Polaron Weights and Measures

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The most natural description a material in terms of microscopic quasiparticles often is developed upon a rigid crystalline lattice, leaving the effects of non-rigidity to be accounted for through interactions with an additional field of vibrational quanta. When such interactions with vibrations are weak, one is often satisfied to regard their effects as “scattering” of the rigid quasiparticles and to neglect distinctions between the rigid and non-rigid descriptions at the quasiparticle level. When interactions with vibrations are strong, however, it becomes imperative to account for the persistent spatial correlations that arise in the frame of the mobile quasiparticle, giving rise to the notion of a co-moving lattice distortion or phonon cloud. Such persistent correlations between a rigid-lattice quasiparticle and the vibrations of the host give rise to the definition of a new quasiparticle of the non-rigid lattice, the polaron.

There are some who reserve the term “polaron” for the strong-interaction case. We find this artificial, as it suggests a distinction that is not in evidence in our results. We find that although polaron properties vary greatly from one regime to another, there is no regime in which significant spatial correlations do not exist, and certainly no interaction threshold below which polaron character is suddenly lost. We speak therefore of polarons as the quasiparticles of deformable materials, and seek to ascertain their properties in all regimes.

1. POLARON GROUND STATE AND RELATED ENERGIES

We consider a single electronic excitation \((a, a^\dagger)\) whose principal characteristic is its finite positive mass and its coupling \((g)\) with optical phonons \((b, b^\dagger)\) as expressed in the Holstein Molecular Crystal Model (here in 1D) \cite{holstein1959}

\[
\hat{H} = -J \sum_n a_n^\dagger (a_{n+1} + a_{n-1}) + \hbar \omega \sum_n b_n^\dagger b_n - g \hbar \omega \sum_n a_n^\dagger a_n (b_n^\dagger + b_n),
\]

wherein \(J\) is the nearest-neighbor hopping integral and \(\omega\) is the optical phonon fre-
quency. Below, we distinguish between the non-adiabatic regime ($J/h\omega < 1/4$), the adiabatic regime ($J/h\omega > 1/4$), and the adiabatic limit ($J/h\omega \to \infty$).

We have analyzed this model using the Global Local variational method [2-5], supported by both weak- and strong-coupling perturbation theory. While each perturbation theory confirms our numerical results in the appropriate limiting regime and provides asymptotic information it is essential to the nature of the polaron problem that both perturbation theories fail in the intermediate regime where the self-trapping transition is found; ultimately it is the correct description of the self-trapping transition that is the heart of the polaron problem. Since perturbation theories are unable to confirm our results in this area, we have made extensive comparisons with other high-quality contemporary methods such as quantum Monte Carlo [6], density matrix renormalization group [7], and cluster diagonalization [8]; as detailed elsewhere, and have found excellent quantitative agreement.

In the following, we have located the self-trapping transition by analyzing the detailed behavior of many distinct and measurable polaron properties over wide ranges of coupling strength and adiabaticity. For each such property, we developed an objective criterion through which we located a point marking a crossover from the behavior typical of that property in the weak-coupling regime to the behavior typical of the strong-coupling regime. These loci are marked in Figures 1, 2, and 5 below, beginning with the ground state energy and its components.

The total energy of the polaron can be viewed as the sum of contributions from the three principal components of the polaron Hamiltonian, the kinetic energy of the exciton ($E_{\text{kin}}$), the phonon energy ($E_{\text{ph}}$) and the interaction energy ($E_{\text{int}}$). While the total energy is clearly the most important single quantity, particularly from the variational perspective, its dissection into components provides more information about what is going on inside the polaron. We see, for example, that each of these four basic energies experience a rapid crossover between characteristic weak-coupling behavior and characteristic strong coupling behavior. When examined in detail, we find that these crossovers occur at coupling values that cluster together along a common trend line well-described by the curve

$$g_{\text{ST}} = 1 + \sqrt{J/h\omega}.$$ 

The clustering of self-trapping loci about $g_{\text{ST}}$ is increasingly tight at higher $J/h\omega$ and more diffuse at lower values; that the central trend of this clustering is simply described by a square root is thus more telling of properties of the adiabatic regime than it is of the non-adiabatic.

We are led to conclude that each energy component constitutes a probe of a single coordinated change in essentially all aspects of polaron structure occurring in a narrow region of the polaron parameter space; this is the self-trapping transition.

2. POLARON MASS AND BAND DISTORTION

Perhaps the most familiar distinguishing characteristics of polarons are the enhancement of the polaron effective mass $m^*$ relative to that of the rigid-lattice mass $m_0$ ($= \hbar^2/2Jl^2$ where $l$ is the lattice constant) and the narrowing of the polaron
energy band. In many approaches these two polaronic effects appear with sufficient similarity that there is an unfortunate tendency for them to be regarded as essentially interchangeable. In the distinctness of these two energy band properties lies some very significant information about polaron structure.

