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# Polaron crossover in molecular solids

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## Abstract

An analytical variational method is applied to the molecular Holstein Hamiltonian in which the dispersive features of the dimension dependent phonon spectrum are taken into account by a force constant approach. The crossover between a large and a small size polaron is monitored, in one, two and three dimensions and for different values of the adiabatic parameter, through the behaviour of the effective mass as a function of the electron–phonon coupling. By increasing the strength of the intermolecular forces the crossover becomes smoother and occurs at higher e–ph couplings. These effects are more evident in three dimensions. We show that our modified Lang–Firsov method starts to capture the occurrence of a polaron self-trapping transition when the electron energies become of order of the phonon energies. The self-trapping event persists in the fully adiabatic regime. At the crossover we estimate polaron effective masses of order  $\sim 5$ –40 times the bare band mass according to the dimensionality and the value of the adiabatic parameter. Modified Lang–Firsov polaron masses are substantially reduced in two and three dimensions. There is no self-trapping in the antiadiabatic regime.

## 1. Introduction

There has been a growing interest in polarons over the last years, partly in view of the technological potential of polymers and organic molecules [1, 2] in which polaronic properties have been envisaged. Theoretical investigations on polarons generally start from the Holstein Hamiltonian [3] originally proposed for a diatomic molecular chain along which hopping of electrons, linearly coupled to the vibrational quanta, takes place according to a tight-binding description. If the local e–ph coupling is sufficiently strong, the induced lattice deformation may dress the electron and transform it into a polaronic charge carrier [4, 5]. The conditions for polaron formation and its mobility properties may, however, also depend on the adiabaticity

ratio, on dimensionality, and on peculiarities and anharmonicities of the lattice structure [6–15]. As the Holstein Hamiltonian can be identically applied to states made of excitons [16, 17] and phonons it also provides a useful tool in optical spectra analysis and transport properties of organic materials [18, 19] with large scale applications.

While the physical properties of polaronic systems change [20, 21] according to the size of the polaronic quasiparticle, a number of theoretical tools [22–26] have been applied to clarify the nature and width of the crossover between a large (with respect to the lattice constant) polaron at weak e–ph coupling and a small polaron at strong coupling for a given value of the adiabatic parameter. Provided that a phase transition is ruled out in the Holstein Hamiltonian with dispersive optical phonons [27] being the ground state energy analytic in the e–ph coupling, such a crossover may still appear as a smooth transition in the antiadiabatic regime, or rather as a sudden (but continuous) event in the adiabatic regime [28]. While the narrowing of the polaron band signals the onset of the crossover, it is certainly from the behaviour of the effective mass that the self-trapping event can be accurately located in the intermediate region of e–ph couplings [29]. Although precisely in the latter region perturbative studies traditionally reveal their shortcomings, an analytical method, the modified Lang–Firsov (MLF) transformation [30], has been developed to overcome the limitations of the standard Lang–Firsov (LF) [31] approach on which strong coupling perturbation theory is based. As an enhancement of the polaron mass should be accompanied by a reduction in the polaron size, the electron–phonon correlation function offers an independent tool to analyse the crossover through the measure of the spread of the lattice deformation. Since the notion of self-trapping transition has often assumed different meanings in the literature, we emphasize that our view of a *self-trapped polaron* is not that of a localized and immobile object but, rather, of a small quasiparticle whose different ground state properties have undergone a transition, driven by the e–ph coupling, at distinct although closely related points in the polaron parameter space [32]. Among these properties, we study in this paper, using the MLF transformation [33, 34], the polaron mass and the correlation function as obtained from a Holstein Hamiltonian in which the *dispersion* of the optical phonon branches is fully accounted for in any dimensionality. Besides depicting a model more appropriate to physical systems, dispersive phonons represent a relevant feature of the Holstein model itself as previously shown by one of us [35]. The role of the intermolecular forces in the crossover of the MLF polarons at different dimensionalities is a main focus of our investigation. The generalities of the model are given in section 2, while the results are presented in section 3 both for the polaron mass and for the static correlation function. Section 4 contains some final remarks.

## 2. The modified Lang–Firsov phonon basis for the Holstein model

We consider the dimension dependent Holstein Hamiltonian consisting of one electron hopping term, an interaction which couples the electronic density and the ionic displacements at a given site and dispersive harmonic optical phonons as

$$H = -t \sum_{\langle ij \rangle} c_i^\dagger c_j + g \sum_i n_i (b_i^\dagger + b_i) + \sum_{\mathbf{q}} \omega_{\mathbf{q}} b_{\mathbf{q}}^\dagger b_{\mathbf{q}}. \quad (1)$$

The first sum is over  $z$  nearest neighbours,  $c_i^\dagger$  and  $c_i$  are the real space electron creation and annihilation operators,  $n_i (=c_i^\dagger c_i)$  is the number operator, and  $b_i^\dagger$  and  $b_i$  are the phonon creation and annihilation operators.  $b_{\mathbf{q}}^\dagger$  is the Fourier transform of  $b_i^\dagger$  and  $\omega_{\mathbf{q}}$  is the frequency of the phonon with vector momentum  $\mathbf{q}$ .

