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Mass enhancement in narrow-band systems

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Abstract. A perturbative study of the Holstein molecular crystal model which accounts for lattice structure and dimensionality effects is presented. Anti-adiabatic conditions peculiar to narrow-band materials and an intermediate-to-strong electron–phonon coupling are assumed. The polaron effective mass depends crucially in all dimensions on the intermolecular coupling strengths which also affect the size of the lattice deformation associated with the small-polaron formation.

1. Introduction

Several studies published over the last few years have addressed questions related to the existence of small polarons with itinerant properties in real systems [1–7]. This issue is central for a possible description of high-T_c superconductivity in terms of (bi)polaronic models [8, 9]. In spite of being well defined quasiparticles, small polarons may lose their mobility either because of a dynamical dephasing between the charge carriers and their surrounding deformation field or because of the heaviness of the effective mass. These effects could however differ significantly according to the regime (adiabatic or anti-adiabatic) and the strength of electron–phonon coupling characterizing the system [10]. Theoretical investigations start generally from the Holstein molecular crystal model [11], a fundamental tool which has revealed a rich variety of behaviours in the polaron landscape through the use of quantum Monte Carlo methods [12, 13], density matrix renormalization group techniques [14], variational methods [7, 15–17], cluster solutions [18–21] and perturbative approaches [22–24]. A numerical study of the polaron bandwidth in the first order of perturbative theory has proved that the phonon momentum dependence is a *key* feature of the Holstein Hamiltonian and that the lattice dimensionality strongly influences the bandwidth values [25]. Unlike other properties such as ground-state energy and effective mass, the bandwidth is not affected by second-order corrections and therefore it provides a useful test bench for alternative, non-perturbative attacks on the polaron problem [26]. Being aware of the importance that the intermolecular forces have in the narrowing of the polaron band, we report here on a perturbative numerical study of the mass enhancement in the strong-coupling and anti-adiabatic regime. My reasons for choosing to start from this regime are threefold:

(i) it is the easiest in the sense that the lattice deformation follows the charge carriers coherently and the above-mentioned dephasing features can be ruled out;
(ii) the unit comprising electron *and* phonon dressing is a stable small polaron—that is, the size of the quasiparticle is not significantly broadened in some portions of our parameter space;

(iii) this regime is relevant to several classes of narrow-band materials whose charge-carrier effective masses merit accurate estimates.

Although the present work assumes that the carriers are coupled to bosonic degrees of freedom having a vibrational origin, anti-adiabatic conditions are likely to occur in excitonic systems where the characteristic frequency $\bar{\omega}$ could easily be of the order of 1 eV and the boson can therefore follow the electron essentially without retardation. In these cases the carrier effective mass is expected to be only moderately enhanced with respect to the bare-electron mass.

In section 2, the dispersive Holstein model is briefly reviewed while the numerical results are displayed in section 3. Some conclusions are drawn in section 4.

2. The Holstein model with dispersive phonons

My starting point is the real-space–momentum-space representation of the Holstein Hamiltonian which reads

$$H = -t\sum_{i\neq j} c_i^\dagger c_j + \epsilon\sum_j c_j^\dagger c_j + \sum_{\boldsymbol{k}} \hbar\omega_{\boldsymbol{k}} a_{\boldsymbol{k}}^\dagger a_{\boldsymbol{k}} + \frac{g}{\sqrt{N}}\sum_{\boldsymbol{k}}\sum_j c_j^\dagger c_j (a_{\boldsymbol{k}} + a_{-\boldsymbol{k}}^\dagger)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j). \tag{1}$$

