Absence of phase transitions in Holstein systems

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We consider a model of a particle, which is positioned at fixed discrete-lattice sites and interacts with the phonons of the lattice, described by a generalized Holstein Hamiltonian. As physically interesting situations, the molecular polaron, the Frenkel-exciton–phonon system in molecular aggregates, and the small polaron in a crystal are included. We prove that, for optical-phonon dispersions, there is no abrupt (nonanalytical) phase transition of the ground state as the phonon coupling increases. This result holds for both finite-N-site models and infinite-site models. For nonzero temperature, the free energy is smooth for arbitrary phonon dispersions. Furthermore, we show that the ground-state wave function of a small polaron is delocalized for any coupling strength. As a consequence, the self-trapping transition is a smooth crossover which is not accompanied by a localization transition or a nonanalytical change of the ground state.

I. INTRODUCTION

The present paper is concerned with the study of the existence of phase transitions in Holstein systems. The Holstein Hamiltonian[1] H describes the interaction of a particle (like an electron or an exciton), which may stay at N different sites, with the phonons of a molecule or a crystal:

$$H = H_{0,s} + H_{0,\mathrm{ph}} + H_I \ , \tag{1}$$

where

$$H_{0,s} = -\sum_{n,m=1}^{N} T_{mn} \mid m \rangle\langle n \mid \tag{2}$$

and

$$H_{0,\mathrm{ph}} = \sum_{\mathbf{k}} \omega(\mathbf{k}) a^{\dagger}(\mathbf{k}) a(\mathbf{k}) \ . \tag{3}$$

Moreover

$$H_I = \alpha^{1/2} \sum_{n=1}^{N} \sum_{\mathbf{k}} \{ g(\mathbf{k}) a(\mathbf{k}) \exp[i\mathbf{k}\cdot\mathbf{R}(n)] + \mathrm{H.c.} \} \mid n \rangle\langle n \mid \ . \tag{4}$$

In (2), $H_{0,s}$ is the Hamiltonian of a single particle which may occupy N distinct lattice sites ($N < \infty$). The $\mid n \rangle$'s are the site states of the particle ($1 \le n \le N$). For the hopping element T_{mn} we assume

$$T_{mn} \ge 0 \quad \text{for } m \ne n \tag{5}$$

and

$$T_{mn} = T_{nm} \ . \tag{6}$$

Thirdly, the $N \times N$ matrix $T \equiv (T_{mn})$ is assumed to be ergodic. This means that for any $m,n \in \{1,\ldots,N\}$ there exists a natural number $p \in \mathbb{N}$ such that

$$\langle m \mid T^p \mid n \rangle \ne 0 \ . \tag{7}$$

The conditions (5)–(7) are, for example, satisfied in the usual near-neighbor interaction

$$T_{mn} = \begin{cases} T > 0 & \text{if the states } n \text{ and } m \text{ are near neighbors} \ , \\ 0 & \text{otherwise} \ . \end{cases} \tag{8}$$

$H_{0,\mathrm{ph}}$ is the usual free-phonon term. $a^{\dagger}(\mathbf{k})$, $a(\mathbf{k})$, $\mathbf{k}$, and $\omega(\mathbf{k})$ are the creation operator, annihilation operator, wave vector, and frequency of the phonons, respectively. The $\mathbf{k}$ sum extends over an infinite discrete-phonon-momentum lattice. (We could also take a finite number of phonon modes or a continuous phonon momentum space without changing the qualitative results.) Obviously,

$$\omega(\mathbf{k}) \ge 0 \ . \tag{9}$$

Henceforth, we specify the spatial dimension d to $d=3$, but all results are readily transferred to arbitrary d.

In (4), α denotes the extracted coupling parameter and $g(\mathbf{k})$ the coupling function where

$$\sum_{\mathbf{k}} \mid g(\mathbf{k}) \mid^2 < \infty \ . \tag{10}$$

$\mathbf{R}(n)$ is the mapping from the numeration of the sites by natural numbers n, $1 \le n \le N < \infty$ to their position in real space.

The associated Hilbert space $\mathcal{H}$ is the product space

$$\mathcal{H} = \mathbb{C}^N \otimes F \ , \tag{11}$$

where

$$F = \bigoplus_{m=0}^{\infty} [l^2(\mathbb{Z}^3)]^{\circledS m} \tag{12}$$

is the usual Fock space of the phonons, ⓢ denoting the symmetrical tensor product. $l^2(\mathbb{Z}^3)$ contains all complex-valued square-summable sequences of the discrete-phonon-momentum lattice isomorphic to $\mathbb{Z}^3$.

Let us now discuss the different physical cases, which are described by H. The two-level system ($N=2$), coupled to bosons, has been studied in great detail in the literature; see Leggett *et al.*[2] for a review. For $N=3$ up to order of ~ 100, the Hamiltonian H describes the interaction of an electron or exciton with the intramolecular vibrations of a molecular aggregate; see Craig and Walmsley,[3] Davydov,[4] and Merrifield.[5] For N very large or $N \to \infty$, we arrive at the concept of small polarons in solids; see, e.g., Holstein,[1] Toyozawa,[6] and Emin.[7] Here, the $\mathbf{R}(n)$'s are the usual periodic positions of the discrete lattice.