The standard practice in dealing with the Hamiltonian (1) is to apply the LF transformation where a phonon basis of fixed displacements (at the electron residing site) is used. Such

a choice of phonon basis diagonalizes the Hamiltonian in the absence of hopping. The hopping term is then treated as a perturbation. However, the LF approach under simple approximations, e.g. within zero-phonon averaging or zeroth order of perturbation, cannot describe the retardation between the electron and the lattice deformations produced by the electron. This retardation induces a spread in the size of the polaron and becomes very important for weak and intermediate e–ph coupling. The MLF phonon basis, where the displacements of the oscillators at different sites around an electron are treated variationally, can describe the retardation and a large to small polaron crossover even within simple approximations [33, 34]. Recently the convergence of the perturbation series within the LF and the MLF methods has been studied in a two-site Holstein model for the ground state [30] as well as for the first excited state [36]. It was found that:

- (i) within the MLF method the perturbation corrections are much smaller than those corresponding to the LF method in the range from weak to intermediate e–ph coupling,
- (ii) the convergence of the perturbation series within the MLF is also much better in that range,
- (iii) in the strong coupling limit the MLF phonon basis reduces to the LF basis and the LF perturbation method works very well in this limit.

The above studies have clearly pointed out that the MLF perturbation method works much better than the LF method when the entire range of the e–ph coupling is considered.

The MLF perturbation method has also been applied to a many-site Holstein model with dispersionless phonons in 1D, and the supremacy of the MLF method over the LF method in predicting the ground state energy and dispersion of the polaron has been observed [37]. For the present case of dispersive phonon we apply the MLF transformation to the dimension dependent Hamiltonian (1):

$$\tilde{H} = e^R H e^{-R} \tag{2}$$

where

$$R = \sum_{\mathbf{q}} \lambda_{\mathbf{q}} n_{\mathbf{q}} (b_{-\mathbf{q}}^\dagger - b_{\mathbf{q}}),$$

$$n_{\mathbf{q}} = \frac{1}{\sqrt{N}} \sum_i n_i e^{-i\mathbf{q} \cdot R_i} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{k}} \tag{3}$$

and  $\lambda_{\mathbf{q}}$  are the variational parameters which represent the shifts of the equilibrium positions of the oscillators (quantized ion vibrations) with momentum  $\mathbf{q}$ . For conventional Lang–Firsov transformation  $\lambda_{\mathbf{q}} = g/\omega_{\mathbf{q}}$ . The MLF transformed Hamiltonian for a single electron case is obtained as

$$\begin{aligned} \tilde{H} = & -\epsilon_p \sum_i n_i - t_p \sum_{ij} c_i^\dagger c_j \exp \left[ \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \lambda_{\mathbf{q}} b_{\mathbf{q}}^\dagger (e^{i\mathbf{q} \cdot R_i} - e^{i\mathbf{q} \cdot R_j}) \right] \\ & \times \exp \left[ -\frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \lambda_{\mathbf{q}} b_{\mathbf{q}} (e^{-i\mathbf{q} \cdot R_i} - e^{-i\mathbf{q} \cdot R_j}) \right] \\ & + \sum_{\mathbf{q}} \omega_{\mathbf{q}} b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \sum_{\mathbf{q}} (g - \lambda_{\mathbf{q}} \omega_{\mathbf{q}}) n_{\mathbf{q}} (b_{-\mathbf{q}}^\dagger + b_{\mathbf{q}}) \end{aligned} \tag{4}$$

where

$$\epsilon_p = \frac{1}{N} \sum_{\mathbf{q}} (2g - \lambda_{\mathbf{q}} \omega_{\mathbf{q}}) \lambda_{\mathbf{q}} \tag{5}$$

is the polaron self-energy and

$$t_p = t \exp \left[ -\frac{1}{N} \sum_{\mathbf{q}} \lambda_{\mathbf{q}}^2 \left( 1 - \frac{\gamma_{\mathbf{q}}}{z} \right) \right] \quad (6)$$

is the polaronic hopping. The coordination number  $z$  is twice the system dimensionality.

$$\gamma_{\mathbf{q}} = \sum_j' e^{i\mathbf{q} \cdot \mathbf{R}_{ij}} = 2 \sum_{i=x,y,z} \cos q_i$$

where  $i$  and  $j$  are nearest neighbour sites. As unperturbed Hamiltonian we choose  $H_0$  as

$$H_0 = -\epsilon_p \sum_i n_i + \sum_{\mathbf{q}} \omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}}. \quad (7)$$