$c_i^\dagger$ (c_i) creates (destroys) a tight-binding electron at the ith molecular site and t is the hopping integral related to the bare-electron half-bandwidth D by $D = zt$, z being the coordination number. ϵ is a reference electronic energy and $\boldsymbol{r}_j$ is the jth-lattice-site vector. N is the number of molecules in the lattice. It is understood that t differs from zero only between first-neighbour sites and this poses a constraint on the $i \neq j$ sum in the first term. $a_{\boldsymbol{k}}^\dagger$ ($a_{\boldsymbol{k}}$) creates (destroys) a $\boldsymbol{k}$-phonon with frequency $\omega_{\boldsymbol{k}}$. The lattice dimensionality enters the problem through the phonon dispersion relations which have been obtained analytically by assuming first-neighbour pairwise intermolecular forces along the linear chain (1D), in the square lattice (2D) and in the simple cubic lattice (3D) [27]:

$$\begin{aligned}
\omega_{1D}^2(k) &= \frac{\beta+\gamma}{M} + \frac{1}{M}\sqrt{\beta^2 + A_x}\\
\omega_{2D}^2(\boldsymbol{k}) &= \frac{\beta+2\gamma}{M} + \frac{1}{M}\sqrt{\beta^2 + 2B_{x,y}}\\
\omega_{3D}^2(\boldsymbol{k}) &= \frac{\beta+3\gamma}{M} + \frac{1}{M}\sqrt{\beta^2 + C_{x,y,z}}\\
A_x &= \gamma^2 + 2\gamma\beta c_x\\
B_{x,y} &= \gamma^2(1 + c_x c_y + s_x s_y) + \beta\gamma(c_x + c_y)\\
C_{x,y,z} &= \gamma^2(3 + 2(c_x c_y + s_x s_y + c_x c_z + s_x s_z + c_y c_z + s_y s_z)) + 2\beta\gamma(c_x + c_y + c_z)
\end{aligned} \tag{2}$$

where $c_x = \cos k_x$, $c_y = \cos k_y$, $c_z = \cos k_z$, $s_x = \sin k_x$ etc. β is the intramolecular force constant and γ is the intermolecular first-neighbour force constant. Let us define $\omega_0^2 = 2\beta/M$ and $\omega_1^2 = \gamma/M$ with M being the reduced molecular mass. N is the number of diatomic molecules in the lattice and g is the local electron–phonon coupling constant. The adiabatic parameter is $\hbar\bar{\omega}/D$, $\bar{\omega}$ being a characteristic phonon frequency which we take as the zone-centre frequency and whose expression is: $\bar{\omega}^2 = \omega_0^2 + z\omega_1^2$.

Throughout this paper we fix $\hbar\omega_0 = 100$ meV and $t = 15$ meV so that the anti-adiabatic condition $\hbar\bar{\omega}/D > 1$ is fulfilled in any dimensionality. Moreover, our perturbative approach requires the occurrence of the condition $D < g$ [28]. By applying the Lang–Firsov unitary transformation [29] and a subsequent $1/\lambda_0$ expansion, with $\lambda_0 \equiv g^2/(\hbar\omega_0 D)$ being the ratio between the polaron binding energy and the electron half-bandwidth [30], H of equation (1) transforms into $\tilde{H} = \tilde{H}_0 + \tilde{H}_P$ with

$$\begin{aligned}
\tilde{H}_0 &= \sum_{\boldsymbol{k}} \hbar\omega_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}} a_{\boldsymbol{k}} + \left(\epsilon - \frac{g^2}{N}\sum_{\boldsymbol{k}}(\hbar\omega_{\boldsymbol{k}})^{-1}\right)\sum_j c^\dagger_j c_j \\
&\quad - \frac{g^2}{N}\sum_{\boldsymbol{k}}\sum_{i\neq j}\frac{\exp\big(\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)\big)}{\hbar\omega_{\boldsymbol{k}}} c^\dagger_j c_j c^\dagger_i c_i \\
\tilde{H}_P &= -t\sum_{i\neq j}\exp\Big[-\frac{2g^2}{N}\sum_{\boldsymbol{k}}(\hbar\omega_{\boldsymbol{k}})^{-2}\sin^2\frac{(\boldsymbol{k}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j))}{2}\Big] \\
&\quad \times \sum_{m=0}^{\infty}\frac{1}{m!}\Big[\frac{g}{\sqrt{N}}\sum_{\boldsymbol{k}}\frac{a^\dagger_{-\boldsymbol{k}}}{\hbar\omega_{\boldsymbol{k}}}\big(\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}-\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j}\big)\Big]^m \\
&\quad \times \sum_{n=0}^{\infty}\frac{1}{n!}\Big[\frac{g}{\sqrt{N}}\sum_{\boldsymbol{k}}\frac{a_{\boldsymbol{k}}}{\hbar\omega_{\boldsymbol{k}}}\big(\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j}-\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}\big)\Big]^n c^\dagger_i c_j.
\end{aligned} \tag{3}$$

