Small-oscillation theory of the one-dimensional large optic polaron

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We study the small oscillations of the one-dimensional large polaron within the Holstein molecular-crystal model. We show that additional stationary solutions are not minimal. We solve analytically the classical equations of motion for the normal modes of the displacements about the minimal polaron solution, both determining the eigenspectrum and constructing the eigenfunctions.

I. INTRODUCTION

Quasi-one-dimensional solids[1] (e.g., anisotropic molecular crystals and especially polymeric crystals) are characterized by considerable anisotropy in their electronic transport properties. Within the framework of tight-binding theory, $J_{||}/J_{\perp} \gg 1$, where $J_{||}$ and $J_{\perp}$ are, respectively, the intrachain and interchain electron-transfer amplitudes. Under these conditions, very general arguments[2–4] indicate that, with any electron-phonon coupling, an excess electron or hole must occur in the form of a quasi-one-dimensional polaron, whose intrachain dimension L is large compared to the lattice spacing a, while still being confined to the single chain. The study of the dynamics of such anisotropic large polarons[5,6] necessitates the development of a formal theory of the small oscillation behavior of the one-dimensional large polaron within a well-defined model. This is the object of this paper. For this purpose we utilize the well-known Holstein molecular-crystal model[7] with its one-dimensional large-polaron solution.

The results of these dynamical studies on one-dimensional polarons[5,6] have implications for the intrachain dynamics of intrinsic electronic defects in quasi-one-dimensional solids [e.g., solitons in $(CH)_x$] (Refs. 8 and 9) and for the scattering theory of topological defects in one-dimensional field theories.[10–14] While the intrachain bandlike motion is the focus of our studies,[5,6] the interchain behavior is presumably characterized by thermally activated hopping.[15–18] The matrix elements associated with such interchain hopping again inherently rely on the intrachain eigenfunctions such as are developed for the specific model studied in this paper.

In Sec. II we introduce the molecular-crystal model and formulate the electron-phonon interaction within the adiabatic approximation. In Sec. III we review the results of the minimal-energy adiabatic solution—the Holstein large polaron.[7] In Sec. IV we discuss additional stationary adiabatic solutions[19] and demonstrate that these solutions are not minimal but rather are saddle-point solutions. In Sec. V we develop the theory of the small oscillations of the large polaron. In Sec. VI we solve for the odd normal modes, and in Sec. VII we solve for the even normal modes. In Sec. VIII we give a few concluding remarks.

II. ADIABATIC THEORY OF POLARON-LATTICE INTERACTIONS FOR THE MOLECULAR-CRYSTAL MODEL

In this section, we formulate the theory of the adiabatic polaron-lattice interaction within the framework of the molecular-crystal model.[7] Our starting Hamiltonian is

$$H=\sum_n \left[\frac{-\hbar^2}{2M}\frac{\partial^2}{\partial u_n^2}+\tfrac{1}{2}M\omega_0^2 u_n^2\right]-J\sum_n a_n^{\dagger}(a_{n+1}+a_{n-1}) -A\sum_n u_n a_n^{\dagger}a_n \ . \tag{2.1}$$

The first term describes the vibrational motion of a chain of isolated diatomic molecules (mass M and Einstein frequency ω_0) as a function of the vibrational displacements, u_n, of the individual diatomic internuclear coordinates from their common equilibrium value. The second term describes electron transfer between adjacent sites (as in conventional tight-binding theory) with overlap matrix element J; the notations $a_n^{\dagger}$ and a_n denote fermion creation and annihilation operators, respectively. Finally, the third term of (2.1) constitutes the electron-lattice interaction; the Holstein molecular-crystal model assumes this to be site diagonal in the electron coordinate and purely local in that it depends only on the vibrational coordinate of the occupied site.

The zeroth-order adiabatic approximation[20] consists of dropping the vibrational kinetic-energy contribution to (2.1), namely,

$$T_L=\sum_n \frac{-\hbar^2}{2M}\frac{\partial^2}{\partial u_n^2} \ . \tag{2.2}$$

For the case of a single electron, the adiabatic electron wave function solves the Schrödinger-type eigenvalue equation

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$$\left[\tfrac{1}{2}M\omega_0^2\sum_p u_p^2 - Au_n\right]a_n(\ldots,u_m,\ldots) - J[a_{n-1}(\ldots,u_m,\ldots)+a_{n+1}(\ldots,u_m,\ldots)] = E(\ldots,u_m,\ldots)a_n(\ldots,u_m,\ldots) \; . \tag{2.3}$$

Here, the one-electron wave function is specified in terms of the amplitudes, $a_n(\ldots,u_m,\ldots)$, for electron occupancy of the nth diatomic site; as in any adiabatic formulation, these amplitudes are parametric functions of the vibrational displacements, u_m. The eigenvalue, $E(\ldots,u_m,\ldots)$, also a parametric function of the displacements u_m, serves as the effective potential energy for vibrational motion. It is conveniently written as

$$E(\ldots,u_m,\ldots) = \tfrac{1}{2}M\omega_0^2\sum_p u_p^2 + \varepsilon(\ldots,u_m,\ldots) - 2J \; , \tag{2.4}$$

where $\varepsilon(\ldots,u_m,\ldots)$ is the energy eigenvalue of the "electronic" equation

$$-J[a_{n+1}(\ldots,u_m,\ldots) - 2a_n(\ldots,u_m,\ldots) + a_{n-1}(\ldots,u_m,\ldots)] - Au_n a_n(\ldots,u_m,\ldots) = \varepsilon(\ldots,u_m,\ldots)a_n(\ldots,u_m,\ldots) \; . \tag{2.5}$$

In the continuum approximation, appropriate for the case of the large polaron, (2.5) takes the form

$$H(\{u_m\})a_n(\{u_m\}) = -J\frac{\partial^2 a_n(\{u_m\})}{\partial n^2} - Au_n a_n(\{u_m\}) = \varepsilon(\{u_m\})a_n(\{u_m\}) \; , \tag{2.6}$$

wherein the aggregate, $\{u_m\}$, now corresponds to a continuous field variable. The electron-lattice interaction plays the role of an effective potential energy in the electron Hamiltonian:

$$H = -J\frac{\partial^2}{\partial n^2} + V(n) = -J\frac{\partial^2}{\partial n^2} - Au_n \; . \tag{2.7}$$

The solution of (2.3) or of (2.6) for arbitrary displacements u_m is extremely difficult. However, within the Born-Oppenheimer approach,[20] one first solves the problem for those values of u_m which minimize $E(\{u_m\})$, and then develops perturbative solutions for small displacements of the u_m about their equilibrium values $u_m^{(0)}$. The first part of this program, namely, obtaining the minimal energy solution, has been accomplished by Holstein[7] and by Rashba.[21] We review the results of this minimal energy solution in the next section.