The remaining part of the Hamiltonian ( $\tilde{H} - H_0$ ) in the MLF basis is considered as the perturbation part. The energy eigenstates of  $H_0$  are given by

$$|\phi_i, \{n_{\mathbf{q}}\}\rangle = c_i^{\dagger} |0\rangle_e |n_{\mathbf{q}_1}, n_{\mathbf{q}_2}, n_{\mathbf{q}_3}, \dots\rangle_{\text{ph}} \quad (8)$$

where  $i$  is the electron site and  $n_{\mathbf{q}_1}, n_{\mathbf{q}_2}, n_{\mathbf{q}_3}$  are the phonon occupation numbers in the phonon momentum states  $\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3$ , respectively. The lowest energy eigenstate of the unperturbed Hamiltonian has no phonon excitations, i.e.  $n_{\mathbf{q}} = 0$  for all  $\mathbf{q}$ . The ground state has an energy  $E_0^0 = -\epsilon_p$  and is  $N$ -fold degenerate, where  $N$  is the number of sites in the system. The perturbation lifts the degeneracy and to first order in  $t$  the ground state energy of the 3D-polaron with momentum  $\mathbf{k}$  is given by

$$E_0(\mathbf{k}) = -\epsilon_p - t_p \gamma_{\mathbf{k}} \quad (9)$$

and the corresponding eigenstate is  $|\mathbf{k}, n_{\mathbf{q}} = 0\rangle = \frac{1}{\sqrt{N}} \sum_i e^{i\mathbf{k} \cdot \mathbf{R}_i} c_i^{\dagger} |0\rangle_e |0\rangle_{\text{ph}}$ .

The second order correction to the ground-state energy of the polaron with momentum  $\mathbf{k}$  is given by

$$E_0^{(2)}(\mathbf{k}) = \sum_{\mathbf{k}'} \sum_{\{n_{\mathbf{q}}\}} \frac{1}{\sum_{\mathbf{q}} n_{\mathbf{q}} \omega_{\mathbf{q}}} |\langle \{n_{\mathbf{q}}\}, \mathbf{k}' | \tilde{H} - H_0 | \mathbf{k}, \{0\} \rangle|^2. \quad (10)$$

It is evident that the second order correction has contributions from intermediate states having all possible phonon numbers, i.e. each  $n_{\mathbf{q}}$  in equation (10) takes values from zero to infinity with the condition that  $n_{\text{TOT}} = \sum_{\mathbf{q}} n_{\mathbf{q}} \geq 1$ .

By minimizing the zone centre ground state energy we get the variational parameters  $\lambda_{\mathbf{q}}$ :

$$\lambda_{\mathbf{q}} = \frac{g}{\omega_{\mathbf{q}} + z t_p \left( 1 - \frac{\gamma_{\mathbf{q}}}{z} \right)} \quad (11)$$

and, by such a choice of  $\lambda_{\mathbf{q}}$ , the one phonon matrix element between the ground state  $|\mathbf{k} = \mathbf{0}, \{n_{\mathbf{q}} = 0\}\rangle$  and the first excited state

$$\langle 1\mathbf{q}, \mathbf{k}' | \tilde{H} - H_0 | \mathbf{k} = \mathbf{0}, \{0\} \rangle = \delta_{\mathbf{k}', -\mathbf{q}} \frac{1}{\sqrt{N}} \left[ -z t_p \lambda_{\mathbf{q}} \left( 1 - \frac{\gamma_{\mathbf{q}}}{z} \right) + (g - \lambda_{\mathbf{q}} \omega_{\mathbf{q}}) \right] \quad (12)$$

vanishes. Then, the one phonon excitation process yields no contribution to the second order correction for the MLF ground state energy. The  $\lambda_{\mathbf{q}}$  appropriate to the 1D, 2D and 3D systems are easily obtained by (11).

The static correlation function involving the electron charge at  $i$ th site and the lattice deformation at the  $i + n$ th site are given by

$$\chi_n = \langle \psi_G | c_i^{\dagger} c_i (b_{i+n}^{\dagger} + b_{i+n}) | \psi_G \rangle / 2\bar{g} \langle n_i \rangle \quad (13)$$

where  $\bar{g} = N^{-1} \sum_{\mathbf{q}} (g/\omega_{\mathbf{q}})$  and  $|\psi_G\rangle$  denotes the ground state for the polaron with momentum  $\mathbf{k} = \mathbf{0}$ . The denominator in equation (13) is used to normalize the correlation function with

respect to its on-site value in the strong coupling limit.  $n_i$  is the electron number operator and  $\langle n_i \rangle = 1/N$  for the one-electron system. While  $c_i$  and  $b_i$  are the bare electron and phonon annihilation operators in the undisplaced oscillator basis respectively, the corresponding operators in the MLF basis are the annihilation operators for the polaron and that of the phonon in the variationally displaced oscillator basis. The correlation function is calculated in the MLF basis within zero phonon averaging.

