Local Modes in Anharmonic Solids and the Kondo Problem

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The quantum theory of local modes in molecules is extended to few-dimensional solids such as polyacetylene. Local modes are found to be present below the phonon band *no matter how weak the anharmonicity*. The problem of the local mode interacting with a phonon background is reduced to a Bose variety of the Kondo problem. Based on this analogy, a theory is constructed of thermal dissociation of local modes and the generation of high local-mode quantum numbers through intense radiation.

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The vibrational excitations of most solids are well described by harmonic normal modes (NM). The effect of anharmonicity is usually included through a finite lifetime for the elementary excitations (phonons). What is less well known in solid-state physics is the fact that molecules such as H_2O and CH_2, containing weakly coupled anharmonic degrees of freedom, are poorly described by the NM scheme.[1] A classical example is the C-H stretch mode in benzene.[2] If this mode contains six vibrational quanta (the sixth overtone) then the lowest-energy state has all six quanta localized on the *same* C—H bond.[3] This type of excitation is called a local mode (LM). The Hamiltonian for the vibrational spectrum of such molecules is known[2,4] and can be easily diagonalized.[5] The spectrum contains, in general, LM's, NM's, and combination bands. Both the spectrum and the optical absorption strength agree very well with experiment. Interestingly, it is much more complex to solve the classical initial-value problem[6] than to find the eigenstates of the quantum Hamiltonian because of the appearance of quasiperiodic and chaotic orbits in the former case.

The remaining degrees of freedom of the molecule such as C-C vibrations can still be described as normal modes. These so-called skeleton modes[7] (SM) form a quasicontinuous background on which the LM's are superimposed.[8] Radiationless energy transfer from the LM into the SM continuum is the main contribution to the width of the LM absorption spectrum.

Recently, there has been much interest in the question of whether LM's can occur in solids and how they may be generated. In this Letter we will outline how the quantum theory of LM's in molecules is extended to chainlike compounds containing anharmonic optical modes,[9] e.g., the C-H mode in polyacetylene (Fig. 1). Our principal results are as follows: If we ignore the SM's then the LM Hamiltonian on a chain can be mapped onto the one-dimensional Bose gas with attractive interaction. The vibrational quanta play the role of the bosons. LM's are simply the bound states of this Hamiltonian and the NM's the scattering states. The LM and NM spectra can be determined through the Bethe *Ansatz* and, no matter how weak the anharmonicity, for a given number of quanta there is always a narrow band of LM's below the NM continuum. In the classical limit these bound states turn into solitons

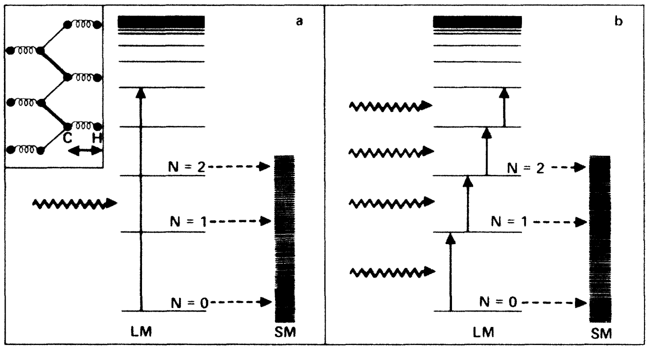

FIG. 1. Optical excitation of a chain of LM anharmonic oscillators (e.g., polyacetylene; see inset) coupled to a skeleton-mode (SM) continuum. (a) Direct excitation by single-photon absorption; (b) multiphoton absorption close to the fundamental.

of the nonlinear Schrödinger equation.[10] This result means that LM's must be present in few-dimensional solids.

To include the effect of the SM's on the LM's we must understand how a local state with self-interaction is affected by interaction with a continuum. The coupling of the SM background of the LM's can be represented as a Bose variety of the Anderson Hamiltonian[11] if we assume a smooth density of states for the background modes. Using the Hartree-Fock approximation, we find that as a function of temperature a first-order phase transition takes place to a state of high LM occupation numbers [Fig. 2(a)].

LM's can be optically excited in two ways. The first option is single-photon absorption from the ground state to the Nth overtone [Fig. 1(a)] and the second is multiphoton absorption with the drive frequency in resonance with the fundamental of the LM [Fig. 1(b)]. The LM hybridizes with the radiation field, as does any optically active mode, to form a polariton. The oscillator strength drops exponentially with N and the spectral width increases linearly with N so that only low overtones can be excited (in molecules $N < 8$). Multiphoton absorption is a "many-body" problem but through the analogy with the Anderson Hamiltonian we find that SM's can transfer vibrational energy to the LM and high overtones *can* be excited if the source is intense. However, the energy transfer from the SM's has again the character of a first-order phase transition and an "energy barrier" separates the regime of low LM occupation numbers from the high occupation numbers [Fig. 2(b)]. The nature of the barrier is obvious from Fig. 1(b): Because of the anharmonicity a drive frequency which could sustain a high overtone cannot excite low overtones.