By computing polaron ground states in each crystal momentum sector, we construct the lowest energy band of the polaron and analyze it as in the previous section [3]. Having already studied the ground state energy we have already accounted for the overall shift of the polaron band, we focus here on polaron band shape.

Traditional measures of polaron band shape are the effective mass, derived from the band curvature at the Brillouin zone center, and the bandwidth, defined as the
difference between the highest and lowest energies in the band. We have studied both of these properties, as well as the band edge curvature (not displayed) which can be thought of as an effective mass measure at the Brillouin zone boundary.

The logarithm of $m^*$ resembles the ground state energy components of the previous section, and a similar analysis to locate crossovers proceeds to similar results. The locus of transition points so determined falls neatly in line with those already discussed. While this qualitative and quantitative agreement is not unexpected, neither is it entirely trivial since the effective mass addresses relationships among distinct crystal momentum states (i.e. dynamics) while the ground state energy does not.

The polaron bandwidth combines characteristics of both the zone center and the zone edge, where distinct behaviors may be found. This is particularly so in the adiabatic regime where the polaron band edge at weak coupling is very flat. To this very small band edge curvature corresponds a large effective mass, and an infinite effective mass in the limit of vanishing coupling where the band edge is rigorously flat. This is so even though the zone-center effective mass is typically an unremarkable finite value near that of the free exciton at the same weak coupling values.

This flatness of the band edge at weak coupling in the adiabatic regime is due to a strong mixing of the free exciton and free phonon states that imparts a strong one-phonon-like character to the outer polaron band. As coupling increases, this one-phonon character gives way to the multi-phonon character we more usually ascribe to polarons; the band edge acquires a non-trivial curvature that reaches a maximum (zone-edge effective mass reaches a minimum) at a characteristic value $g \approx g_N$ and then reverses as the band flattens again as the familiar strongly-coupled polaron character sets in. Importantly, this happens before any dramatic change occurs at the Brillouin zone center, and in complementary fashion, no dramatic change occurs at the zone edge when the more familiar self-trapping transition occurs at $g \approx g_{ST}$.

Explicit calculation of many band structures by the Global Local variational
method shows that the polaron bandwidth experiences three distinct regimes:

\( g < g_N \), the polaron band edge is quite flat, the polaron band center is characteristic of the free exciton, and all polaron properties are very weakly dependent upon \( g \).

\( g_N < g < g_{ST} \), the polaron band narrows relatively rapidly through a finite interval of coupling strength, and band center properties begin to change more rapidly.

\( g_{ST} < g \), the polaron bandwidth continues to narrow as coupling strength increases, but with a coupling dependence characteristic of the strong-coupling regime, and essentially all polaron properties reflect similar dependences on the coupling.

This three-phase behavior of the polaron bandwidth poses significant challenges to a variety of approaches to polaron theory. There are many approaches that either do not contain the self-trapping transition at all, misidentify it, or locate it somewhere other than along \( g_{ST} \). Of those that do make a reasonable identification of the self-trapping transition, relatively few are sufficiently faithful to the quantum mechanical nature of the polaron to identify the onset of band narrowing at \( g_N \) as well.

3. ELECTRON-PHONON CORRELATIONS AND POLARON SIZE

Much of what is considered known about polarons has to do with their spatial localization; the self-trapping transition, in particular, is widely regarded as a localizing transition. To get at this notion of spatial localization and to quantify it in parallel with other measurable polaron properties, we use a correlation function that quantifies spatial relationships between the electronic and vibrational components of the polaron. Since it is such persistent spatial correlations that define the polaron as a quasiparticle, the spatial extent of those correlations can be taken as a measure of polaron size. To this end we use the correlation function (in \( D \) dimensions) \([5,9,10]\)

\[
C^{[D]}_F = \langle \hat{C}^{[D]}_F \rangle = \frac{1}{2g} \sum_{\vec{n}} d^\dagger_{\vec{n}} a_{\vec{n}} (b^\dagger_{\vec{n} + \vec{r}} + b_{\vec{n} + \vec{r}}) \]

evaluated in the global ground state at the Brillouin zone center and normalized such that \( \sum_{\vec{r}} C^{[D]}_F = 1 \). Defined this way, the leading result in weak-coupling perturbation theory \([9,10]\) is non-vanishing and rigorous in the limit \( g \rightarrow 0 \). In the left panel of Figure 3, we show typical examples of exact weak-coupling traces in 1D, 2D and 3D for an isotropic case. The most important message of the dimensional comparison is that the weak coupling limits in each dimension are qualitatively similar, and in their quantitative aspects show no remarkable differences; each experiences a steady and unremarkable radial decay from a central peak, and none is characterizable as being either completely localized or completely extended.

