these two configurations is equal to the activation barrier for diffusion of the one-centre polaron (see, for example, the discussion in [74]). However, in some crystals such as alkali halides, alkaline earth fluorides [44], and possibly alumina [75], the two-centre state of the hole polarons is stabilized by the formation of a chemical bond between the two anions sharing the hole. These effects can be sensibly understood only on the basis of more sophisticated quantum mechanical calculations. Combined with the calculation of optical absorption energies, as well as other observables like magnetic resonance parameters and activation energies for diffusion, they can provide quantitative comparison between theory and experiment.

As was pointed out by Flynn and Stoneham [76], in many cases the wavefunctions of the localized polaron states may be treated as sensibly exact eigenfunctions of the total Hamiltonian. They bear the same relation to the exact eigenstates that Wannier functions bear to Bloch functions. Note, too, that for the mean energy of the band of the localized states both Bloch and Wannier representations have exactly the same value. Just as in the construction of Wannier functions, the localized functions of different sites may be orthogonalized. Nevertheless, they are mixed by the exact crystal Hamiltonian, and the transitions induced between different polaron configurations may be related to the polaron

hopping motion through the crystal. This approach has been used, for instance, by Holstein [10]. In the latter work the electronic-overlap term of the total Hamiltonian, which is responsible for the polaron jumps between sites, was treated as a small perturbation. In zeroth order, i.e. in the absence of this term, the polaron may be treated as permanently localized at a given site. Within the static approach, which concerns the microscopic characteristics of the small polaron rather than the dynamics of its diffusion, this state is treated as approximately stationary.

The pioneering calculations of small polaron against large polaron stability in actual (rather than model) systems were those of Gilbert [25] (described in [77] by Fowler). The idea of Gilbert was to introduce a two-step procedure: (i) to localize the polaron from completely delocalized state onto several lattice sites; (ii) to calculate the energy gain due to the lattice relaxation from this state into the final polaron state. These calculations were primitive, but very illuminating. They suggested a calculation scheme, which was taken up in many other static approaches to the problem of polaron structure and stability. In particular, they showed why holes self-trap in alkali metal halides but electrons do not; in essence the difference comes from conduction bands, which are wider than valence bands, and from the chemical binding forces within the anion molecular ions.

It is interesting to compare these Mott-Littleton calculations with those of earlier workers (see [78], p 60 for a summary). The argument then was that the localization of the polaron produced a potential well from ionic polarization (so involving ϵ_{ion} a dielectric constant determined by the ionic polarization and defined by

$$1/\epsilon_{\text{ion}} = 1/\epsilon_{\infty} - 1/\epsilon_0 \quad (3)$$

in terms of high-frequency and static dielectric constants); the potential well would be Coulombic, screened by the ionic polarization, outside the polaron radius R_p and roughly constant inside the well. Minimizing the total energy, including kinetic energy, gives R_p in terms of ϵ_{ion} , etc. For the small polaron, the effective radius becomes small, comparable with or less than interatomic spacings. In the fuller analysis the kinetic energy is replaced by band parameters, and the ionic polarization is modelled atomistically using the shell model and the Mott-Littleton method. However, the different roles of electronic and ionic polarizations continue to be essential, and the simple dielectric picture is still of value.

In the later discussion we shall focus on the static approach, which is widely used in crystal calculations, although some comments will be made concerning the results of dynamic simulation.

3.1. Static approach

The scaling argument suggested by Emin and Holstein [13] asserts that if we change the length scale of the (normalized) eigenfunction, the energy as a function of the scale factor should have a minimum at the scale corresponding to the actual eigenstate. Within the more sophisticated technique developed by Toyozawa and co-workers, both states (delocalized and localized polaron) may be treated using the same model Hamiltonian [11, 18]. However, neither method allows us to take into account the microscopic structure of the polaron in the real solid. This is only possible by employing some atomistic approach. In particular, one can assume the polaron to be localized in a small area comprising of several tens of ions or molecules, which are embedded in the remaining media and vary the radius of its wavefunction whilst simultaneously minimizing the total energy of the crystal with respect to the atomic coordinates. In this way, both the short-range and long-range contributions into the total energy may readily be taken into account. This approach is used for the

quantum molecular dynamics simulations of an excess electron in water [61, 62] and small clusters [65, 66]. A similar technique, though with the static model for the crystalline lattice and a very restricted basis set, was used for the simulation of the self-trapped excitons in alkali halides by Song and Leung [79]. In both cases only one electron is treated rigorously, whereas other species are represented by their pseudopotentials. In the many-electron calculations the localized and the delocalized states usually belong to different Hamiltonians. However, it is possible to derive a reliable estimate by taking *differences* between the energies calculated by each method, and using the most appropriate methods at each stage in their calculation.

Essentially, two energies are compared in these calculations: the kinetic energy gain from having a delocalized carrier in an undistorted lattice, and the polarization and distortion energy gain from having a localized carrier. The self-trapping energy is thus the difference:

$$E_{st} = E_{loc} - E_{rel}. \quad (4)$$

When one uses a standard stationary quantum chemical technique, one must introduce an artificial intermediate state, Φ_i , as a common reference point for the calculation of E_{loc} and E_{rel} [80, 81]. It corresponds to the point F in figure 3. Two steps are needed. First, one needs to construct an electronic state Φ_i in the perfect lattice qualitatively the same as the localized configuration. Second, one assumes the magnitudes of the electronic polarization produced by this state and the completely delocalized polaron state are the same (or, occasionally, are related in some other simple way). The validity of the latter approximation was analyzed by Fowler [27]. In this case, polaron localization energy is given in terms of H_{ee} , the electronic Hamiltonian, by

$$E_{loc} = \langle \Phi_i | H_{ee} | \Phi_i \rangle - \langle \Phi_{del} | H_{ee} | \Phi_{del} \rangle \quad (5)$$

where Φ_{del} is the wavefunction of the delocalized state. The lattice relaxation energy is given in terms of the total Hamiltonian, H , by

$$E_{rel} = \langle \Phi_i | H | \Phi_i \rangle - \langle \Phi_{st} | H | \Phi_{st} \rangle \quad (6)$$

where Φ_{st} is the wavefunction of the self-trapped states. Note that, in the approximation that the electronic polarization of the crystal and the self-energy of the polaron in the delocalized and the intermediate states compensate each other, the localization energy is simply the change in the kinetic energy of the localizing particle. The electronic polarization of the perfect lattice in the intermediate state has to be taken into account in calculating the relaxation energy.

If E_{st} is found to be positive the localized state is certainly unstable and the polaron can exist only as the delocalized state. In such cases localized states may form in the presence of a defect, or near an interface. If the calculated value of E_{st} is negative, the localized state is considered to be stable. However, the real behaviour of the localized polaron is determined not only by the sign and the value of E_{st} but, also by the barriers and the transfer matrix elements, $|H_{LL'}|$, for its diffusion between different localized states.

3.2. Calculation of the localization energy

The commonest and simplest form of the electronic Hamiltonian is the tight-binding form, with only the largest matrix elements between the nearest sites; the density of states of the valence band then has a symmetric form as a function of energy. The localization energy of the particle on one lattice site (i.e. the expectation value of a Wannier function at that site) is then equal to the halfwidth of the band of delocalized states. Such a picture is an appropriate

representation of the polaron states, to the extent that the s atomic orbitals centred on the sites are true Wannier functions, as for the $1s$ core anion holes in the transition metal oxides. However, in many crystals the wavefunction of the valence hole polaron has p or d orbital characteristics. In these cases the simple approach described above leads to a substantial overestimation of the localization energy [81–83]. Since the localization and relaxation energies are usually similar in magnitude, and their difference is much smaller than the width of the band of the delocalized states, the accuracy of the calculation of E_{loc} is crucial in the estimating the self-trapping energy, E_{st} . As has been shown in [80–82], accounting for the angular dependence of the matrix elements of the tight-binding Hamiltonian improves the accuracy of the calculation of E_{loc} .

The situation becomes still more complicated when the valence band is a mixture of the states originated from two or more sublattices. This is the case for AgCl, alumina, silica, transition-metal oxides and halides, and for other crystals where the self-trapping of holes is under discussion. A calculation scheme for the mixed band case based on a model Hamiltonian technique and the tight-binding approximation has been proposed in [80]. It takes into account the nature of the hole polaron states and real atomic orbitals of surrounding ions.

Both methods mentioned above are based on the idea that the matrix elements of the tight-binding Hamiltonian, constructed using Wannier functions, may be calculated using the matrix elements obtained from some band structure calculation for the perfect crystal. The link becomes possible if we assume that: (i) the band of free holes coincides with the valence band taken with the opposite sign, i.e. the bottom of the hole band corresponds to the top of the valence band; (ii) the atomic orbitals of anions and cations may be used as Wannier functions; and (iii) the wavefunction of the intermediate state, Φ_i , calculated in the cluster approximation is *physically equivalent* to the Wannier function localized at certain perfect lattice sites. However, as was discussed in section 2, in many interesting cases as a result of electronic relaxation the wavefunction of electronic polaron is different from those of the valence band electrons. This is only partly taken into account within the methods discussed in [80–83]. Therefore, the localization energy calculated using frozen wavefunctions of the perfect crystal may be inaccurate, and a more flexible variational approach should be used to calculate the localization and relaxation energy terms accurately.

