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COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in **Physical Review B.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on ''Dynamical properties of small polarons''

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We show that the conclusion on the breakdown of the standard small polaron theory made recently by E. V. de Mello and J. Ranninger [Phys. Rev. B **55**, 14 872 (1997)] is a result of an incorrect interpretation of the electronic and vibronic energy levels of the two-site Holstein model. The small polaron theory, when properly applied, agrees well with the numerical results of these authors. Also we show that their attempt to connect the properties of the calculated correlation functions with the features of the intersite electron hopping is unsuccessful. [S0163-1829(99)02014-7]

1. In a recent publication[1] de Mello and Ranninger have analyzed numerically the familiar two-site Holstein model[2,3] of a single electron coupled to an intrasite vibration mode. The model is the electronic doublet ϕ_1, ϕ_2, describing an electron localized on sites 1 and 2, respectively, plus the interaction with a vibration mode. The overlap of ϕ_1 and ϕ_2 leads to a splitting $2t$ of the doublet in the absence of the interaction, where

$$t=\int \phi_1^* H_{\rm el}\phi_2\, dV; \tag{1}$$

$H_{\rm el}$ is the electron Hamiltonian. The Hamiltonian of the model is given by

$$H=\frac{p^2}{2M}+\frac{M\omega_0^2x^2}{2}-gx(a_1^\dagger a_1-a_2^\dagger a_2)-t(a_1^\dagger a_2+a_2^\dagger a_1). \tag{2}$$

Here p,x are the momentum and coordinate of the vibration mode, M,ω_0 its mass and frequency, respectively, and $a_i^\dagger, a_i$ $(i=1,2)$ are the electron operators. Equation (2) is an invariant with respect to the inversion $x\to -x$, $(1,2)\to(2,1)$ and the parity is conserved. This model is an extreme simplification of the small polaron model. $2t$ is the analog of the electron bandwidth in a crystal.

2. One of the basic results of the small polaron theory[2,4–7] is the narrowing of the electron band due to the electron-phonon (vibron) coupling. In the strong-coupling regime, when $g^2\to\infty$, the narrowing is described by a simple exponential dependence on g as

$$t^*=t\exp(-{\rm const}\cdot g^2). \tag{3}$$

The exponential dependence, Eq. (2), is readily derived by the use of the familiar double-well potential model.[2] Polaron tunnels coherently within the narrow band at low temperatures (while the thermally activated hopping dominates at high temperatures[5,6]). The numerical solution for several vibrating molecules coupled with one or two electrons[8–12] revealed an excellent agreement of the numerical bandwidth with the analytical Holstein and Lang-Firsov (LF) results at large g.

3. However, de Mello and Ranninger[1] arrived with an opposite conclusion. On the basis of numerical analysis of the same problem authors[1] claim in Sec. III that:

> ''...the LF approach, which is generally believed to become exact in the limit of antiadiabaticity and an electron-phonon coupling going to infinity, actually diverges most from the exact results precisely in this limit...'' (p. 14 885).

In Ref. 1 the ''LF approach'' is identified with the lowest ($\sim t$) order in perturbation theory. We do not agree with this identification, since to go beyond the lowest approximation was a central point for the authors of Refs. 4, 6, and 7. These authors did not provide any physical explanation for their drastic disagreement with all earlier results starting from the pioneering work by Holstein and including the kinetic theory of strongly coupled electron-phonon systems, in particular with the theory of high-frequency conductivity.[6,13]

4. In Ref. 14 we have recently developed the analytical approach to the two-site model by the use of the expansion technique, which provides the electronic and vibronic terms as well as the wave functions in any order in powers of t. In the second order in t the doublet energy of the ground state $E_\pm$ is given by

$$E_\pm = \pm t^* - \frac{t^2}{4E_p}, \quad t^* \equiv t\exp(-2E_p/\hbar\omega_0). \qquad (4)$$

Here $E_p = g^2/2M\omega_0^2$ is the polaron shift (the following designation is used in Ref. 1: $E_p = \alpha^2\hbar\omega_0$). The first term describes the splitting of the doublet (components of the doublet have opposite parity) corresponding to the bandwidth in a crystal, as discussed above, while the second term is a correction to the polaron shift of the whole band due to the virtual transitions to the nearest-neighbor site. The exponential reduction factor was found in all orders of t of the perturbation expansion[14] in agreement with the standard result, Eq. (2). On the other hand, the corrections to the atomic level are relatively small as $1/g^2$ rather than exponential.