In any case, mentioned above, the problem of self-trapping is of fundamental significance. For weak coupling α, one expects that the electron behaves as a free particle and it should be delocalized over all sites, whereas for very strong coupling it is conceivable that the electron is self-trapped by the phonons. A self-trapping transition is understood as a drastic change in the mass, in the number of virtual phonons of the ground state, in the degree of spatial delocalization, or as an abrupt change in the ground-state energy or the free energy of the system as a function of α. It is essential to understand whether it is a continuous or discontinuous transition. In the latter case the ground-state energy and the mass, etc., were nonanalytic at a certain critical coupling α_c.

For a two-level system coupled to a bath of oscillators with nonzero frequency (molecular polaron), Manka[8] and Moraweck[9] get discontinuities in mean-field theories. Prelovsek[10] and Beck *et al.*[11] find an abrupt change in the physical quantities. On the other hand, Rivier and Coe,[12] Shore and Sander,[13] and Stolze and Brandt[14] get smooth crossovers. The situation is quite similar for the molecular Frenkel exciton-phonon system and the small polaron. Toyozawa (see, e.g., Refs. 6, 15–17; see also Cho and Toyozawa[18]) investigated the small polaron within the adiabatic approximation, where he does find an abrupt transition and a discontinuous change of the polaron mass. Furthermore, Emin,[7] and Yarkony and Silbey[19] get temperature-dependent sharp transitions, too, whereas Scherer *et al.*[20] found a continuous transition; see also Venzl and Fischer.[21] The small-polaron problem can also be attacked by Monte Carlo calculations. De Raedt and Lagendijk (see Ref. 22 and references therein) found drastic changes in the polaron quantities.

The method, used in the publications quoted above, is either a variational or a Monte Carlo approach. Without subtracting from the merits of these techniques, it is clear that they are not able to decide whether or not a transition is continuous or discontinuous. A variational calculation yields an upper bound on the energy (but not the energy as such) and the Monte Carlo method because of its finite sampling time will always give a continuous transition. In this paper, we use a functional analytical approach in order to study the exact nature of the self-trapping transition. We prove that for optical-phonon dispersions, the ground state, the ground-state energy, the number of virtual phonons in the ground state, and the polaron mass are analytical functions of the coupling parameter. For nonzero temperature also acoustical dispersions result in analytical physical quantities. Therefore, the self-trapping transition is smooth and no discontinuous phase transition exists. These results apply to all cases $N=2,3,\ldots$ mentioned above, including $N \to \infty$.

If the $\mathbf{R}(n)$'s are periodic, the total momentum is a conserved quantity. We prove that the ground state respects this translational symmetry belonging to zero total momentum for any coupling strength. Thus a phonon-induced localization does not occur.

It should be remarked that there may still be smooth peak structures in the derivatives of the energy with respect to the coupling constant. If ω is a mean value of the phonon frequencies and T the electron bandwidth, then the adiabatic approximation ($\omega/T \equiv 0$) can predict a true phase transition (see again Toyozawa, Refs. 15–17). In view of our result, this transition smears out for $\omega/T > 0$. However, for $\omega/T \ll 1$, there is still a sharp peak structure in the corresponding derivative. Therefore, it should be possible to detect this peak experimentally for small ω/T. However, the structure of the peak is not to be interpreted as an original discontinuous structure which is smeared out exclusively by other effects like impurity scattering, lattice defects, potential fluctuations, etc., but it is really a *per se* continuous peak. The properties of a small polaron cannot be classified within a phase-transition concept.

For a large polaron, the existence of phase transitions was first critically studied by Peeters and Devreese.[23] In fact, utilizing functional analytical methods of J. Fröhlich,[24] similar analyticity results were proved in Refs. 25–28. The two differences to our system are the continuum character of the model (whereas we take the discrete nature of the lattice into account) and the infinite electron bandwidth in contrast to our finite electron bandwidth. Therefore it is *a priori* not clear at all whether or not the results for the large polaron are transferrable to the physically different Holstein system (see, e.g., De Raedt and Lagendijk[22] for a discussion). Using methods which are based upon previous work,[25–28] we do show that the nature of the self-trapping transition is the same irrespective of the kind of polaron model.

This paper is organized as follows: Firstly, in Sec. II, we show that the ground state of the finite-site model is analytic in all parameters. We transfer this result to the case $N \to \infty$ in Sec. III. Finite-temperature results are obtained from the path-integral representation of the free energy and are listed in Sec. IV. Finally, in Sec. VI, we mention possible extensions and conclude our results.

II. SPECTRAL PROPERTIES OF THE FINITE-SITE HOLSTEIN MODEL

In this section, we assume the optical-phonon dispersion

$$\omega(\mathbf{k}) \geq \omega_0 > 0 \tag{13}$$

and inversion symmetry of $\omega(\mathbf{k})$ and $g(\mathbf{k})$. Furthermore, the sites $\{\mathbf{R}(n)\}$ should be inversion symmetric with respect to a fixed point in space. Let E be the ground-state energy of H. Because of (10) and since the interaction is linear in the phonon operators, we get, according to a result of Nelson,[29] that H_I is a Kato potential with respect to $H_{0,\mathrm{ph}}$ with relative bound zero. That means that for any $\epsilon>0$ there exists a constant b such that for all $|\psi\rangle \in D(H_{0,\mathrm{ph}})$

$$\|H_I\Psi\| \leq \epsilon\|H_{0,\mathrm{ph}}\psi\| + b\|\psi\| \ . \tag{14}$$

Since $H_{0,s}$ commutes with $H_{0,\mathrm{ph}}$, and $H_{0,s}$ is bounded, there exists also a constant c such that

$$\|H_I\psi\| \leq \epsilon\|(H_{0,\mathrm{ph}}+H_{0,s})\psi\| + c\|\psi\| \ . \tag{15}$$

Consequently, by the Kato-Rellich theorem,[30] H is a well-defined self-adjoint operator which is bounded from below.

