

Basic theory and phenomenology of polarons

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Polarons are defined and discussed at an introductory, conceptual level. The important subcategories of polarons—large polarons, small polarons, and bipolarons—are considered in turn, along with the basic formulas and qualitative behaviors. Properties that affect electrical transport are emphasized.

I. Introduction

In a typical covalently-bonded crystal (such as typical Group IV or III-V semiconductors), electrons and holes can be characterized to an excellent approximation by assuming that they move through a crystal whose atoms are frozen into place. The electrons and holes can scatter off phonons, of course, but when no phonons are present (say, at very low temperature), all ionic displacement is ignored in describing electron and hole transport and properties.

This approach is inadequate in ionic or highly polar crystals (such as many II-VI semiconductors, alkali halides, oxides, and others), where the Coulomb interaction between a conduction electron and the lattice ions results in a strong electron-phonon coupling. In this case, even with no *real* phonons present, the electron is always surrounded by a cloud of *virtual* phonons. The cloud of virtual phonons corresponds physically to the electron pulling nearby positive ions towards it and pushing nearby negative ions away. The electron and its virtual phonons, taken together, can be treated as a new composite particle, called a *polaron*. (In particular, the above describes an *electron polaron*; the *hole polaron* is defined analogously. For brevity, this paper will generally discuss only electron polarons, and it will be understood that hole polarons are analogous.)

The concept of a polaron was set forth by Landau in 1933 [1,2]. The many-body quantum theory describing a polaron proved difficult to solve, but progress was made steadily over the following decades, particularly using the newly-developed tools of quantum field theory. Even today, there is ongoing research regarding the theory of polarons, including the basic theory, but also their behavior in more specialized situations such as high-temperature superconductors, quasi-two dimensional systems, and in magnetic fields.

Conventional polarons, the subject of this paper, result from the interaction of electrons with longitudinal-optical (LO) phonons. It is noted for completeness that there are a number of polaron-type quasiparticles that result from other interactions, such as a spin polaron (electron interacting with atomic magnetic moments) [1,3], a piezopolaron (electron interacting with acoustic phonons), and others [1].

II. Large polarons

In many materials, the radius of a polaron is much larger than the lattice constant of the material. In this case, the polaron is called a *large polaron* (another term is *Fröhlich polaron*). The properties of such a polaron are parameterized primarily by a unitless number called the *Fröhlich coupling constant*, denoted α , defined by [1]

$$\alpha = \frac{e^2}{\hbar c} \sqrt{\frac{m_b c^2}{2\hbar\omega_{LO}}} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right), \quad (1)$$

where ϵ_0 is the static dielectric constant, ϵ_∞ is the high-frequency dielectric constant, m_b is the effective mass given by the band structure (i.e., not adjusted for polaronic effects), and ω_{LO} is the LO-phonon angular frequency. The parameter α is approximately twice the total number of phonons in the phonon cloud of a given electron or hole [4], and therefore polaronic effects are likely to start to become significant when α becomes order-unity or larger. In real crystals,

measured values of α are in the range 0.02-0.2 for common III-V semiconductors, up to 0.3-0.5 in II-VI materials, typically 2-4 in alkali halides, and as high as 4.5 in the perovskite SrTiO₃ [1].

The effective mass of a polaron is larger than the mass of the underlying electron. Loosely speaking, the electron must drag the lattice distortion with it as it moves, creating a larger inertia. There is no known exact formula describing the mass increase, but one approximation due to Richard Feynman gives [1]:

$$m^* \approx m_b (1 + \alpha/6) \text{ (for } \alpha \ll 1), \quad m^* \approx m_b (0.02\alpha^4) \text{ (for } \alpha \gg 1), \quad (2)$$

The mobility of a large polaron is often limited (at least in certain temperature ranges) by scattering due to (real) optical phonons, as a result of the strong electron-optical-phonon coupling in these materials. The number of (real) optical phonons in the material is proportional to $(\exp(\theta/T)-1)^{-1}$, where T is the temperature and $\theta = \hbar\omega_{LO}/k_B$ is the crystal's Debye temperature; therefore, the mobility is proportional to $(\exp(\theta/T)-1)$ [1,4]. More precisely, the mobility equals $F(\alpha) \exp(\theta/T)$, where F is a certain theoretically-predicted function [1,4]. This behavior is indeed seen in some polaronic materials, such as high-purity AgBr [5].

