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Polaron self-trapping in a honeycomb net

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Abstract

Small-polaron behaviour in a two-dimensional honeycomb net is studied by applying the strong-coupling perturbative method to the Holstein molecular crystal model. We find that small optical polarons can be mobile also if the electrons are strongly coupled to the lattice. Before the polarons localize and become very heavy, there is in fact a window of electron–phonon couplings in which the polarons are small and have masses of order $\simeq$5–50 times the bare band mass according to the value of the adiabaticity parameter. The two-dimensional honeycomb net favours the mobility of small optical polarons, in comparison with the square lattice.

1. Introduction

The transport properties of real systems are strongly affected by the presence of nonlinear potentials in the lattice [1–3]. Nonlinearities may arise because of embedded impurities in the host lattice which favour trapping of the charge carriers [4–7] in any dimensionality [8] or nonlinearities may be intrinsic to the system and driven by the electron–lattice interaction as assumed in the molecular crystal model first proposed by Holstein [9] in the form of a discrete nonlinear Schrödinger equation for electrons coupled to harmonic phonons. Several theoretical methods have been developed in the last few decades [10–19] to analyse the ground-state and finite-temperature properties of the unit comprising the electron plus the surrounding local lattice deformation, namely the polaron. Central to these investigations is the concept of self-trapping traditionally denoting a transition between an infinite-radius state at weak electron–phonon coupling and a finite-radius polaron at strong e–ph coupling. The narrowing of the polaron band and the abrupt increase of the polaron effective mass versus e–ph coupling are the classical and related indicators of the transition event which may occur or not according to the degree of adiabaticity and the dimensionality of the system. When the characteristic phonon energy $\bar{\omega}$ becomes larger than the electronic bandwidth, the antiadiabatic regime is attained. In this case it is generally accepted that the polaron wave function spreads over a few lattice sites (small polaron) with the polaron mass being a smooth function of the e–ph

coupling. Instead, the polaron self-traps in the adiabatic regime and there is growing evidence that this event takes place in any dimensionality [15, 19, 20].

When the lattice polarizations is confined to one or a few unit cells the carrier feels the details of the local structure: recent generalizations of the Holstein model have shown that the inclusion of on-site lattice anharmonicity can substantially modify the size [21] and the mass [22] of the polaronic quasiparticle. While these findings could contribute to locating with more accuracy the self-trapping event in parameter space, it is still unclear whether and how the transition depends on the lattice structure. To address this problem we focus here on the polaron mass renormalization in a two-dimensional honeycomb net which can be viewed as a triangular Bravais lattice with a basis of diatomic molecules at the vertices. The Holstein model is briefly reviewed and the results are discussed in section 2. The conclusions are drawn in section 3.

2. The Holstein model Hamiltonian

The Hamiltonian for the single electron in the Holstein model reads

$$H = -t\sum_{i\neq j} c_i^\dagger c_j + g\sum_i c_i^\dagger c_i (a_i + a_i^\dagger) + \sum_{\boldsymbol{k}} \omega_{\boldsymbol{k}} a_{\boldsymbol{k}}^\dagger a_{\boldsymbol{k}} \tag{1}$$

where the dimension dependence explicitly appears in the momentum-space Hamiltonian for the harmonic lattice vibrations. $c_i^\dagger$ (c_i) creates (destroys) a tight-binding electron at the i-site and t is the first-neighbour hopping integral related to the bare electron half-bandwidth D by $D = zt$, z being the coordination number. $a_{\boldsymbol{k}}^\dagger$ ($a_{\boldsymbol{k}}$) creates (destroys) a $\boldsymbol{k}$-phonon with frequency $\omega_{\boldsymbol{k}}$. g is the overall electron–phonon coupling constant.