$\tilde{H}_0$ is diagonal except for a second-order term in the electron density operator which could cause an attractive electron–electron interaction [8]. The perturbation $\tilde{H}_P$ displays the fundamental features of the polaronic quasiparticle such as the hopping integral narrowing (the first factor in equation (3)) plus the peculiar mixing of fermionic and bosonic variables. At any electron–phonon interaction vertex, m (n) phonons can be emitted from (absorbed by) the cloud surrounding the electron provided that the total crystal momentum is conserved. By choosing a transformed ground state with no phonons we see that the first-order dispersive contribution $E^{(1)}$ to the ground-state polaron band arises only from the $n = m = 0$ term in equation (3) and hence from the zero-phonon scattering process. In 3D and taking a lattice spacing $a = |\boldsymbol{r}_i - \boldsymbol{r}_j| = 1$, one finds

$$E^{(1)}(\boldsymbol{p}) = -2t(\cos p_x + \cos p_y + \cos p_z)\exp\Big[-\frac{2g^2}{N}\sum_{k_x}\sin^2\frac{k_x}{2}\sum_{k_x,k_y}(\hbar\omega_{\boldsymbol{k}})^{-2}\Big] \tag{4}$$

where the total crystal momentum $\boldsymbol{p}$ coincides with the electron momentum due to the absence of self-energy corrections. The second-order perturbative contribution requires summation over all intermediate states having m $\boldsymbol{k}$-phonons more than the vacuum and one electron on a first neighbour i of the initial site j. Moreover, the final electronic position f can either coincide with j (this process does not introduce dispersive effects in the polaron band) or be a first neighbour of the i-site. The latter scenario is clearly dimension dependent: in 1D the final site is a second neighbour of j, in 2D f can be either a second or a third neighbour of j and in 3D the fourth-neighbour site can also be reached via hopping. While the detailed study of these dispersive effects (which can become relevant in adiabatic conditions) is postponed to a later paper, we turn now to computing the polaron effective mass. It should be remarked that the second-order corrections decrease the mass values calculated in first-order perturbative theory which therefore should be taken to provide upper bounds for the polaron mass.

3. Polaron effective masses

The polaron mass m^* can be obtained according to the definition

$$\frac{m^*}{m_0} = \frac{zt}{\nabla^2 E(\boldsymbol{p})|_{\boldsymbol{p}=0}} \tag{5}$$

where m_0 is the bare-band mass and the dispersive polaron band is given by equation (4). The polaron binding energy obviously has no $\boldsymbol{p}$-dispersion. Then, m^*/m_0 is at first order independent of t and coincident simply with the reciprocal of the band-narrowing factor. This picture holds in the strong-coupling regime assumed here. In figure 1(a), the computed ratios m^*/m_0 for 1D, 2D and 3D are shown versus the first-neighbour intermolecular force constant ω_1. While the polaron masses strongly depend on the dimensionality d and are very large at small ω_1, the ratios become essentially d-independent in the upper portion of the parameter range and tend to converge to 2. The value of the polaron binding energy $\lambda_0 > 1$ signals that the energy gain associated with the lattice deformation is larger than the kinetic energy due to the tight-binding hopping in the bare band. Therefore it is energetically convenient to the electron