III. REVIEW OF THE MINIMAL ENERGY ADIABATIC SOLUTION

The "equilibrium" displacements, $u_m^{(0)}$, corresponding to the minimal energy $E(\{u_m^{(0)}\})$, are given by

$$u_n^{(0)} = \frac{A}{M\omega_0^2}\,|a_n^{(0)}|^2 \; , \tag{3.1}$$

in terms of the, as yet undetermined, electron wave function, $a_n^{(0)}$. Substituting (3.1) into (2.4), yields the so-called nonlinear Schrödinger equation

$$J\frac{\partial^2 a_n^{(0)}}{\partial n^2} + \left[\frac{A^2}{M\omega_0^2}\,|a_n^{(0)}|^2 + \varepsilon\right]a_n^{(0)} = 0 \; . \tag{3.2}$$

The unusual delocalized Bloch states

$$a_n^{(0)} = N^{-1/2}e^{ikna} \; , \tag{3.3}$$

correspond to "electronic" eigenvalues

$$\varepsilon = Jk^2a^2 \; , \tag{3.4}$$

i.e., to total energy

$$E = -2J + Jk^2a^2 \; , \tag{3.5}$$

and describe the bottom of the single-particle electron band.

In addition, as is well known, the nonlinear Schrödinger equation (3.2) possesses an exact self-trapped[22–24] solution, namely,

$$a_n^{(0)} = \left[\frac{\gamma}{2}\right]^{1/2}\operatorname{sech}[\gamma(n-\xi/a)] \; , \tag{3.6}$$

which is normalized according to

$$\int_{-\infty}^{\infty}|a_n|^2 dn = 1 \; . \tag{3.7}$$

The parameter

$$\gamma = \frac{A^2}{4M\omega_0^2 J} \tag{3.8}$$

characterizes the size, $L = a/\gamma$, of the polaron, where a is the lattice spacing, and may be used to define a natural length scale transformation

$$z = \gamma n \; . \tag{3.9}$$

The variable ξ denotes the polaron-centroid coordinate; the translational invariance of the polaron is reflected in the ξ independence of (3.2).

Using (3.1), the equilibrium displacements are given by

$$u_n^{(0)} = \frac{A}{2M\omega_0^2}\gamma\operatorname{sech}^2[\gamma(n-\xi/a)] \; . \tag{3.10}$$

The electronic energy is obtained from (3.2)

$$\varepsilon = -J\gamma^2 \; , \tag{3.11}$$

whence the total energy (2.4) of the coupled electron-lattice system is

$$E_p=\varepsilon+\tfrac{1}{2}M\omega_0^2\sum_n |u_n^{(0)}|^2=-J\gamma^2/3 . \tag{3.12}$$

The energy E_p represents the polaron binding energy; it gives the minimum value $E(\{u_m^{(0)}\})$ of the self-trapped state (3.6) relative to the corresponding (3.5) minimum, $-2J$, for the delocalized Bloch electron state (3.3). This minimal-energy polaron solution (3.6) and (3.10) is shown in Fig. 1.

The self-consistent electron-lattice interaction is

$$V^{(0)}(n)=-Au_n^{(0)}=-2\gamma^2 J\,\mathrm{sech}^2[\gamma(n-\xi/a)] . \tag{3.13}$$

Using (3.13), one may rewrite (3.2) in the form

$$\frac{d^2a_n}{dn^2}+\{2\gamma^2\,\mathrm{sech}^2[\gamma(n-\xi/a)]-\gamma^2\}-a_n=0 . \tag{3.14}$$

IV. ADDITIONAL STATIONARY ADIABATIC SOLUTIONS

In addition to the self-consistent solution $a_n^{(0)}$, Eq. (3.2) possesses a hierarchy of other solutions[19]

$$a_n^{(m)}=\frac{\beta k}{\sqrt{2\gamma}}\mathrm{cn}\{\beta(n-\xi/a);k\} , \tag{4.1}$$

with increasing electronic energy

$$\varepsilon^{(m)}=J\beta^2(1-2k^2) . \tag{4.2}$$

Here $\mathrm{cn}\{u;k\}$ is the Jacobi elliptic function (of modulus k) that reduces to the cosine in the limit $k\to 0$. While $\mathrm{cn}\{u;k\}$ has periodicity 4 K [where $\mathsf{K}(k)$ is the complete elliptic integral of the first kind], it is antiperiodic over 2 K:

$$\mathrm{cn}\{u+2\,\mathsf{K};k\}=-\mathrm{cn}\{u;k\} . \tag{4.3}$$

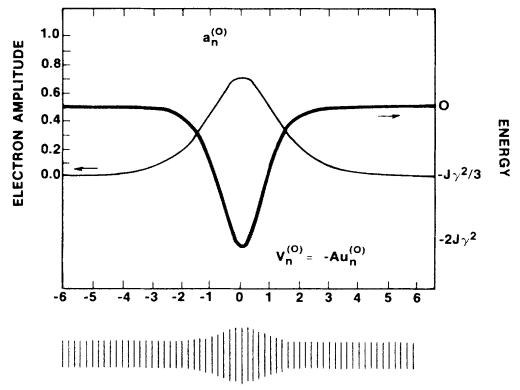

FIG. 1. The self-consistent minimal solution for the large polaron. The bold solid curve gives the potential energy $V_n^{(0)}=-Au_n^{(0)}$ seen by the self-trapped electron; the solid curve gives the adiabatic electron wave function $a_n^{(0)}$. Sketched at the bottom is a linear diatomic crystal, with nuclei displaced by u_n, indicating the presence of the polaron. The bottom of the Bloch energy band is the zero of energy. The maximum depth of the potential well is $2J\gamma^2$. The self-trapped polaron state is bound relative to the Bloch band by $-J\gamma^2/3$. Shown in the sketch is the case $\gamma=10$.