We introduce a uv cutoff $r<\infty$ in the coupling, which is removed later, and we define $H_{I,r}$ by replacing $g(\mathbf{k})$ in (4) by $g_r(\mathbf{k})\equiv g(\mathbf{k})\Theta(r-k)$. Furthermore let $H_r = H_{0,s}+H_{0,\mathrm{ph}}+H_{I,r}$ and let E_r be the associated ground-state energy. Now the number of phonons with momentum $k>r$ is conserved and we may classify the Hamiltonian after its eigenvalues, i.e.,

$$H_r = \sum_{k(>r)} \sum_{n_{\mathbf{k}}=0}^{\infty} H(\{n_{\mathbf{k}}, k>r\}) \ , \tag{16}$$

where

$$H(\{n_{\mathbf{k}}, k>r\}) = H_{0,r}+H_{I,r}+\sum_{k(>r)} \omega(\mathbf{k})n_{\mathbf{k}} \tag{17}$$

and

$$H_{0,r} = \sum_{k(\leq r)} \omega(\mathbf{k})a^{\dagger}(\mathbf{k})a(\mathbf{k}) + H_{0,s} \ . \tag{18}$$

Now, because of (13), $H_{0,r}$ has a purely discrete spectrum for $r<\infty$. Since $H_{I,r}$ is a Kato potential with relative bound zero with respect to $H_{0,r}$, even $H(\{n_{\mathbf{k}}, k>r\})$ has a purely discrete spectrum. From (16), (17), and (13) it follows that the spectrum of H_r remains discrete in the energy interval $[E_r, E_r+\omega_0[$.

If $r\to\infty$, we get [because of (14)] that $H_r \to H$ in norm resolvent convergence. Consequently, $E_r \to E$ as $r\to\infty$ and the spectrum of H remains discrete in the energy interval $[E, E+\omega_0[$. Thus, we have proven the existence of a discrete ground state of H.

The uniqueness of the ground state is proven by showing that $\exp(-H)$ has a strictly positive integral kernel in the electron-site representation and in the phonon Q space; see Reed and Simon.[31] Here, the phonon Q space may be thought of as the Schrödinger (position) representation of the phonons written as distinct harmonic oscillators. We choose such a representation because H_I acts as multiplication operator in this representation. Then the Trotter formula ensures us that all we need to prove is showing that $\exp(-H_{0,s}-H_{0,\mathrm{ph}})$ has a strictly positive integral kernel in the chosen representation. Now, $\exp(-H_{0,\mathrm{ph}})$ clearly has a strictly positive integral kernel in the phonon Q space. As for details for the last two steps, we refer to Gerlach and Löwen,[25] who described this steps more extensively in the case of a large polaron. It remains to show that $\exp(-H_{0,s})=\exp(T)$ has a strictly positive kernel in the electronic site representation, i.e., to show that

$$\langle m \mid \exp(T) \mid n \rangle > 0 \quad \text{for any } |m\rangle, |n\rangle \ . \tag{19}$$

This follows from the expansion

$$\langle m \mid \exp(T) \mid n \rangle = \sum_{n=0}^{\infty} (n!)^{-1} \langle m \mid T^n \mid n \rangle \tag{20}$$

and our ergodicity assumption of T (7). Thus the ground state is unique.

We add a remark: If one classifies the wave function after a total momentum $\mathbf{Q}$ (see, e.g, Scherer *et al.*[20] and Sec. III), the ground-state energies of the Hamiltonian to fixed subspace belonging to $\mathbf{Q}$ and $-\mathbf{Q}$ are equal, because of our assumption of inversion symmetry. Since the ground state of H is unique, it follows that it must belong to $\mathbf{Q}=\mathbf{0}$, i.e., it is translation invariant.

Having shown that the ground state of H is discrete and nondegenerate for any α, the analytical perturbation theory of Kato[30] is applicable. This theory ensures us that the ground state and the ground-state energy of H are analytical in $\alpha\geq 0$ [because of (15)] and in T_{mn} (because $H_{0,s}$ is a bounded operator). The same holds for the number of virtual phonons in the ground state. Consequently, there exists no discontinuous phase transition.

III. THE LIMIT OF INFINITE SITES

In view of our results of Sec. II, one expects that a true nonanalyticity, if at all, should only take place with the help of some limit, for example the limit of infinite sites $N\to\infty$. In this section, we prove that even for $N\to\infty$ the physical quantities remain analytical. We consider the infinite-site Holstein Hamiltonian on a Bravais lattice generated by the three linearly independent vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, i.e., the lattice positions are

$$\mathbf{R}(\mathbf{n}) = n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3, \quad n_i\in\mathbb{Z}, \ \mathbf{n}=(n_1,n_2,n_3) \ . \tag{21}$$

In our Hamiltonian

$$H = H_{0,s}+H_{0,\mathrm{ph}}+H_I \tag{22}$$

we have now

$$H_{0,s} = -\sum_{\mathbf{m},\mathbf{n}} T_{\mathbf{m}-\mathbf{n}} |\mathbf{m}\rangle\langle\mathbf{n}| \ . \tag{23}$$

Here, a summation over a vector $\mathbf{n}=(n_1,n_2,n_3)$ means three summations over n_1, n_2, and n_3 independently in the range from $-\infty$ up to ∞. In contrast to the finite site case we have labeled each site by three natural numbers in order to make the connection to a real three-dimensional lattice clear.