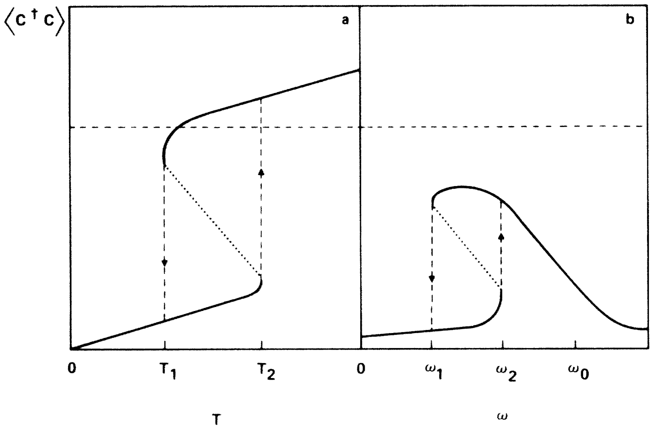

FIG. 2. Phase diagram of an anharmonic chain-like compound with local modes of fundamental ω_0 coupled to a continuum background: (a) as a function of temperature, and (b) as a function of the drive frequency ω. The dissociation threshold for the occupation number $\langle c^\dagger c\rangle$ is indicated by a dash-dotted line, and unstable solutions of the self-consistency equation by a dotted line.

We start by constructing the LM Hamiltonian for a chain of anharmonic oscillators. The spectrum of most observed anharmonic vibrational modes is well fitted by the Birge-Sponer relation[12]:

$$E(N) = \hbar\omega_0 N - \Delta E N^2 \quad (N = 1, 2, 3, \ldots), \tag{1}$$

with $\hbar\omega_0 \simeq 3000$ cm^{-1} for the C-H stretch mode and $\Delta E \simeq 50$ cm^{-1}. Note that when N is of order $\hbar\omega_0/2\Delta E$, $E(N)$ stops increasing with N. This corresponds to dissociation of the bond. The chain couples nearby oscillators (Fig. 1). In the molecular case kinetic coupling between adjacent oscillators is sufficient to explain the observed spectra.[4,13] Kinetic coupling between oscillators has the form $[G(1,2)/M]\sum_i P(i) \times P(i+1)$, where $P(i)$ is the momentum of the ith oscillator, M is the oscillator mass, and $G(1,2)$ is of order 0.1–0.01. We will use a Hilbert space spanned by the eigenfunctions of the individual anharmonic oscillators and a second-quantized form of the Hamiltonian where the Bose creation operator $c^\dagger(i)$ adds one quantum of vibration to the ith site. If we use a Morse potential for the C—H bond then the spectrum of Eq. (1) is exact. The largest matrix elements of P between two Morse eigenfunctions connect modes whose occupation numbers differ by 1. In second-quantized notation this means that we can approximate P as $i(M\hbar\omega_0/2)^{1/2}(c^\dagger - c)$, as for a harmonic oscillator. The LM Hamiltonian in second-quantized form is then

$$\begin{aligned}\mathcal{H} = \sum_i \{\hbar\omega_0 c^\dagger(i)c(i) - \Delta E c^\dagger(i)c(i)c^\dagger(i)c(i) + \tfrac{1}{2}G(1,2)\hbar\omega_0[c^\dagger(i)c(i+1) + \text{c.c.}] \\ - \tfrac{1}{2}G(1,2)\hbar\omega_0[c^\dagger(i)c^\dagger(i+1) + \text{c.c.}]\}. \end{aligned} \tag{2}$$

