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What do polarons owe to their harmonic origins?

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Abstract

Polaron (and related) soliton concepts are based on the assumption that quasiparticles are in linear interaction with harmonic oscillators. The discrete nonlinear Schrödinger equation and its semiclassical relatives are also based on this assumption. Study of the effects of nonlinearity in interaction, and anharmonicity in the restoring force of the oscillators, has led to notable results such as saturation of nonlinearities and counterintuitive pheonomena such as destruction of self-trapping on increasing the nonlinearity. We report on these and related results. The general aim of the investigation is to determine what polarons owe to their harmonic (and linear) origins and how a generalized conceptual framework may be built which includes known polaron physics as a subset. Copyright © 1998 Elsevier Science B.V.

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1. Introduction

The purpose of the present lecture/article is to delve into the interesting question as to what polarons [1–3] owe to their harmonic origins. The first report of such work was presented at another conference in Greece eight years ago [4]. The question has been revived recently [5–7] and work is being carried out on several new fronts [8–10]. Among new results and ideas that we present in this article are an analysis of anharmonic alternatives to the harmonic origins of the polaron which we discuss in the language of Stokes diagrams, an appropriate expression for the so-called 'logarithmically hard oscillator' along with a distinction between it and the 'logarithmically soft oscillator', and a discussion of self-trapping when the 'oscillator' with which the quasiparticle interacts is extremely nonlinear in that it has a vanishing frequency, i.e., is a free particle constrained in a box. The layout of this article is as follows. In Section 2 we describe what we mean by polarons and explain what harmonic origins are of concern to us here, in Section 3 we describe our method of attack and describe results for the so-called rotational polarons, in Section 4 we comment on stationary states of these rotational polarons and mention other cases of anharmonicity, and in Section 5 we touch upon current and planned work on the microscopic description of these effects.

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2. Polarons and their harmonic origins

A polaron is, by definition, a quasiparticle such as an electron, an exciton, a vibrational excitation, or a light interstitial particle, e.g. a muon, in such *strong* interaction with oscillations, such as lattice vibrations or intramolecular motions, that it displays unusual properties in its transport and other characteristics. Unusual properties of this kind include dramatic features such as self-trapping and counterintuitive behavior such as an increase in the mobility with increasing temperature. The physical picture accompanying these phenomena is that the quasiparticle 'digs its own well' as a result of its strong interactions with the oscillations, thus causing self-trapping. An increase in temperature helps the quasiparticle to climb out of its well and thus to move *more* efficiently than at lower temperatures. This is in contrast to the nonpolaronic situation wherein an increase in temperature results merely in greater scattering through an increase in the oscillation amplitudes: the quasiparticle moves *less* efficiently than at lower temperatures [1–3]. Polaronic descriptions have been useful in a wide variety of materials and systems and continue to present fascinating challenges to the theorist. The approach incorporating the Davydov soliton [11] is an example of such a description. Dressing transformation approaches [12–14], the method of the discrete nonlinear Schrödinger equation [4,15,16], and 'numerically exact' procedures [17,18] constitute other examples of polaronic descriptions.

In order to understand what harmonic origins are of interest to us here, it is best to state the basic Hamiltonian H which describes the usual polaronic system studied. In standard notation which we will not describe here for want of space,

$$H = \sum_m \varepsilon_m a_m^+ a_m + \sum_{m,n} V_{mn} a_m^+ a_n + \sum_m \hbar\omega_q \left(b_q^+ b_q + \frac{1}{2} \right) + N^{-1/2} \sum_{m,q} \hbar\omega_q g_q \exp(\mathrm{i} q \cdot R_m)(b_q + b_{-q}^+) a_m^+ a_m. \tag{2.1}$$