In this section, we modify our standard assumptions (5)–(7); we assume positivity and translational and inversion invariance

$$T_{\mathbf{mn}} \geq 0, \quad T_{\mathbf{mn}} = T_{\mathbf{m}-\mathbf{n}}, \quad T_{\mathbf{n}} = T_{-\mathbf{n}} . \tag{24}$$

Furthermore, it is assumed that the Fourier transform $\varepsilon(\mathbf{k})$ of $T_{\mathbf{m}}$ exists and is a bounded function of $\mathbf{k}$.

$H_{0,\mathrm{ph}}$ is given by (3), but one may think about the discrete $\mathbf{k}$ summation also as a continuous integration for example over the first Brillouin zone. All cases are tractable in our formalism; however, we always assume optical dispersions; see (13).

The interaction H_I is still given by (4); however, the n summation now extends over all $\mathbf{n}$ and $\mathbf{R}(\mathbf{n})$ one has to insert (21). We assume square summability of the coupling; see (10).

The underlying Hilbert space is now $l^2(\mathbb{Z}^3) \otimes F$, where F is given by (12).

It is possible to cancel the electron coordinate by classifying the eigenstates after the conserved total momentum $\mathbf{q}$. We first perform a Lee-Low-Pines transformation:[32]

$$U = \sum_{\mathbf{n}} \exp[-i\mathbf{P}_{\mathrm{ph}} \cdot \mathbf{R}(\mathbf{n})] \, | \, \mathbf{n} \rangle \langle \mathbf{n} \, | \ , \tag{25}$$

where

$$\mathbf{P}_{\mathrm{ph}} = \sum_{\mathbf{k}} \mathbf{k} a^{\dagger}(\mathbf{k}) a(\mathbf{k}) \tag{26}$$

is the phonon momentum. Then the transformed Hamiltonian reads as follows:

$$U^{-1} H U = H^T = H^T_{0,s} + H_{0,\mathrm{ph}} + H_{I,N} \ , \tag{27}$$

where

$$H^T_{0,s} = - \sum_{\mathbf{m},\mathbf{n}} T_{\mathbf{m}-\mathbf{n}} \exp\{ i\mathbf{P}_{\mathrm{ph}} \cdot [\mathbf{R}(\mathbf{m}) - \mathbf{R}(\mathbf{n})] \} \, | \, \mathbf{m} \rangle \langle \mathbf{n} \, | \tag{28}$$

and

$$H_{I,N} = \alpha^{1/2} \sum_{\mathbf{k}} [g(\mathbf{k}) a(\mathbf{k}) + \mathrm{H.c}] \ . \tag{29}$$

Note that $H_{I,N}$ does not depend on the electron coordinate. All we have to do is to diagonalize $H^T_{0,s}$. This is done by performing a unitary transformation to the electron Fourier space introducing the new states

$$| \, \mathbf{q} \rangle = (\Omega_B)^{-1/2} \sum_{\mathbf{n}} \exp[-i\mathbf{q} \cdot \mathbf{R}(\mathbf{n})] \, | \, \mathbf{n} \rangle, \quad \mathbf{q} \in B \ . \tag{30}$$

Here B denotes the associated first Brillouin zone of the lattice and $\Omega_B = \int_B d^3q$ is the volume of the first Brillouin zone.

Note that the representation of the electronic Hilbert space changes from $l^2(\mathbb{Z}^3)$ to $L^2(B)$.

Written in these states, the Hamiltonian is diagonal

$$H^T = \int_B d^3q \, H(\mathbf{q}) \, | \, \mathbf{q} \rangle \langle \mathbf{q} \, | \ , \tag{31}$$

where $H(\mathbf{q})$ lives merely on the phonon Fock space and is given by

$$H(\mathbf{q}) = \varepsilon(\mathbf{q} + \mathbf{P}_{\mathrm{ph}}) + H_{0,\mathrm{ph}} + H_{I,N} \ . \tag{32}$$

Here, the band-structure function $\varepsilon(\mathbf{k})$ is the Fourier transform of $T_{\mathbf{n}}$:

$$\varepsilon(\mathbf{k}) = - \sum_{\mathbf{n}} T_{\mathbf{n}} \exp[-i\mathbf{k} \cdot \mathbf{R}(\mathbf{n})] \ . \tag{33}$$

The structure of the Hamiltonian $H(\mathbf{q})$ is known from the theory of large polarons and is qualitatively well understood. We can therefore shorten our discussion concerning spectral properties. In particular, they can be analyzed in the same manner as Fröhlich[24] does (see also Spohn).[33] Let $E(\mathbf{q})$ denote the ground-state energy of $H(\mathbf{q})$. Especially it follows that the spectral interval $[E(\mathbf{q}), \Delta(\mathbf{q})[$ is discrete where

$$\Delta(\mathbf{q}) = \inf_{\mathbf{k}} [\omega(\mathbf{k}) + E(\mathbf{q} + \mathbf{k})] \ . \tag{34}$$

