Quantum Vibrational Impurity Embedded in a One-dimensional Chain *

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Abstract

We perform a fully quantum mechanical numerical calculation for the problem of a single electron (or excitation) propagating in a $N$-site one-dimensional chain in the presence of a single Holstein impurity. We compute the long-time averaged probability for finding the electron on the impurity site as a function of the nonlinearity parameter, defined in terms of the electron-phonon coupling strength and the oscillator frequency. The results, in the intermediate nonlinearity parameter range, differ substantially from the ones obtained through the use of the discrete nonlinear Schrödinger equation, even in the high-frequency regime.

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Interest concerning issues related to the interplay between nonlinearity and disorder in discrete systems lead us to consider some time ago, the problem of a single nonlinear (cubic power) impurity embedded in a discrete, linear, one-dimensional lattice. By using the lattice Green functions in a selfconsistent manner we were able to derive analytically all the bound state properties and the transmission coefficient through the impurity[1, 2]. We found an impurity nonlinearity threshold below which, there is no bound state, in marked contrast with the linear impurity case[3]. The dynamics of the problem showed the presence of a selftrapping transition, when the impurity nonlinearity exceeded a threshold value[2, 4, 5]. We also considered the case of a generalized impurity and, by using either an appropriate \textit{ansatz}[6] or the Green function formalism[7], were able to construct analytically a phase diagram in parameter space showing regions with different number of bound states. Extensions of the nonlinear impurity problem to a dimerized chain and to higher dimensions have been recently investigated[8].

In all of the above studies, the evolution of a quasiparticle propagating in the lattice is given by the discrete nonlinear Schrödinger equation (DNLS):

\[
\frac{idC_n}{dt} = V(C_{n-1} + C_{n+1}) - \chi |C_n|^{\sigma-1} C_n \delta_{n0}
\]

where \(C_n(t)\) denotes the probability amplitude for the quasiparticle to be at site \(n\), \(V\) is the nearest-neighbor transfer energy integral, \(\chi\) is the nonlinearity parameter and \(\sigma\) is the nonlinearity exponent. In the Holstein impurity context, the DNLS (for the cubic nonlinearity, \(\sigma = 3\)) describes the time evolution of an electron which is strongly coupled to the vibrational degrees of freedom of a molecule at the impurity site. In this case \(\chi = g^2/\omega\) where \(g\) is the electron-phonon coupling and \(\omega\) is the phonon frequency.

However, several doubts have been raised concerning the general applicability of the semiclassical approximation on which the DNLS is based to the fully quantum mechanical Holstein problem[9 - 13]. This has motivated us to calculate the effect of quantum fluctuations in these impurity systems. In the present letter we perform a fully quantum mechanical numerical calculation for a single vibrational impurity coupled to an electron (or excitation) at a given site \((j = 0)\) of a finite chain with periodic boundary conditions and compare the results to the DNLS predictions. The Hamiltonian is

\[
H = \sum_{j=0}^{N-1} \left\{ C_j^\dagger C_{j+1} + C_{j+1}^\dagger C_j \right\} + \omega a^\dagger a + g(a + a^\dagger) C_0^\dagger C_0
\]
electron-phonon coupling at the impurity site. The most general eigenfunction has the form
\[ |\Psi_E\rangle = \sum_{j=0}^{N-1} \sum_{\nu=0}^{\infty} \alpha_j^{(\nu)} |\nu\rangle \otimes |j\rangle \]
where \(|\nu\rangle = (\alpha_0^{(\nu)})^{\nu} / \sqrt{\nu!} |0\rangle_{ph} \) and \(|j\rangle = C_j^{\dagger} |0\rangle_e\). The states \(|0\rangle_{ph}\) and \(|0\rangle_e\) are the phonon and electron vacuum, respectively. After inserting Eq. (3) into the eigenvalue equation \(H|\Psi_E\rangle = E|\Psi_E\rangle\), we obtain
\[ \sum_{j=0}^{N-1} \sum_{\nu=0}^{\infty} [E - \omega \nu] \alpha_j^{(\nu)} C_j^{\dagger} |\nu\rangle = V \sum_{j=0}^{N-1} \sum_{\nu=0}^{\infty} [\alpha_{j-1}^{(\nu)} + \alpha_{j+1}^{(\nu)}] C_j^{\dagger} |\nu\rangle + g C_0^{\dagger} \sum_{\nu=0}^{\infty} \left[ \alpha_{0}^{(\nu+1)} \sqrt{\nu+1} + \alpha_0^{(\nu-1)} \sqrt{\nu} \right] |\nu\rangle \]