In the strong-coupling regime the Lang–Firsov approach [23] is reliable [24, 25] and the polaron mass m^* can be obtained via a perturbative method. In d dimensions the ratio between m^* and the bare band mass m_0 is [20]

$$\begin{aligned}
\left(\frac{m^*}{m_0}\right)_d &= \frac{\exp(\bar{g}^2)}{1 + z^2 t \exp(-\bar{g}^2) f(\bar{g}^2)/(\hbar\bar{\omega})} \\
\bar{g}^2 &= \frac{2g^2}{N}\sum_{k_x} \sin^2\frac{k_x}{2} \sum_{k_x,k_y} (\hbar\omega_{\boldsymbol{k}})^{-2} \\
f(\bar{g}^2) &= \sum_{s=1}^{+\infty} \frac{(\bar{g}^2)^s}{ss!}.
\end{aligned} \tag{2}$$

The series expansion in the last of equations (2) reflects the fact that the second-order polaron self-energy comprises the emission and absorption of an arbitrary number of phonons; hence it is a sum over an infinite number of diagrams each having s phonons between the two interaction vertexes. The second order of perturbative theory also introduces the effect of the adiabaticity parameter $zt/\hbar\bar{\omega}$ on m^* which, in general, depends on dimensionality through: (i) $g^2 \propto d$, (ii) the first-neighbour number z, (iii) the Brillouin zone sums and (iv) the features of the phonon spectrum.

We take a 2D honeycomb net equivalent to a triangular lattice with a two-point basis. Each lattice site is a diatomic molecule with coordination number $z = 6$. Hence, the phonon spectrum has both acoustic and optical branches whose analytical expressions can be deduced by means of a force constant parametrization scheme:

$$\begin{aligned}
\omega^2(k_x, k_y) &= \frac{\beta + 3\gamma}{M} \pm \frac{1}{M}\sqrt{\beta^2 + \gamma^2 H(k_x, k_y) + \beta\gamma G(k_x, k_y)} \\
H(k_x, k_y) &= 3 + 2(c_x c_y + s_x s_y + c_{3x} c_y + s_{3x} s_y + c_{2x}) \\
G(k_x, k_y) &= 2(2c_x c_y + c_{2x})
\end{aligned} \tag{3}$$

with: $c_x = \cos(k_x\sqrt{3}a/2)$, $c_y = \cos(k_y 3a/2)$, $c_{2x} = \cos(k_x\sqrt{3}a)$, $c_{3x} = \cos(k_x 3\sqrt{3}a/2)$, $s_x = \sin(k_x\sqrt{3}a/2)$, $s_y = \sin(k_y 3a/2)$, $s_{3x} = \sin(k_x 3\sqrt{3}a/2)$. a is the lattice constant and M is the reduced molecular mass. β and γ are the *intra*molecular and *inter*molecular force constants respectively in terms of which one defines: $\omega_0^2 = 2\beta/M$, $\omega_1^2 = \gamma/M$ and the zone-centre optical frequency $\bar{\omega} = \sqrt{\omega_0^2 + z\omega_1^2}$.

Previous investigations of the Holstein Hamiltonian [26] have shown that the intermolecular forces have to be sufficiently strong in order to predict the correct polaron bandwidth trend versus dimensionality. Thus the ground-state properties of the Holstein model essentially depend on the strength of ω_1 which should be of order $\simeq\omega_0/2$. When this condition is fulfilled the polaron mass turns out to be substantially dimension independent. Larger ω_1-values are admitted in the model although they encounter the obvious upper bound $\omega_1 \leqslant \omega_0$ in a molecular lattice. This result (which has been proven in a large portion of parameter space ranging from fully adiabatic to antiadiabatic conditions) introduces a novel feature in the polaron landscape corroborated by Monte Carlo simulations [27], density matrix renormalization-group studies [15] and variational approaches.