Essentially every standard polaron theory is built on the basis of (2.1). We draw the reader's attention to the third and fourth terms in the right-hand side of (2.1). The third term describes excitations of harmonic oscillators, i.e., oscillators in which the restoring force follows the (linear) Hooke's law. The fourth term describes a quasiparticle–oscillation interaction in which the site energy of the quasiparticle is modulated by an amount linear in the oscillation amplitude. The question under investigation here is: what are the consequences of taking the oscillators to be *not* Hookian, and/or the quasiparticle–oscillation interaction to be *not* linear in the oscillation amplitude. Our interest is not in slight excursions from harmonicity or linearity, which can be easily addressed through perturbation methods, but in *qualitatively* significant departures from traditional analyses of the polaron. The proper way of addressing the question raised is at the microscopic level [8–10] described by the Hamiltonian (2.1). However, we will focus in this article on studies based on the discrete nonlinear Schrödinger equation (DNLSE) [2,11,15,16], which has been widely thought to be a consequence of (2.1) under two known approximations: the semiclassical approximation, and the timescale disparity approximation. Our essential question can be understood graphically as follows. The standard 'Stokes shift diagram' shows the essence of the traditional polaron through the graphical fact that a straight line (linear interaction) when added to a parabola (harmonic interaction) produces a parabola which is shifted (displacement of the oscillator) and lowered (polaronic binding energy). Our present question can be stated pictorially (see Fig. 1) as being related to the addition of a *nonlinear* curve to an *anharmonic* interaction. One instructive example is the addition of a saturating interaction such as that represented by the hyperbolic tangent (of the oscillation amplitude) to a saturating potential such as a hyperbolic secant. They reduce, respectively, to a straight line and a parabola for small amplitudes. Another instructive example, and one which we will analyze below more in detail, is provided by the addition of a sinusoidal interaction to a cosinusoidal potential. Graphical inspection of Fig. 1 already suggests the possibility of saturation and indicates what may be expected from the analysis below.

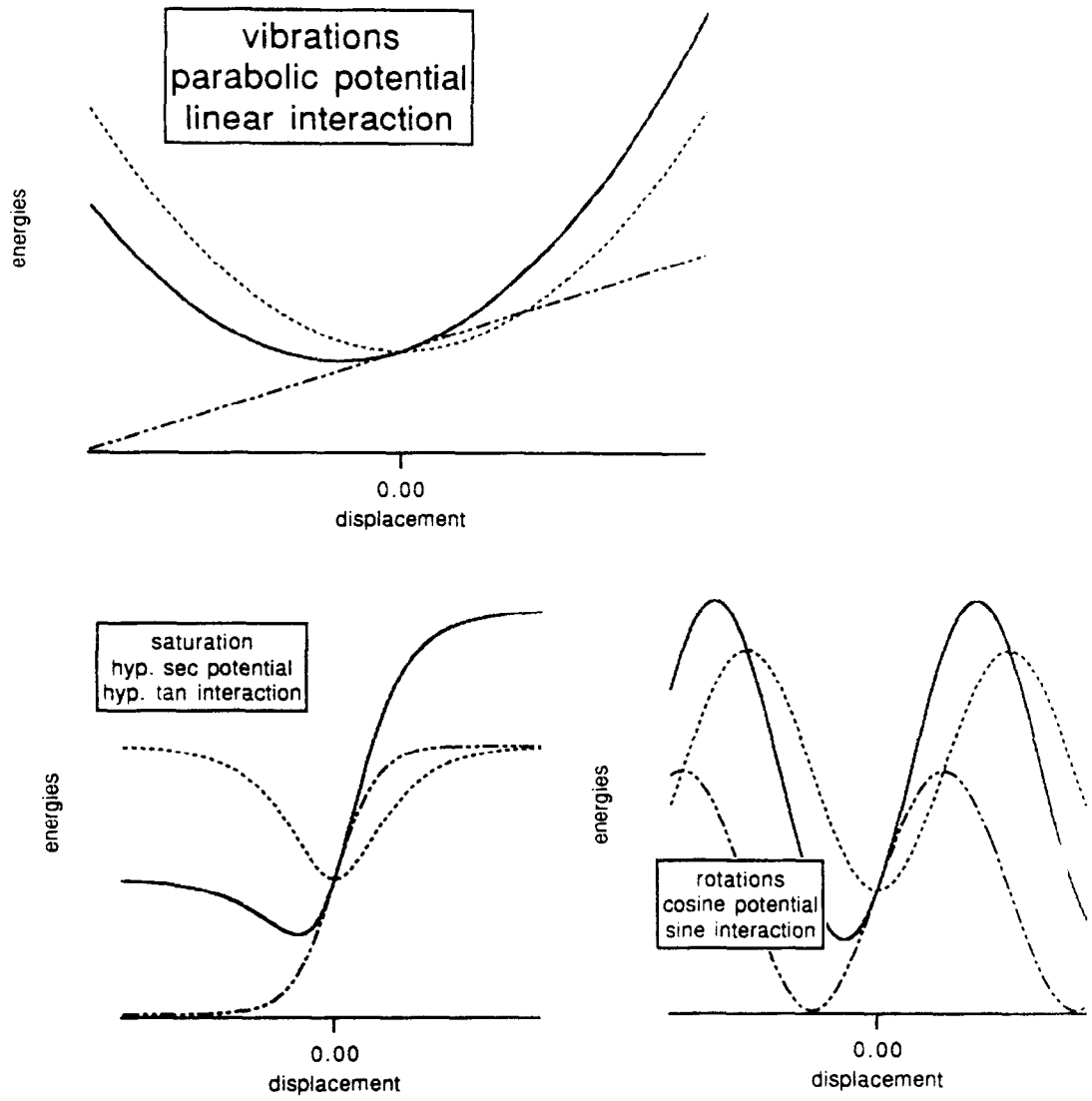

Fig. 1. Graphical depiction of anharmonicities and interactions.