An alternative approach to address these problems is based on cluster calculations. The wavefunction of the intermediate polaronic state in the perfect lattice, which should be equivalent to the wave function of the localized polaron state, is often a broken symmetry solution of the Hartree–Fock equations. Nieuwpoort and Broer suggested a method for the calculation of the Hamiltonian matrix elements between broken symmetry wavefunctions, with holes localized on different equivalent sites. It is based on a variational procedure and provides a fruitful approach for investigation of ‘electronic polaron’ bands [55–57], and thus for evaluation of the polaron localization energy. The important advantage of their approach is that the matrix elements needed to evaluate both the localization and the relaxation energies of the polaron may be calculated employing the same quantum chemical technique and set of parameters. There is a further problem for electron (as opposed to hole) polarons, since the calculations for the conduction band and the crystal electron affinity are still very unreliable.

3.3. Microscopic structure of small polarons and calculation of the relaxation energy

Most model Hamiltonian methods used in studies of self-trapping assume that the harmonic approximation suffices, and the energy of interaction between the particle and the medium is linear in coordinates representing the deformation of the medium from its equilibrium

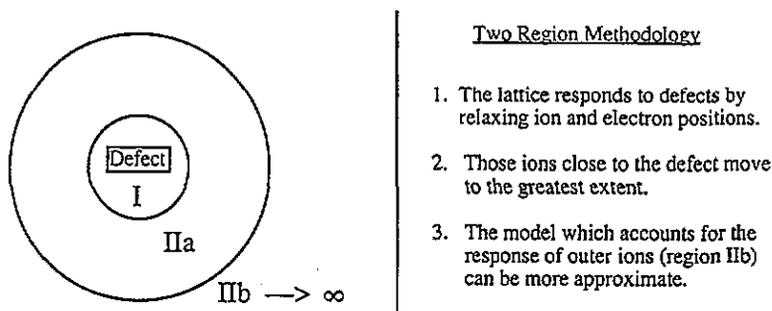


Figure 5. Two-region methodology for defect calculations in a polarizable lattice. In region I, electronic structure is calculated self-consistently as forces on the ions are relaxed to zero. In region II, simpler approximations are sufficient to embed region I. Thus ionic positions and polarizations are estimated from a continuum model. Region IIa is created to link the two regions properly; in many calculations the ions in region IIa are discrete, but with displacements and dipole moments derived from continuum models.

configuration [8, 11]. These are rather dubious approximations for strong lattice distortions. It is in calculating this lattice relaxation that the Mott–Littleton method and related techniques come into their own; indeed this was done in early work by generalizing an approach to the vacancy problem [25]. Gilbert’s calculations were the basis for more extensive work of Jette and co-workers [84], who made extensive estimates for alkali metal fluorides and chlorides, showing that the self-trapped holes could be regarded rather well as halogen molecular ions in a polarizable distortable matrix. These calculations were done within a polarizable point-ion model, a model which has been superseded for most serious estimates by the shell model. Later work in the same spirit, but using the shell model, has been published for a wide range of systems: for the alkali metal halides (including mixed alkali metal halides) by Cade and co-workers [85, 86], for the Cs structure alkali metal halides by Monnier and co-workers [87] and by Norgett and Stoneham [88] for the alkali earth metal halides. The ‘molecule in a crystal’ model for the hole polarons in alkali metal halides (V_K centre) has been examined by Stoneham [44], by Tasker and Stoneham [89] and by Cade and co-workers [85]; here a diatomic molecular ion is studied quantum mechanically [90], and then embedded into a classical ionic host. In this case one has strong covalent bonding within the molecular ion X_2^- , but ionic interactions with the rest of the crystal.

A more sophisticated approach combines a quantum mechanical treatment of a small molecular cluster, in which the polaron is localized, with the Mott–Littleton calculation of the polarization of the rest of the crystal (for a review see Catlow and Stoneham [24]; see also [28, 91–93]). The crystal is divided into two regions: an inner region (I), containing the defect and its immediate surroundings, and an outer region (II) which responds as a dielectric continuum (see figure 5). The quantum cluster is placed at the centre of region I. This quantum chemical approach has recently been used for studies of several alkali metal halides [28] and oxides [94], and has provided satisfactory microscopic models for the self-trapped holes and excitons in these crystals. In particular, the quantum chemical calculations of the V_K centre in several alkali halides [81, 83, 95, 96] give atomic displacements similar to those obtained by Cade and co-workers using the classical Mott–Littleton technique [85]. Similar results were also obtained with both techniques for the lattice distortion around the hole in MgO [82, 97]. However, the main advantage of the quantum mechanical methods is that they provide a stronger connection between the localized and delocalized states.

Although the atomic structures of point defects in ionic crystals can be studied more or less routinely, this is certainly not the case with the calculation of the relaxation energy. The most substantial problem is the choice of the path for the localization of the polaron and, as a consequence, of the intermediate state, which provides the reference point for the calculation of the relaxation energy [81]. Another point concerns the accuracy of the calculation, since the self-trapping energy rarely exceeds several tenths of an eV and is the difference of two large and similar values.

The situation is not simple even for the 'dielectric' polaron, in which electrons or holes in a polar lattice interact mainly with the long-range polarization. According to the phenomenological theory, the radius of the dielectric polaron should be large rather than small. An example of the problems can be seen for MgO, where trapping of the holes has been modelled quite extensively. All the calculations of the lattice relaxation predict that the hole should be strongly localized on one oxygen ion. The relaxation energy, which is the energy difference between the final completely relaxed state and the intermediate state (the latter corresponds to the hole on one oxygen in the perfect lattice where only electronic relaxation is taken into account), was calculated using different methods to be 1.7–2.4 eV [82, 97, 98]. This large energy is fully consistent with a theoretical analysis of the observed charge-state stabilities of transition metal impurities in MgO. The localization energy according to the existing estimations [82] is 2.0–2.4 eV. The value of 2.4 eV is equal to half of the experimental magnitude of the valence band width (4.8 eV [99]) and so gives an upper limit [100]†. Recent calculations [82], in which both relaxation and localization energies were treated using the same quantum chemical technique, indicated a self-trapping energy of about –0.4 eV. In simple treatments of small dielectric polarons, the hopping energy for diffusion motion is less than this, and probably less than half of the self-trapping energy, so the polaron should be very mobile. Therefore, despite the strong localization in the cluster calculation and the large relaxation energy, it will be hard to distinguish the behaviour of the polaron from that of the large polaron at appreciable temperatures. Apparently the transfer matrix elements $|H_{LL'}|$ are substantial and the stationary localized state on one site is not a good approximation.

In the case of the 'molecular' polaron the self-trapping is caused by the short-range interaction, and the situation is complicated by the possibility of coexistence of both types of polarons. The V_K centre is the classical example. For instance, it is not clear *a priori* if one should consider the localization in the one-centre form first and then calculate the additional energy gain due to the formation of the chemical bond between two anions, or if the two-centre localization is preferable from the very beginning (see the discussion in section 2).

As should be clear from the above discussion, the relaxation energy only makes sense as a part of the self-trapping energy, for it depends on the intermediate state(s) chosen in its calculation. It cannot be measured directly, although it may be estimated on the basis of energy cycles, which combine available experimental and theoretical data, as demonstrated by Itoh and co-workers [101] for self-trapped excitons in alkali metal halides. Relaxation energies contribute substantial terms to a wide range of observable quantities, including defect formation energies and optical charge-transfer processes. Moreover, the observed systematics of behaviour (e.g. which charge states of transition metals are stable in a given host) gives strong support to theoretical estimates of relaxation energies.

† The experimentally observed total valence band width of 4.8 ± 0.3 eV is in a good agreement with the result of the Hartree-Fock calculation by Causà and co-workers, which gives 5.1 eV. However, recent experiments by French and co-workers, using valence band x-ray photoemission spectroscopy, and LDA calculations gave for the valence band width in MgO the value of 6 eV.

We should note that the self-trapping energy is defined relative to the bottom of the band of free polaron states, which in turn depends on the crystal under study. Thus whilst $E_{st} \leq 0$ may be used as a criterion of self-trapping in each particular crystal, it does not provide a good basis for comparison of different or mixed crystals. Such a comparison is possible on the basis of energy cycles aiming at the calculation of the defect formation energy. This formation energy may also be compared with the crystal ionization and excitation thresholds, and in this way connected with the effectiveness of the polaron or exciton production.

3.4. Small polaron formation energy

Although the general idea is quite transparent, energy cycles differ from one case to another and, moreover, there are alternative cycles for each particular case (see, for example [28, 85, 101]). Let us consider, for example, the V_K type of self-trapped hole in alkali metal halides, caesium halides or alkaline earth fluorides. Despite the differences in the crystalline structure, the hole in all these cases is sensibly regarded as an X_2^- molecular ion, which occupies two anion lattice sites (see [44] for a discussion).

The energy required to form a V_K centre may be considered as the sum of energies for several distinct steps [85]. (i) The energy required to remove the two X^- lattice ions to infinity (separately)—the vacancy energy E_v . (ii) The energy of formation of X_2^- (gaseous) + e^- from two X^- anions. The internuclear separation R for X_2^- may be taken as R_e for free X_2^- , although other values of R do not change the final result. (iii) The energy associated with introducing X_2^- into the prepared (perfect) vacancy site—the interstitial energy E_i . (iv) The energy arising from relaxation of ions in region I, region II, and of course, within the V_K centre—the relaxation or lattice energy E_R . It is necessary to consider the electron released in step (ii), and this is usually placed at the bottom of the conduction band of the crystal. The associated energy for this process is the electron affinity of the crystal, χ . The V_K centre formation energy may be written in the form

$$E_D = E_v + E_i + E_R + [A(X) - \chi] \quad (7)$$

where $A(X)$ is the electron affinity of the halide X . The values of electron affinity for crystals are not well known, but values are quoted in the range 0.1–1.5 eV [102]. The result is that the defect energy has a consistent reference point within a given crystal, but comparisons of different energies involving different crystals do not have identical reference points.