In the Appendix, we prove that

$$E(\mathbf{0}) < E(\mathbf{q}) \quad \text{for any } \mathbf{q} \in B \setminus \{\mathbf{0}\} \ . \tag{35}$$

Let us briefly discuss the physical consequences of (35). Firstly, it shows that the ground state of H belongs to total momentum zero and that it is delocalized for any coupling strength α. We refer also to the discussion of Gerlach and Löwen[25] in the case of a large polaron. Secondly, we conclude that there is no drastic "symmetry breaking" of the translational symmetry in the ground state and that no localization transition occurs. An intuitive discussion of possibilities and nonpossibilities of symmetry breaking was given by De Raedt and Lagendijk.[34] Furthermore, (34) and (35) imply that the spectral interval $[E(\mathbf{0}), E(\mathbf{0}) + \omega_0[$ of $H(\mathbf{q})$ is discrete such that the ground state of $H(\mathbf{0})$ is discrete.

Having established the discreteness of the ground state of $H(\mathbf{0})$, we proceed as in Sec. II to prove its uniqueness. By assumption the operator $\varepsilon(\mathbf{q} + \mathbf{P}_{\mathrm{ph}})$ is a bounded operator and it is defined anywhere on the underlying Hilbert space. We firstly note that then

$$\exp[-\varepsilon(\mathbf{q} + \mathbf{P}_{\mathrm{ph}})] = \sum_{n=0}^{\infty} (n!)^{-1} [-\varepsilon(\mathbf{q} + \mathbf{P}_{\mathrm{ph}})]^n \ . \tag{36}$$

Inserting (33), we state that $\exp[-\varepsilon(\mathbf{P}_{\mathrm{ph}})]$ has a positive integral kernel in the phonon Q space, since $\exp(i\mathbf{P}_{\mathrm{ph}} \cdot \boldsymbol{\lambda})$ has a positive integral kernel in the phonon Q space for all $\boldsymbol{\lambda} \in \mathbb{R}^3$. Since $H_{I,N}$ acts as a multiplication operator and $\exp(-H_{0,\mathrm{ph}})$ has a strictly positive integral kernel in the Q space and since $H_{0,\mathrm{ph}}$ commutes with $\varepsilon(\mathbf{q} + \mathbf{P}_{\mathrm{ph}})$, we finally get that $\exp[-H(\mathbf{0})]$ has a strictly positive integral kernel in the phonon Q space. Consequently, the ground state of $H(\mathbf{0})$ is nondegenerate.

Now, as in Sec. II, we turn to analytical perturbation theory. We obtain that the ground state of $H(\mathbf{0})$ and consequently also the ground-state energy of H as well as expectation values of the ground state are analytical in α.

It was proposed (see, e.g., Toyozawa[16]) to define a polaron mass proportional to $[\partial^2 E(\mathbf{0})/\partial q^2]^{-1}$. Analytical perturbation theory in $\mathbf{q}$ around $\mathbf{q} = \mathbf{0}$ ensures us that the polaron mass is analytic in α, too.

IV. FINITE-TEMPERATURE RESULTS

In this section, we comment briefly on analyticity results for finite temperatures $1/\beta > 0$. In doing so, we con-

sider the (formal) free energy F in the path-integral representation. For the large polaron the analyticity proof was already done by Gerlach and Löwen.[26,27] In our case one may proceed along similar lines. We assume (5)–(7), (10), and

$$\int d^3k \mid g(\mathbf{k}) \mid^2/\omega(\mathbf{k}) < \infty \ , \tag{37}$$

which we have written in a continuous-phonon-momentum space. This includes acoustical dispersions which are not too singular. The free energy $F=-(1/\beta)\ln(Z)$ is derivable from a partition function Z where

$$Z = \mathrm{tr}\exp(-\beta H)/\mathrm{tr}\exp(-\beta H_{\alpha\equiv 0}) \ . \tag{38}$$

By the standard Feynman-Kac construction, Z can be represented by a functional integral

$$Z = \langle \exp(\alpha S_I[\sigma]) \rangle \ , \tag{39}$$

where

$$\langle A[\sigma] \rangle = \sum_{n=1}^{N} \int \mu_n^T(d\sigma(\cdots)) A[\sigma] \Big/ \sum_{n=1}^{N} \int \mu_n^T(d\sigma(\cdots)) \ . \tag{40}$$

$\mu_n^T(d\sigma(\cdots))$ is the path-integral measure generated by the Hamiltonian $H_{0,s}$, i.e., by the matrix T. Because of (7) it is a strictly positive measure. It is concentrated on piecewise constant paths $t\in[0,\beta]\to\sigma(t)$ taking as values the natural numbers $1,2,\ldots,N$ with the boundary condition $\sigma(0)=\sigma(\beta)=n$. As for further details see Spohn and Dümcke.[35]

$S_I[\sigma]$ is explicitly given by

$$S_I[\sigma]=\tfrac{1}{2}\int_0^\beta dt \int_0^\beta ds \int d^3k \mid g(\mathbf{k}) \mid^2 \exp\{i\mathbf{k}\cdot[\mathbf{R}(\sigma(t))-\mathbf{R}(\sigma(s))]\}\cosh[\omega(\mathbf{k})(\mid t-s \mid -\beta/2)]/\sinh[\beta\omega(\mathbf{k})/2] \ . \tag{41}$$

The existence of Z is proven by a trivial estimation of S_I requiring (37). By dominated convergence, Z is representable as a power series

$$Z = \sum_{n=0}^{\infty} \alpha^n/(n!)\langle S_I^n[\sigma] \rangle \ , \tag{42}$$

which is absolutely convergent for all α. Consequently, the free energy is analytic in α. We remark that the same can be done for the limit of infinite sites ($N\to\infty$).