3. Method of attack and rotational polarons

Consider for simplicity dispersionless (Einstein) oscillators of frequency ω in (2.1). Under the semiclassical assumption (the assumption that the oscillations may be treated classically), (2.1) leads to

$$i\hbar \frac{dc_m}{dt} = \sum_n V_{mn} c_n + E_0 x_m c_m, \tag{3.1}$$

$$\frac{d^2 x_m}{dt^2} + \omega^2 x_m + S|c_m|^2 = 0, \tag{3.2}$$

where c_m is the amplitude for the quasiparticle to be at site m, x_m is the (now classical) amplitude of the oscillation at site m, and E_0 and S are constants related to the coupling constant. Through an argument of timescale disparity which allows one to neglect the first term in (3.2), (3.1) is often written as the DNLSE [15,16]

$$i\hbar \frac{dc_m}{dt} = \sum_n V_{mn} c_n - \chi |c_m|^2 c_m, \tag{3.3}$$

where χ is the nonlinearity parameter (the energy lowering due to polaronic effects) and is given by $E_0 S/\omega^2$.

We now pose our question at the level of description of (3.3): how is (3.3), along with its well-known consequences such as self-trapping, modified when the oscillators in the system are not *Hookian* and/or the interaction with the quasiparticle is not linear in the oscillation amplitude?

The last terms in (3.1) and (3.2) arise from the last term in (2.1). At a semimicroscopic level, the latter may be represented by an interaction of the form

$$\mathcal{E}(x_m, c_m) = E_0 x_m |c_m|^2, \tag{3.4}$$

which yields the respective terms in (3.1) and (3.2) through differentiation with respect to c_m and x_m, respectively. There are two assumptions of linearity in the above standard procedure, both of which arise from a Taylor series argument. The interaction term $E_0 x_m |c_m|^2$ in (3.4) is linear in x_m and so is the restoring force in (3.2). We now investigate the consequences of relaxing these linearity assumptions in the two terms. We are thus interested in generally nonlinear restoring force $f(x_m)$ for the molecular oscillator and in generally nonlinear potentials $E(x_m)|c_m|^2$ for the interaction between the oscillations and the quasiparticle.

Since no molecular oscillator is truly Hookian and no interaction energy is truly linear in the oscillator displacement, it should be clear that our investigation has considerable physical relevance. Systems in which the nonlinearities might be particularly interesting are the ones in which x_m is a rotation rather than a vibration. For notational purposes in such rotational situations, we will denote it by an angle variable θ_m. The system could thus be an electron/exciton moving among the sites m of a chain, there being a rotator (for instance a dipole) at each site m whose angle from a fixed direction is θ_m. Periodicity in θ_m being essential at least at every interval of 2π, the nonlinear effects could be quite important for rotations which are not too small compared to 2π. We replace the standard Hooke's linear restoring force by a general nonlinear force proportional to a function $f(\theta_m)$ of the rotational coordinate, and the standard linear interaction potential (2.4) by the general nonlinear potential

$$\mathcal{E}(\theta_m, c_m) = E(\theta_m)|c_m|^2. \tag{3.5}$$

Eqs. (3.1) and (3.2) are now generalized to

$$i\hbar \frac{dc_m}{dt} = \sum_n V_{mn} c_n + E(\theta_m) c_m, \tag{3.6}$$

$$\frac{d^2\theta_m}{dt^2} + \omega^2 f(\theta_m) + R E'(\theta_m)|c_m|^2 = 0, \tag{3.7}$$

where, for this rotational case, the constant R is essentially the reciprocal of the moment of inertia of the rotator. The resulting generalization of the DNLSE (3.3) is

$$i\hbar \frac{dc_m}{dt} = \sum_n V_{mn} c_n - h(|c_m|^2) c_m, \tag{3.8}$$

where $h(|c_m|^2)$ is simply $-E(\theta_m)$, the quantity θ_m being expressed as a function of $|c_m|^2$ obtained as the solution of $f(\theta_m) = -(R/\omega^2) E'(\theta_m)|c_m|^2$.