5. In Ref. 14, Sec. VI, it was demonstrated that the aforesaid statements of authors of Ref. 1 do not correspond to reality and are only due to the fact that they failed to notice the above-mentioned difference between the splitting of the doublet's components and their shift as a whole. This is the result of the methodological defect of the approach which was employed in Ref. 1. Instead of a direct solution of the quantum-mechanical problem (to determine the energy spectrum and the wave functions), they calculated a value (which has no direct physical meaning)

$$E^i_{\mathrm{kin}} \sim t\langle a_1^\dagger a_2\rangle_i, \qquad (5)$$

$\langle\cdots\rangle_i$, $(i=+,-)$ is a quantum-mechanical average on the one of the doublet's component. This approach would eliminate the possibility to make such an error to a considerable extent. They accepted implicitly an assertion that E^i_{kin} is the analog of the electron bandwidth. No explicit wording of this assertion is given in Ref. 1. However, this wrong interpretation of E^i_{kin} is forced, because the authors of Ref. 1 have compared it just with a small polaron bandwidth.[2,4] In other cases such comparison would be irrelevant, since authors of Refs. 2 and 4 never calculated E_{kin}.

As it was shown in Ref. 14, this assertion is incorrect. Let us denote as ΔE^i a correction term to the energy level i which is generated by the last term $\sim t$ of the Hamiltonian (2). In fact:

1. E^i_{kin} is proportional to $\partial\Delta E^i/\partial t$ (rather than to ΔE^i). The average (5) decreases when $|g|$ increases as a power of g^2 ($\sim g^{-2}$ for $g^2 \rightarrow \infty$; see Ref. 15), but not exponentially.

2. Analog of the electron bandwidth is the difference $\delta E = |\Delta E^+ - \Delta E^-|$, but not ΔE^i alone. δE contains the exponential factor (3).

In other words, in Ref. 1, authors had compared the values of the essential different nature. This is the source of the above-mentioned drastic disagreement.

6. In Ref. 1, Sec. V, authors have calculated the electron dipole momentum (the authors of Ref. 1 have connected this correlator with the charge fluctuations which is not quite correct) and the vibronic coordinate correlators (deformation dynamics correlator in Ref. 1):

$$\chi_{\mathrm{nn}}(\tau) = \langle (n_1 - n_2)_\tau (n_1 - n_2)\rangle_0, \quad \chi_{\mathrm{xx}}(\tau) = \langle x_\tau x\rangle_0, \qquad (6)$$

where $\langle\cdots\rangle_0$ is the average over the ground state Ψ_0. No analytical examination was made. The authors of Ref. 1 pointed out that the calculated curves which represent a functional dependence $\chi(\tau)$ (Figs. 11 and 12 of Ref. 1) may be presented as a superposition of slow and fast oscillations with the frequencies of the fast oscillations $\tilde{t}$ and $\tilde{\omega}$, accordingly for $\chi_{\mathrm{nn}}(\tau)$ and $\chi_{\mathrm{xx}}(\tau)$ (we do not see any reason to identify $\tilde{t}$ with ‘‘renormalized intrinsic hopping integral t’’). They claim that when these frequencies (which are certainly $>\omega_0$, see Table I in Ref. 1) draw together, the qualitative changing of the electron transport mechanism takes place. No physical argumentation (even of a qualitative nature) to support this assertion of the authors has been given.

7. We note that $\chi(\tau)$ may be represented as

$$\chi(\tau) = \sum_{m\neq 0} a_m^2 e^{-i\omega_{m0}\tau}, \quad \hbar\omega_{m0} = E_m - E_0,$$
$$a_m = \langle \Psi_m A \Psi_0\rangle, \qquad (7)$$

Ψ_m, E_m are eigenfunctions and eigenvalues, accordingly, of the Hamiltonian Eq. (2), $A = n_1 - n_2$ or x. The summation in Eq. (7) is performed over the states Ψ_m with parity opposite to the parity of the ground state Ψ_0 (selection rules for the operator A). We note that the frequency spectra of χ_{nn} and χ_{xx} are identical.