Alternative energy cycles might be useful; for example, the uncertainty in χ can be eliminated if the electron is removed from the conduction band and placed on an 'electron trap', i.e. it reduces a metal ion doped into the crystal for this purpose. Typically, for V_K centre formation, Pb^{2+} , Tl^+ or Ag^+ cations are employed as electron traps. The energy scale (zero) involving the electron trap corresponds more to what is involved in practice in self-trapped hole formation, and in that sense this zero point may be more satisfying. However it has serious technical drawbacks, especially if the Mott–Littleton technique is employed for calculations. These concern the pair potentials between the host lattice ions and impurities in different charge states and the accuracy of the relaxation energy calculation for the impurity states. However, the location of the electron on a trap preserves the crystal neutrality and permits comparison with uncharged defects on a common ground. It enables one to use the periodic boundary conditions in the calculations of charged polaronic states.

One simple estimate of the energy E_Γ of a hole at the top of the valence band of an undistorted crystal assumes [87] that the centre of the valence band corresponds to the Madelung potential at the anion, so that

$$E_\Gamma = \frac{M}{a_0} - \frac{1}{2} E_{val} \quad (8)$$

where M is the Madelung constant, a_0 is the lattice constant, and E_{val} is the valence band width. The corresponding approximate condition for self-trapping becomes:

$$-E_{\text{D}} - \frac{M}{a_0} + \frac{1}{2}E_{\text{val}} \leq 0 \quad (9)$$

an equation that has been widely used in previous calculations (see for example [85, 87, 88]).

3.5. Specific properties of the self-trapped exciton state

The structure and characteristics of a self-trapped exciton (STE) involve both the basic issues of self-trapping, and the interaction and correlated behaviour of the electron and the hole. The conditions for the exciton self-trapping have been studied extensively phenomenologically as reviewed by Ueta and co-workers [11] and Rashba [8]. The theory predicts that an exciton can self-trap even if neither an electron nor a hole can do so alone. Another remarkable prediction is that, in certain circumstances, the parity of the relative motion of an electron and a hole may be broken [11]. In particular, this may happen when a hole has a very large effective mass and its interaction with an electron consists of the long-range Coulomb attraction and short-range strong repulsion. These predictions of the phenomenological theory have been supported by the results of recent quantum mechanical calculations.

Starting from the first calculations by Wood [103] and Stoneham [104], successful attempts have been made to use for self-trapped excitons the methods developed for calculations of point defects [105]. As was noted above, such an approach is only possible when the exciton is well localized in a small region of the crystal host. Even then there are clear distinctions between the ground or excited state of the localized point defect and the STE.

An exciton is an excited state of an otherwise perfect (but deformable) lattice. A key characteristic of the STE is its luminescence: STE are short-lived luminescent states of excited crystals, with properties very different from those for the crystal ground state (see for reviews [21, 40, 41] and references therein). The initial states for the luminescence are treated as approximately stationary, and correspond to the minima of the adiabatic potential of the excited crystal. However, the methods and basis sets which were developed for the calculation of the properties of the crystal ground state are not well suited for its excited state. Moreover, usual adiabatic calculations are meaningful only in the close vicinity of these minima, for which atomic structures are considered as models of STE [28]. The dynamics of the processes leading to these states requires further concepts and complexities.

The electron and the hole overlap strongly, but become localized in the lattice for different reasons. In alkali halides and fluorides, in effect, the hole is self-trapped and localized in the form of a quasi-molecule, whereas the electron is localized mainly by its Coulomb interaction with the hole. In crystalline quartz the holes do not self-trap, while the self-trapping of excitons gives rise to the luminescence with a very large Stokes shift. According to experimental ESR data, the electron of the STE in these crystals is less localized than the hole. Further, the self-trapping of the exciton in many crystals is accompanied by its decay, producing primary Frenkel defects [42]. The degree of localization of the electronic component of the nearest-neighbour defect pair depends sharply on the relative position of the hole component. Since the radius of the electron localization is large and changes significantly during the calculation of the adiabatic potential for the exciton localization and decomposition, special efforts are needed in order to make the basis set flexible enough and to take into account the resulting changes in polarization and other energies.

Another issue arises with the wavefunction of the STE. Experimentally, in the alkali metal halides both singlet and triplet states of the self-trapped exciton have been detected or inferred. In crystalline quartz only the triplet state of the STE has been observed so far. Nevertheless, most of the theoretical studies concern only the triplet excited state of the crystal. This is solely for technical reasons. In wide-gap insulators, as all of these crystals indeed are, the crystal triplet state automatically means the excited state. For the lowest multiplicity it may be treated in the single-determinant unrestricted Hartree-Fock approximation. This approach has been employed in all the many-electron calculations made so far. It is much more time-consuming to treat the singlet excited state using a many-determinant approximation for the wavefunction of the crystal. The first calculations for the singlet state of the STE in NaCl were performed by Stoneham [104]. Similar calculations using the generalized valence bond (GVB) technique in several alkali metal halides have been made only recently [106].

3.6. How good are the results?

3.6.1. Stability of the small polaron form: will self-trapping occur?

Self-trapped holes. In all cases studied seriously, the correct prediction is achieved. For the halides, the margin is substantial, where the hole small polaron is stable by several tenths of a volt [80–85]. Typical relaxation energies (i.e. the energy to relax a hole localized on a single halogen to the V_K centre geometry) are 1.0–1.5 eV. The situation is less clear for oxides, principally because of lack of direct experimental evidence. Theoretically there are substantial problems with the calculation of the localization energy due to the mixed character of the valence band. Once again, relaxation energies are quite large (for instance, about 2 eV for the one-centre hole on oxygen in MgO [82, 97]). Recent quantum chemical cluster simulation of the self-trapped hole in α -Al₂O₃ [75] suggested a model with the hole shared between two anions, analogous to that in alkali halides. The energetically most favourable configuration appears to involve a strong inward Jahn-Teller displacement of two O ions (on which about 80% of the hole density is localized), accompanied by the outward displacement of the two nearest Al atoms. The self-trapping energy predicted for this configuration is -2.7 eV [75]. EPR experiments [107] suggested that the holes can self-trap in fused silica in the form of O₂³⁻ molecular centres. However, hole trapping in a glass network could be assisted by charge and density fluctuations. Quantum chemical simulations [108] made in a periodical model for an idealized SiO₂ structure (β -cristobalite) have shown that the holes most probably cannot self-trap on the one anion site in this material. The two-centre-type localization of the hole in pure silica has not been simulated so far.

In these crystals the holes (if self-trapped) are localized onto one or two anions. In AgCl the situation is qualitatively different. The structure of the self-trapped hole has been studied using various experimental techniques and reliably established [109–111]. AgCl has the rock salt structure, but a different character of chemical bonding and valence band electronic structure. In particular, the top of the valence band in AgCl is determined by the d states of the silver ions. This is certainly an important factor: for alkali halides the holes are self-trapped in the anion sublattice and form V_K centres; for AgCl the cation can change charge state without a large energy cost, and the hole is localized on one cation. Indeed, the simulation of the hole self-trapping on chlorine ions in AgCl [80] revealed a hole density redistribution from the chlorine ions to silver because the silver states have higher energy in the valence band. The chemical bond sharing the hole between two chlorines

does not form because the lattice polarization encourages the hole transfer. The value of the hole self-trapping energy obtained in [80] is equal to -0.1 eV (where the zero of energy corresponds to the bottom of the free hole band (see figure 3)) which is close to ~ 0.12 eV, the experimentally observed activation energy for the thermo-stimulated ionization of the self-trapped hole in AgCl [112]. About two thirds of the hole spin density is localized on the $d_{x^2-y^2}$ atomic orbital of the silver ion. The remaining third of the spin density is delocalized by p_{xy} orbitals of four nearest chlorine ions. This model agrees well with the ESR data [111].

Holes trapped near impurities. The commonest examples are the so-called V^- and $[Me]^0$ centres (Me = Li, Na) in II-VI compounds, where the theory has been applied successfully (see [113] for a review). In these systems holes were trapped near impurities or vacancies. In many cases impurities can trap holes by simply changing charge state. The best known cases are mercury-like centres in alkali halide crystals. The peculiarity of these centres is that their optical excitation releases the hole back from the impurity ion. The effect of optical delocalization of the holes from mercury-like A^{2+} centres (A = Tl, In, Ga) has been observed in KCl crystals [85]. A simple explanation of this effect in terms of one-electronic states [115] is based on the idea that the charged activator ion A^{2+} strongly perturbs the occupied 3p states of at least two spheres of surrounding Cl ions. This results in either split-off from the valence band edge of local occupied states or the formation of resonant states within the valence band. The electron transition from these states to the impurity state formed by the mixture of ns A^{2+} and 3p Cl states is accompanied by formation of the hole in the valence band, or essentially by the hole transfer from impurity to surrounding anions. The holes created rapidly become self-trapped in the lattice. Theoretical calculations [116] suggested that this effect should be observable for any centres that are charged or strongly perturb their crystalline ionic environment. Before self-trapping and/or at high temperatures, the released holes are very mobile and can participate in further defect processes.