For optical dispersions, this result was expected since the ground-state energy is analytical and the influence of a finite temperature is—intuitively—to smoothen the result. However, the free energy is also analytical for acoustical dispersions, fulfilling (37), whereas we were not able to clarify the zero-temperature analytical properties in this case.

V. GENERALIZATIONS AND CONCLUSIONS

In this section, we extend our method to two interesting cases. Firstly, we consider the influence of an impurity potential on the phase-transition problem and secondly we discuss phonon-position-dependent transfer energies.

One may add an impurity potential at site $\mathbf{R}(\mathbf{n}_0)$ like

$$-\lambda \mid \mathbf{n}_0 \rangle\langle \mathbf{n}_0 \mid , \quad \lambda > 0 \tag{43}$$

to the Hamiltonian (22). In doing this, the problem one deals with is the bound small polaron. The spectral properties of this Hamiltonian can be studied by the same methods as developed by the author in Ref. 28 for the large bound polaron (see also Ref. 36). To obtain qualitative results, we can admit more general potentials of type

$$V = -\lambda \sum U_n \mid \mathbf{n} \rangle\langle \mathbf{n} \mid , \quad \lambda, U_{\mathbf{n}} > 0 \tag{44}$$

with the additional requirement that for all $\epsilon>0$ there exists a decomposition $U_{\mathbf{n}}=l_{\mathbf{n}}+b_{\mathbf{n}}$ such that $\sum_{\mathbf{n}} \mid l_{\mathbf{n}} \mid^2 < \infty$ and $\mid b_{\mathbf{n}} \mid < \epsilon$ for any $\mathbf{n}$.

We only mention the results without providing a proof (it can be found in Ref. 36). The continuum edge of the Hamiltonian H with potential (44) begins exactly at the energy $\min[E(\lambda)+\omega_0, E(\lambda=0)]$. Here we have assumed a continuous phonon $\mathbf{k}$ space, $\omega_0>0$ is the minimum of the phonon dispersion, and $E(\lambda)$ denotes the ground-state energy of the Hamiltonian $H+V$. If T is ergodic, the ground state is unique, as far as it exists. For vanishing electron-phonon coupling, the occurrence of bound states was already extensively studied (see, e.g., Economou, Ref. 37). It turns out that for short-range potentials, e.g., for (43), in three-dimensional lattices, λ must exceed a critical value λ_c, in order to form a bound state. This is connected with a nonanalyticity of the ground-state energy and a localization transition of the ground state. This transition does persist for $\alpha>0$; we can prove that there exists an α-dependent critical unique value $\lambda_c(\alpha)$ with $0\le\lambda_c(\alpha)<\infty$ such that the ground-state energy is nonanalytic in λ.

Shinozuka and Toyozawa[38] called this phenomenon extrinsic self-trapping. For the case (43), they also give the phase-diagram in the $\alpha\lambda$ plane. We remark that their phase diagram intersects the α axis and this is interpreted as a discontinuous self-trapping transition in α for $\lambda\equiv 0$. This is not true, for we have shown the analyticity of the ground-state energy for $\lambda\equiv 0$. For $\lambda>0$, however, there exists a nonanalyticity as an intrinsic property of the Hamiltonian, i.e., a true phase transition induced by the impurity potential.

Our second concern is to discuss phonon position transfer energies, i.e., the matrix T is assumed to depend additionally on the phonon position operator. A phonon-modified transfer is essential in the Su-Schrieffer-Heeger-model.[39] Then except for some technical as-

sumptions the same proof is possible, as long as the transfer energies remain negative. For a Peierls-Hubbard system, for instance, this was extensively proved in Ref. 40. Consequently, such phonon-position-dependent transfer energies cannot generate a phase transition of the ground state.

In conclusion, we have shown that for several situations the ground-state energy of a Holstein type Hamiltonian is analytic in the electron-phonon parameter. This casts new light on the mathematical nature of the self-trapping process. In fact, from a fundamental point of view, the properties of a molecular polaron, a Frenkel exciton-phonon system and a small polaron cannot be classified by a phase-transition concept. In practice, e.g., for small values of ω/T (where ω is a mean value of the phonon frequencies and T is the electron-exciton bandwidth) there may be large but analytical changes in the physical quantities such that from this point of view the self-trapping process has experimental consequences.

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APPENDIX A: ABSENCE OF PHONON-INDUCED LOCALIZATION FOR THE SMALL POLARON

In this Appendix, we prove

$$E(\mathbf{0})<E(\mathbf{q}) \quad \text{for } \mathbf{q}\in B\setminus\{\mathbf{0}\}\ , \tag{A1}$$

which was mentioned in Sec. III; see (35). We take the dimension d as $d=1$, omitting hereafter the vector notation; the generalization to arbitrary d is straightforward. We assume $g(k)\in L^2(\mathbb{R})$ and optical dispersions. In addition to the standard assumptions at the beginning of Sec. III, we assume, for the matrix T, $T_1>0$. We have $q\in[0,2\pi/a[$, a denoting the one-dimensional lattice constant.