There is a connection between correlators (6), (7), and corresponding generalized susceptibilities $\kappa_a(\omega)$ (see Ref. 16). Here ω is the frequency of an external disturbance. For example, the complex polarizability $\kappa(\omega)$ of the considered model may be expressed by the Fourier transform of the correlator (6)

$$\kappa(\omega) = \frac{ie^2l^2}{\hbar}\int_0^\infty e^{i(\omega+i\delta)\tau}[\chi_{\mathrm{nn}}(\tau) - \chi_{\mathrm{nn}}(-\tau)]\,d\tau,$$
$$\delta > 0,\ \delta \rightarrow 0. \qquad (8)$$

l is a constant with dimensionality of the length. An imaginary part of $\kappa(\omega)$ is

$$\kappa''(\omega) = \frac{ie^2l^2}{\hbar}\sum_m a_m^2[\delta(\omega - \omega_{m0}) - \delta(\omega + \omega_{m0})]. \qquad (9)$$

The value $\omega\kappa''(\omega)$ determines an absorption coefficient of electromagnetic radiation, and the value $\omega_m a_m^2$ determines an absorption intensity for the transition $0 \rightarrow m$. Due to the presence of the δ functions in Eq. (9), the absorption process in the given frequency range cannot be linked causally with another one in the other frequency range. For example, a dc conductivity of the semiconductor does not depend on a higher empty band contribution (and vice versa, the intensity of the interband absorption does not depend on dc conductivity mechanism).

It is natural to identify the frequencies in Ref. 1, Figs. 11 and 12, in the following way: the slow oscillation corresponds to the width $\delta E = 2t^*$ of the lowest doublet, Eq. (4); the fast oscillations correspond the frequencies $> \delta E/\hbar$ in $\chi_{\mathrm{nn}}(\tau)$ and $\chi_{\mathrm{xx}}(\tau)$ for that the weights a_m^2 [see Eq. (7)] are maximal. The slow and fast oscillations are located in different frequency regions, therefore changes in the high-frequency region cannot modify the low-frequency electron-transport mechanism cardinally.

For these reasons, the aforesaid assertion (see above, point 6) is unfounded. And again, the source of this error is of methodological character. This situation would be excluded, if instead of $\chi(\tau)$, which have no direct physical meaning, they have considered the complex polarizability $\kappa(\omega)$.

In Ref. 1 the authors touch upon the subject of a boundary where a localized regime changes to an itinerant one. In our opinion the boundary is determined by the parameter $\eta_1 = t/2E_p$ [η_1 is the parameter which was introduced by T. Holstein; the small polaron appears when $\eta_1 < 1$. Also this parameter determines a correction ($\sim t$) to the overlap integral between the site-localized functions]. For $\eta_1 < 1$ the lowest adiabatic potential curve has two minima, which are separated by the energetic barrier (localized regime), for $\eta_1 > 1$ the barrier vanishes (itinerant regime), Ref. 14. We state, that in the range of the parameters, which considered in Ref. 1 the itinerant regime was not yet realized.

8. We have checked and proved that (under right interpretation, naturally) the numerical calculations presented in Secs. III and V of Ref. 1 agree satisfactorily with the Holstein-LF approach for $t/\hbar\omega_0 < 1$. The deviations which arise when $t/\hbar\omega_0 \geqslant 1$ may be explained qualitatively in the framework of the adiabatic approach.

Finally, we note that the authors' assertion in Sec. V,[1]

> ''We notice that the charge dynamics qualitatively tracks globally the behavior expected on the basis of the LF approximation in the antiadiabatic limit . . . '' (p. 14 882),

obviously clashes with their statement in Sec. III (see above, the quotation in our point 3). No comments on this discrepancy are given in Ref. 1.

In conclusion, we state that although the numerical calculations in Ref. 1 were performed fairly enough, their interpretation is untenable.

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