That these are perturbative results, formally rigorous only at vanishing coupling, naturally recommends that some caution and discretion be exercised when regarding them to be representative of polaron structure at finite \( g \). Considering, however, that every other quantity so far investigated in this paper has exhibited weak or very weak leading dependence upon the coupling (see all panels of Figures 1 and 2), there is reason to anticipate that this perturbative description of correlations may persist meaningfully to non-trivially-finite \( g \). This proves to be true over a broad range of
adiabaticity, giving support to the utility of weak-coupling perturbation theory as a tool through which one can elaborate upon many aspects of polaron structure that are resistant to analysis by any other means.

In order to examine electron-phonon correlations at all coupling strengths, it is necessary to use non-perturbative methods. In the right panel of Figure 3, we present results obtained from by using Global Local variational method in 1D. This shows that there is a broadest polaron corresponding to the $g = 0$ case of perturbation theory, as expected. Further, as expected, discernible change in the correlation function occurs relatively slowly with increasing $g$. It is clear that even at coupling values as high as $g = 2.5 \rightarrow 3.0$ the character of correlations bears a much closer resemblance to that of the $g = 0$ limit than to the self-trapped case. The contraction of correlations clearly accelerates as the self-trapping transition is approached, but it is clear, too, that a substantial amount of spatial contraction occurs before the self-trapping transition. Although this contraction continues into the strong-coupling limit, the phase of rapid localization can be considered to be essentially completed by the time $g \approx g_{ST}$. Clearly, there is something both qualitatively and quantitatively distinct about the two phases of spatial contraction separated by the self-trapping transition.

We can gain a more quantitative handle on this localization phenomenon by constructing a measure of the width of spatial correlations. This is straightforwardly done by constructing a spatial variance tensor $\sigma^2$ and contracting it along a desired measurement direction $\mu$.

$$\sigma^2 = \mu \cdot \sigma^2 \cdot \mu.$$ 

The components of $\sigma^2$ can be computed from

$$\sigma^2_{ij} = \sum_{\vec{r}} r_i r_j C_{\vec{r}}^{(D)} ,$$

where $i, j$ label crystal axes and $\vec{r}$ runs over all lattice sites. The weak-coupling limit
yields the exact result $\sigma^2_{ij} = \delta_{ij} 2J_i/\hbar \omega$; i.e., the width of spatial correlations in any direction is finite and given by the adiabaticity in that direction.

Since the polaron width decreases monotonically from this finite limiting weak-coupling value to zero in the strong-coupling limit, it would appear that the adiabaticity provides the natural scale parameter for polaron size. Further, $g_{ST}$ provides the natural coupling scale for the self-trapping transition. It is natural, therefore, to use these scales to organize a comparison of polaron widths from many different calculations in a single scaling plot that might reveal characteristic features of the manner in which polarons undergo spatial localization. Such a compilation has been made in Figure 4 based on many fixed-adiabaticity scans obtained by the Global Local method. (This data contains some artifacts at the weak-coupling end of each trace that have been retained here only to illustrate the limitations of the Global Local method for this particular purpose; only the descending data are meaningful.)

The coalescence of these data along an apparent limiting curve suggest that there is a very typical narrowing behavior underlying self-trapping, and that with increasing adiabaticity ($J/\hbar \omega \to \infty$) this typical behavior approaches a scaling relationship

$$\frac{\sigma^2}{\sigma_0^2} = F(\frac{g}{g_{ST}}) \quad g < g_{ST}$$

$$= 0 \quad g > g_{ST}$$

Our data is not sufficiently constraining to give great confidence in the specific form of the scaling function $F(x)$; however, for the purposes of illustration we have included the curve $F(x) = \sqrt{1 - x}$ in Figure 4. [5]

The polaron width thus appears to play the role of an order parameter for the self-trapping transition, particularly in the adiabatic limit - being finite and spelling out a characteristic parametric relationship below the transition, and being essentially vanishing above the transition. What is of importance here is not the formality of a phase transition, which at best materializes in the extreme adiabatic limit, but the distinct scaling regimes above and below the generally finite-width transition.
Through a more detailed analysis, we have shown that the scaling properties of our computed correlation functions and their widths above the self-trapping transition are the same as result from both strong-coupling perturbation theory and various forms of adiabatic theory including soliton theories. On the other hand, the same detailed analysis shows that distinct scaling properties prevail below the transition that are incompatible with those descriptions. The inescapable conclusion is that the adiabatic approximation breaks down below the self-trapping transition ($g < g_{ST}$) in such a way that the polaron width cannot be concluded from it without substantial correction.