This would be a 1D Bose gas were it not for the last term in $\mathcal{H}$. Now, for $G(1,2) = 0$ the number of bosons N is conserved. The ground state in the N-particle sector is then an N-particle bound state with all N quanta on the same site. This state would be highly degenerate because of the different choices of that site. Excited states in that sector are separated by ΔE from the ground state (they are the combination bands). Different sectors are separated from each other by $\hbar\omega_0$ which always is far larger than ΔE. For $G(1,2)$ finite the degeneracy is broken and N is no longer conserved. However, if we include mixing between states of different N perturbatively, then to lowest order in $G(1,2)$ the effect is of order $G(1,2)^2$ which is very small. Allowing the perturbation to mix only degenerate states or states separated by ΔE means that we can neglect the last term in H which reduces the problem to finding the spectrum of the 1D Bose gas with attractive on-site interaction. The $N=1$ eigenstates (or $|1\rangle$ states) of this Hamiltonian are NM plane waves with dispersions $E^1(k)$:

$$E^1(k)=\hbar\omega_0-\Delta E+G(1,2)\hbar\omega_0\cos k. \tag{3}$$

The $N=2$ eigenstates are two NM plane waves ($|1,1\rangle$) and one two-particle bound state ($|2\rangle$) with a binding energy E_b^2 below the $|1,1\rangle$ continuum:

$$E_b^2=2|G(1,2)\hbar\omega_0|-2\{[G(1,2)\hbar\omega_0]^2+\Delta E^2\}^{1/2}, \tag{4}$$

and another bound state above the continuum.

For general N and strong anharmonicity, the single-oscillator spectrum, Eq. (1), remains essentially valid. For general N and weak anharmonicity the Hamiltonian can be diagonalized by the Bethe *Ansatz*,[14] and the binding energy of the N-boson bound state $|N\rangle$ below the N-particle NM band edge is

$$E_b^N=-\tfrac{1}{4}[\Delta E^2/G(1,2)\hbar\omega_0]N^2(N-1). \tag{5}$$

An N-particle bound state has an effective mass proportional to N, and so the LM dispersion is reduced by $1/N$ compared with the NM dispersion. For large N the boson probability density of an N-particle bound state centered at the origin is[15]

$$\rho_N(x)=\frac{N^2[6\Delta E^2/G(1,2)\hbar\omega_0]^{1/2}}{4\cos h^2\{\frac{1}{2}N[6\Delta E^2/G(1,2)\hbar\omega_0]x\}}, \tag{6}$$

and so the LM width is proportional to $1/N$. This is also the one-soliton solution of the nonlinear Schrödinger equation[10] which is indeed the classical continuum limit of our 1D Bose system.[16] Thus for any N the LM is the lowest-energy excitation and for large N the LM reduces to a classical soliton. A LM in a solid thus behaves like a particle slowly tunneling from site to site. The coupling to SM's will have two important effects: It suppresses tunneling[17] and leads to LM decay. For large N, the LM effective mass is large and, to first order, we can neglect tunneling, restricting ourselves to a LM on just a single site [see Eq. (6)]. This approximation means that we cannot discuss LM transport properties. The coupling of the LM to the SM's is then taken over from the case of molecules[18]:

$$\mathcal{H}\simeq\textstyle\sum_k\epsilon(k)a_k^\dagger a_k+\hbar\omega_0c^\dagger c-\Delta Ec^\dagger cc^\dagger c+[c^\dagger\sum_k V(k)a_k+\text{c.c.}], \tag{7}$$

where k is the wave vector of a SM with dispersion $\epsilon(k)$ and creation operator $a^\dagger(k)$. $V(k)$ is the coupling strength. Since the background consists of contributions of many different degrees of freedom, $V(k)$ is assumed to be a random function. This Hamiltonian is a Bose variety of the Anderson Hamiltonian which is used to treat magnetic impurities in metals, the Kondo problem, with the occupation number of the LM corresponding to the impurity moment. As is true for the Kondo problem, we may gain qualitative insight using the Hartree-Fock (HF) approximation. In the HF approximation we assume that the ground-state wave function is the product of single-particle states $|n\rangle$, each of which is a hybridized combination of a SM and the LM. The single-particle states $|n\rangle$ diagonalize the HF Hamiltonian:

$$\mathcal{H}_{\text{HF}}=\textstyle\sum_k\epsilon(k)a_k^\dagger a_k+\hbar\omega_0c^\dagger c-2\Delta E\langle c^\dagger c\rangle c^\dagger c+[c^\dagger\sum_k V(k)a_k+\text{c.c.}], \tag{8}$$

where $\langle c^\dagger c\rangle$ is the expectation value of the number of quanta in the LM $|c\rangle$. The most important quantity is the probability per unit energy $\rho_c(\epsilon)=\sum_n\delta(\epsilon-\epsilon_n)\times|\langle c|n\rangle|^2$ for a vibrational quantum of energy ϵ to find itself in the LM (the LM density of states). This LM density of states is the imaginary part of the projection of the Green's function on the LM. The Green's function of a quadratic H-F Hamiltonian is easily found and the result for $\rho_c(\epsilon)$ is a Lorentzian,

$$\rho_c(\epsilon)=\frac{1}{\pi}\frac{\Delta}{(\epsilon-\hbar\omega_0+2\Delta E\langle c^\dagger c\rangle)^2+\Delta^2}, \tag{9}$$

centered close to the fundamental. The width Δ of the Lorentzian is $\pi\langle V^2\rangle\rho$, where ρ is the SM density of states. The time τ spent by a vibrational quantum in the LM is $\hbar/\Delta$. The width of the LM density of states is also the spectral width for optical absorption at the fundamental frequency as follows from the optical theorem. Typically, $\Delta\simeq 20\ \text{cm}^{-1}$ for the C-H stretch.