### 3. Polaron mass and correlation functions

Previous investigations have pointed out that the Holstein model with a dispersionless spectrum ( $\omega_1 = 0$ ) or with weak intermolecular forces ( $\omega_1 \ll \omega_0$ ) would predict *larger polaron bandwidths in lower dimensionality* against physical expectations [35]. Moreover, as pointed out by Holstein in his original papers [3], dispersionless phonons would lead to an unphysical *divergent site jump probability* for the polaronic quasiparticle [38]. Hence, intermolecular forces are a *key ingredient* of the Holstein model.

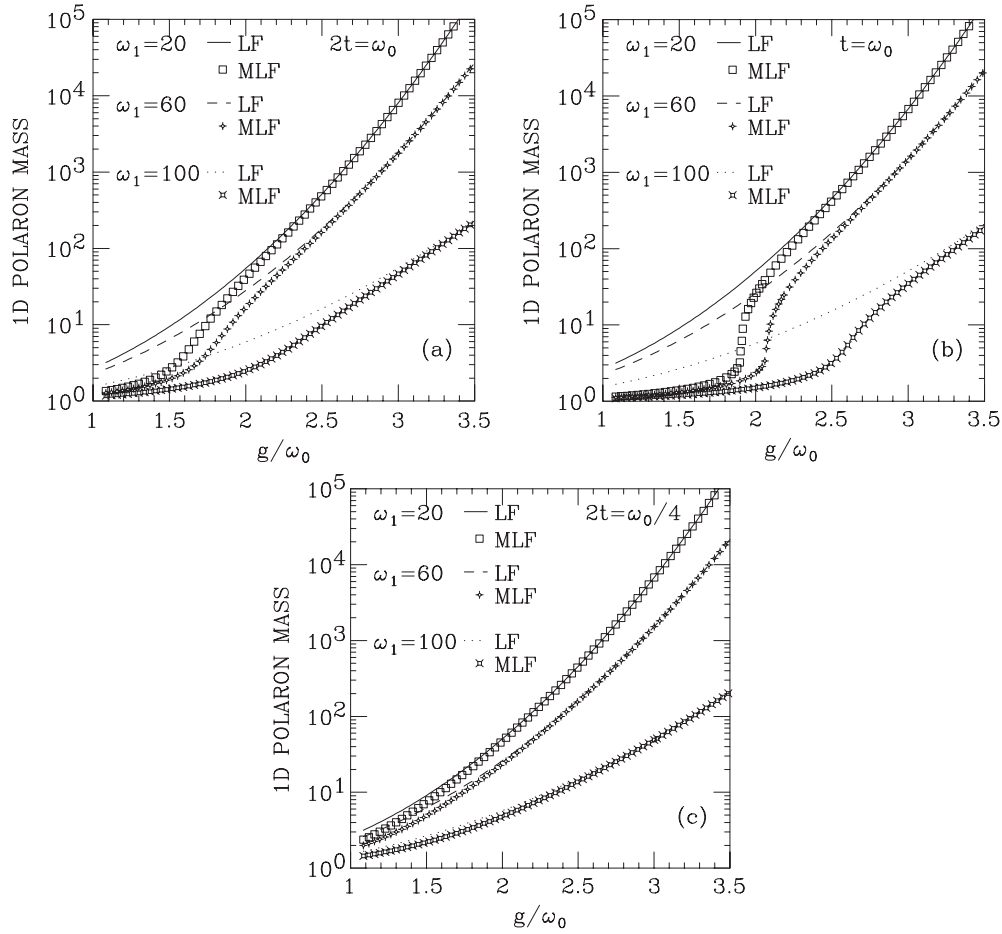
Numerical analysis [35] has shown that the bandwidths  $\Delta E_d$  grow faster versus the intermolecular energy  $\omega_1$  in higher dimensionality  $d$ , thus providing a criterion to fix the minimum  $\omega_1$  which ensures the validity of the Holstein model. Imposing the inequalities criterion  $\Delta E_{3D} \geq \Delta E_{2D} \geq \Delta E_{1D}$  we set the *threshold value*  $\bar{\omega}_1$  which turns out to be a function of the breathing mode energy  $\omega_0$  and of the  $d$ -independent e-ph coupling  $g_0 = g/\sqrt{d}$  ( $g$  scales  $\propto \sqrt{d}$ ): thus, at intermediate  $g_0$  ( $\simeq 1-1.5$ , in units of  $\omega_0$ )  $\bar{\omega}_1$  is  $\simeq \omega_0/2$ , while at strong  $g_0$  ( $\geq 2$ )  $\bar{\omega}_1$  should be at least  $\simeq 2\omega_0/3$  in order to ensure the correct bandwidths trend. On the other hand, the intermolecular energies encounter the upper bound  $\omega_1 < \omega_0$  given by the value of the coupling energy between the two atoms in the basic unit of the molecular solid. Moreover, too large  $\omega_1$  may invalidate strong coupling perturbative treatments of the Holstein model for 3D systems in fully adiabatic regimes [39].