Two quantities play a central role in polaron theory. The first, defined by

$$\lambda = Ng^2 \Big/ \left(D \sum_{k} \hbar\omega_k \right)$$

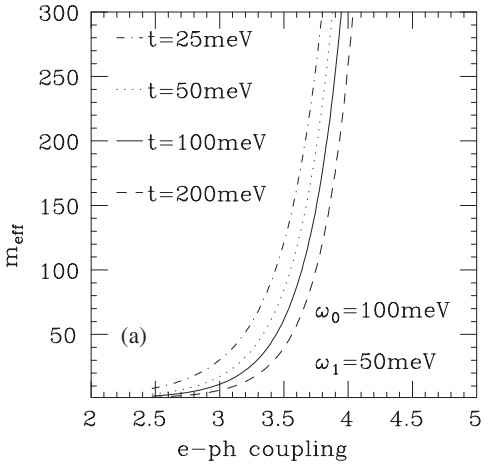
(N being the number of molecular sites), represents the ratio [28] between the polaron binding energy and the electronic half-bandwidth. It yields the energetical gain due to small-polaron formation with respect to the bare electronic state. The second, defined by

$$\alpha = Ng \Big/ \left(\sum_{k} \hbar\omega_k \right)$$

measures the lattice deformation associated with the quasiparticle formation. While in adiabatic systems the condition $\lambda > 1$ signals the existence of the small-polaron state, in antiadiabatic systems $\alpha > 1$ is a more restrictive condition for small-polaron formation [29].

Recent analysis [30–32] on the mobility of small polarons also in conjunction with models on polaronic high-T_c superconductivity [33–35] have led to reconsideration of the concept of self-trapped state which, although intimately related to the small size of the quasiparticle, *is not* synonymous with the small-polaron state. Thus, if the narrowing of the polaron bandwidth (induced by an increasing e–ph coupling) marks the onset of the transition between large and small states, there is still a range of g-values for which the polaron, although spread over a few lattice sites only, is not trapped and retains mobility properties. The self-trapping event can be instead associated with a rapid but continuous effective-mass increase which is precisely located by looking at the curvature of the logarithm of the effective mass versus g. In our view this method, beyond embodying the full physical significance of the transition process, offers a simple criterion for selecting a 'critical g-value' as an inflection point either in the logarithm of the effective mass or in its first derivative. While the former case would identify the point of most rapid increase of the effective mass, the occurrence of the latter case distinguishes a peculiar point in the *mass versus g* plot although the concavity–convexity change is absent.

In figure 1(a), four plots of the polaron mass (in units of the bare band mass) as a function of the g-coupling are reported, while the corresponding curvatures of the logarithm of the mass are shown in figure 1(b). High optical phonon frequencies are assumed. Our selected plots range from an extreme adiabatic ($t = 200$ meV) to a moderately antiadiabatic ($t = 10$ meV) regime. At a fixed g the antiadiabatic polaron is always heavier than the adiabatic polarons but some peculiar points, resolved as the minima of the curves displayed in figure 1(b), show *decreasing* g-values on decreasing the degree of adiabaticity. Then, an antiadiabatic polaron



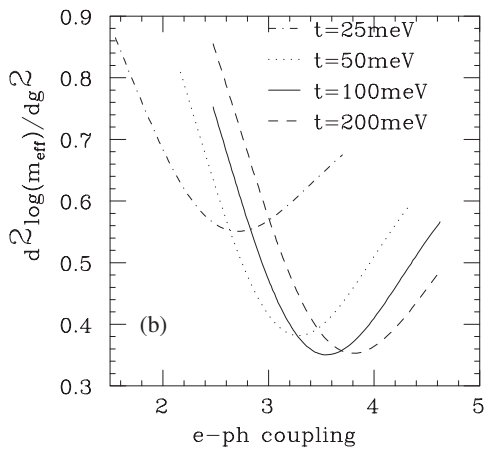
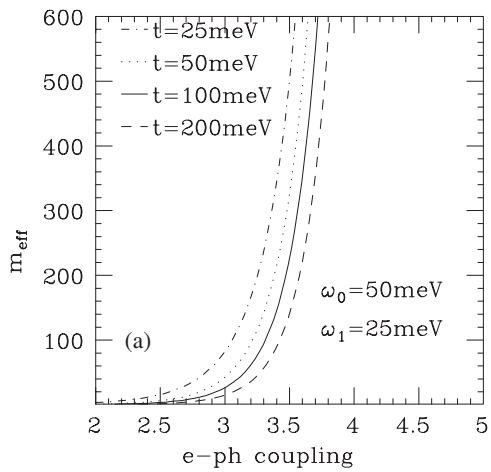