Thus we may consider an "m-well" solution, with alternating electronic amplitude from well to well,

$$\beta N=m\mathsf{K} , \tag{4.4}$$

where N is the total number of sites in the chain. Normalization (3.7) of the electronic amplitude identifies

$$\beta=\frac{\gamma/m}{\mathsf{E}-k'^2\,\mathsf{K}} , \tag{4.5}$$

where $\mathsf{E}(k)$ is the complete elliptic integral of the second kind, and where $k'^2=1-k^2$. Equations (4.4) and (4.5) together determine the modulus k of the elliptic functions and integrals. The electronic energy is given by

$$\varepsilon^{(m)}=J\left[\frac{\gamma}{m}\right]^2\frac{1-2k^2}{(\mathsf{E}-k'\,\mathsf{K})^2} . \tag{4.6}$$

In the limit the self-trapped wells are sufficiently separated ($k\to 1$)

$$\beta\to\gamma/m , \tag{4.7}$$

and the electronic energy becomes

$$\varepsilon^{(m)}\to\varepsilon_0^{(m)}=-J(\gamma/m)^2 . \tag{4.8}$$

In terms of the total energy

$$E\to-2J-\frac{J}{3}\left[\frac{\gamma}{m}\right]^2 . \tag{4.9}$$

In this limit, the wave function takes the approximate form of m noninteracting wells

$$a_n^{(m)}\to\frac{1}{m}\left[\frac{\gamma}{2}\right]^{1/2}\sum_{p=0}^{m-1}(-1)^p\,\mathrm{sech}\left[\frac{\gamma}{m}(n-2p\,\mathsf{K}-\xi/a)\right] , \tag{4.10}$$

where we have normalized (4.10) according to (3.7). We thus have an entire hierarchy of lattices of self-trapped bound states. It remains to be seen, however, whether these represent minimal or only stationary solutions. A typical such lattice solution is sketched in Fig. 2.

A second-order variation, similar to the calculation presented in Sec. VI, gives the eigenfrequencies ω_α of the normal modes as solutions to

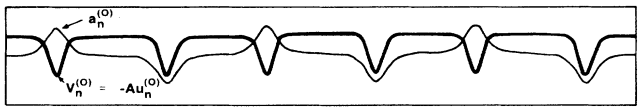

FIG. 2. A typical stationary state, comprised of a lattice of wells (nuclear displacements u_n denoted by the bold solid curve) with alternating electron amplitude (solid curve). Such a lattice is unstable with respect to a relative displacement of the wells (acoustic mode), and hence is not a minimal solution.

$$\left[\frac{d^2}{dz^2}+2\left[1+\frac{2}{1-\omega_\alpha^2/\omega_0^2}\right]k^2\,\mathrm{cn}^2\{z;k\}+(1-2k^2)\right]f_\alpha(z)=\frac{2\beta}{\gamma}\frac{k^4}{1-\omega_\alpha^2/\omega_0^2}\mathrm{cn}\{z;k\}\int_{-\infty}^{\infty}dz'\,\mathrm{cn}^3\{z';k\}f_\alpha(z')\,, \tag{4.11}$$

where the function $f_\alpha(z)$ is defined by

$$\delta u_n=\frac{8\gamma}{1-\omega_\alpha^2/\omega_0^2}a_n^{(m)}f_\alpha(z)\,, \tag{4.12}$$

where δu_n is the atomic displacement deviation from the stationary solution, and where [similar to (3.9)] $z=\beta n$. For the odd modes, the left-hand side of (4.11) vanishes

$$\left[\frac{d^2}{dz^2}+2\left[1+\frac{2}{1-\omega_\alpha^2/\omega_0^2}\right]k^2\,\mathrm{cn}^2\{z;k\}+(1-2k^2)\right]f_\alpha(z)=0\,. \tag{4.13}$$

Unfortunately, (4.13) is a Lamé equation of, in general, nonintegral order, whose eigenspectrum is not known. With the change of variable

$$u=\mathrm{sn}\{z;k\}\,, \tag{4.14}$$

Eq. (4.13) takes the form

$$\frac{d}{du}\left[(1-u^2)^{1/2}(1-k^2u^2)^{1/2}\frac{df_\alpha}{du}\right]+\left[2\left[1+\frac{2}{1-\omega_\alpha^2/\omega_0^2}\right]k^2\left[\frac{1-u^2}{1-k^2u^2}\right]^{1/2}+\frac{1-2k^2}{(1-u^2)^{1/2}(1-k^2u^2)^{1/2}}\right]f_\alpha(u)=0\,. \tag{4.15}$$

In the limit $k\to 1$, this reduces to

$$\frac{d}{du}\left[(1-u^2)\frac{df_\alpha}{du}\right]+2\left[1+\frac{2}{1-\omega_\alpha^2/\omega_0^2}\right]f_\alpha(u)-\frac{1}{1-u^2}f_\alpha(u)=0\,, \tag{4.16}$$

which is the equation (6.5) of the small oscillation spectrum of odd modes for the isolated self-trapped solution. This suggests that the additional m-well lattice solutions are stable with respect to opticlike distortions, similar to the stability of the single-well solution to such distortions. The limit $k\to 1$, however, eliminates the branch cuts emanating from $u=\pm 1$ and $u=\pm k$ and does not give any information as to the stability of the m-well solutions with respect to collective, or acousticlike, distortions; these acousticlike modes disappear in the limit $k\to 1$, as the first Brillouin-zone boundary moves[25] to $k=0$. For completeness, under the transformation (4.14), the general normal mode equation (4.11) becomes in the limit $k\to 1$

$$\frac{d}{du}\left[(1-u^2)\frac{df_\alpha}{du}\right]+\left[2\left[1+\frac{2}{1-\omega_\alpha^2/\omega_0^2}\right]-\frac{1}{1-u^2}\right]f_\alpha(u)=\frac{2}{1-\omega_\alpha^2/\omega_0^2}\frac{1}{(1-u^2)^{1/2}}\int_{-1}^{1}du'(1-u'^2)^{1/2}f_\alpha(u')\,. \tag{4.17}$$

In order to investigate the stability with respect to lattice displacements, we juxtopose the exact m-well solution (4.1) with m noninteracting wells (4.10). Comparing (4.8) with (4.6) gives an "interaction" energy

$$\Delta\varepsilon=\varepsilon^{(m)}-\varepsilon_0^{(m)}=J\left[\frac{\gamma}{m}\right]^2\left[\frac{1-2k^2}{(\mathsf{E}-k'^2\mathsf{K})^2}+1\right]\,, \tag{4.18}$$

which, in the limit of sufficiently separated wells ($k\to 1$), reduces to

$$\Delta\varepsilon=-\tfrac{1}{2}J\left[\frac{\gamma}{m}\right]^2k'^2[\ln(4/k')-\tfrac{7}{2}]\,. \tag{4.19}$$

The interaction per pair,

$$\Delta\varepsilon\,|_{\mathrm{pair}}=-\frac{J\gamma^2k'^2}{2m^3}[\ln(4/k')-\tfrac{7}{2}]\,, \tag{4.20}$$

is thus seen to be attractive. Evaluating the periodicity,

$$\Delta n=2\,\mathsf{K}=2\ln(4/k')+O(k'^2\ln k')\,, \tag{4.21}$$

allows the interaction per pair to be written

$$\Delta\varepsilon\,|_{\mathrm{pair}}=\frac{-4J\gamma^2}{m^3}e^{-\Delta n}(\Delta n-7)\,, \tag{4.22}$$

where Δn is the number of sites between interacting wells.