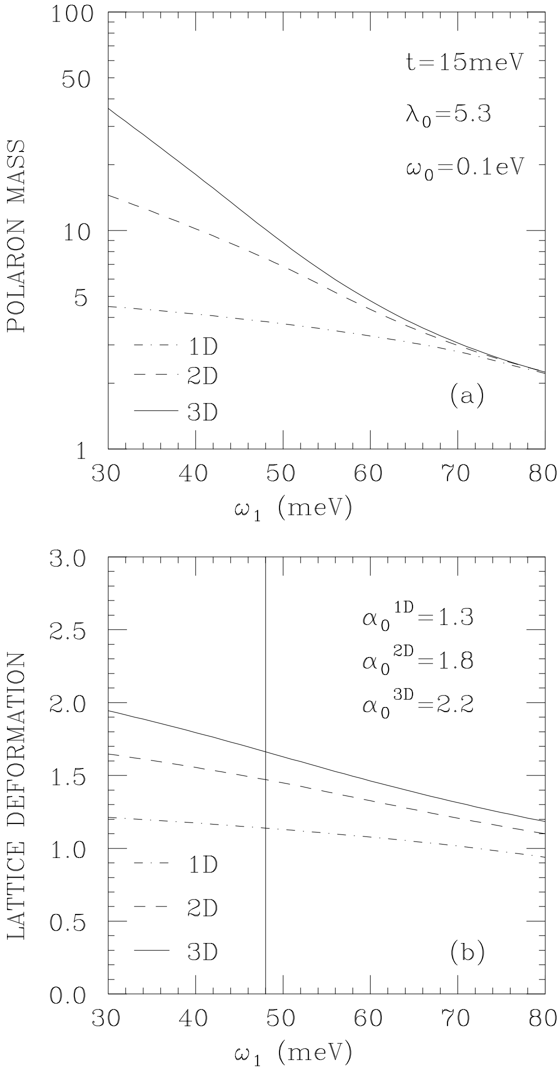

Figure 1. (a) One-, two- and three-dimensional polaron masses (in units of the bare-band mass) versus the first-neighbour intermolecular energy. The dispersionless polaron binding energy is 5.3, in units of the bare-electron kinetic energy $D = zt$. (b) One-, two- and three-dimensional lattice deformations versus the first-neighbour intermolecular energy. The α_0^d are the lattice deformation values in a dispersionless model ($\omega_1 = 0$). $\bar{\omega}_1 = 48$ meV marks the lower bound for the validity of the model (see the text).

to be dressed by the phonon cloud and become a quasiparticle. Actually, in anti-adiabatic regimes, the more restrictive condition concerning the lattice deformation $\alpha_0 \equiv g/(\hbar\omega_0) > 1$ needs to be fulfilled to guarantee that our quasiparticle *is a small polaron*. While λ_0 and α_0 refer to a system with dispersionless phonons it is clear that both the polaron binding energy and the lattice deformation parameter will change after switching on the intermolecular interactions. The role of the intermolecular couplings is not simply that of increasing the characteristic phonon frequency but rather that of establishing the correct Holstein model dependence on dimensionality. Ignoring the intermolecular couplings would yield a 1D polaron band ΔE_{1D} that was larger than the 2D polaron band ΔE_{2D} and $\Delta E_{2D} > \Delta E_{3D}$ which is clearly unphysical since the polaronic wave-function overlap is larger for higher dimensionality. This wrong trend would hold for any value of the intramolecular frequency ω_0. Thus, as observed by Holstein himself in his original paper [11], the phonon dispersion is a vital ingredient of the theory and this observation motivates our numerical investigation.