With this caveat we study the polaron mass both in the Lang–Firsov and in the modified Lang–Firsov scheme, taking a lattice model in which first neighbours molecular sites interact through a force constants pair potential. Then, the  $d$ -dependent optical phonon spectrum is given by

$$\begin{aligned}
 \omega_{1D}^2(q) &= \frac{\alpha + \gamma}{M} + \frac{1}{M} \sqrt{\alpha^2 + 2\alpha\gamma \cos q + \gamma^2} \\
 \omega_{2D}^2(\mathbf{q}) &= \frac{\alpha + 2\gamma}{M} + \frac{1}{M} \sqrt{\alpha^2 + 2\alpha\gamma g(\mathbf{q}) + \gamma^2(2 + h(\mathbf{q}))} \\
 \omega_{3D}^2(\mathbf{q}) &= \frac{\alpha + 3\gamma}{M} + \frac{1}{M} \sqrt{\alpha^2 + 2\alpha\gamma j(\mathbf{q}) + \gamma^2(3 + l(\mathbf{q}))} \\
 g(\mathbf{q}) &= \cos q_x + \cos q_y \\
 h(\mathbf{q}) &= 2 \cos(q_x - q_y) \\
 j(\mathbf{q}) &= \cos q_x + \cos q_y + \cos q_z \\
 l(\mathbf{q}) &= 2 \cos(q_x - q_y) + 2 \cos(q_x - q_z) + 2 \cos(q_y - q_z)
 \end{aligned} \tag{14}$$

where the intramolecular force constant  $\alpha$  and the intermolecular first neighbours force constant  $\gamma$  are related to  $\omega_0$  and  $\omega_1$  by  $\omega_0^2 = 2\alpha/M$  and  $\omega_1^2 = \gamma/M$ , respectively.  $M$  is the reduced molecular mass. In terms of  $\omega_0$ , the dimensionless parameter  $zt/\omega_0$  defines the adiabatic ( $zt/\omega_0 > 1$ ) and the antiadiabatic ( $zt/\omega_0 < 1$ ) regime.

Second order perturbative theory introduces the polaron mass  $m^*$  dependence on the hopping integral  $t$ , hence on the adiabatic parameter, which would be absent in the first order Lang–Firsov theory. Generally,  $m^*$  can vary with  $t/\omega_0$  in two ways:  $m^*$  becomes lighter either by increasing  $\omega_0$  at fixed  $t$ , or by increasing  $t$  at fixed  $\omega_0$ . As the mass variation due to  $\omega_0$  is



**Figure 1.** Ratio of the 1D polaron mass to the bare band mass versus e–ph coupling according to the Lang–Firsov and the modified Lang–Firsov methods. The adiabatic parameter is set at: (a) the intermediate value,  $2t/\omega_0 = 1$ ; (b) a fully adiabatic regime,  $2t/\omega_0 = 2$ ; (c) an antiadiabatic regime,  $2t/\omega_0 = 0.25$ .  $\omega_0 = 100$  meV and  $\omega_1$  (in units meV) are the intramolecular and intermolecular energies of the diatomic molecular chain, respectively.

much stronger than that due to  $t$ , for a given adiabatic parameter, we may get different mass values according to the absolute values of  $\omega_0$  and  $t$ . However, for sufficiently strong e–ph couplings which make the perturbative method applicable, the LF mass changes only slightly with  $t$ , and second order corrections are small unless the intramolecular phonon energies are low ( $\omega_0 < 50$  meV) [39]. Hereafter we set  $\omega_0 = 100$  meV and select the adiabatic parameter by tuning  $t$ .

In figure 1, we plot the ratio of the 1D polaron mass to the bare band mass against the e–ph coupling calculated both in the Lang–Firsov scheme and in the modified Lang–Firsov expression.

An intermediate regime  $2t = \omega_0$  is assumed in figure 1(a) while the intermolecular energy spans a range of weak to strong values. The striking different behaviour between the LF and the MLF mass occurs for intermediate  $g$ , while at very strong couplings the MLF plots converge, as expected, towards the LF predictions. The LF method overestimates the polaron mass for  $g \in [\sim 1-2]$  (according to the value of  $\omega_1$ ) and, mostly, it does not capture the rapid

mass increase found instead in the MLF description. Note that, around the crossover, the MLF polaron mass is of order ten times the bare band mass in the case  $\omega_1 = 60$  meV. Large intermolecular energies enhance the phonon spectrum thus reducing the effective masses in both figures. In the MLF method, large  $\omega_1$  tend also to smooth the mass behaviour in the crossover region.