We still must determine the occupation number $\langle c^\dagger c\rangle$. The self-consistency requirement is

$$\langle c^\dagger c\rangle=\frac{1}{\pi}\int\frac{d\epsilon\,\Delta\,n(\epsilon)}{(\epsilon-\hbar\omega_0+2\Delta E\langle c^\dagger c\rangle)^2+\Delta^2}, \tag{10}$$

where $n(\epsilon)$ is the mean occupation number of the hybridized single-particle levels. If we use the Bose occupation-number distribution then the self-consistency equation reduces to

$$\langle c^\dagger c\rangle\simeq\frac{k_{\text{B}}T}{\pi}\Delta\frac{\Lambda}{[\hbar\omega_0-2\Delta E\langle c^\dagger c\rangle]^2+\Delta}, \tag{11}$$

with $\Lambda\cong\ln(k_{\text{B}}T/\epsilon_{\min})$ for $k_{\text{B}}T<<\hbar\omega_0$ and $\Lambda\cong\ln(\hbar\omega_0/\epsilon_{\min})$ for $\hbar\omega_0>>k_{\text{B}}T$, where $\epsilon_{\min}$ is a low-frequency cutoff for the SM's. The resulting phase diagram can be constructed graphically. For low temperatures there is only a single solution to Eq. (11), with $\langle c^\dagger c\rangle \simeq (k_B T/\pi)\Delta\Lambda/(\hbar\omega_0)^2$, quite small. For $T > T_1$, with $k_B T_1 = (\pi\Delta/\Lambda)(\hbar\omega_0/2\Delta E)$, three solutions appear, two of them stable. The new stable solution has a high occupation number: $\langle c^\dagger c\rangle \simeq \hbar\omega_0/2\Delta E$, just below the threshold for dissociation of the LM. However, the intervening unstable solution is an energy maximum creating an energy barrier between the two solutions. Only at much higher temperatures, $T > T_2$, where $k_B T_2 = \frac{4}{27}(\pi/\Delta\Lambda)(\hbar\omega_0)^3/2\Delta E$, does the small $-\langle c^\dagger c\rangle$ solution disappear. This thermally induced dissociation is a collective energy transfer from the SM background to the LM's and is similar to a first-order phase transition [Fig. 2(a)].

If the LM induces a polarization oscillation, then it can be excited by a radiation field. The frequency-dependent dielectric constant can be computed in linear response. However, the oscillator strength for exciting an N-quantum LM drops exponentially fast with N. In the strong-anharmonicity limit[19] $\ln f(N) \simeq -(a+bN)$ with $a \simeq 4.28$ and $b \simeq 1.22$ for the C-H stretch mode. For weak anharmonicity our Bethe *Ansatz* gives a similar exponential dependence on N. In addition, the LM lifetime also drops with N, $\tau(N) \simeq \tau/N$, and so high overtones cannot be excited in this way. High overtones could be excited by intense radiation in resonance with the fundamental (multiphoton absorption). Linear response is not appropriate, but we can use the HF self-consistenty condition. The Bose distribution must then be replaced with the appropriate steady-state nonequilibrium distribution. We will discuss two limiting cases for $n(\epsilon)$. If the optically excited phonons thermalize rapidly, then we may still use the Bose distribution but now with an *effective* temperature T^*. We then simply find our previous results but replace T by T^*. If the excited phonons do not thermalize at all, then the occupation probability peaks at $\epsilon = \hbar f\omega$, where ω is the frequency of the radiation. The self-consistency equation is then

$$\langle c^\dagger c\rangle \cong \frac{1}{\pi}\frac{\Delta\langle n\rangle\Gamma}{[\hbar(\omega-\omega_0)+2\Delta E\langle c^\dagger c\rangle]^2+\Delta^2}, \qquad (12)$$