With $\hbar = 1$, (3.8) leads to the nonlinear Von Neumann equation

$$i\frac{d\rho_{mn}}{dt} = \sum_s (V_{ms}\rho_{sn} - V_{sn}\rho_{ms}) - \rho_{mn}[h(\rho_{mn}) - h(\rho_{nn})] \tag{3.9}$$

for the density matrix ρ. Eqs. (3.8) and (3.9) thus allow us to study the effect on polaronic evolution of restoring forces and interaction potentials which are nonlinear in the rotational coordinate θ_m. Physically rich solutions can be obtained immediately for a two-site system in which m, n take the values 1 and 2. Thus, p, the probability difference of the quasiparticle occupation at the two sites, can be shown to obey a closed equation in terms of a quantity $g(p)$ defined, up to an arbitrary constant, through

$$\frac{dg(p)}{dp} = h(\rho_{11}) - h(\rho_{22}) \tag{3.10}$$

and solved explicitly to display striking behavior [4–6]. We now examine the solutions for the simple case when the restoring force $f(\theta)$ and interaction energy $E(\theta)$ are simple sinusoidal functions of θ:

$$f(\theta) = \frac{\sin(\Lambda\theta)}{\Lambda}, \qquad E(\theta) = \frac{E_0}{\Lambda}\sin(\Lambda\theta). \tag{3.11}$$

The limit $\Lambda \to 0$ gives the linear, harmonic, case, i.e., the standard polaron, with $\chi = E_0^2 R/\omega^2$. Our interest is in examining nonzero Λ. An important energy in this general case is

$$\Delta = \frac{E_0}{\Lambda}, \tag{3.12}$$

which describes (see (3.12)) the ceiling on the quasiparticle-oscillation interaction energy and will be seen below to measure the (static) site energy lowering that every site in the crystal feels for high values of nonlinearity. In the usual polaronic case, this saturation energy Δ is infinitely large. One immediately anticipates saturation effects. The ratio of Δ to other key parameters such as χ and V will be seen to play a crucial role in determining new aspects of polaronic evolution.

The explicit form of the generalized DNLSE for the rotational polaron is

$$i\hbar\frac{dc_m}{dt} = \sum_n V_{mn}c_n - \frac{\chi|c_m|^2}{\sqrt{1 + (\chi/\Delta)^2|c_m|^4}}c_m. \tag{3.13}$$

It reduces to the standard DNLSE (3.3) for small χ/Δ but predicts substantially different transport features for nonnegligible values of χ/Δ. Thus, whereas increase in the nonlinearity χ leads in the traditional case (3.3) to merely stronger nonlinear effects, (3.13) shows that such increase leads first to stronger nonlinear effects but eventually to a total *disappearance* of nonlinear features. Indeed, for large values of χ/Δ, (3.13) reduces to a *linear* equation which, unlike (3.3), exhibits no self-trapping whatsoever!

The function $g(p)$ defined in (3.10) becomes, for the rotational case,

$$g(p) = \Delta\left[\sqrt{(p+1)^2 + (2\Delta/\chi)^2} + \sqrt{(p-1)^2 + (2\Delta/\chi)^2} - 2\sqrt{1 + (2\Delta/\chi)^2}\right], \tag{3.14}$$

the arbitrary constant in $g(p)$ having been chosen to make $g(0) = 0$. The dynamics of the rotational polaron can be described graphically by plotting the effective dynamic potential $U(p)$ obtained from (3.14) through

$$U(p) = 2V^2(p^2 - p_0^2) + \tfrac{1}{2}[g(p) - g(p_0)]^2 - 2Vr_0[g(p) - g(p_0)], \tag{3.15}$$

p_0 being the initial value of the probability difference. For simplicity, we consider the initial condition of complete localization at one of the two sites. We then have $p_0 = 1$. We have taken a fixed saturation energy Δ in Fig. 2. In