Self-trapped excitons. Self-trapping of excitons has been observed in many insulating crystals, such as alkali metal halides, quartz, rare-gas solids, alkaline earth halides, perovskite-structured halides of the $KMgF_3$ family, and other systems [3,6]. Extensive experimental studies on STE in insulators have been carried out during the last few decades (see [21,40,41,117] and references therein), and these show how self-trapping drastically alters the optical, luminescent and energy transport properties of the crystal.

For a rough evaluation of the exciton relaxation energy, one can consider the excited state of the perfect lattice, and try to find local ionic displacements that localize the exciton. Such an approach has been used by Shluger and Stefanovich [108] in their study of the STE in SiO_2 with the β -cristobalite structure. Periodic boundary conditions for the supercell Si_8O_{16} resulted in the equivalence of all the perfect lattice sites. The triplet-excited state remained delocalized for small ionic displacements. The displacement of one oxygen ion from its site by about 0.1 Å localized the hole on this oxygen. Starting from this point one can try to find the lowest minimum of the adiabatic potential energy surface (APES), which corresponds to the bound electron-hole pair and yields the luminescence energy and other spectroscopic data in agreement with experiment. (We should note that there are several other minima, corresponding to defect pairs). Clearly, within the accuracy of the calculation technique both the structure and spectroscopic parameters may be found only approximately. However, two completely different methods, employed by Fisher and co-workers [118] and in [108,119] give qualitatively very similar models for the STE in SiO_2 . Although the differences between the crystal excitation energy and the minima of the APES calculated by these workers are large, they cannot be attributed directly to the exciton relaxation energy.

The reason is twofold: first, the short-range crystal distortion, which localizes the exciton in these calculations, depends quantitatively on the shape and size of the cluster and/or boundary conditions; second, the exciton excitation energies calculated using both periodic and cluster models are much smaller than the experimental value because of the restricted basis set. This is one case where we cannot readily identify an adiabatic route from the delocalized to the localized forms; indeed, the adiabatic approximation may fail.

The alkali halides are regarded as prototype materials in which both holes and excitons self-trap. The microscopic features of exciton self-trapping processes have been studied extensively. However, the experimental determination of the model of the STE in these crystals is still far from complete. Many theoretical investigations of STE in alkali halides have been made, as reviewed in [41, 105]. First it was assumed that the STE in alkali halides consisted of a diffuse electron bound to a self-trapped hole or V_K centre, the so called $(V_K + e)$ model [120]. After the ENDOR experiments on the STE in KCl [121], which suggested asymmetry, it was shown that the $(V_K + e)$ configuration, which has D_{2h} symmetry, could be unstable [122]. It is suggested that the STE is an off-centred $(V_K + e)$, in which the D_{2h} symmetry is broken by the pseudo-Jahn-Teller interaction of the electron with the local lattice vibrations. Extensive studies of the off-centre model of the STE have been carried out by Song and Leung, using a one-electron pseudopotential extended-ion technique (see [79, 123] and references therein). In most of these calculations the hole component of the STE was treated as a frozen X_2^- molecular ion, repelling the electron, which is localized in the crystalline potential (as in an F centre) rather than due to the Coulomb interaction with the molecular core of the V_K centre.

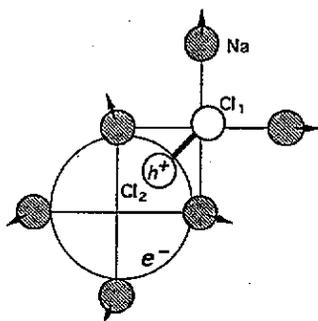


Figure 6. Off-centre model for exciton geometries in alkali halide crystals (here NaCl). The shaded circles represent the Na^+ ions, and the two open circles the Cl ions that make up a Cl_2^- ion. The charge on this molecular ion is such that one ion (labelled h^+) is roughly neutral (Cl^0) and the other is close to Cl^- . The large circle identifies what is effectively an anion vacancy containing an electron (essentially an F centre).

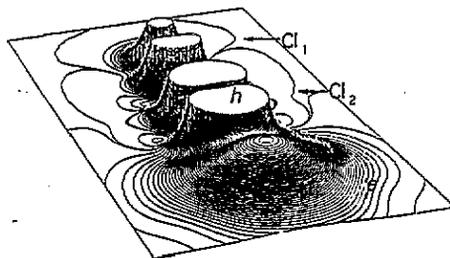


Figure 7. Spin density distribution of two unpaired electrons of the triplet STE in NaCl. This is a schematic not normalized picture. The three main features correspond to the configuration shown in figure 6. The electron is that of the nascent F centre, the hole (Cl_2) is that of the Cl ion (approximately Cl^0) moving away from its site to join with the next ion (Cl_1) on the close-packed row of halogens.

Recent *ab initio* many-electron calculations [28, 95, 96, 106, 124, 125] have supported this conclusion, and simultaneously emphasized the importance of the many-electron approach to the problem. It has been shown that an X_2^- molecular ion, displaced from the D_{2h} position (see figure 6), is polarized in such a way that the hole is mainly localized on that anion located closer to the anion vacancy (created by the axial motion of the X_2^- ion) which is trapping the electron (see figure 7, which represents the spin density distribution calculated for the STE in NaCl [125]). This points to what seems to be a common feature of the STE structure, not only in the alkali halide crystals but also in silicon dioxide and

lithium oxide [126]. As was discussed by Shluger and co-workers [127], in all these STE the electron is trapped on a lattice anion site and the hole is localized onto the anion displaced from this site.

Nevertheless a number of crucial problems remain unsolved. These concern, first, the APES for the ground triplet state of the STE (see [28, 125] for a discussion). Hartree-Fock calculations of the APES for the triplet exciton in alkali halides and SiO₂ have demonstrated that the potential energy is remarkably flat near its minima with respect to further spatial separation of the electronic and hole components of the STE. However, a rigorous location of the minimum corresponding to the STE and barrier for its decay into primary Frenkel defects in each particular case has not been determined reliably. Consequently, the models of the STE are not finally established. The APES for the singlet excited state of the crystal (singlet STE) has not been considered in detail. Electron correlation must be included to solve these problems [125]. There is possible experimental support for the view that the energy surface is flat from the observation of muon-induced fluorescence [128]. The observed luminescence occurs after the decay of the muon, at an energy not far from the normal triplet luminescence; the data are consistent with the idea that the muon stabilizes the self-trapped exciton in a minimum different from its normal one.

Second, the exciton self-trapping energy was not considered seriously. The width of the energy dispersion of a free exciton in alkali halides was regarded as roughly equal to that of the hole in the valence band [58]. This reflected the common view that the exciton self-trapping in these crystals is governed by the hole localization at the first place. The situation is unclear in oxides, where the holes do not self-trap. Calculation of the self-trapping energy for the STE in KCl using the energy cycle approach was performed in [28]. Since the quantitative characteristics of the model of the STE in this crystal are still unclear these calculations were unable to give a reliable number. However, they demonstrated that the self-trapping energy is probably more than 2.7 eV, which is larger than that for the V_K centre in this crystal (~ 1.9 eV [44]). Qualitatively the same conclusion has been drawn by Itoh and co-workers [101], on the basis of somewhat different energy cycle.

3.6.2. Optical spectra and spin resonance data. There are two main types of optical transition associated with polarons. First, there are the 'intramolecular' or 'intraionic' transitions, where the distorted and polarized host merely weakly alters a transition identifiable from some free ion (X₂⁻ molecular ion in the V_K centre). Here one may use free molecular ion data plus calculated distortions [44, 85, 129] (giving effectively the 'molecule in a crystal' approach).

Second, there are charge-transfer transitions, in which an electron moves from one site to another (or to another group of sites). These are the dominant transitions, for instance, in cation vacancy centres like V-type centres in oxides (see figure 8). The transition energy for this type of transitions is determined by polarization and distortion energy and is very sensitive to the relaxation of the surrounding lattice. In particular, the displacements—and hence the polarization potential—are different for the anion carrying the hole and for the other anions [130]. This leads to an additional splitting of the hole electronic states and affects optical absorption energies of the hole especially in the one-centre state. Note that since the optical transition is a Franck-Condon transition (the nuclei remain at their original positions) only the electronic part of lattice polarization should be taken into account in the final state (see [131] for a discussion of the Zn vacancy in ZnSe, where the simplest models are demonstrably inconsistent).