with $\langle n\rangle$ the average occupation number of the hybridized LM-SM's of frequency ω, and Γ the width of the steady-state distribution, presumed small compared to Δ. Far from resonance $\langle c^\dagger c\rangle$ is small, of order $\pi^{-1}\Delta\langle n\rangle\Gamma/[\hbar(\omega-\omega_0)]^2$. If we *increase* ω from zero, we first reach a threshold $\omega_1 = \omega_0 - 2\Delta E\langle n\rangle\Gamma/\hbar\pi\Delta$, where a second solution appears with a large value of $\langle c^\dagger c\rangle$, of order $\pi^{-1}\langle n\rangle\Gamma/\Delta$, which may or may not be below the dissociation threshold. The second solution is again separated by a barrier from the first. For larger ω, the first solution vanishes above $\omega_2 = \omega_0 - \hbar^{-1}[(27/2\pi)\langle n\rangle\Gamma\Delta E\Delta]^{1/3}$, while $\langle c^\dagger c\rangle$ drops rapidly for the remaining solution. If on the other hand we *reduce* ω from $\omega \gg \omega_0$, we start on the second solution, and high values of $\langle c^\dagger c\rangle$ can be reached without having to overcome the barrier [Fig. 2(b)]. This appears as a promising possibility to excite high overtones.

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[1] B. R. Henry and W. Siebrand, J. Chem. Phys. **49**, 5369 (1968). For reviews on LM's in molecules, see B. R. Henry, Acc. Chem. Res. **10**, 207 (1977); M. L. Sage and J. Jortner, Adv. Chem. Phys. **47**, 293 (1981).

[2] M. S. Burberry and A. C. Albrecht, J. Chem. Phys. **71**, 4631 (1979), and references therein.

[3] R. L. Swofford, M. S. Burberry, J. A. Morrell, and A. C. Albrecht, J. Chem. Phys. **66**, 5245 (1977).

[4] R. Wallace, Chem. Phys. **11**, 189 (1975).

[5] H. S. Møller and O. Sonnich Mortensen, Chem. Phys. Lett. **66**, 539 (1979).

[6] C. Jaffé and P. Brumer, J. Chem. Phys. **73**, 5646 (1980); E. L. Sibert, W. P. Reinhardt, and J. T. Hynes, J. Chem. Phys. **77**, 3583 (1982).

[7] D. F. Heller and S. Mukamel, J. Chem. Phys. **70**, 463 (1979); M. L. Sage and J. Jortner, Chem. Phys. Lett. **62**, 451 (1979).

[8] R. G. Bray and M. J. Berry, J. Chem. Phys. **71**, 4909 (1979).

[9] Chains of *classical* anharmonic oscillators also show focusing of energy in local modes: E. Fermi, J. R. Pasta, and S. M. Ulam, Los Alamos Scientific Laboratory Report No. LA-1940 (unpublished). The classical limit is, however, again complicated by chaotic solutions.

[10] V. E. Zakharov and A. B. Shabat, Zh. Eksp. Teor. Fiz. **61**, 118 (1971) [Sov. Phys. JETP **34**, 62 (1972)].

[11] P. W. Anderson, Phys. Rev. Lett. **41**, 124 (1971). Note that this is not simply the Fano problem.

[12] R. T. Birge and H. S. Sponer, Phys. Rev. **20**, 259 (1926),

[13] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

[14] J. B. McGuire, J. Math. Phys. **5**, 622 (1964); C. N. Yang, Phys. Rev. **168**, 1920 (1968).

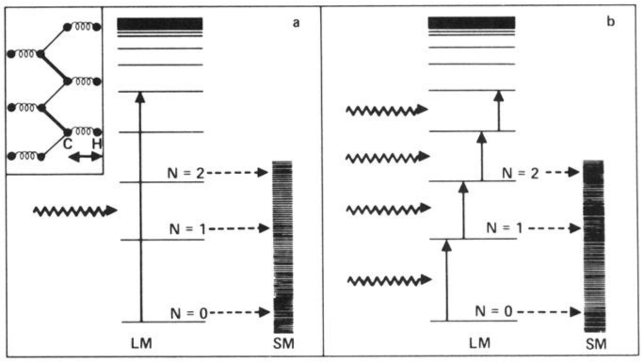
[15] B. Yoon and J. W. Negele, Phys. Rev. A **16**, 1451 (1977).

[16] A. Klein and F. Krejs, Phys. Rev. A **18**, 1343 (1978).

[17] See, for instance, J. P. Sethna, Phys. Rev. B **25**, 5050 (1982), or A. O. Caldeira and A. J. Leggett, Phys. Rev. Lett. **46**, 211 (1982).

[18] Sage and Jortner, in Ref. 1.

[19] M. S. Burberry and A. C. Albrecht, J. Chem. Phys. **70**, 147 (1979).



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