The use of the transfer matrix formalism and periodic boundary conditions allows us to express all the \(\alpha_j^{(\nu)}\) in terms of the \(\alpha_0^{(\nu)}\) viz.,
\[ \alpha_j^{(\nu)} = \frac{\alpha_0^{(\nu)}}{\sinh(NK_\nu)} \left[ \sin(jK_\nu) + \sin((N - j)K_\nu) \right] \]
where the wavevector \(K_\nu\) is defined by \(A_\nu \equiv (E - \omega \nu) / 2V = \cos(k_\nu)\) and the eigenvalue equation reduces to
\[ (g/V) \sinh(NK_\nu) \left\{ \alpha_0^{(\nu+1)} \sqrt{\nu+1} + \alpha_0^{(\nu-1)} \sqrt{\nu} \right\} = 2 \alpha_0^{(\nu)} \sin(k_\nu) \sinh(NK_\nu) - 1 \]

When \(|A_\nu| > 1\), \(k_\nu \rightarrow iK_\nu + \{0, \pi\}\) where the left (right) choice corresponds to \(A_\nu > 1\) (\(A_\nu < -1\)) and where \(K_\nu\) is given by \(K_\nu = \log(|A_\nu| + \sqrt{A_\nu^2 - 1})\). The trigonometrical equations (3), (6) change to a hyperbolic form:
\[ \alpha_j^{(\nu)} = \frac{\alpha_0^{(\nu)}}{\sinh(NK_\nu)} \left[ (\pm 1)^N \sinh(jK_\nu) + \sinh((N - j)K_\nu) \right] (\pm 1)^j \]
\[ (g/V) \sinh(NK_\nu) \left\{ \alpha_0^{(\nu+1)} \sqrt{\nu+1} + \alpha_0^{(\nu-1)} \sqrt{\nu} \right\} = \pm 2 \alpha_0^{(\nu)} \sinh(K_\nu) \sinh(NK_\nu) \}

where the \(\pm\) sign corresponds to the sign of \(A_\nu\). Equations (3) and (8) constitute an infinite set of “three-terms” recursion relations of the form:
\[ c_\nu \alpha^{(\nu-1)} + b_\nu \alpha^{(\nu)} + a_\nu \alpha^{(\nu+1)} = 0 \]

The eigenvalue equation associated to this (infinite) tridiagonal equation can be solved by a standard method. However, some care must be taken in order to avoid numerical
instabilities: we iterate Eq. (9) from two directions, “up” from $\nu = 0$ up to $L$ and “down” from $\nu_{\text{max}}$ down to $L$, where $\nu_{\text{max}}$ is an appropriate phonon number cutoff. The eigenvalue equation is then obtained by imposing that both iterations yield the same value for $\alpha_0^{(L+1)}/\alpha_0^{(L)}$ at the “gluing” point $\nu = L$, chosen to ensure the numerical stability of the iteration process. The precision of the numerical computation is monitored through several tests:

(a) Evaluation of

$$\left| \left\{ \frac{\alpha_0^{(L+1)}}{\alpha_0^{(L)}} \right\}_{\text{up}} - \left\{ \frac{\alpha_0^{(L+2)}}{\alpha_0^{(L+1)}} \right\}_{\text{up}} \right| + \left| \left\{ \frac{\alpha_0^{(L+1)}}{\alpha_0^{(L-1)}} \right\}_{\text{down}} - \left\{ \frac{\alpha_0^{(L+2)}}{\alpha_0^{(L+1)}} \right\}_{\text{down}} \right|$$

(b) Orthogonality relations: for instance, $\sum_{\mu} \alpha_{0,\mu}^{(0)} \alpha_{0,\mu}^{(\nu)} = \delta_{\nu,0}$ where the index $\mu$ runs over all the eigenstates.

(c) A general test based on the Hamiltonian: If $A$ is an arbitrary operator, then the mean value of $\Omega \equiv [A, H]$ over any eigenstate of $H$ is identically zero. For instance, if we take $A = a$, the phonon destruction operator, the identity $0 = \langle \Omega \rangle$ leads to the condition $\omega < a > + g < C_0^\dagger C_0 > = 0$.

Once in possession of all the eigenenergies $E_\mu$ and the amplitudes $\alpha_{j,\mu}^{(\nu)}$, we are ready to compute dynamical observables. As the initial condition for the electron we use the one that places it completely on the impurity site at $t = 0$ and focus on the probability $P_0(t)$ for finding it there at an arbitrary time $t$ later. For the phonon part we use two different initial conditions: an undisplaced oscillator (zero phonons present) and a naturally “relaxed” oscillator (a coherent state). Due to absence of degeneration, the long-time average probability $< P_0 > = \lim_{T \to \infty} (1/T) \int_0^T P_0(t) \, dt$ can then be expressed in terms of the $\alpha_{0,\mu}^{(\nu)}$ as

$$< P_0 > = \sum_{\mu} \left[ \sum_{\nu=0}^{\infty} \alpha_{0,\mu}^{(\nu)} \right]^2 \left[ \sum_{n=0}^{\infty} p_n \alpha_{0,\mu}^{(n)} \right]^2$$

where

$$p_n = \begin{cases} \frac{1}{\sqrt{n!}} \left( \frac{-g}{\omega} \right)^n \exp\left[-(g/\omega)^2/2\right] & \text{undisplaced oscillator} \\ \delta_{n,0} & \text{coherent state case} \end{cases}$$