In the exciton case the optical spectra are more complicated. The STE comprises a hole, usually well localized on an ion (O⁻ in quartz or Ag²⁺ in AgCl) or molecular ion (X₂⁻,

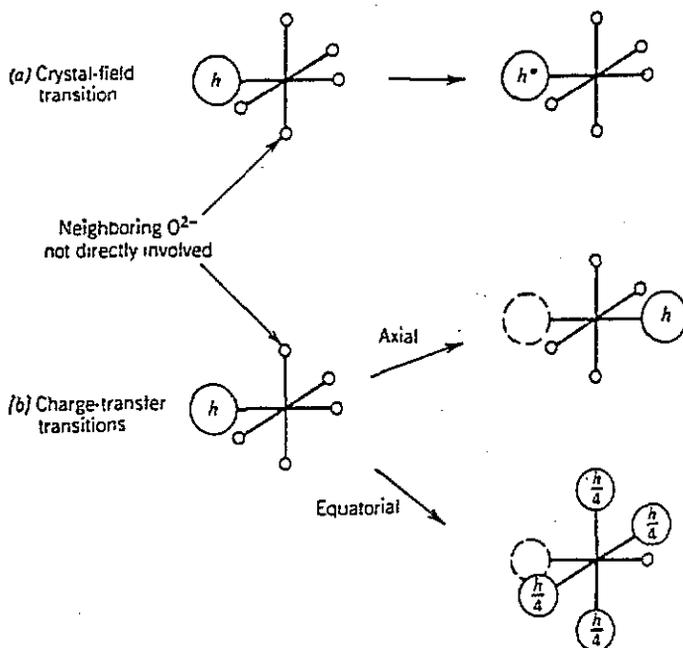


Figure 8. Optical transitions of the V-type centres in MgO. In (a), h^* indicates an excited state of O^- reached in a crystal field transition. In (b), the hole fractions on each neighbour in the excited state are shown before lattice relaxation. These charge-transfer transitions dominate the optical absorption. The equatorial transition will be split by electron exchange terms between the four oxygens. Note that h always indicates that the lowest crystal-field state of oxygen is occupied or partly occupied; h^* indicates that an excited crystal-field state is occupied.

where X is a halogen in alkali halides and alkali fluorides [41, 117]), and an electron which is much more delocalized. In some cases like, for example, in alkali halides, the electronic and the hole component of the STE are apparently spatially separated. Decomposition of the STE in these crystals can be accompanied by the formation of Frenkel defects: F and H centres [42]. Although optical absorption spectra of the STE in alkali halides and in quartz resemble the combined spectra of the defect pair qualitatively, there are considerable quantitative distinctions. These are caused by the strong electron-hole interaction and mutual perturbation of the electron and the hole components of the STE compared to the separated pair.

A helpful way to display data for a large number of crystals of the same structure is the so-called Mollwo-Ivey plot, where energies are expressed as a power of lattice spacing. This has been done [91] for the energies of the electron transitions of the STE in alkali halides and the interionic distance in the lattice as for isolated F centres [133] (see also section 15.1 of [44]). However, at least three groups of alkali halides have different Mollwo-Ivey plots. A similar categorization has been made on the basis of an analysis of the luminescent states in various alkali halides [134]. The physical nature of this grouping of all alkali halides according to the optical and luminescence properties of the STE is still unclear. The results of theoretical calculations of the electron and hole transitions in several alkali halides are summarized in [28, 135]. The agreement in all cases is satisfactory, but is not sufficient to distinguish between different (on-centre against off-centre) models of STE. However, we should note that these are most difficult calculations, which presently require the use of the ΔSCF technique. For the delocalized excited states the convergence of this method is very

poor. For the well localized excitations of the hole component of the STE the agreement with experiment is better [95, 135]. However, the energies of these transitions are also sensitive to the displacement of the X_2^- molecular ion.

For paramagnetic polarons, such as V_K centres, it is important to calculate spin resonance characteristics like the g tensor and hyperfine parameters. For the calculation of the g tensor the Stone equation [136] is widely used, derived from second-order perturbation theory (PT2) applied to the spin-orbit and Zeeman interactions of an unpaired electron orbital momenta with the magnetic field. However, for high symmetry defects, such as V_K or H centres in alkali halides, PT2 yields zero shifts of the longitudinal components of a tensor, $\Delta g_{\parallel} = g_{\parallel} - g_0$, ($g_0 = 2.0023$) because of the zero value of the relevant matrix elements between ground and all excited states. As is shown in [97–99], in this case much better agreement with experimental data can be achieved by taking into account third-order perturbation corrections (PT3). A novel technique has recently been derived by Heifets [138] which allows one to calculate g tensors for an arbitrary total electron spin of the paramagnetic defect by means of quantum chemical methods based on PT2 and PT3 corrections. This technique has been successfully applied to the V_K centre calculations in KCl [83]. The g -tensor calculations for the hole trapped in the $[Li]^0$ -centre in MgO [82] demonstrated that in this case, unlike the 'molecular' type V_K centre, all optical and ESR active transitions depend very strongly on the values of the ion displacements. Therefore good agreement with experiment of both optical transition energies and g tensor indicates that the geometry of the hole centre has been determined reliably.

Hyperfine parameters are even more crucial, particularly when the nuclei on which the unpaired spin resides have naturally abundant magnetic isotopes. In this case one can make estimates of the orbital composition of the polaron electronic wavefunction, i.e. the relative s and p character of the wavefunction on each nucleus. The relationship between hyperfine parameters and the geometry of point defects in non-metallic solids has been examined in ch. 13 of [44] (see also [139]). The compact configuration of the STE in alkali halides, where the centre of the electron distribution is located only about 1.7 \AA from the hole nucleus (see figures 6 and 7), suggests that contributions of both unpaired electrons should be taken into account in calculating the hyperfine interaction for both ions of the X_2^- molecular ion. Reliable many-electron calculations of the hyperfine parameters have been performed so far only for the STE in quartz [118].

3.6.3. Entropy of formation and vibrational properties. Study of vibrational properties of small polarons is important for gaining an understanding of their structure and localization processes as well as thermodynamical characteristics of materials. Local modes [140], as well as the optical linewidth, the broadening of spin resonance lines, spin-lattice relaxation and Raman data [141], have all been exploited and tested against theory. The calculated and experimental values for the frequencies of the stretching vibration of X_2^- molecular ions in V_K centre and STE in several alkali metal halides and alkaline earth fluorides are collected in [28, 140]. Calculations presented in [22] determine the local lattice dynamics of a self-trapped exciton in NaI and KI, its relaxation law and the shape of the hot emission spectra.

Lattice distortions and spectroscopic characteristics discussed above are usually calculated at constant lattice parameter. Thus the lattice does not expand or contract because of the presence of the polaron, although the ion displacements are calculated at long range. So these are essentially internal properties at constant volume (the distinction between constant volume and constant lattice parameter is negligible for our purposes). This point was argued in detail by Gillan [142] and reviewed recently by Catlow and

co-workers and Harding [143,144]. Its recognition is most important for the calculation of defect formation energies and diffusion parameters because these values are usually compared with polaron parameters obtained by fitting to experimental conductivity or diffusion data. These parameters are enthalpies since the experiments are performed at constant pressure. The relationship between the constant-pressure parameters (enthalpy and entropy of formation) and constant-volume parameters (internal energy and entropy at constant volume) was discussed in several papers (see, for example, [143,144]). The formation energy at constant volume and zero temperature is the main energy parameter calculated using the static approach.

The entropy of formation of a point defect or polaron at constant volume $\Delta s = S$ (defect crystal) $-S$ (perfect crystal) in the harmonic approximation in the high-temperature limit may be written in the form [144]

$$\Delta s = -k_B \ln \frac{\prod_{i=1}^{3N'} \omega'_i}{\prod_{i=1}^{3N} \omega_i} + 3k_B(N' - N)(1 - \hbar/k_B T) \quad (10)$$

where ω' and ω are the lattice frequencies for the defective and perfect lattice, respectively, and k_B is the Boltzmann constant. Evaluation of Δs thus requires the summation over all these modes in the crystal. It should be noted that a calculation of only a few lattice vibrations localized around the defect and ignoring the rest gives wrong values for the entropies of formation of point defects. Existing methods for the calculation of the thermodynamical parameters of point defects in ionic solids were discussed by Harding [144].

The vibrational entropy associated with thermal generation of electron-hole pairs is of considerable significance for an understanding of the anomalous thermal properties of uranium dioxide at high temperatures, as was emphasized by MacInnes [145]. In particular, in most materials the thermal conductivity decreases monotonically with temperature; in UO_2 , though, it goes through a pronounced minimum at about 2000 K, and increases by about 60% of the minimum value before the melting point is reached at 3210 K [146].

As has been suggested in several papers (see, for example, [147-149]) this is because of the existence of an ambipolar contribution; there is transport of energy down the thermal gradient by the creation of electron-hole pairs at high temperature and their recombination at low temperature. This electronic contribution was considered using the small polaron model. According to [147-149] the electron and hole small polarons make a substantial contribution to certain properties—thermal conductivity and specific heat—at temperatures near the melting point. These properties, in turn, are needed in assessing the safety cases for several hypothetical reactor incidents.

Quantitatively, the early study of Harding and co-workers [147] was one of the first to make a serious attempt at entropy calculations for small polarons within the shell model. Recent calculations by Harding and Martin [149], data from Hampton and co-workers [148], and a molecular dynamics study of the thermal conductivity of UO_2 by Lindan and Gillan [150], confirmed the importance of the polaron contribution in a heat conduction mechanism in UO_2 .

3.6.4. Pressure dependence. The atomic positions involve a balance between several types of force: short-range repulsion, polarization and intramolecular bonding. Cade and co-workers [86] showed that, as the pressure was increased, there was a striking change to be expected in the V_K centre optical transition for KCl. This should occur at pressures that should be accessible. The defect energy is also sensitive to any decrease of a_0 , although

this did not affect qualitatively the stability of the hole. Since the width of the valence band increases as the lattice constant becomes smaller, this also affects the self-trapping energy.