As the pairwise interaction is attractive, the m-well solution is unstable with respect to collapse. To show this explicitly, consider a lattice of such interacting wells, separated by Δn sites. If one of the wells is displaced by δn, the change in energy of the lattice is

$$\delta\varepsilon^{(m)}=J\frac{8\gamma^2}{m^3}e^{-\Delta n}\{(\Delta n-7)[1-\cosh(\delta n)]+\delta n\sinh(\delta n)\}\,, \tag{4.23}$$

which, for small displacements $\delta n/\Delta n\ll 1$, reduces to

$$\delta\varepsilon^{(m)} = -\frac{8J\gamma^2}{m^3}\Delta n\, e^{-\Delta n}[\cosh(\delta n)-1]\ , \tag{4.24}$$

i.e., we can lower the energy of the stationary solutions (4.1) by distorting the lattice. Thus, while these m-well lattice solutions are stable with respect to opticlike modes (4.16), they are unstable with respect to acousticlike modes (4.24). Therefore these solutions (4.1) are not minimal but rather saddle-point solutions and hence will not be relevant for the small oscillation spectrum nor for a transport discussion of the large polaron.[5,6]

V. SMALL OSCILLATIONS OF THE LARGE POLARON—FORMULATION

We now consider the electronic problem for vibrational configurations in the vicinity of the minimal configuration [specified by the $u_m^{(0)}$ of (3.10)]. We study the modifications of the electronic wave function, electronic energy, and total vibrational potential energy, for small departures

$$\delta u_m = u_m - u_m^{(0)} \tag{5.1}$$

from the minimal configuration. The starting point of this analysis is Eq. (2.6), which we solve perturbatively, obtaining corrections to the electron wave function $a_n(\ldots,u_m^{(0)},\ldots)$ and energy $\varepsilon(\ldots,u_m^{(0)},\ldots)$ to first and second orders in the δu_m, respectively.

The Hamiltonian (2.7) may be decomposed into an equilibrium piece and a perturbation due to the departure of the nth nucleus from its equilibrium position

$$H = H_0 + \lambda\delta V_n \mid_{\lambda=1}\ , \tag{5.2}$$

with

$$H_0 = -J\frac{\partial^2}{\partial n^2} + V_0(n) = -J\frac{\partial^2}{\partial n^2} - Au_n^{(0)} \tag{5.3}$$

and

$$\delta V_n = -A\,\delta u_n\ . \tag{5.4}$$

Within Rayleigh-Schrödinger perturbation theory

$$\varepsilon = \sum_{p=0}^{\infty}\lambda^p\varepsilon^{(p)} \tag{5.5}$$

and

$$a_n = \sum_{p=0}^{\infty}\lambda^p a_n^{(p)}\ , \tag{5.6}$$

where the corrections $a_n^{(p)}$ are orthogonal to the zeroth-order wave function (3.6):

$$\int_{-\infty}^{\infty} a_n^{(p)*}a_n^{(0)}\,dn = 0\ . \tag{5.7}$$

To first order in λ,

$$(H_0-\varepsilon^{(0)})a_n^{(1)} = (\varepsilon^{(1)}-\delta V_n)a_n^{(0)}\ . \tag{5.8}$$

Multiplying by $a_n^{(0)*}$ and integrating over the length of the chain, using the Rayleigh-Schrödinger orthogonality condition (5.7), the first-order correction to the energy is given by

$$\varepsilon^{(1)} = \sum_n |a_n^{(0)}|^2\delta V_n = -A\frac{\gamma}{2}\sum_n \operatorname{sech}^2[\gamma(n-\xi/a)]\delta u_n\ . \tag{5.9}$$

This is manifestly linear in the nuclear displacements δu_n. The first-order correction to the wave function then satisfies

$$\left[\frac{\partial^2}{\partial n^2} + 2\gamma^2\operatorname{sech}^2[\gamma(n-\xi/a)] - \gamma^2\right]a_n^{(1)} = \frac{A}{J}\left[\frac{\gamma}{2}\sum_m \operatorname{sech}^2[\gamma(m-\xi/a)]\delta u_m - \delta u_n\right]a_n^{(0)}\ . \tag{5.10}$$

Defining the Green's function $G(n,n')$ as that solution of the equation

$$\left[\frac{\partial^2}{\partial n^2} + 2\gamma^2\operatorname{sech}[\gamma(n-\xi/a)] - \gamma^2\right]G(n,n') = -\delta(n-n') + \frac{\gamma}{2}\operatorname{sech}(\gamma n)\operatorname{sech}(\gamma n') \tag{5.11}$$

which is orthogonal to the electronic ground-state wave function $a_n^{(0)}$, i.e., for which

$$\int_{-\infty}^{\infty} G(n,n')\operatorname{sech}(\gamma n)\,dn = 0\ , \tag{5.12}$$

the first-order correction to the wave function is given by

$$a_n^{(1)} = \frac{A}{J}\int_{-\infty}^{\infty} G(n-\xi/a,n'-\xi/a)a_n^{(0)}\delta u_{n'}\,dn'\ . \tag{5.13}$$

An explicit solution for $G(n,n')$ can be obtained[6] but will not be needed for our discussion here. As can be readily verified from the explicit solution, $G(n,n')$ is symmetric with respect to the interchange of the variables n and n'.