Figure 1. (a) Polaron masses (in units of the bare band electron mass) versus g in adiabatic and antiadiabatic regimes with high-frequency optical phonons: $\bar{\omega} =$ 158 meV. (b) The second derivative of the logarithm of the effective mass with respect to g.



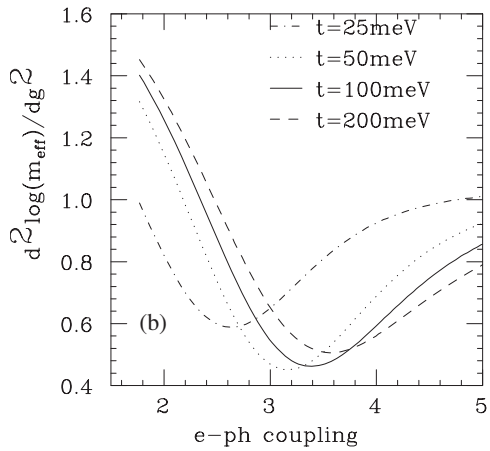


Figure 2. (a) Polaron masses (in units of the bare band electron mass) versus g in adiabatic and antiadiabatic regimes. The characteristic frequency of the optical phonons is: $\bar{\omega} = 79$ meV. (b) The second derivative of the logarithm of the effective mass with respect to g.

may already be self-trapped at $g \simeq 2.7$, weighing $m_{\rm eff} \simeq 14$, while an extreme adiabatic polaron self-traps only at $g \simeq 3.8$, with $m_{\rm eff} \simeq 123$. The correctness of our perturbative approach is monitored by the λ- and α-values which are larger than one at all the displayed points consistently with the assumption on the existence of small polarons. In the intermediate adiabatic cases $t = 100$ and 50 meV, we find $m_{\rm eff} \simeq 73$ at $g \simeq 3.5$ and $m_{\rm eff} \simeq 40$ at $g \simeq 3.3$ respectively. Thus, a 2D honeycomb net seems to sustain mobile adiabatic polarons in a window of strong-coupling regimes approximately defined by $2.5 \leqslant g \leqslant 3.3$. In figure 2, the phonon frequencies are still high, although much reduced with respect to figure 1. As a main effect the polaron masses are roughly doubled while the peculiar minima of the second derivative of the logarithm of the effective mass (figure 2(b)) do not shift substantially versus g with respect to the corresponding cases in figure 1(b). To emphasize the role of the lattice structure we have compared the adiabatic polaron (with $t = 100$ meV) in the present 2D honeycomb net with the previously investigated [20] square lattice. As an example, provided that: (i) the same overall