Measurements of the pressure dependence of dielectric constants and of polaron transport in uranium dioxide give additional information, which can be used to separate the binding and motion energy contributions to the observed Arrhenius energies in polaron transport. The point is that the number of carriers depends mainly on ϵ_0 , which determine the binding of holes on U ions to oxygen interstitials, whereas the hole mobility depends on $\epsilon_\infty^{-1} - \epsilon_0^{-1}$.

3.6.5. Elastic properties. The volume change and the related elastic dipole tensor [151, 152] have been calculated in several ways, and compared with experiment [153]. Agreement is not good, perhaps because the result is sensitive to details of the precise potentials assumed for the molecular ion's interaction with its host (a point also suggested by relations among the hopping energies for the several possible transitions in other systems [88]). The displacement field has also been monitored by spin resonance, and more recently the potential of neutron scatter in such studies has been assessed [154].

4. Small polaron diffusion

4.1. Basic ideas

In the standard approach to ionic migration, a key energy is that of a 'saddle point' relative to the initial state. In simple cases, where the initial and final states are symmetrical, and where there are no complications like change of charge state during the jump process, this classical saddle point is obtained as follows. The moving ion is placed at the mid-point of its path, and held there whilst the other ions are relaxed (both shells and cores if the shell model is used). The energy of this saddle point relative to the initial state can be related to the dynamics of classical diffusion. In small polaron migration, there is a quantum component too.

The analogue of the saddle point is the 'coincidence site' (see figure 9). This is the lowest-energy distortion (in practice the configuration of the cores is what is defined, for the shells are treated separately) which is such that the carrier (which could be ion, like a proton, but is normally a hole or an electron) would have the same energy if localized at the initial or the final site. There may still be a barrier in the adiabatic energy surface between the two sites, but the particle is able to tunnel between them for this geometry.

Suppose for this coincidence geometry the tunnel frequency is ν . We anticipate that the rate will be proportional to the probability that the energies associated with the two sites will be equal to within $\hbar\nu$, and hence to $\hbar\nu \exp(-W/k_B T)$ at higher temperatures. Since the rate, once the energies are equal to this accuracy, is then proportional to ν (albeit with an upper bound related to phonon frequencies) an overall rate proportional to $\nu^2 \exp(-W/k_B T)$ is expected.

This is shown by fuller calculations [9, 10, 76] by explicit summation of the component transition probabilities over vibronic states, plus thermal averaging over initial states and summing over final vibrational states. This fuller calculation can only be carried through with some quite strong assumptions (normally an harmonic lattice and single vibration frequency), so there are undoubtedly deeper questions remaining.

Clearly the saddle-point energy for classical diffusion can be calculated by the Mott-Littleton method. What Norgett and Stoneham [88] showed was that the coincidence site energy for small polaron motion could also be calculated by this method.

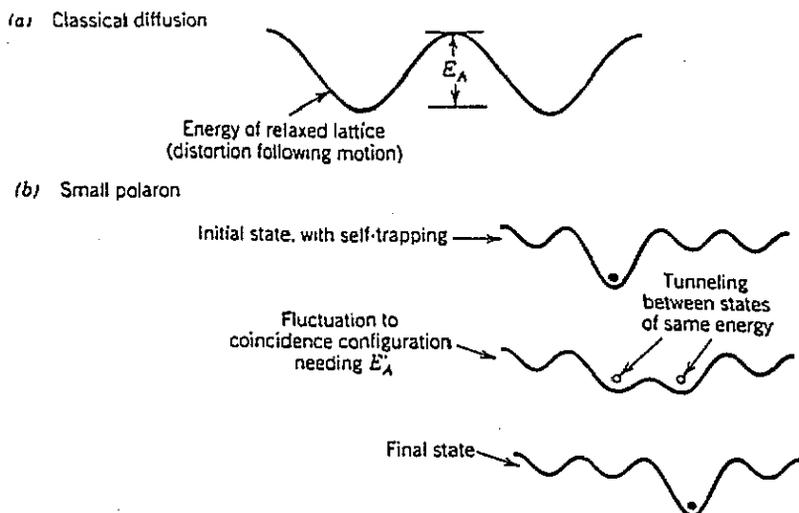


Figure 9. (a) Classical diffusion and (b) small polaron motion. In (a) the energy surface shown is that in which the lattice relaxes around the moving particle at each state, and E_A is the activation energy for motion. In (b) there is a thermal fluctuation (requiring energy E'_A) from the initial self-trapped state to the coincidence configuration, in which tunnelling can occur between states of the same energy on two adjacent sites.

4.2. Working approximations

4.2.1. Charge redistribution during motion. The Mott–Littleton method, plus a knowledge of the key interatomic potentials, is still not quite sufficient. There are decisions to be taken about the response of host lattice electrons and cores and about the disposition of charge at various stages of the coupled carrier–lattice motion. The details depend on the system under study and, at least in principle, can be obtained from quantum chemical calculations.

Consider first a transition metal oxide (essentially a system in which the hole is localized on one site). Initially there is a $3+$ ion on site 1 and a $2+$ ion on site 2. An electron jumps from site 2 to site 1 (or the hole from 1 to 2). Let us first use the language of the classical shell model [155]. We shall assume that the electronic polarization can follow the motion of the polaron (hole), so that the shells of the ions are always in their optimum sites for a given hole position. The positions of the ion cores, therefore, must be such that the hole has the same energy whichever of the two sites is occupied (in the harmonic limit this actually means that the energy does not change even if the hole were transferred gradually; the shell model is not fully harmonic because of the short range forces, however). The sequence of steps used is this: (i) find the relaxed (shells and cores) initial state (E' , x' say). (ii) Find the relaxed (shells and cores) state with both initial and final states equally occupied (E'' , x'' say). Note that this needs assumptions about whether the half hole is on the shells or the cores, and note too that the half hole on one site does not interact with its other half on the other site. (iii) Decide whether or not the transfer is rapid.

This third point needs more careful consideration. If the hole transfer between two sites takes place adiabatically, i.e. the hole follows the nuclei all the time, the transition state for the hole transfer corresponds to the state in which the hole is equally shared between two sites. Whether or not the transition is adiabatic should be determined by the value of the transfer matrix element between two sites and the effectiveness of the vibrational relaxation process.

4.2.2. *Adiabatic or non-adiabatic?* The approximate quantum mechanical model of electron transfer in a polar media, including the dynamics of the reaction coordinates relaxation, has been presented in [156]. It suggests an 'adiabaticity' parameter G , defined as

$$G = 2\pi |T|^2 / \hbar\omega_c E_R \quad (11)$$

where T is the electron transition matrix element between the initial and the final states, $1/\omega_c$ is the characteristic vibrational relaxation time of the reaction coordinate, and E_R is the system reorganization energy. The reaction is considered to be adiabatic ($G \gg 1$) or non-adiabatic ($G \ll 1$) depending on the size of G ; G may be qualitatively interpreted as the ratio between the time spent by the 'reaction coordinate' in the barrier region and the time taken by the one electron transition between the initial and the final states. In order to estimate the value of G we need to calculate T and E_R for hole transfer between the nearest anion sites. According to the conventional definition E_R may be calculated as the difference between the energy at the adiabatic potential energy minimum, corresponding to the hole localization in its initial state, and the final hole state, but with the crystal relaxation remaining the same as in the first case. The calculation of T is much less straightforward [157]. An approximate way of estimating T for the case of the resonant hole transfer in a crystal was discussed in [82]. If the value of G for the polaron transition between the two sites is much greater than 1, one resonant jump of the electron (hole) takes place much faster than the decay of the resonant state for electron (hole) transfer due to the relaxation process of the local vibrations. Hence the electron will be able to make many transitions between the two sites and the loss of the phase coherence between these states becomes an important question. As shown in [158], the reaction rate at this limit is similar to what one would obtain by assuming that the hole followed the nuclei adiabatically. If so, then the adiabatic barrier height (not yet what is observed in an Arrhenius plot!) is $E'' - E'$. If not, i.e. slow transfer, keep the cores fixed at x'' but put the hole solely on the original site and allow shells alone to relax. This state has higher energy still, say $E'' + e''$; the magnitude of the barrier (in the same sense as above) is $E'' + e'' - E'$.

It seems likely that the e'' term should be ignored, in that the transfer integrals for the hole band in oxides seem to be bigger than the longitudinal optic phonon energy (see for example discussion in [51]). If so, then in crystals where both electrons and holes are on the same sublattice (e.g. MnO, FeO, CoO, NiO, UO₂) it can be shown that *the electron mobility and the hole mobility will be the same to lowest order*. This is important in the ambipolar contribution to thermal conductivity in UO₂, where one wishes to know its dependence on stoichiometry (i.e. the O/U ratio).

Consider next a halide in which the V_K centre moves. The basic initial defect involves a hole shared on two sites, 1 and C (the central site), and this transfers to a hole shared on the two sites, C and 2. We may assume again that the shells respond rapidly. However, we might identify at least two types of intermediate state. One type corresponds to the case when the carrier tunnels to what is in effect the final charge distribution ($G \leq 1$). The other type assumes a molecular ion is formed as an intermediate state ($G \gg 1$), with charges on sites (1, C, 2) of $(-A, [A - 1], -A)$, with A usually taken to be the proton charge (this value is also uncertain in the absence of additional calculations). Which type is correct needs self-consistent calculations outside the Mott-Littleton framework. Good agreement with experiment has been found for the V_K centre in KCl [83] and Al₂O₃ [75] using the quantum chemical embedded molecular cluster approach, but the experiments themselves still leave much to be desired as a test of the prediction (see discussions in [75, 83, 159]).