To second order in λ,

$$(H_0-\varepsilon^{(0)})a_n^{(2)} = (\varepsilon^{(1)}-\delta V_n)a_n^{(1)} + \varepsilon^{(2)}a_n^{(0)}\ . \tag{5.14}$$

Multiplying by $a_n^{(0)*}$, integrating and using the Rayleigh-Schrödinger orthogonality conditions (5.7), the second-order energy is given by

$$\varepsilon^{(2)} = \sum_n a_n^{(0)*}\delta V_n\, a_n^{(1)}\ . \tag{5.15}$$

Substituting for $a_n^{(0)}$ and $a_n^{(1)}$ yields

$$\varepsilon^{(2)} = -\tfrac{1}{2}M\omega_0^2\sum_{nn'}\mathscr{G}(n-\xi/a,n'-\xi/a)\delta u_n\,\delta u_{n'}\ , \tag{5.16}$$

where

$$\mathscr{G}(n,n') = 4\gamma^2 G(n,n')\operatorname{sech}(\gamma n)\operatorname{sech}(\gamma n')\ . \tag{5.17}$$

Thus to second order in the small displacements δu_n, the total electron-lattice energy (2.4) is given (parametrically as a function of the displacements δu_n) by

$$E(\ldots,u_m,\ldots) = \varepsilon^{(0)}+\varepsilon^{(1)}+\varepsilon^{(2)}-2J + \tfrac{1}{2}M\omega_0^2\sum_m (u_m^{(0)}+\delta u_m)^2\ . \tag{5.18}$$

The cross term in the last sum precisely cancels the first-order correction $\varepsilon^{(1)}$ to the electronic energy [as it must, since the adiabatic solution (3.6) is minimal] leaving

$$E(\ldots,u_m,\ldots)=-2J-J\gamma^2/3+\tfrac{1}{2}M\omega_0^2\left[\sum_n(\delta u_n)^2-\sum_{nn'}\mathcal{G}(n-\xi/a,n'-\xi/a)\delta u_n\,\delta u_{n'}\right]. \tag{5.19}$$

We now are in a position to investigate the normal modes of vibration associated with the new vibrational potential-energy function, $V(\ldots,\delta u_m,\ldots)$, as given by (5.19). The odd modes have previously been studied analytically by Melnikov,[26] while the even eigenfrequencies only have been treated numerically by Shaw and Whitfield.[27] The principal utility of these modes is their incorporation of translational invariance in a relatively straightforward and automatic way, thereby serving as a convenient vehicle for our study[6] of the interaction between the translational motion of the polaron and the other (nontranslational) vibrational degrees of freedom.

Assuming harmonic time dependence $e^{i\omega t}$ for the nuclear displacements, the small oscillations are the eigenmodes of the classical dynamical equations

$$M\frac{\partial^2}{\partial t^2}\delta u_n=-\frac{\partial V(\ldots,\delta u_m,\ldots)}{\partial u_n}. \tag{5.20}$$

Using (5.19) for the potential and rearranging

$$(\omega_0^2-\omega^2)\delta u_n=\omega_0^2\sum_{n'}\mathcal{G}(n,n')\delta u_{n'}. \tag{5.21}$$

We remark that, in differentiating the double sum contained in (5.19), we have utilized the symmetry of $\mathcal{G}(n,n')$ in the variables n and n'. Moreover, in writing down these expressions we are tacitly considering the polaron centroid coordinate ξ as being located at the origin. Equation (5.21) has the form of a standard linear homogeneous integral equation, the solution of which, subject to a normalizability boundary condition, constitutes a complete set of normal-mode functions $u_\alpha(n)$, with associated eigenfrequencies ω_α.

Upon introducing (5.17) into (5.21), we have

$$(1-\omega^2/\omega_0^2)\delta u_n=4\gamma^2\,\mathrm{sech}(\gamma n)\sum_{n'}G(n,n')\mathrm{sech}(\gamma n')\delta u_{n'}. \tag{5.22}$$

Defining the function

$$f(n)=\sum_{n'}G(n,n')\mathrm{sech}(\gamma n')\delta u_{n'}, \tag{5.23}$$

(5.22) becomes

$$\delta u_n=\frac{4\gamma^2}{1-\omega^2/\omega_0^2}\mathrm{sech}(\gamma n)f(n). \tag{5.24}$$

We remark that a direct consequence of the orthogonality condition (5.12) is the result

$$\int_{-\infty}^{\infty}u_\alpha(n)dn=0. \tag{5.25}$$

Differentiating (5.23) and using (5.11), we have

$$\frac{d^2f}{dn^2}+\gamma^2[2\,\mathrm{sech}^2(\gamma n)-1]f(n)=-\mathrm{sech}(\gamma n)\delta u_n+\frac{\gamma}{2}\mathrm{sech}(\gamma n)\int_{-\infty}^{\infty}\mathrm{sech}^2(\gamma n')\delta u_{n'}dn', \tag{5.26}$$

where we have replaced the n sum by an integral over a continuous variable n. Using (5.24) in (5.26), we have

$$\frac{d^2f}{dn^2}+\gamma^2\left[\left[2+\frac{4}{1-\omega^2/\omega_0^2}\right]\mathrm{sech}^2(\gamma n)-1\right]f(n)=\frac{2\gamma^3\,\mathrm{sech}(\gamma n)}{1-\omega^2/\omega_0^2}\int_{-\infty}^{\infty}\mathrm{sech}^3(\gamma n')f(n')dn'. \tag{5.27}$$

Introducing the length scale transformation (3.9) into (5.27), yields

$$\frac{d^2f}{dz^2}+\left[\left[2+\frac{4}{1-\omega^2/\omega_0^2}\right]\mathrm{sech}^2z-1\right]f(z)=\frac{2\,\mathrm{sech}z}{1-\omega^2/\omega_0^2}\int_{-\infty}^{\infty}\mathrm{sech}^3(z')f(z')dz'. \tag{5.28}$$

Equation (5.28) constitutes an integro-differential equation which, with appropriate boundary conditions [normalizability and the orthogonality condition (5.25)] is equivalent to the integral equation (5.21). The latter clearly has the form of a standard linear homogeneous integral equation, the solution of which yields a complete set of normal-mode functions $u_\alpha(n)$, with associated eigenfrequencies, ω_α. Equivalently, the solutions of (5.28) yield the eigenfunctions $f_\alpha(z)$, with the same eigenfrequencies, ω_α. Finally, we note that (5.28) is invariant with respect to the replacements $z\to-z$, $z'\to-z'$. Thus the eigenfunctions $f_\alpha(z)$ may be classified as either even or odd.