Because of our definitions, λ_0 does not depend on d whereas α_0 is $\propto\sqrt{d}$. In figure 1(b) we see that the lattice deformation

$$\alpha = N^{-1} g \sum_{k} (\hbar\omega_k)^{-1}$$

is in all dimensions a decreasing function of the intermolecular force constant and, in 1D, the system does not fulfil the small-polaron condition at the largest ω_1-values. This case has been presented to point out how the starting condition $\alpha_0^{1D} = 1.3$ sets the 1D system rather in an intermediate-coupling regime where a broadening of the polaron size can take place [31, 32]. Under these conditions the same perturbative method based on the Lang–Firsov transformation becomes questionable†. Below $\bar{\omega}_1 = 48$ meV the polaron bandwidth inequalities $\Delta E_{3D} > \Delta E_{2D} > \Delta E_{1D}$ are not satisfied [25] as expected on general grounds; hence, the dispersionless and the weakly dispersive Holstein Hamiltonians yield erroneous estimates of the effective masses. The straight line in figure 1(b) marks therefore the lower bound for the intermolecular coupling which guarantees the validity of the model.

Increasing the electron–phonon coupling—see figure 2(a)—leads to a strong mass enhancement (particularly in 3D) at small ω_1 while the mass ratios converge to 5 at large intermolecular coupling strengths. Note (figure 2(b)) that the polaron is small for all d throughout the whole ω_1-range; hence the Lang–Firsov method works well in this case. The threshold value for the validity of the Holstein model is set here at $\bar{\omega}_1 = 59$ meV. The inequalities $m^*_{3D} > m^*_{2D} > m^*_{1D}$ keep on being satisfied for a range of ω_1-values above the threshold before convergence is achieved, but second-order perturbative terms (being larger for higher dimensionality) are expected to partly correct this trend. Figures 3 show that a stronger e–ph coupling, with $\lambda_0 = 21.3$, yields a mass ratio of $\simeq$25 and shifts the threshold $\bar{\omega}_1$ to 65 meV, indicating the relationship between the features of the phonon spectrum and the strength of the g-coupling. Also in this case the polaron size remains *small* throughout the whole ω_1-range (see figure 3(b)), thus confirming the reliability of the Lang–Firsov method in a regime of strong e–ph coupling with anti-adiabatic conditions.

Next, I have varied g in the range 1–4 (in units of $\hbar\omega_0$) and found, at any g, the minimum intermolecular coupling $\bar{\omega}_1(g)$ at which the bandwidth inequalities $\Delta E_{3D} > \Delta E_{2D} > \Delta E_{1D}$ are satisfied. This criterion yields an empirical relation, $\bar{\omega}_1(g) \simeq \bar{\omega}_1(1)(1 + \ln(g))$, which allows one to obtain a reliable estimate of the polaron effective mass. In figure 4 the 1D mass ratio is plotted versus the dimensionless $g/(\hbar\omega_0)$ both in the first and the second order of perturbative theory: it turns out that second-order corrections are negligible in 1D systems

† The questions related to the validity of the perturbative approach both in the adiabatic and the anti-adiabatic regime will be discussed in detail in a forthcoming paper.