4.2.3. *Interatomic potentials.* A further technical issue in both approaches is that it is not clear that the short-range repulsive forces should be independent of charge state. Of the several theoretical studies using pair potentials and aimed at estimating the activation energy of V_K centre reorientations in cubic lattices [87, 88, 160], the most comprehensive were concerned with the mechanism of this process in alkaline earth fluorides [88] and caesium halides [87]. Here, a check of sensitivity to the interatomic potentials showed that modest changes of short-range potential with ionic charge state affected the relative activation energies for jumps with different angles of reorientation. Thus one potential might indicate the 90° jump had lowest energy, another potential favouring the 180° jump. Yet for oxides, studies of charge state stability [161] show that keeping the same repulsive forces for both charges is a good first-order approximation. However, the calculated adiabatic barriers (which are smaller energies and so more sensitive to details) for the hole jumps in MgO are unreasonably large [97]. These issues are being addressed by the current state of electronic structure plus Mott–Littleton methods, as discussed in [28, 94, 82].

4.2.4. *Polarization and electron correlation effects.* Recent quantum chemical calculations [83] show that the activation energy required for V_K centre reorientation in KCl includes what can be described as the excitation of translational and rotational modes, and is strongly affected by a change in the crystal polarization energy. The polarization energy itself, near the coincidence configuration, is 0.2 eV greater than that for the equilibrium V_K geometry, simply because the hole is more strongly localized onto a single site in the intermediate state (see [54, 74] for general discussion of this point). For KCl, the repolarization energy (i.e. the difference of polarization energies at the coincidence site and the equilibrium configurations) *reduces* the reorientation adiabatic barrier by about one third. This is quite different from the one-centre hole jumps in MgO [82], where the hole is delocalized over two nearest oxygens at the coincidence site for the hole diffusion. The polarization of the crystal lattice at the coincidence state is then smaller than for the equilibrium one-centre polaron state, so the repolarization energy *raises* the barrier height in MgO.

In both the Mott–Littleton-type atomistic simulation [97] and the quantum chemical Hartree–Fock [82] calculations of the barrier for the one-centre hole jumps in MgO the intraionic part of the electron correlation was effectively included in a semi-empirical manner through the electronic part of the lattice polarization and the experimental values of the ionic polarizabilities used in the calculation. The adiabatic barrier to hole transfer is given by the energy difference between the state in which the hole is completely localized on one oxygen centre and that in which it is equally distributed over the two adjacent oxygen sites. Within this model the barrier results from the larger polarization of the surrounding lattice in the one-centre configuration. However, in order to take into account the difference in the electron correlation and in the kinetic energy of the hole in the two states the wavefunction of the hole in both states should have much more variational freedom. In particular, the barrier is found to be 1.05 eV at the *ab initio* Hartree–Fock level, while inclusion of the configuration interaction (CI) technique for the valence electrons reduces this value to 0.23 eV [82]. Within the CI method the wavefunction of the system is constructed as a linear combination of Slater determinants corresponding to all possible single and double electronic excitations from the ground state of the system. At the transition state, the local symmetry of the system is D_{2h} and the main excitation involves the promotion of an electron from the doubly occupied Σ_g orbital to the singly occupied Σ_u , and of a second electron to an unoccupied orbital. In the case of the localized hole state, the electronic configurations with the largest coefficients in the CI expression do not involve excitations to or from the singly occupied orbital. Hence the majority of the correlation energy in the one-centre state is due to electrons in the

doubly filled valence orbitals. Consequently, at the barrier point to hole migration, the hole is distributed over several orbitals in the CI expression, giving rise to an extra contribution to the kinetic and correlation energies.

4.2.5. Exciton motion and decomposition. In the exciton case the joint motion of an electron and a hole has to be considered. Because of the high symmetry of the lattice (especially in alkali metal halides and Li_2O) the adiabatic potential energy surface of the lowest state of the exciton may have two or more equivalent minima near the same anion site, separated by some energy barrier. (In the alkali halides the X_2^- molecular ion in the off-centre configuration of the STE may be displaced to the left or to the right from the anion site as shown in figure 6). As has been pointed out by Chen and Song [162], in the framework of the off-centre model of the STE, the mechanism for its diffusion in alkali halides may be considered as comprising two steps: (i) a joint motion of the electron and the hole along the (110) axis; (ii) rotation of the hole component of the STE which changes its direction by 60° (see figure 10); the process strongly resembles the 60° reorientation of the V_K centre. This has been studied within the many-electron approach for the STE in NaCl [125].

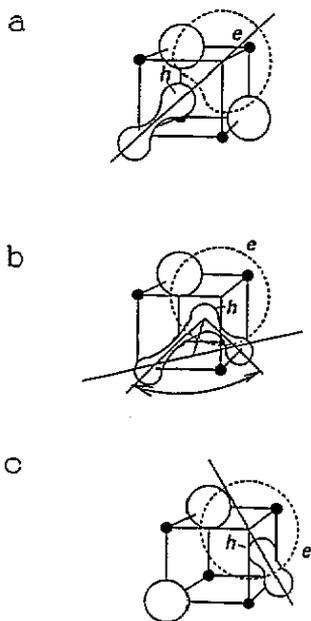


Figure 10. A schematic presentation of the process of 60° reorientation of the STE in NaCl. (a) The initial configuration (see also figures 6 and 7). (b) The saddle point. (c) The final configuration.

Exciton decomposition into a pair of primary defects is an example of a chemical reaction in the solid state. The evaluation of the barrier for this process is a formidable task. Although the crystal relaxation energies are usually large, the barriers for the processes of the STE decay into defects, for diffusion of the STE and for migration of the hole component of the primary defect pair, rarely exceed 0.1 eV [21, 40, 41]. Such an accuracy is hard to achieve reliably, even for simple defects, within even the best current theoretical methods (see [28] for a discussion).

4.3. Comparison with experimental data

Experimentally, there are several distinct measures of activation energies. Each is usually fitted to an Arrhenius or altered Arrhenius expression locally, and we must ask what

precautions are needed to relate to the Arrhenius energy the activation energy calculated. (i) Small polaron theory does not predict simply Arrhenius rates for hopping, but a more complex form (see [88] for analytical and numerical expressions) which has a $T^{-1/2}$ prefactor in some limits (T large). At low T the apparent Arrhenius energy should be very small, even for quite large activation energies. (ii) The Nernst-Einstein relation between mobility and diffusion constant brings in another factor T in some situations, dependent on what is measured, and this must be allowed for. (iii) There will often also be trapping energies in the Arrhenius energy, and these must be included. In some cases (e.g. O interstitials in UO_2) a trap may accommodate two holes, and these defects will give two trap energies, depending on whether it is the first or second hole removed. (iv) There may be several distinct jumps (as for V_K centres in fluorites). Note that reorientation can be spectroscopically detected by decay of polarization with time, whereas linear motion (180° jumps) can be detected only by decay of intensity.

There is a hidden assumption that the process being considered is indeed thermally activated, i.e. an Arrhenius expression in which a physical meaning can be given to the activation energy [163]. This is not always the case, especially for systems that have (or appear to have) small activation energies. In these cases, one- or two-phonon processes may be dominant, and the correct dependence is then often a power of T . If the rate varies as T^n , then the apparent activation energy at temperature T is nkT ; thus with $n = 7$ for two-phonon processes [76], at room temperature the activation energy would appear to be about 0.16 eV. Experimentally, it is very hard to decide between activated and power-law dependences without data over a wide range of temperatures.

4.4. Special cases

Whereas the halides are understood reasonably well (especially qualitatively), the oxide systems have caused considerable controversy, not least because of the experimental difficulties faced in avoiding problems of impurities or near-surface non-stoichiometry. The position for alkali metal doped oxides is much clearer, with sensible (rather than precise) accord of theory with experiment for both binding and activation energies. For free polarons, the experimental position is less clear: for MnO there appears to be a small polaron [164]; for FeO again a small polaron [165, 166] with its motion strongly influenced by defect clusters [166]; CoO probably has a small polaron [164] too. NiO is especially interesting, apparently having a small polaron, but with a large apparent activation energy [164]; a surface contribution must be eliminated in experiment [164, 167].

The result for NiO raises an interesting possibility [167, 168], namely that the motion is by excitation from a small polaron form into the large polaron form. Precise theoretical estimates need values for both the localization energy and for the crystal-field terms. We note that transitions may occur for coincidences corresponding to more than one final state because of the several crystal field levels (see below), and these uncertainties are sufficiently large to make a clear decision almost impossible. Nevertheless, this small-to-large excitation mechanism seems to be one of the most sensible explanations of the experiments in NiO. Thermally induced small-large transitions could also be important in the very different system MgO, where only one or two phonons would be needed to change the state.