VI. SMALL OSCILLATIONS OF THE LARGE POLARON—ODD MODES

The odd-parity solutions have been previously obtained by Melnikov[26] and by Shaw and Whitfield.[27] For the odd-parity solutions, the integral term on the right-hand side of (5.27) vanishes:

$$\frac{d^2f_\alpha}{dz^2}+\left[\left[2+\frac{4}{1-\omega_\alpha^2/\omega_0^2}\right]\mathrm{sech}^2z-1\right]f_\alpha(z)=0. \tag{6.1}$$

Introducing the transformation

$$u=\tanh z \tag{6.2}$$

into (6.1), yields

$$\frac{d}{du}\left[(1-u^2)\frac{df_\alpha}{du}\right]+\left[\left[2+\frac{4}{1-\omega_\alpha^2/\omega_0^2}\right]-\frac{1}{1-u^2}\right]f_\alpha(u)=0\ , \tag{6.3}$$

which, upon defining

$$2+\frac{4}{1-\omega_\alpha^2/\omega_0^2}=l(l+1)\ , \tag{6.4}$$

becomes

$$\frac{d}{du}\left[(1-u^2)\frac{df_l}{du}\right]+\left[l(l+1)-\frac{1}{1-u^2}\right]f_l(u)=0\ . \tag{6.5}$$

The normalizable eigenfunctions of (6.5) with odd parity are the associated Lengendre polynomials

$$f_l(u)=P_l^1(u)=(1-u^2)^{1/2}\frac{dP_l}{du}\ , \tag{6.6}$$

with eigenvalues

$$l=2,4,6,\ldots \tag{6.7}$$

[odd l being excluded by the requirement that $P_l^1(u)$ be an odd function of z, and hence of u]. The odd-parity solutions trivially satisfy (5.25). The odd eigenfunctions of (6.1) are conveniently written as

$$f_s(z)=P_{s+2}^1(\tanh z)=(1-u)^{1/2}\frac{dP_{s+2}(u)}{du}\bigg|_{u=\tanh z}\ , \tag{6.8}$$

where

$$l=s+2\ ,$$
$$s=0,2,4,\ldots\ . \tag{6.9}$$

The eigenvalue equation (6.4) then takes the form[26,27]

$$\omega_s^2/\omega_0^2=1-\frac{4}{s^2+5s+4}\ . \tag{6.10}$$

The actual normal modes (5.24) become

$$u_s(z)=(\tfrac{1}{2})^{1/2}\left[\frac{2s+5}{(s+2)(s+3)}\right]^{1/2}(1-u^2)\frac{dP_{s+2}(u)}{du}\bigg|_{u=\tanh z}\ , \tag{6.11}$$

which is normalized by an integral over all space in variable z. We note that the lowest eigenfrequency, $\omega_{s=0}$, vanishes; the other eigenfrequencies converge with increasing s towards an accumulation point at ω_0.

We now comment on the physical implications of the above results. By far, the most important of these is the lowest frequency mode, namely

$$f_0(z)\sim \mathrm{sech}z\tanh z\ . \tag{6.12}$$

To understand the physical meaning of this mode, let us consider the corresponding displacement functions, $u_s(z)$, as given by (5.24). According to (6.11), we have

$$u_0(z)\sim \mathrm{sech}^2 z\tanh z\ . \tag{6.13}$$

Upon comparing (6.13) with (3.10), we note that

$$u_0(z)\sim\frac{\partial u^{(0)}(z-\xi/a)}{\partial\xi}\bigg|_{\xi=0}\ . \tag{6.14}$$

From (6.14) it is clear that, if we displace the polaron centroid from its initial value (zero) by an infinitesimal increment, $\delta\xi$, we find the change

$$u^{(0)}(z-\delta\xi/L)-u^{(0)}(z)\sim u_0(z)\delta\xi\ . \tag{6.15}$$

Thus, the existence of a nonvanishing vibrational amplitude associated with the zero-frequency mode, $u_0(z)$, corresponds just to a rigid displacement of the self-consistent polaronic distortion, $u^{(0)}(z)$. This result, of course, expresses the invariance of the self-consistent solution with respect to infinitesimal displacements (translational invariance).

In the usual theory of lattice dynamics, the determination of the normal modes of vibration constitutes the essential problem. Once these modes are found, the usual harmonic-oscillator theory takes over, yielding the well-known picture of noninteracting phonons. However, in the present problem, having found one mode—the translational mode—for which the "stiffness" constant, $M\omega_{\alpha=0}^2$, vanishes, we now encounter a fundamental difficulty. The motion associated with such a mode is clearly *not* oscillatory, as the "displacement" amplitude, Q_0, may become indefinitely large. Under these circumstances, the small amplitude assumption for the displacements, δu_n, about a fixed centroid coordinate, as defined by (5.1), is completely inadequate for dynamical problems. In particular, the harmonic form of the potential function $V(\ldots,\delta u_n,\ldots)$, given by (5.19), will not properly describe the vibrational dynamics of the system in which extended translational motion of the polaron is necessarily involved. In view of the above essential difficulty, the $\omega=0$ translational (Goldstone) mode must be separated from the other (small oscillation) modes and treated *to all orders* in the amplitude. This complication is inherent in the strong coupling of the electron and phonon degrees of

freedom that give rise to the Holstein large polaron; to adequately deal with this difficulty requires a major departure from conventional noninteracting phonon theory. A consistent formalism for so separating out the Goldstone mode is contained in Ref. 6.

VII. SMALL OSCILLATIONS OF THE LARGE POLARON—EVEN MODES

We now study the integro-differential eigenvalue equation (5.28) for the even modes. The numerical eigenfrequencies of these even-parity prodes have previously been obtained by Shaw and Whitfield.[27] We compare our analytic results to their numerical results at the end of this section (Table I). Defining

$$g(u)=(1-u^2)^{1/2}f(u) \tag{7.1}$$

and using the definition (6.4), (5.28) becomes

$$(1-u^2)\frac{d^2g}{du^2}+l(l+1)g(u) = \frac{(l+2)(l-1)}{2}\int_{-1}^{1}g(u')du' . \tag{7.2}$$

Differentiating,

$$\frac{d}{du}\left[(1-u^2)\frac{dg'}{du}\right]+l(l+1)g'(u)=0 , \tag{7.3}$$

we recover the Legendre equation, where $g'=dg/du$. Thus

$$g(u)=\alpha\int^{u}P_l(u')du'+\beta\int^{u}Q_l(u')du'+\gamma , \tag{7.4}$$

or equivalently

$$g(u)=\alpha\int^{u}P_l(u')du'+\beta\int^{u}P_l(-u')du'+\gamma , \tag{7.5}$$

depending upon which linearly independent set [$P_l(u)$ and $Q_l(u)$, or $P_l(u)$ and $P_l(-u)$ for nonintegral l] of solutions to the Legendre equation we choose to use. In what follows, we utilize the set specified in (7.5). The constant γ is determined by resubstituting the solution (7.5) to (7.3) back into the original equation (7.2). For this purpose, a useful relation is[28]