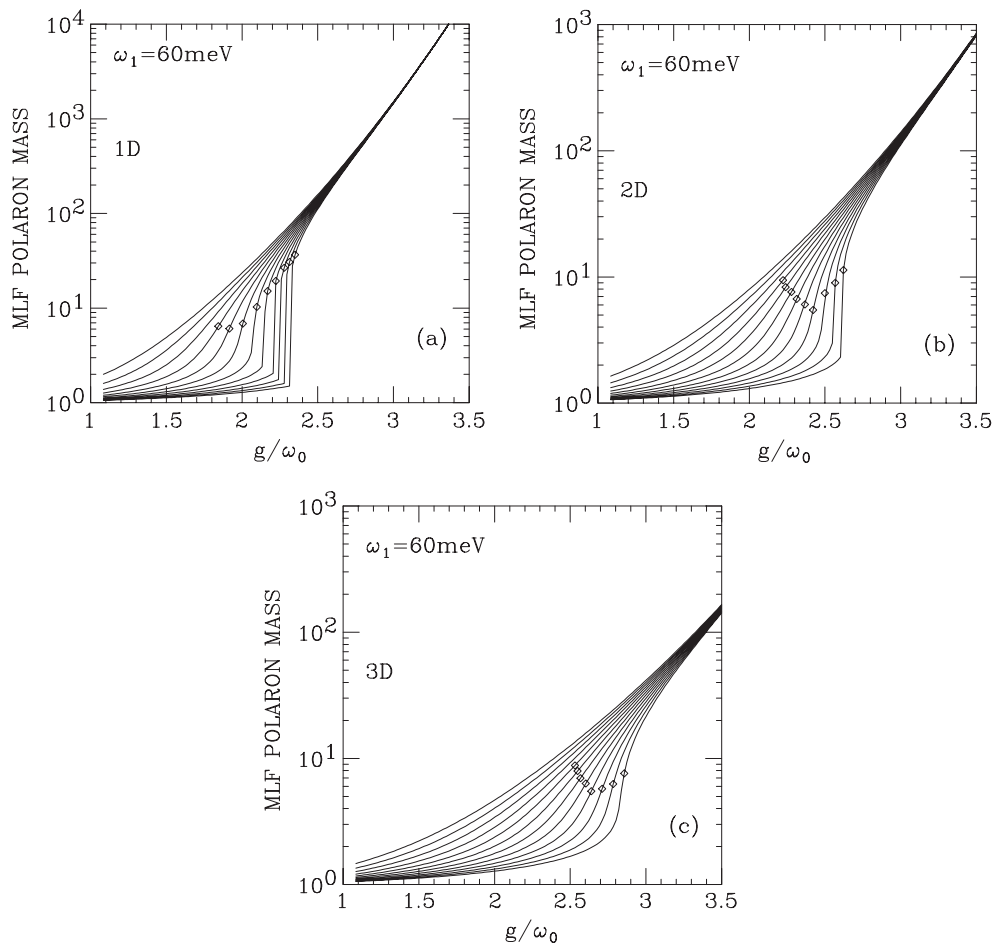
Going to a fully adiabatic regime (see figure 1(b)) the discrepancies between the LF and MLF plots are even more pronounced, and the range of e–ph couplings in which the two methods converge shrinks considerably. There is scarce renormalization in the MLF curves up to the crossover which is clearly signalled by a sudden *although continuous* mass enhancement whose abruptness is significantly smoothed for the largest values of intermolecular energies. In the antiadiabatic case shown in figure 1(c), the picture changes drastically, and we recover a nearly coincident mass behaviour in the LF and MLF methods throughout the whole range of couplings. The convergence is favoured at large  $\omega_1$ . As mentioned above, the LF plots show a strong resemblance in going from figures 1(a) to (c): in fact, the LF method slightly depends on the hopping integral in 1D systems with large intramolecular energy. The results we have displayed so far make us reconsider the concept of *self-trapping* traditionally indicating an abrupt, but continuous, transition between an infinite size states at weak e–ph couplings and a finite (small) size polaron at strong e–ph couplings. According to the adiabatic polaron theory [11, 40] there is no self-trapping event in 1D as the polaron solution is always the ground state of the system. Instead, in higher dimensionality a minimum coupling strength is required to form finite size polarons, hence self-trapped polarons can exist at couplings larger than that minimum. As a shrinking of the polaron size yields a weight increase, the polaron mass behaviour is accepted to be the most reliable indicator of the self-trapping transition. The latter appears to us as a crossover essentially dependent on the degree of adiabaticity of the system and crucially shaped by the internal structure of the phonon cloud which we have modelled by tuning the intermolecular forces. We are then led to relocate the self-trapping event in the parameter space of 1D systems admitting also that finite size polarons can self-trap if a sudden change in their effective mass occurs for some values of the e–ph couplings in some portions of the adiabatic regime. As fluctuations in the lattice distortions around the electron site are included in our variational wavefunction, discontinuities in the polaron mass should not appear at the onset of the transition [41]. Mathematically we select the crossover points through the simultaneous occurrence of a maximum in the first logarithmic derivative and a zero in the second logarithmic derivative of the MLF polaron mass with respect to the coupling parameter: such inflection points, corresponding to the points of most rapid increase for  $m^*$ , are reported on in figure 2, where the mass ratios are plotted for a wide choice of antiadiabatic to adiabatic regimes and a sizeable value of  $\omega_1$  in 1D, 2D and 3D.