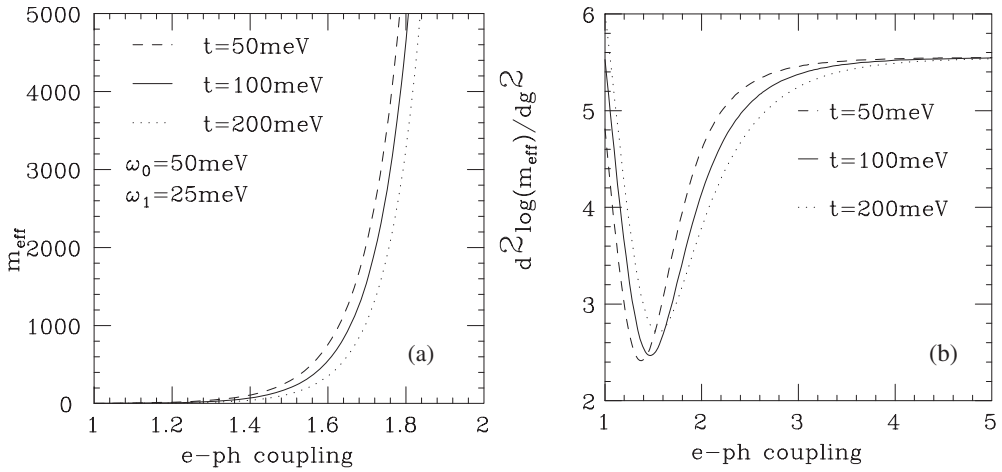


Figure 3. (a) Polaron masses (in units of the bare band electron mass) versus g in three adiabatic regimes. The electron couples here to the acoustic phonon branch. (b) The second derivative of the logarithm of the effective mass with respect to g.

e–ph coupling $g = 3.38$ is taken, (ii) the same values of intramolecular and intermolecular force constants are assumed ($\omega_0 = 50$ meV and $\omega_1 = 25$ meV) and these values are consistent with the strong-coupling perturbative method, we find $m_{\rm eff} \simeq 140$ for the honeycomb net polaron against $m_{\rm eff} \simeq 1200$ for the square lattice. Also the intermediate adiabatic polaron ($t = 50$ meV) behaves in a similar manner, with $m_{\rm eff} \simeq 200$ for the honeycomb net polaron against $m_{\rm eff} \simeq 1700$ in the square lattice assuming the same input parameters as above. We have also considered the effect of the acoustic branch of the phonon spectrum on the polaron properties. In all cases, with different degrees of adiabaticity, the minima of the second derivative (figure 3(b)) occur at much lower g-values than for optical polarons. However, no physical meaning can be attached to these values since they are well outside the range of validity of the Lang–Firsov-based perturbative method. When the method holds ($g > 2.5$) no peculiar point can be resolved in the polaron behaviour versus g, which is anyway characterized by a huge mass renormalization. Figure 3 has been provided also to show that the occurrence of distinctive features in the mass or mass derivative curves, far from being a cogent criterion for the self-trapping event, just indicates a trend which needs to be corroborated by the analysis of other independent quantities.

3. Conclusions

We have developed a perturbative study of the molecular crystal model assuming the existence of strong electron–phonon coupling conditions which favour the formation of small polarons. The Lang–Firsov method permits us to calculate the mass renormalization for specific structures once the phonon spectrum is known. Rather than applying the model to real systems as was previously done for simple lattices, we have examined whether alternative structures such as the 2D honeycomb net may host polarons which are both small and mobile. In fact we have found that adiabatic small polarons are lighter by roughly a factor of eight than in the square lattice once the same input parameters are assumed. Adiabatic polarons have been studied as a function of the e–ph coupling and distinctive points in the mass behaviour (versus g) have been selected and placed in relation with a possible occurrence of the self-trapping event.

Although not ultimate, this criterion seems plausible provided that such 'self-trapping g-points' are obviously well within the range of applicability of the Lang–Firsov scheme. We find that small optical polarons in the honeycomb net can self-trap if the electron–lattice system couples in the range $3 < g < 4$. The exact location of the transition depends on the adiabaticity parameter with intermediate adiabatic polarons lying in the lower portion of that range. Our results suggest that adiabatic optical polarons can be mobile in the honeycomb net although a strong-coupling regime holds. The small-polaron effective mass is of order $\simeq$5–50 times the bare band mass before the self-trapping point is attained, with more adiabatic polarons being lighter once the e–ph coupling is fixed.