TABLE I. Eigenfrequencies of the lowest normal modes of small oscillation about the minimal polaron solution.

l	ω/ω_0	l	ω/ω_0
2	0	14	0.990 34
2.5229	0.647 51	14.7172	0.991 23
4	0.881 92	16	0.992 56
4.6065	0.912 21	16.7262	0.993 19
6	0.948 68	18	0.994 10
6.6479	0.958 18	18.7337	0.994 55
8	0.971 01	20	0.995 20
8.6740	0.975 28	20.7402	0.995 53
10	0.981 31	22	0.996 02
10.6923	0.983 61	22.7459	0.996 28
12	0.986 93	24	0.996 65
12.7062	0.988 31	24.7508	0.996 85

$$P_l(u)=\frac{1}{2l+1}\left[\frac{dP_{l+1}}{du}-\frac{dP_{l-1}}{du}\right] , \tag{7.6}$$

which, upon introduction into (7.5), yields

$$g(u)=\alpha[P_{l+1}(u)-P_{l-1}(u)] +\beta[P_{l+1}(-u)-P_{l-1}(-u)]+\gamma . \tag{7.7}$$

The constant γ is then determined to be

$$\gamma=\frac{(l+2)(l-1)}{4}(\alpha+\beta) \times\int_{-1}^{1}du'[P_{l+1}(u')-P_{l-1}(u')] . \tag{7.8}$$

The constants α and β must be determined from the boundary conditions at infinity.

Both an explicit evaluation of (7.8) and a determination of the constants α and β require an examination of the singularity properties of the Legendre functions $P_l(u)$. In particular, while normalized to $P_l(1)=1$, $P_l(u)$ has a branch cut emanating from $u=-1$ to $u=-\infty$. Using the representation[29]

$$P_l(u)=F\left[-l,l+1;1;\frac{1-u}{2}\right] \tag{7.9}$$

of $P_l(u)$ in terms of the hypergeometric function, the behavior on the real axis near the branch cut may be evaluated[30]

$$P_l(-1+\delta)=\frac{\sin(l\pi)}{\pi}\left[\ln\left[\frac{\delta}{2}\right]+2C+2\psi(l+1)\right] +\cos(l\pi) , \tag{7.10}$$

where $0<\delta\ll 1$. Here C is Euler's constant, and ψ is the digamma function. Using (7.10) to evaluate the integral (7.8) yields

$$\gamma=(\alpha+\beta)\frac{\sin(l\pi)}{\pi}\frac{2l+1}{l(l+1)} . \tag{7.11}$$

We may thus satisfy the integro-differential equation (5.27) with (7.7), where the constant γ is given by (7.11).

We now investigate the asymptotic behavior of the solution. As $z\to\infty$, $u\to 1$, and the solution

$$g(u)\to-\beta\frac{2\sin(l\pi)}{\pi}\frac{2l+1}{l(l+1)}+\gamma . \tag{7.12}$$

Similarly, as $z\to-\infty$, $u\to-1$, and the solution

$$g(u)\to-\alpha\frac{2\sin(l\pi)}{\pi}\frac{2l+1}{l(l+1)}+\gamma . \tag{7.13}$$

For even modes we require $g(u\to 1)=g(u\to-1)$, whence $\alpha=\beta$. It is straightforward to show that, with $\alpha=\beta$, as $z\to\pm\infty$, $g(u)\to 0$.

We now impose the orthogonality condition (5.25)

$$\int_{-1}^{1}\frac{g(u)}{1-u^2}du=0 . \tag{7.14}$$

Using the relation[31]

$$\frac{dP_l}{du}=\frac{-l(l+1)}{2l+1}\frac{1}{1-u^2}[P_{l+1}(u)-P_{l-1}(u)] \quad (7.15)$$

and (7.11), yields the eigenvalue equation

$$\frac{2\sin l\pi}{\pi}[C+\psi(l+1)]+\cos(l\pi)=1\ , \quad (7.16)$$

which may also be expressed as

$$\frac{2}{\pi}[\psi(l+1)-\psi(1)]=\tan\left[\frac{l\pi}{2}\right]\ . \quad (7.17)$$

It is curious that the eigenvalue condition (7.16) is also satisfied by the odd modes of Sec. VI, for which l is an even integer. An evaluation of the transcendental eigenvalue equation (7.16) yields the eigenvalues listed in Table I, which are identical to those found by purely numerical means.[27] The several lowest modes, both even and odd, are shown in Fig. 3.