Large polarons have optical signatures in the THz frequency range (the frequency range where the photon frequency is comparable to ω_{LO}). For example, in a polaron, the electron sits in a (self-induced) potential well. A photon can excite the electron into a higher-energy state within that well, and this gives rise to an absorption peak [1].

III. Small polarons

In a polaron, the electron sits in a potential well resulting from the ionic displacements it created. In some materials, the shape and strength of this potential well is such that the electron can be confined to a volume of approximately one unit cell or less. In this case, the polaron is called a *small polaron*. A proper theoretical analysis of a small polaron requires *ab initio*

techniques that account for the motion of each atom in the few unit cells nearest the electron; nevertheless a good deal can be said about their general properties and behavior.

The transport of small polarons is generally via thermally-activated hopping. In particular, under certain approximations, the mobility has an Arrhenius-like dependence [1]:

$$\mu_{\text{drift}} \propto T^{-1} \exp(-W_{\text{H}}/k_{\text{B}}T), \quad \mu_{\text{Hall}} \propto T^{-1/2} \exp(-W_{\text{H}}/3k_{\text{B}}T), \quad (3)$$

where W_{H} is half the polaron binding energy. (The drift mobility and Hall mobility differ, as indicated by the two different expressions.) In the theory of small-polaron transport, a distinction is made between *adiabatic* hopping, in which the electron is at all times relaxed in the potential well of its lattice distortion, and *anti-adiabatic* hopping, in which the electron jumps out of the potential well, and then the lattice moves to equilibrate with the electron's new position. (In reality, the behavior is always somewhere between these two extremes.)

Small polaron effects are present in a variety of materials, including most transition-metal oxides, many amorphous materials, and many polymers, including DNA. They are identified and characterized in a variety of ways, including electrical transport, thermopower, photoemission [6], and infrared absorption [7].

IV. Bipolarons and polaronic excitons

Although two electrons (or two holes) repel by the Coulomb interaction, two electron polarons (or two hole polarons) can in theory have a net attractive force, due to the attraction of each to the lattice distortion induced by the other. A bound state of two electron polarons (or two hole polarons) is called a *bipolaron*. A bipolaron is similar to a Cooper-pair in the BCS theory of superconductivity, in that two electrons are bound by the exchange of virtual phonons, except that the electrons in a Cooper-pair are paired in k-space, while the electrons in a bipolaron are

paired in real space. Stable bipolarons are known to exist in a few materials, including polyacetylene and a number of oxides [1].

A bound pair consisting of an electron polaron and hole polaron is called a *polaronic exciton*, or *polaron exciton*. The presence of lattice distortions can affect the exciton in a number of subtle ways, affecting both the binding energy and the associated optical features [8,9].

V. Conclusions

Polarons are the proper way to describe electrons and holes within any conducting material, but are only important in highly polar or ionic solids. Properties of polarons can be measured through electrical measurements, optical characterization, Raman spectroscopy, photoemission, and various other methods, most beyond the scope of this paper. A polaron may be “large” or “small”, depending on how its radius compares to the lattice constant. Other than size, the most important differences between large and small polarons are in their electrical transport: Large polarons tend to have band-like transport, while small polarons usually undergo hopping transport. Two polarons of like charge can bind into a bipolaron, and two polarons of opposite charge can bind into a polaronic exciton. Polarons are an immensely rich and deep field, both theoretically and experimentally, and the reader is referred to Ref. 1 for a much more detailed introduction to this still-active area of research.

References

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