To prove (A1), we use the same trick as utilized by Gerlach and Löwen in Ref. 25 for a large Fröhlich polaron. Let us briefly recall the basic steps of this trick. The original Hamiltonian, whose ground-state energy $E(q)$ is under study, is $H(q)$, where q is a c number. But to study $E(q)$ as a function of q and to prove (A1), it is profitable to reintroduce formally an operator p, i.e., to reintroduce an additional auxiliary electronic Hilbert space, on which the new Hamiltonian $H(p)$ is defined. p is not the usual momentum operator; this would be unfavorable in the proof, for then p would not possess any eigenfunctions. To overcome this difficulty, p is chosen as a momentum operator on a discrete momentum lattice $\Gamma=\{q_n\}$. Then the possible ground states of $H(p)$ are really eigenfunctions. Now we choose a fixed representation of the underlying Hilbert space and show that $\exp[-H(p)]$ has a strictly positive integral kernel in this representation. This implies that the ground state of $H(p)$ is nondegenerate, i.e., the set $\{E(q_n)\,|\,q_n\in\Gamma\}$ has a unique smallest element. By inversion symmetry $E(q_n)=E(-q_n)$, and hence $E(0)<E(q_n\neq 0)$ for all $q_n\in\Gamma$. Since the lattice Γ can be chosen arbitrarily, it finally follows that $E(0)<E(q)$ for all $q\neq 0$.

We are now going to apply this trick to our Hamiltonian. Let $K\in]0,\pi/a[$ be fixed and assume

$$E(0)\geq E(K)\ . \tag{A2}$$

Then we deduce a contradiction.

We have to distinguish two cases (i) and (ii): (i) $r\equiv aK/(2\pi)$ is irrational, and (ii) $r\equiv aK/(2\pi)$ is rational.

In the first case (i) we introduce an infinite electronic momentum lattice Γ with lattice constant K; the associated Hilbert space $l^2(\mathbb{Z})$ is spanned by the $|\,q_n\,\rangle$'s:

$$l^2(\mathbb{Z})\equiv\overline{\{\,|\,q_n\,\rangle\,|\,q_n=nK,\ n\in\mathbb{Z}\}}\ . \tag{A3}$$

On this space, p is defined as multiplication operator such that $p\,|\,q_n\,\rangle=q_n\,|\,q_n\,\rangle$. The associated Fourier space of this lattice space $l^2(\mathbb{Z})$ is the position space $W=L^2([0,2\pi/K[)$. The functions of this space are considered as periodically continued to $\mathbb{R}$. Then $\exp(i\lambda p)$, $\lambda\in\mathbb{R}$ causes a translation about λ in W. Now we choose the phonon Q space and the electronic W space as fixed representation of the underlying Hilbert space of $H(q)$. Then $\exp(-H_{0,\mathrm{ph}})$ has a strictly positive integral kernel in the Q space, $H_{I,N}$ is a multiplication operator. We prove that $\exp[-\varepsilon(p+P_{\mathrm{ph}})]$ has a strictly positive integral kernel in the electronic W space and a positive integral kernel in the Q space of the phonons. By (33) and (36) we obtain

$$\exp[-\varepsilon(p+P_{\mathrm{ph}})] = \sum_{m=0}^{\infty}(m!)^{-1}\left[\sum_n T_n\exp(-inap)\exp(-inaP_{\mathrm{ph}})\right]^m . \tag{A4}$$

Now, $\exp(-inaP_{\mathrm{ph}})$ has a positive kernel in the phonon Q space. Since $T_1>0$ and since π/K and a are incommensurable (because r is irrational), there exists for any positive functions $|\,f\,\rangle, |\,g\,\rangle\in W$ a natural number m such that the backfolded translation about $-ma$ has a nonvanishing matrix element, i.e.,

$$\langle f\,|\exp(-imap)\,|\,g\,\rangle>0\ .$$

Consequently, $\exp[-\varepsilon(p+P_{\mathrm{ph}})]$ has a strictly positive integral kernel in the electronic W space and a positive integral kernel in the phonon Q space. Thus, it follows that $\exp[-H(p)]$ has a strictly positive integral kernel in the W representation of the electronic space and in the phonon Q space. Therefore the ground state is unique. But since $K\in]0,\pi/a[$ and $E(K)=E(2\pi/a-K)$ (because of inversion symmetry), we get a contradiction to (A2).

In the second case (ii) we can no longer construct an infinite lattice, since then equivalent lattice points occur repeatedly and the ground state is no longer unique. Here we take a finite lattice with periodic boundary conditions.

Let $r=u/v$ where $u,v\in\mathbb{N}$ have no common prime factors. The finite lattice consists of v points and the associ-

ated electronic Hilbert space $\mathbb{C}^v$ is spanned by

$$\{\,|\,q_n\rangle\,|\,q_n=nK \quad \text{with } n=0,1,\ldots,v-1\}\,. \tag{A5}$$