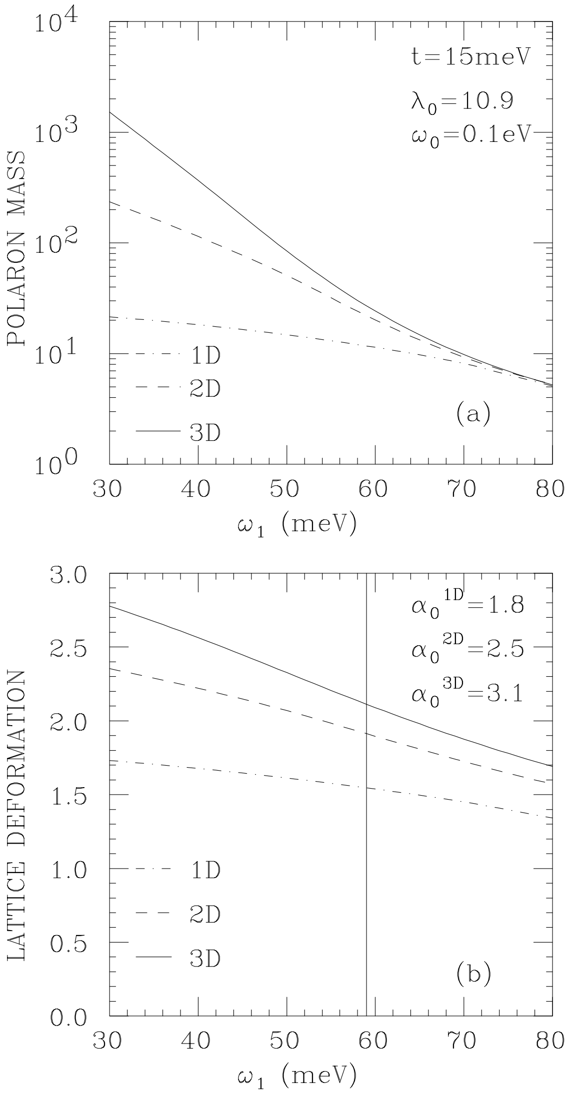

Figure 2. (a) As figure 1(a), but with a dispersionless polaron binding energy $\lambda_0 = 10.9$. (b) As figure 1(b), but with larger lattice deformation values. The lower bound for the validity of the model is set at $\bar{\omega}_1 = 59$ meV.

with anti-adiabatic conditions such as those that we have assumed. I wish to point out that the mass values reported in figure 4 correspond, at any g, to the minimum ω_1 (the threshold) which ensures the smallness of the ground-state polaron. Thus, they are upper bounds for the 1D mass in the sense that the presence of larger intermolecular forces would yield lower mass values. As expected on general grounds [33, 34], the small-polaron solution is the ground state of the discrete Holstein model in the regime of intermediate-to-strong e–ph coupling considered here, while, on decreasing the coupling, a continuous crossover to large-polaron solutions can take place in 1D [31]. We have however seen (figure 1(b)) that the dispersive features of the phonon spectrum could affect the transition by inducing a spreading of the lattice deformation. Anyway, the smoothness of our m^* versus α_0 curve (persisting also in the lower α_0-range not