Some well known features of the antiadiabatic polaron landscape are confirmed by our analytical variational model in all dimensionalities:

- (i) antiadiabatic polarons are generally heavier than adiabatic ones although, at very strong couplings, the mass values converge at the Lang–Firsov results, and
- (ii) there is no self-trapping in the fully antiadiabatic regime as the electron and the dragged phonon cloud form a compact unit, a small polaron, also at intermediate e–ph couplings.

Then, the mass increase is smooth in the antiadiabatic regime. Instead, in the more controversial [42] antiadiabatic to adiabatic transition region, we start to detect the signatures of the crossover which persist in the fully adiabatic regime and form a line of self-trapping events whose features however change considerably versus dimensionality. In 1D (figure 2(a)), the crossover occurs for  $g$  values between  $\sim 1.8$  and  $2.3$ , and the corresponding self-trapped masses are of order  $\sim 5$ – $50$  times the bare band mass, thus suggesting that relatively light



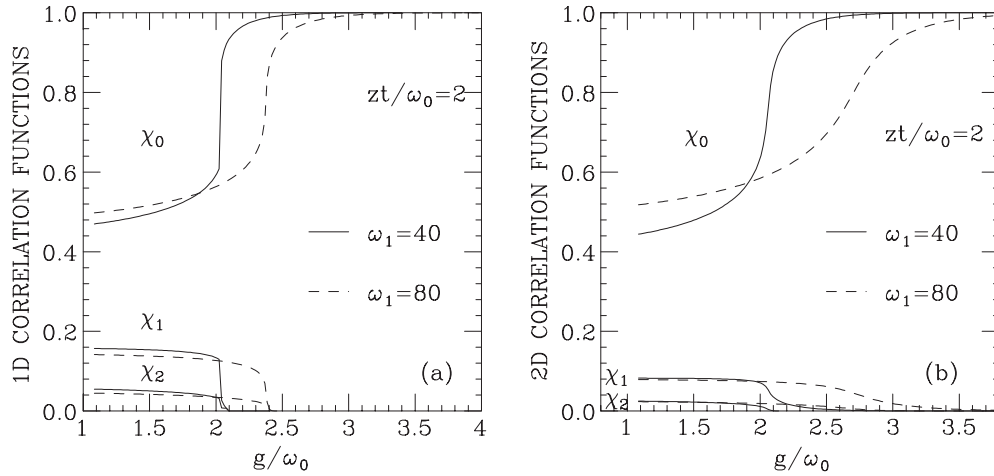


**Figure 2.** The ratio of the modified Lang-Firsov polaron mass to the bare band mass versus e-ph coupling in (a) 1D, (b) 2D and (c) 3D. A set of 12  $zt/\omega_0$  values ranging from the antiadiabatic to the adiabatic regime is considered. From left to right:  $zt/\omega_0 = 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.25, 2.5, 2.75, 3.0$ .  $\omega_0 = 100$  meV. The diamonds mark the occurrence of the self-trapping event.

small polarons can exist in 1D molecular solids with high phonon spectrum. The self-trapped mass values grow versus  $g$  by increasing the degree of adiabaticity, and the incipience of the self-trapping line is set at the intermediate value  $2t/\omega_0 = 1$ . We note that these findings are in good qualitative and quantitative agreement with refined variational results supporting the existence of self-trapped polarons also in 1D. Although in the deep adiabatic regime we find a quasi-steplike increase, the 1D polaron mass is a continuous and derivable function of the e-ph coupling [23].

The 2D lattice introduces some significant novelties in the MLF mass behaviour, as shown in figure 2(b):

- (i) at a given e-ph coupling and adiabaticity ratio, the 2D mass is lighter than the 1D mass and the 2D LF limit is attained at a value which is roughly one order of magnitude smaller than in 1D;



**Figure 3.** (a) 1D and (b) 2D static correlation functions versus e–ph coupling in the adiabatic regime,  $zt/\omega_0 = 2$ .  $\omega_0 = 100$  meV. Two values of intermolecular energies,  $\omega_1 = 40$  and  $80$  meV, have been taken.

- (ii) the crossover region is shifted upwards along the  $g$  axis with the self-trapping events taking place in the range  $g \sim 2.2$ – $2.6$ , and the corresponding masses are of order  $\sim 5$ – $10$  times the bare band mass;
- (iii) the curve connecting the self-trapping points is parabolic, with an extended descending branch starting at the intermediate value  $4t/\omega_0 = 1$ ;
- (iv) in the deep adiabatic regime, the lattice dimensionality smoothens the mass increase versus  $g$ .