The thermal and electronic conductivities of non-stoichiometric oxides like UO_2 present one further problem, namely the high jump rates that are needed to understand some experiments. High prefactors would not be a problem (though entropies of motion have yet to be calculated), but there are difficulties when the hopping rate itself appears faster than the maximum phonon frequency, since that is an upper bound on the average rate that the coincidence site can be reached. That problem is not resolved. One possibility concerns

the multiplet structure from the crystal-field splitting. For many transition metal ions, the partly filled shell of d- or f-electrons leads to low-lying levels, which may be 0.1 eV or less above the ground state. This can help in two ways: there are more accessible coincidence states (e.g. the initial state may correspond to one of these low-lying levels, the final state to another) and there is also a greater possibility of multiple jumps. However, why the rates are high may have yet another explanation. In oxides the level of non-stoichiometry is significant (one charged defect every 100–1000 molecular units is common). These charged defects have two effects. One effect is to make certain sites inaccessible, hence the Heikes formula [169], which gives a rate proportional to $c(1 - c)$ for fractional concentration c . Another is to give random electric fields, which can be very large (up to 10^8 V cm⁻¹ at these concentrations [170]), so that the jumps may be forced by these fields, rather than simply the thermal motion a single polaron would have in an otherwise perfect crystal.

A further interesting situation exists for a completely different system: the excess electron in liquid water provides a classical example of a small 'dielectric' electron polaron. The hydrated electron has been treated using various quantum simulation techniques [62, 65, 171]†. The experimental estimate for the diffusion coefficient of the hydrated electron (from the conductivity via the Nernst–Einstein equation) shows that it is about 2.5 times larger than that for negative halide ions Cl⁻ or Br⁻ in aqueous solutions (see, for example, [172]). Recent quantum molecular dynamics simulations of the hydrated electron have shown that to a good approximation the excess electron wavefunction *adiabatically* follows the fluctuations in the electron–water potential caused by thermal motion of surrounding water molecules [173], so the high mobility of electrons relative to classical ions comes from the absence of inertial effects [172]. The coupling between solvent dynamics and that of the solute should be rather different in the inertial and adiabatic cases. As was shown by Schnitker and Rossky [173], the electron is capable of following the high-frequency solvent polarization fluctuations associated primarily with the rapid solvent vibrational motions, whereas the solvent, in its turn, responds to a substantially shifted electrostatic source (diffusive electron) also on short timescales. However, recent simulation [47] demonstrated clearly that the enhancement of the electronic diffusion rate in the quantum simulations over the rate exhibited by classical ions can be attributed only partly to the adiabatic dynamics of the excess electron *per se*, although it is essential. The specific features of the solute–solvent interaction potential are also essential to the description of the mobility of the hydrated electron. These features include, first, the relatively weak forces that derive from the variation of the quantum kinetic energy with the spatial confinement of the excess electron. Note that very similar problems are characteristic for the simulation of polaron localization in crystalline materials within the static approach (see section 3.2 for a discussion).

4.5. Muons as small polarons

That light interstitial atoms in metals behave as small polarons in some respects was recognized several years ago [76]. The description of these systems needed concepts and analysis beyond the standard polaron theories (e.g. moving beyond the Condon approximation), and indeed hydrogen in metals proved to be one of the first systems for

† Several different models of solvation were proposed. In particular, Ovchinnikov has shown that the shape and the thermal behaviour of the optical absorption spectra of the hydrated electron in water can be reasonably understood if the excess electron is localized on the water molecule situated in the centre of a cavity. However, since the electronic affinity of the water molecule is most probably very small (if any) this model requires much more extensive many-electron calculations.

which detailed realistic models were attempted [36,163]. The subsequent experiments using muons pointed to new features again. Not only could the incoherent hopping regime be studied, but the coherent motion of small polarons was also accessible. Moreover, the electron gas in metals had dramatic effects on muon dynamics in this coherent regime [174]. For our purposes, it is muon behaviour in non-metals that is of more importance, though we shall confine our comments to an illustration of the range and variety of polaron behaviour once one goes beyond the standard idealized models. Most of the studies are for muonium, i.e. a muon with an associated electron. A general review is given by Cox [175].

4.5.1. Metastable states. Muons are slowed rapidly to thermal or near-thermal energies, certainly on timescales short compared with the instrumental resolution of nanoseconds. It is sensible to assume that the muon will quickly reach the lowest-energy relaxed state, and that it is this state that is seen prior to muon decay after a few microseconds. There are several clear exceptions to that argument. First, in the cubic semiconductors (Si, Ge and diamond) the metastable (tetrahedral site) 'normal' muonium is formed as well as the stable (bond centre site) 'anomalous' muonium, and interconversion is thermally activated. Second, in the ionic semiconductor CuCl, muonium exists in two forms at the same tetrahedral site (that with four Cu neighbours): Cu(I) is metastable and mobile (locally: there is no long-range diffusion), and Cu(II) is quasi-stationary below 30 K, both on the timescale of the muon lifetime [176]. It is not clear whether the difference is vibronic, or whether electronic excitation is involved, or whether it corresponds to what one might describe as delayed self-trapping ([177] discussed some of the ways in which delayed self-trapping might occur; note too [30] for the STE). Third, in KBr there is an anomalous fluorescence induced by muons with an efficiency of perhaps 25% at the lowest temperatures [128]. This fluorescence occurs after muon decay and appears to be related to, but distinct from, the spin-forbidden luminescence from the ground state of the self-trapped exciton. One possibility is that the muon has stabilized the exciton into a distinct metastable state on the lowest-energy surface, a possibility consistent with much recent evidence that this lowest adiabatic energy surface is relatively flat and that different routes to it lead to apparently different behaviour.

4.5.2. Mobility and local environment. Experimentally, one of the key quantities is a relaxation function. This usually contains two pieces of information: a mean-square field from magnetic dipole interactions with nearby nuclei, and a correlation time associated with dynamic behaviour such as diffusion. The dipolar interactions and their dependence on the direction of any applied field can be used to identify the site the muon occupies. One fascinating experiment [178] shows that muonium in KCl has a diffusion rate falling as the cube of T at lower temperatures. This leads to some puzzles not yet resolved. The natural interpretation [179] is to say that the muon is moving coherently as a small polaron, and that there is deformation-potential scattering by acoustic phonons†. However, this would yield another problem [183]. If the polaron is moving coherently over N sites between such scattering events (and these alone lead incoherence in the wavefunction) then the mean-square field should be reduced by a factor N [54,184], which is not the case.

† The same conclusion may be reached far more easily [180] by calculating the standard deformation-potential scattering. This is given by Kittel [181] for large polarons; the same formula holds unaltered for coherently moving small polarons, though the temperature range is different, and this affects integrals over phonon occupation numbers. This scatter time can then be inserted in the standard expression for a small polaron in the band regime, with well defined wavevector [182]. The cubic dependence on temperature appears to correspond to that observed, though other problems remain.

5. Conclusions

Our first observation must be how widespread the application of the small polaron concept is. The range of materials that show features characteristic of small polarons is very wide; indeed, we have not discussed important cases like borides, or more exotic materials. Partly the range stems from links of polaron ideas to conventional defect issues, where lattice deformation and polarization is a crucial component of defect processes and spectroscopy. The lattice relaxation which drives self-trapping is similar to the lattice relaxation which stabilizes a range of charge states, which determines optical spectra, and which contributes to characteristic activation energies. The link is at its clearest when a defect might be regarded as a small polaron trapped by an impurity (such as a self-trapped hole bound to an Na ion in CsI). Indeed, the interactions of small polarons with defects, or with other small polarons, are especially important in polaron dynamics at finite concentrations, as in non-stoichiometric solids. But, just as the small polaron ideas give a new way of looking at certain defect states, so do defect ideas point to small polaron ideas which were not evident in Landau's original paper. The electronic excited states of self-trapped excitons (again not discussed in any detail in this review), and especially the variety according to whether it is the electron or hole (or both) that is excited indicates an important area of spectroscopy. Trapped small polarons (like the V^- centre in MgO, where a hole is localized on an oxygen next to a cation vacancy) have contrasting forms of excitation, too, both charge transfer (the hole moving to other oxygens) and electronic excitation of the oxygen ion itself.

This leads to a second point, and indeed to the reason for this survey. Many workers regarded (and may still regard) small polarons as a simple extrapolation of large polarons. Their theories use single phonon frequencies with couplings appropriate for long wavelengths, and with little or no attempt to be system-specific. Certainly significant qualitative results can be obtained this way, but it is hard to relate most of them directly to the recent range of quantitative experiments, and such theories are of little help in unravelling the complex dynamical behaviour of many systems. Quantitative modelling has been very successful, now exploiting quantum chemistry alongside accurate interatomic potentials. There are still technical problems, of course, partly because the energies that are needed are relatively small. The momentum of polaron studies comes from their importance in defect processes. It seems to us that the areas which will attract most attention relate to polaron dynamics: the self-trapping step, their motion (whether coherent or incoherent), and the non-adiabatic transitions amongst electronic excited states.

The third point is more general: why do small polarons matter? Are they a mere scientific curiosity? In the halides, the technological impact is present but not dominant: there are links to the understanding of the photographic process for silver halides; there are polaron aspects to the operation of x-ray phosphors like CsI:Na; the sputtering and selective desorption processes have associations with small polaron processes. It is to the oxides that one turns to see great practical significance, and especially the non-stoichiometric oxides. For these, discussions of sensor operation or of catalytic behaviour will normally involve small polaron concepts. Perhaps the clearest example, though, concerns the thermal properties of urania at high temperatures, where the specific heat and thermal conductivity are important parameters in safety cases for hypothetical reactor incidents. Both these properties are dominated by small polaron behaviour at temperatures near to the melting temperature. Such conditions are extremely difficult experimentally, so the case of urania reinforces the point made above: good quantitative modelling is a vital complement to experiment.

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