Again we choose p defined on this space such that $p\,|\,q_n\rangle=q_n\,|\,q_n\rangle$. Then, on $\mathbb{C}^v$, $\exp(iap)$ is represented as a unitary diagonal $v\times v$ matrix with diagonal elements $1,\exp(i2\pi u/v),\ldots,\exp[i2\pi u(v-1)/v]$. This matrix is unitarily equivalent to the unitary $v\times v$ matrix U,

$$U\equiv\begin{vmatrix} 0 & 0 & \cdots & \cdots & \cdots & \cdots & 0 & 1 \\ 1 & 0 & \cdots & & & & 0 & 0 \\ 0 & 1 & 0 & \cdots & & & 0 & 0 \\ \vdots & 0 & 1 & 0 & \cdots & & 0 & 0 \\ \vdots & & & & & & & \vdots \\ 0 & \cdots & \cdots & \cdots & \cdots & 0 & 1 & 0 \end{vmatrix}, \tag{A6}$$

since this matrix has the same eigenvalues $1,\exp(i2\pi u/v),\ldots,\exp[i2\pi u(v-1)/v]$. We now choose the representation of the electronic Hilbert space $\mathbb{C}^v$ such that $\exp(iap)$ acts as the matrix U in the representation just given in (A6). Clearly, such a representation exists. As usual, we take for the phonons the Q space. Utilizing (A4) and (A6) and the fact $T_1>0$, we finally get by similar arguments as in case (i) that $\exp[-H(p)]$ has a strictly positive integral kernel in the chosen representation and that $E(K)=E(2\pi/a-K)$ leads to a contradiction to (A2).

Our final result is $E(0)<E(q)$ for $q\in]0,2\pi/a[$, $q\neq\pi/a$. What about $q=\pi/a$? Here, the argument is slightly different. The analysis of Gross[41] shows that $E(0)\leq E(q)$, even for $q=\pi/a$. From the uniqueness of the ground state in case (ii), it then follows that $E(0)<E(\pi/a)$. Consequently (A1) is proved.

[1]T. Holstein, Ann. Phys. **8**, 343 (1959).
[2]A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
[3]D. P. Craig and S. H. Walmsley, *Excitons in Molecular Crystals* (Benjamin, New York, 1968).
[4]A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).
[5]R. E. Merrifield, J. Chem. Phys. **40**, 445 (1964).
[6]Y. Toyozawa, Prog. Theor. Phys. **26**, 29 (1961).
[7]D. Emin, Adv. Phys. **22**, 57 (1973).
[8]R. Manka, Phys. Status Solidi B **94**, K67 (1979).
[9]M. Moraweck, Diploma thesis, University of Dortmund, 1980.
[10]P. Prelovsek, J. Phys. C **12**, 1855 (1979).
[11]R. Beck, W. Götze, and P. Prelovsek, Phys. Rev. A **20**, 1140 (1979).
[12]N. Rivier and T. J. Coe, J. Phys. C **10**, 4471 (1977).
[13]H. B. Shore and L. M. Sander, Phys. Rev. B **7**, 4537 (1973).
[14]J. Stolze and U. Brandt, J. Phys. C **16**, 5617 (1983).
[15]Y. Toyozawa, Physica B + C **117&118B**, 23 (1983).
[16]Y. Toyozawa, in *Relaxation of Elementary Excitations,* edited by R. Kubo and E. Hanamura (Springer, Berlin, 1980).
[17]Y. Toyozawa, in *Organic Molecular Aggregates,* edited by P. Reineker *et al.* (Springer, New York, 1983).
[18]K. Cho and Y. Toyozawa, J. Phys Soc. Jpn. **30**, 1555 (1971).
[19]D. Yarkony and R. Silbey, J. Chem. Phys. **65**, 1042 (1976); **67**, 5818 (1977).
[20]P. O. J. Scherer, E. W. Knapp, and S. F. Fischer, Chem. Phys. Lett. **106**, 191 (1984).
[21]G. Venzl and S. F. Fischer, Phys. Rev. B **32**, 6437 (1985).
[22]H. De Raedt and A. Lagendijk, Phys. Rep. **127**, 233 (1985).
[23]F. Peeters and J. T. Devreese, Phys. Status Solidi B **112**, 219 (1982).
[24]J. Fröhlich, Fortschr. Phys. **22**, 159 (1974).
[25]B. Gerlach and H. Löwen, Phys. Rev. B (to be published).
[26]B. Gerlach and H. Löwen, Phys. Rev. B **35**, 4291 (1987).
[27]B. Gerlach and H. Löwen, Phys. Rev. B **35**, 4297 (1987).
[28]H. Löwen, J. Math. Phys. (to be published).
[29]E. Nelson, J. Math. Phys. **5**, 1190 (1964).
[30]T. Kato, *Pertubation Theory for Linear Operators* (Springer, New York, 1966).
[31]M. Reed and B. Simon, *Analysis of Operators,* Vol. IV of *Methods of Modern Mathematical Physics* (Academic, New York, 1978).
[32]T. D. Lee, F. E. Low, and D. Pines, Phys. Rev. **90**, 297 (1953).
[33]H. Spohn, Ann. Phys. **175**, 278 (1987).
[34]H. De Raedt and A. Lagendijk, Phys. Rev. B **27**, 6097 (1983).
[35]H. Spohn and R. Dümcke, J. Stat. Phys. **41**, 389 (1985).
[36]H. Löwen, Ph.D. thesis, University of Dortmund, 1987.
[37]E. N. Economou, *Green's Functions in Quantum Physics* (Springer, Berlin, 1979), p. 92.
[38]Y. Shinozuka and Y. Toyozawa, J. Phys. Soc. Jpn. **46**, 505 (1979).
[39]W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1980).
[40]H. Löwen, Z. Phys. B (to be published).
[41]L. Gross, J. Funct. Anal. **10**, 52 (1972).