The latter effect is even more evident in 3D, see figure 2(c), as there are no signs of abrupt mass increase even for the largest values of the adiabatic parameter. At the crossover, 3D masses are of order  $\sim 5$ – $10$  times the bare band mass with the self-trapping points lying in the range  $g \sim 2.5$ – $2.9$ . At large couplings the *effective mass over bare band mass* ratio becomes independent of the  $t$  value and converges towards the LF value. In this region (and for the choice  $\omega_1 = 60$  meV) the 3D Lang–Firsov mass is one order of magnitude smaller than the 2D mass. As the coordination number grows versus dimensionality, large intermolecular forces are more effective in hardening the 3D phonon spectrum, thus leading to lighter 3D polaron masses than 2D ones.

In figure 3 we plot the correlation functions  $\chi_0$ ,  $\chi_1$  and  $\chi_2$  in 1D (a) and 2D (b) respectively, as obtained by (13) for the adiabatic regime  $zt/\omega_0 = 2$  with  $\omega_0 = 100$  meV. Two values,  $\omega_1 = 40$  and  $80$  meV, have been chosen to point out the role of the intermolecular forces in the transition between a large polaron at weak couplings and a small polaron at strong couplings. For sufficiently strong  $g$  values the LF limit is obtained, i.e.  $\chi_0$  becomes 1 while  $\chi_1$  and  $\chi_2$  become zero, implying that the resulting polaron is an on-site small polaron. The small to large polaron crossover is manifested by a strong reduction of  $\chi_0$  along with an enhancement in the values of  $\chi_1$  and  $\chi_2$ . By increasing  $\omega_1$ , the crossover is slightly smoothed and shifted upwards along the  $g$  axis. Accordingly,  $\chi_1$  and (to a lesser extent)  $\chi_2$  acquire some weight throughout a larger portion of e–ph coupling values. As a main feature we note that the crossovers indicated by the correlation functions of the 1D system, for the two selected cases, occur at  $g/\omega_0 \sim 2$  and  $\sim 2.35$ , respectively. These values match the corresponding crossover points extracted by the polaron mass slopes. In 2D, the self-trapping transition takes place at larger (than in 1D)

$g$  values, and non-local e–ph correlations persist in the adiabatic polaron up to  $g/\omega_0 \sim 3$ . The crossover is generally smooth, and the softening effect of the intermolecular forces is more pronounced than in the 1D system.

#### 4. Conclusions

We have developed a variational analytical method to study the Holstein polaron problem versus dimensionality in the entire range of (anti)adiabatic parameters characterizing the molecular system. The essential role of the phonon dispersion in the Holstein model has been accounted for, including the intermolecular interactions, by means of a force constant approach. Unlike the traditional Lang–Firsov scheme, the modified Lang–Firsov method permits us to describe the fact that, in the intermediate and adiabatic regimes, the lattice deformation does not instantaneously follow the electron motion, thus leading to a spreading in the quasiparticle size. Under these circumstances we have examined the behaviour of the polaron mass as a function of the strength of the e–ph coupling, and critically analysed the occurrence of the self-trapping event signalling a shrinking of the polaron size in real space. This crossover has been also monitored through the computation of the static e–ph correlation functions which provide a complementary tool corroborating our conclusions. By varying the adiabatic parameter and selecting the points of most rapid increase for the effective mass, we have found a set of self-trapping points originating, in 1D and 2D, in the intermediate regime ( $zt/\omega_0 = 1$ ) and continuing in the fully adiabatic regime. In 3D, the self-trapping events occur at  $zt/\omega_0 > 1$ . While, in 1D, the curve connecting the inflection points in the adiabatic regime is a monotonic growing function of the e–ph coupling, in 2D and 3D we find distinctive parabola-like curves whose minima (of order  $\sim 5$  times the bare band mass) are located at larger  $g$  in higher  $d$ . Hence small polaron formation is favoured in low  $d$  whereas very large e–ph couplings are required to shrink the size of adiabatic polarons in 3D. As intermolecular forces play a stronger role in more closely packed structures, lattice dimensionality is expected to shape the polaron behaviour. In fact, our results show that the crossover from large to small polarons is, in 2D and even more in 3D, smoother than in the case of the 1D adiabatic polaron at a fixed value of intermolecular energy. After pointing out the quantitative differences in the polaron mass according to the dimensionality, one should however notice a qualitative similarity in all dimensions regarding the occurrence of the self-trapping event. Finally we observe that, although polaron masses become generally lighter in higher  $d$ , also in 1D the *effective mass over bare band mass* ratio is  $\sim 5$  at the crossover when phonons and electrons compete on the energy scale. Small polarons having mobility properties may therefore be expected in low dimensional molecular systems with sufficiently strong intermolecular forces.

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