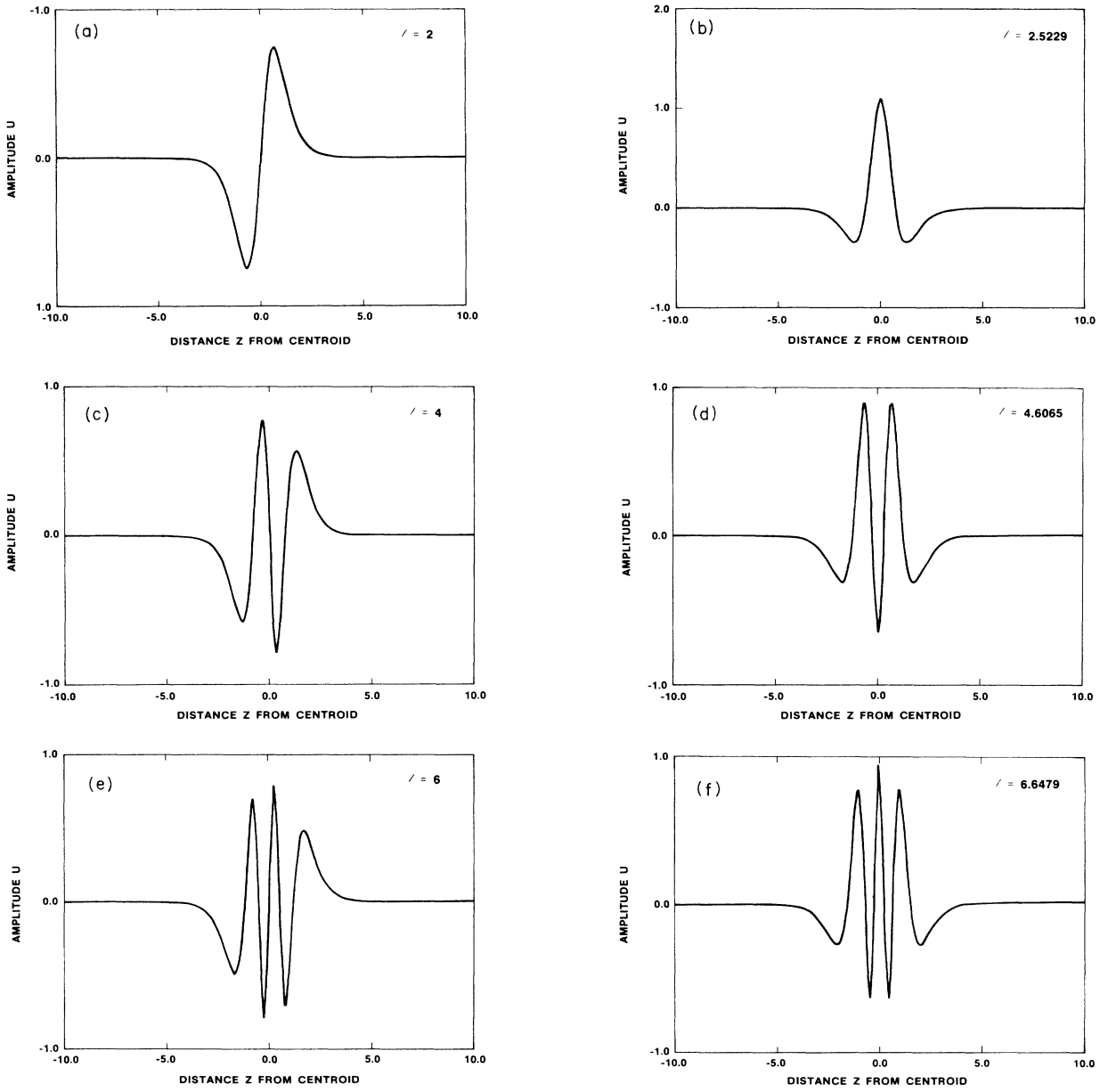

FIG. 3. The nine lowest normal modes of small oscillation about the large polaron solution. The lowest Goldstone (zero-frequency) mode ($l=2$) arises from an infinitesimal translation of the polaron. The remaining modes possess finite frequencies, which quickly approach ω_0.

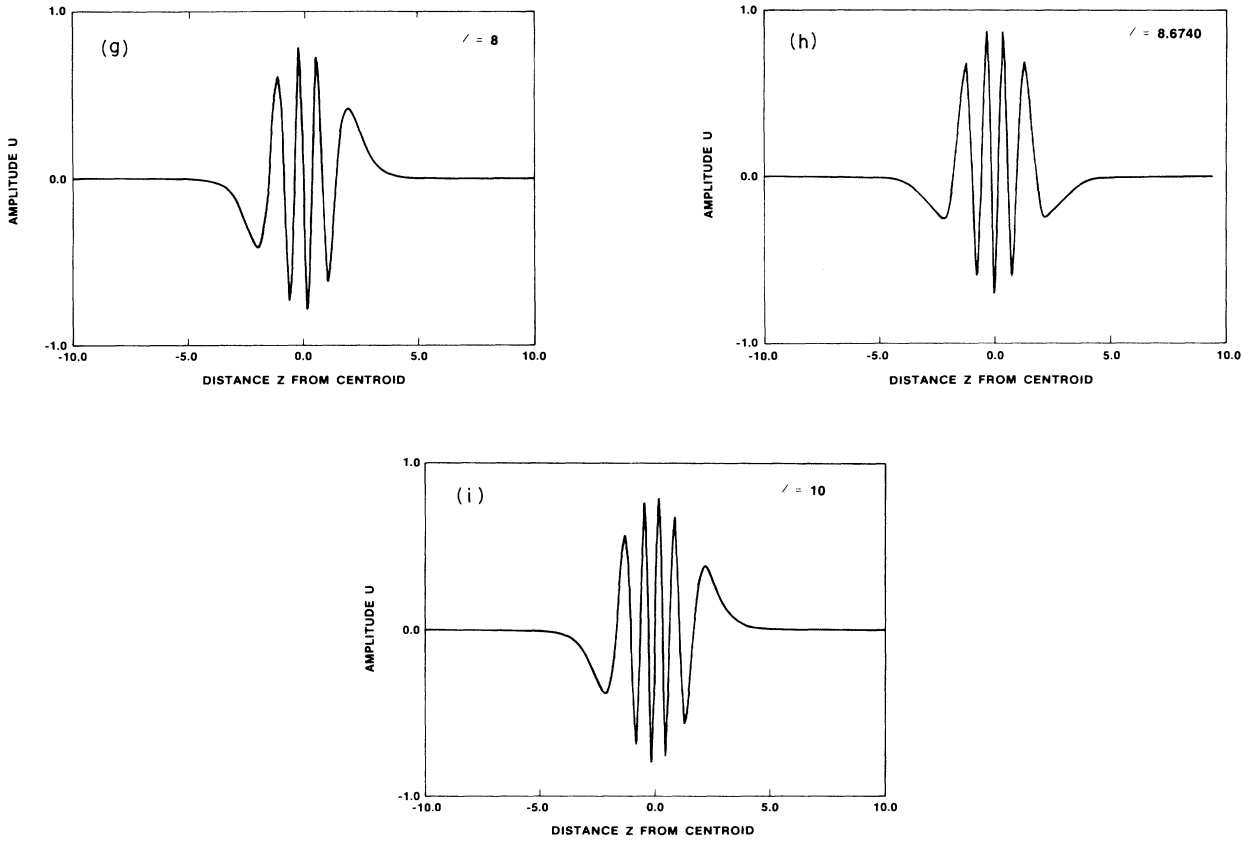

FIG. 3. (*Continued*).

VIII. CONCLUSION

In this paper we have studied the small oscillations of the one-dimensional large polaron within the Holstein molecular-crystal model. We have reviewed the minimal energy adiabatic solution for the Holstein large polaron and have shown that additional stationary adiabatic solutions are spurious—namely, that these solutions are not minimal but rather are saddle-point solutions, being unstable with respect to acousticlike small oscillations. We have solved analytically the classical equations of motion for the normal modes of the displacements about the minimal solution, both determining the eigenspectrum and constructing the eigenfunctions. Both eigenspectrum and eigenfunctions are essential for any systematic discussion of the transport and dynamics of such one-dimensional topological entities. A natural result of our small oscillation analysis is the appearance of the translational (zero frequency) Goldstone mode for the polaron. As this mode lacks a restoring force, it must be treated separately, and to all orders in its amplitude, in any consistent discussion of transport and dynamics.

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