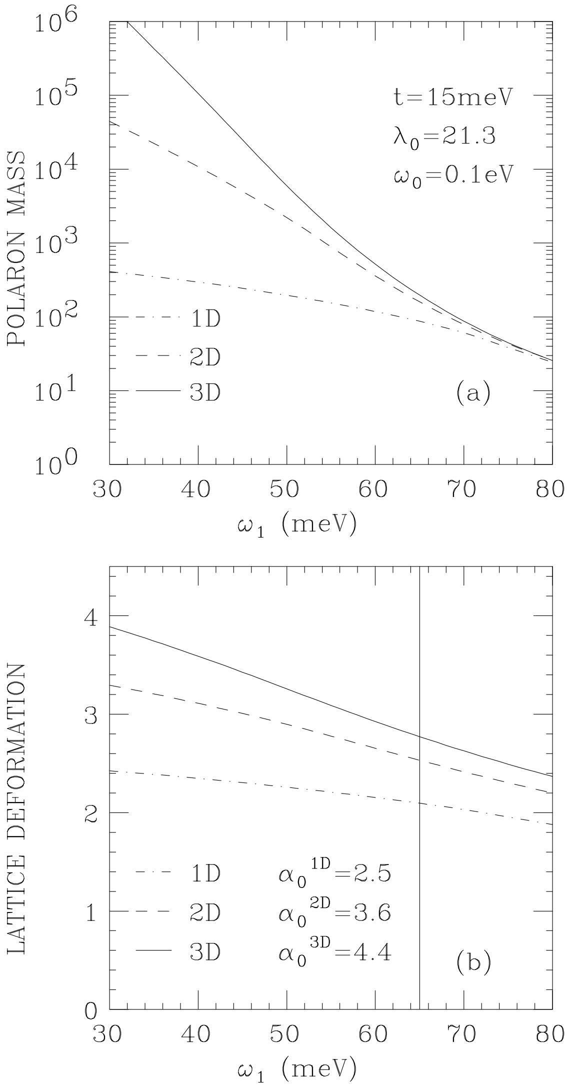

Figure 3. (a) As figure 1(a), but with a dispersionless polaron binding energy $\lambda_0 = 21.3$. (b) As figure 1(b), but with larger lattice deformation values. The lower bound for the validity of the model is set at $\bar{\omega}_1 = 65$ meV.

displayed in figure 4) confirms that no self-trapping is found in 1D anti-adiabatic regimes, whereas recent variational [35] and perturbative investigations signalling a rapid growth of m^* versus e–ph coupling support the existence of the self-trapping transition between polaron states of different structure in 1D adiabatic systems. In any case, phase transitions in Holstein models are ruled out, since the ground-state energy is an analytic function of the e–ph coupling.

4. Concluding remarks

I have presented the first results from a perturbative approach to the polaron problem which focuses on the lattice dimensionality effects. Having chosen the anti-adiabatic regime of

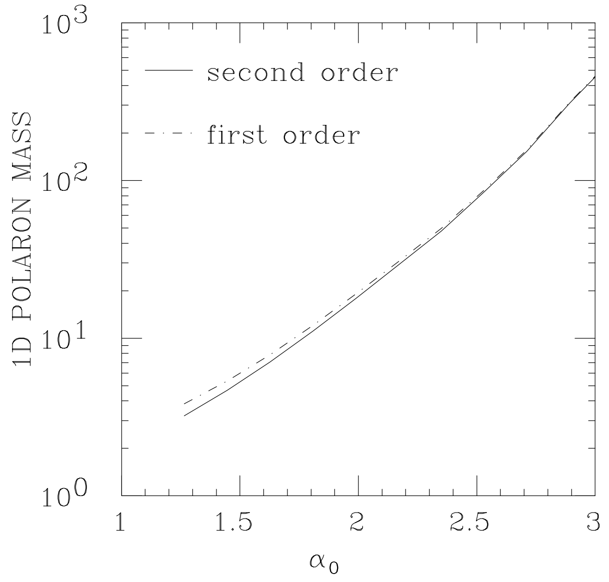

Figure 4. One-dimensional polaron mass (in units of the bare-band mass) versus the lattice deformation parameter. Both the first- and second-order perturbative results are displayed.

the Holstein molecular crystal model, we are confident of the accuracy of the first-order perturbative theory for one-dimensional systems with strong e–ph coupling, whereas some significant second-order corrections can occur for higher dimensionality. While a previous work [25] had shown that a dispersionless Holstein model leads to (i) erroneous estimates of the polaron bandwidth versus dimensionality and (ii) unphysical divergences in the site jump probability [36], the present study reveals that the polaron effective mass is in all dimensions very sensitive to the strength of the forces which tie the molecules in the lattice. We obtain polaron masses between 2 and 25 times the bare-band mass by varying the e–ph coupling in the range $\simeq$1–2.5 and these values become essentially dimension independent when the intermolecular forces are sufficiently strong. The molecular lattice structure has been described by means of a single parameter, the first-neighbour intermolecular coupling, it being understood that the range of the interactions should be extended in real systems if least-squares fitting of the experimental phonon frequencies can provide effective values for the next neighbours and long-range force constants [37]. The anti-adiabatic regime with strong e–ph coupling ensures the validity of the quasiparticle picture for the small polaron; nonetheless we have seen that some broadening of the phonon cloud can arise at intermediate e–ph couplings for strong values of the intermolecular forces with consequent lowering of the lattice deformation parameter. This interesting feature suggests that the intermolecular forces influence the quasiparticle size and, incorporating the effects of the e–ph coupling, have a role in driving the continuous transition between large and small polarons.

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