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References

[1] Mott N F 1987 *Conduction in Non-Crystalline Materials* (Oxford: Clarendon)
[2] Heeger A J, Kivelson S, Schrieffer J R and Su W-P 1988 *Rev. Mod. Phys.* **60** 781
[3] Devreese J T 1996 Polarons *Encyclopedia of Applied Physics* vol 14 (New York: VCH) p 383
[4] Wipf H, Magerl A, Shapiro S M, Satija S K and Thomlinson W 1981 *Phys. Rev. Lett.* **46** 947
[5] Scharf R and Bishop A R 1991 *Phys. Rev.* A **43** 6535
[6] Molina M I and Tsironis G P 1993 *Phys. Rev.* B **47** 15 330
[7] Gupta B C and Lee S B 2001 *Phys. Rev.* B **63** 144302
[8] Dunlap D H, Kenkre V M and Reineker P 1993 *Phys. Rev.* B **47** 14 842
[9] Holstein T 1959 *Ann. Phys., NY* **8** 325
Holstein T 1959 *Ann. Phys., NY* **8** 343
[10] Toyozawa Y 1961 *Prog. Theor. Phys.* **26** 29
[11] Emin D and Holstein T 1976 *Phys. Rev. Lett.* **36** 323
[12] De Raedt H and Lagendijk A 1983 *Phys. Rev.* B **27** 6097
De Raedt H and Lagendijk A 1984 *Phys. Rev.* B **30** 1671
[13] Kopidakis G, Soukoulis C M and Economou E N 1995 *Phys. Rev.* B **51** 15 038
[14] La Magna A and Pucci R 1996 *Phys. Rev.* B **53** 8449
[15] Jeckelmann E and White S R 1998 *Phys. Rev.* B **57** 6376
[16] de Mello E V and Ranninger J 1998 *Phys. Rev.* B **58** 9098
[17] Robin J M 1998 *Phys. Rev.* B **58** 14 335
[18] Alexandrov A S and Kornilovitch P E 1999 *Phys. Rev. Lett.* **82** 807
[19] Romero A H, Brown D W and Lindenberg K 1999 *Phys. Rev.* B **59** 13 728
Romero A H, Brown D W and Lindenberg K 1999 *Phys. Rev.* **60** 14 080
[20] Zoli M 2000 *Phys. Rev.* B **61** 14 523
[21] Zolotaryuk Y, Christiansen P L and Rasmussen J J 1998 *Phys. Rev.* B **58** 14 305
[22] Voulgarakis N K and Tsironis G P 2001 *Phys. Rev.* B **63** 14 302
[23] Lang I J and Firsov Y A 1963 *Sov. Phys.–JETP* **16** 1301
[24] Gogolin A A 1981 *Phys. Status Solidi* b **103** 397
[25] Firsov Y A, Kabanov V V, Kudinov E K and Alexandrov A S 1999 *Phys. Rev.* B **59** 12 132
[26] Zoli M 1998 *Phys. Rev.* B **57** 10 555
[27] Kornilovitch P E and Pike E R 1997 *Phys. Rev.* B **55** R8634
[28] Zoli M 1999 *Physica* C **324** 71
[29] Zoli M 2000 *J. Phys.: Condens. Matter* **12** 2783
[30] Farias G A, da Costa W B and Peeters F M 1996 *Phys. Rev.* B **54** 12 835
[31] Emin D 1996 *Phys. Rev.* B **53** 1260
[32] de Mello E V and Ranninger J 1997 *Phys. Rev.* B **55** 14 872
de Mello E V and Ranninger J 1999 *Phys. Rev.* B **59** 12 135
[33] Alexandrov A S and Mott N F 1994 *Rep. Prog. Phys.* **57** 1197
[34] Mustre de Leon J, Batistić I, Bishop A R, Conradson S D and Trugman S A 1992 *Phys. Rev. Lett.* **68** 3236
[35] Fehske H, Röder H, Wellein G and Mistriotis A 1995 *Phys. Rev.* B **51** 16 582