So what does the order parameter tell us about the regime below the self-trapping transition? The finite value of the order parameter tells us that the scaling properties of the polaron width in this regime are essentially the same as those found in the weak coupling limit. This is a non-trivial statement, since weak-coupling perturbation theory is not strictly valid over this entire regime. Moreover, continuation of weak-coupling perturbation theory to higher orders is not helpful in leading one naturally to this conclusion. The regime between the weak-coupling limit ($F(\approx 0) \approx 1$) and the self-trapping transition ($F(\approx 1) \approx 0$) appears to be essential non-perturbative territory within which extrapolations from either above or below cannot be presumed valid; indeed, many such familiar extrapolations are demonstrably false. The device of the order parameter validated by our calculations provides a means of approximating polaron size over a large regime where no other valid measure currently exists.

4. PHASE DIAGRAM

In the foregoing sections we have explicitly discussed more than half a dozen measurable polaron properties that constitute probes of the self-trapping transition, and implicitly have touched on others not presented. Collectively, these provide an abundance of information that should impose heavy constraints on the notion of a self-trapping line. In Figure 5, we compile self-trapping points from nine distinct measured properties as determined by the Global Local method. Owing to the large amount of overlapping data, we have compiled in one panel those points derived from the ground state energy ($E_0$), the kinetic energy ($E_{kin}$), the phonon energy ($E_{ph}$), the interaction energy ($E_{int}$), and the effective mass ($m^*$), and in a second panel those points derived from correlation function values near the center of the polaron ($C_0$, $C_1$, $C_2$, and $C_3$). Clearly, the self-trapping picture conveyed by each measured property is both qualitatively and quantitatively consistent with all of the others, with all self-trapping points clustering tightly around the curve $g_{ST} = 1 + \sqrt{J/\hbar \omega}$.

5. CONCLUSIONS

Polarons as quasiparticles in solids have been a centerpiece of condensed matter physics for many decades. Throughout the bulk of that time, however, our understanding of polarons and their properties have been limited by the essential complexity of the problem and its resistance to analysis by almost any method. The common understanding of polarons which developed over these decades has necessarily been
Figure 5. Polaron phase diagram in 1D. Solid curves follow $g_{ST}$. Dashed curves follow $g_N$. **Left:** Based on energies and the effective mass. **Right:** Based on the correlation function at its center and near-center sites. [4,5]

abstracted from a mosaic of incomplete descriptions whose incompleteness lay rooted in some essential, if sometimes inobvious problem with virtually every approach. In a great majority of cases, it is the self-trapping transition that can be implicated as the hard core of the problem against which most techniques have been blunted.

We are fortunate now that there are a small handful of computational techniques [2-8] that are capable of faithfully describing polaron properties in essentially all regimes, including the self-trapping transition. Besides affording quantitative accuracy to the description of important polaron properties, it is now possible to resolve many ambiguities and conflicts that have long been tied to the mosaic character of polaron theory. Indeed, it is possible to dispense with the mosaic completely and give a comprehensive, quantitatively accurate and internally-consistent description spanning all regimes. The measurables displayed throughout this paper are representative of one such description.

An essential consequence of these developments is the realization that the conventional polaron wisdom that has achieved widespread acceptance is critically flawed. By this we do not mean mere quantitative inaccuracies that one expects to be narrowed in the normal course of progress, but some essential defects in the paradigm.

At the root of much of this difficulty lies the adiabatic approximation. As discussed in section 3, the adiabatic approximation as widely used breaks down below the self-trapping transition and is inconsistent with the scaling relationships that characterize the large polaron regime. Since the common notion of the large polaron (and its relative, the envelope soliton) are rooted in the adiabatic approximation, we are forced to the semantically-awkward conclusion that the traditional large polaron, as historically understood, does not exist in the large polaron regime.

It would tragically overstate the case to extrapolate from this that large polarons do not exist, or that the appropriate description of the polaron quasiparticle below the self-trapping transition is that of a “weakly-scattered” or “quasi-free” electron in which electron-phonon correlations have a merely peripheral role. The large polaron regime is indeed occupied by spatially-extended, persistently-correlated
electron-phonon quasiparticles. The crux of the matter is simply that the properties of these real large polarons are not those that were/are commonly expected.

If the true character of large polarons has escaped the historical paradigm, then perhaps it is not so surprising that the true character of the self-trapping transition has been missed as well. That there is a fundamental inconsistency is perhaps best illustrated by the effects of dimensionality: Conventional polaron wisdom holds that there is no self-trapping transition in 1D, and that there is an abrupt self-trapping transition in both 2D and 3D. Multiple independent and high-quality methods have now shown with mutual consistency that this is not true; a non-abrupt and qualitatively similar self-trapping transition exists in all dimensions. In 1D, this transition is well-located by the self-trapping line $g_{ST}$, and generalizations of this to higher dimensions and even anisotropic scenarios have been proposed [10].

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REFERENCES