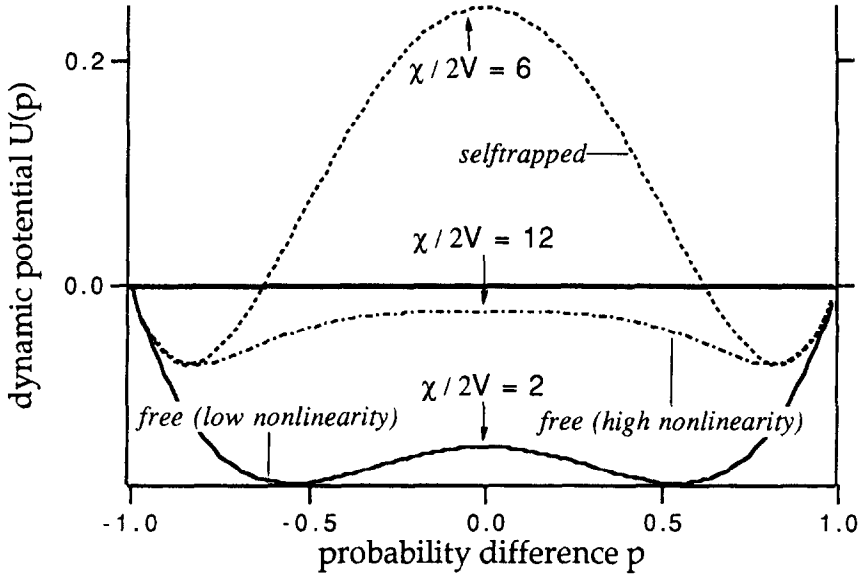

Fig. 2. The dynamic potential $U(p)$ showing graphically the occurrence and eventual disappearance of self-trapping on increasing nonlinearity. $\Delta = 6V$ for all curves. The case $\chi/2V = 2$ shows free motion resulting from a low value of nonlinearity. A higher value of nonlinearity, viz. $\chi/2V = 6$, shows the occurrence of self-trapping. A further increase in nonlinearity, $\chi/2V = 12$, shows the destruction of self-trapping. By contrast, the results of the standard DNLSE would be to make self-trapping always more effective as nonlinearity is increased.

units of $2V$, it equals 3. Whether the motion is self-trapped or free is clear from the vertical location of the horizontal line depicting the "constant energy" of the fictitious oscillator representing the evolution. If it lies always above $U(p)$, the motion is free. Otherwise, the motion is self-trapped, the intersection of the horizontal line with the $U(p)$ curve being indicative of the extent of values that the probability difference p can take. For small values of the nonlinearity there is free motion as is clear from the $\chi/2V = 2$ case. An increase in the nonlinearity χ results in self-trapping as expected: the $\chi/2V = 6$ curve shows that the probability difference oscillates between 1 and about 0.6. The surprising new consequence of our analysis is evident from the $\chi/2V = 12$ curve. We see that a further increase of nonlinearity *frees* the quasiparticle rather than self-trapping it more effectively, as would happen in the DNLSE, i.e., in the limit that Δ/χ tends to infinity.

The above analysis addresses the time evolution of the dimer for given initial conditions. The stationary states of the dimer also show interesting variation with nonlinearity which we describe in the following section.

4. Stationary state effects

We refer the reader to [6] for the details of the stationary state analysis. The general result valid for arbitrary interaction nonlinearity and anharmonicity is that the stationary state probability differences are obtained as the solutions of

$$2V_p \pm \sqrt{1-p^2}\frac{\mathrm{d}}{\mathrm{d}p}g(p) = 0. \tag{4.1}$$

For the rotational polaron represented by (3.14), self-trapped stationary states are the solutions of

$$\frac{4V}{\chi}p - \sqrt{1-p^2}\left(\frac{1+p}{\sqrt{1+(\chi/2\Delta)^2(1+p)^2}} - \frac{1-p}{\sqrt{1+(\chi/2\Delta)^2(1-p)^2}}\right) = 0 \tag{4.2}$$

with nonzero p. New effects such as the disappearance of self-trapping (as manifested in the stationary states) on increasing the nonlinearity may be described through bifurcation diagrams of p versus χ/V as in [4,6]. For small values of the ratio χ/V, the probability difference in the stationary state p is seen to be vanishing (no self-trapping) until a critical value is reached, to bifurcate, giving equal and opposite values showing a localized stationary state whose localization increases as χ/V is increased, and then to drop off to zero again on reaching another critical value of χ/V, signifying the eventual destruction of self-trapping.