We have examined the behavior of Eq. (11) as a function of the nonlinearity parameter $\chi/V \equiv g^2/\omega V$, for different oscillator frequencies ($\omega \propto 1/\sqrt{\text{mass}}$), for chains with $N = 2, 3, 4$ and 5, the chain corresponding to $N = 2$ being the only nonperiodic
one. We show the results for $N = 2$ and $N = 4$ in figures 1-4 where we also compare with the quantity $< P_0 >$ evaluated though the DNLS equation. We observe significant departure from the DNLS prediction for intermediate nonlinearity, even for very large $\omega$. In the case of an (initially) undisplaced oscillator, while $< P_0 >$ increases with $\chi$ on average, it also shows oscillatory behavior with $\chi$ for large oscillator mass. For smaller masses, the oscillatory behavior decreases setting into a monotonic curve for the smallest mass examined. This case, which is closer to the antiadiabatic limit where the DNLS equation should work, still differs significantly from the DNLS prediction. For the case of an (initially) displaced oscillator, $< P_0 >$ increases always monotonically with the nonlinearity parameter. In both cases, as the oscillator mass decreases, the curves converge to a linear-like impurity curve\[1, 3\], remaining significantly away from the DNLS prediction, down to the lowest mass considered here. For $\omega = 100V$ the curve is almost undistinguishable from the one corresponding to a static, linear impurity of strength $\chi$. We note, in particular, the dramatic difference in the slopes of the quantum mechanical versus the DNLS curve in the small coupling limit. The quantum mechanical impurity results approach the DNLS impurity results only in the very large coupling limit $\chi \to \infty$. Similar results are found for the $N = 3$ and $N = 5$ case.

The equivalence of model (2) with a static impurity can be understood as follows: Let us perform the canonical transformation $H \to \tilde{H} = UHU^{-1}$ with $U = \exp[\lambda(a - a^\dagger)C_0^\dagger C_0]$. With the choice $\lambda = -g/\omega$, the transformed Hamiltonian becomes:

$$\tilde{H} = \sum_j [ V_j C_j^\dagger C_{j+1} + \text{h.c.} ] + \omega a^\dagger a - (g^2/\omega) C_0^\dagger C_0$$

(13)

where

$$V_j = \begin{cases} V \exp\left(\frac{g}{\omega}(a - a^\dagger)\right) & j = 0 \\ V \exp\left(-\frac{g}{\omega}(a - a^\dagger)\right) & j = -1 \\ V & j \neq 0, -1 \end{cases}$$

(14)

In the limit $\omega \to \infty$ with fixed $\chi = g^2/\omega$

$$\tilde{H} \to \sum_j [ V C_j^\dagger C_{j+1} + \text{h.c.} ] + \omega a^\dagger a - (g^2/\omega) C_0^\dagger C_0$$

(15)

which is the Hamiltonian for a chain with a single static, linear impurity. Therefore, in the limit $\omega \to \infty$ ($\omega \sim 100V$ is good enough) with fixed $\chi = g^2/\omega$, our Hamiltonian becomes equivalent to the one of a single, static, linear impurity. The DNLS limit is never achieved.

We have directly shown in the present work that the problem of a single vibrational impurity embedded in a finite linear chain, when treated in a completely quantum-mechanical framework, does not approach the predictions based on the DNLS. We
conclude that, for the Holstein impurity problem the DNLS fails to describe correctly the selftrapping process. Our results agree with recent studies\cite{13} on a coupled quasiparticle-boson system which also finds that the DNLS has a limited range of validity in the context of this problem. It would be interesting to test the DNLS in a system possessing translational symmetry where the enhancement of trapping due to the single impurity character of the present model would be absent. Work in that direction is currently under way by our group.

Finally, it is worthwhile pointing out that the general solutions for DNLS-like impurity problems that have been obtained earlier retain their validity and usefulness in classical problems where DNLS is valid. Examples of these problems are typically furnished from nonlinear optical applications.

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FIGURE CAPTIONS

**Figure 1:** $N = 2$ chain: Long-time average probability of finding the electron (excitation) on the impurity versus the nonlinearity parameter $\chi/V = g^2/\omega V$, for different oscillator frequencies (masses). The oscillator is initially undisplaced.

**Figure 2:** Same as in figure 1, but for the case of an initially *displaced* oscillator.

**Figure 3:** $N = 4$ chain: Long-time average probability of finding the electron (excitation) on the impurity versus the nonlinearity parameter $\chi/V = g^2/\omega V$, for different oscillator frequencies (masses). The oscillator is initially undisplaced.

**Figure 4:** Same as in figure 3, but for the case of an initially *displaced* oscillator.