An interesting question is whether the second critical value of χ/V can, in a certain sense, be smaller than the first critical value, i.e., whether a physical situation can occur in which self-trapped stationary states can cease to exist for *all* values of χ/V. An answer can indeed be given [6]. A stability analysis shows that at the self-trapping transition, the quantity $z \equiv (\chi/2\Delta)^2$ must satisfy the cubic equation

$$z^3 + 3z^2 + [3 - (\Delta/V)^2]z + 1 = 0. \tag{4.3}$$

The two real roots of (4.3) correspond, respectively, to the appearance and the disappearance of self-trapping states. For large enough values of the saturation energy Δ, these roots always exist. However, as Δ becomes smaller, the roots become identical to each other at a critical point and then become imaginary signifying the absence of self-trapping stationary states independently of the value of χ/V. The critical condition for this novel prediction is seen easily from (4.3) to be $(\Delta/V)^2 < 27/4$.

From standard polaronic treatment we have known that self-trapping is governed by the ratio of the polaron binding energy to the quasiparticle bare bandwidth, roughly χ/V. The present analysis shows that, for rotational polarons of the kind considered here, the effect of this ratio can be superseded by that of the ratio of the saturation energy (a new quantity introduced in this analysis) to the bandwidth, if the latter ratio is small enough. Physically, this means that increases in the nonlinearity parameter do not succeed in overpowering the intersite motion of the quasiparticle because of the ceiling determined by the saturation energy.

Rotational polarons are of interest generally in any system in which a quasiparticle (an electron, or electronic or vibrational excitation) interacts with angular oscillations so strongly that the presence of the quasiparticle has an appreciable effect on the equilibrium direction of the molecule. Liquid crystals [19], which consist of partially ordered aggregates of molecules possessing directed shapes such as rods or discs, provide an example.

5. Ongoing work, microscopic evolution, and concluding remarks

The new effects we have described above for the rotational polaron, viz., saturation of nonlinearity, destruction of self-trapped states, and occurrence of multiple stationary states, are neither particular to the specific similarities in the coordinate dependence of the restoring force and the interaction energy exemplified in (3.11), nor even to rotations. Indeed, it has recently been shown [7] that a *linear* quasiparticle–oscillation interaction along with the anharmonicity represented by the oscillation potential [2]

$$\mathcal{U}(x) = \frac{1}{2}ka\left[(a-|x|)\ln\left(1-\frac{|x|}{a}\right)+|x|\right] \tag{5.1}$$

[2] The potential (5.1) which leads to (5.2) and to the analysis of exponential saturation given in [7] was earlier written and plotted as $\mathcal{U}(x) = (1/2)ka[(a+|x|)\ln(1+|x|/a) - |x|]$ as a result of a consistent sign error. This 'logarithmically soft oscillator' contains physics different from the model presented in [7] which should be properly termed the "logarithmically hard oscillator". The nature of the transition is considerably altered by the sign change.

will result in the generalized DNLSE

$$i\hbar\frac{dc_m}{dt} = \sum_n V_{mn}c_n - \chi_0[1 - e^{-(\chi/\chi_0)|c_m|^2}]c_m \tag{5.2}$$

and to essentially all the effects described for the rotational polaron. A partial analysis of the general conditions necessary in an arbitrary system for the occurrence of the saturation effects elucidated here has been carried out and will be reported in a forthcoming publication [20].

While other ongoing work addresses these effects in extended systems and explicit consequences on the temperature dependence of the mobility, we believe the most important issue at the moment to be the investigation of what in the predicted effects survives when we refrain from making the semiclassical and the timescale disparity assumptions. The effects described result from a generalization of the DNLSE. The microscopic validity of the DNLSE, and generally of semiclassical constructs, has, however, come under strong criticism recently. Objections to semiclassical equations of motion have existed for quite some time [21]. Recent work has made clear the precise sources of the shortcomings [17,22] and shown under what conditions semiclassical equations can provide a reasonable description [18]. The domain of validity of the DNLSE as a consequence of (1.1) emerges, as a result of this recent work, to be surprisingly (indeed alarmingly) small. It is, therefore, of obvious importance to study which of the exciting consequences of the generalized DNLSEs explained above persist when the point of departure is directly the appropriate generalizations of (1.1). A number of such studies have been carried out and others are under way. One such investigation [9,10] addresses self-trapping from the two-site version of (1.1) when the 'oscillator' is a free particle constrained in a box of length L. A comparison is carried out between this case and the harmonic oscillator case, taking L to be equal to $\hbar/Mw$, where M is the oscillator mass. The latter is the value of the displacement of the oscillator whose classical potential energy equals one quantum of vibrational energy. Clear similarities in the two cases, as well as differences, have been found. Other work along these microscopic directions has included a study of the fully quantum mechanical oscillator evolution for the rotational case [8] and attempts at a generalization of the standard displaced oscillator (dressing) transformation [12]. It is hoped that a clear picture will soon emerge.

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