Localized vibrational modes in Fermi liquids. General theory

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There exist an abundance of physically realized situations in atomic, chemical, molecular, nuclear, and solid-state physics which are modeled as a discrete state interacting with a continuum. One of these situations, a localized oscillator coupled to be the particle-hole excitation continuum of a Fermi liquid, forms the area of inquiry here. Special emphasis is placed on the electron-hole pair excitations of a metal, although the results are more general. In particular, an exactly soluble model, in which a localized harmonic oscillator is coupled to the pair-density fluctuations of a random-phase-approximation Fermi liquid by an interaction linear in both oscillator displacements and density operators, is considered. It is shown that this model is equivalent to a system of coupled harmonic oscillators, and, as such, the eigenstates are obtained via a straightforward normal-mode analysis. Expressions for the local spectral function of the oscillator are obtained in terms of level-shift and broadening functions which are evaluated in closed form in the density-of-states limit. Parametric calculations for vibrational line shapes are made, and the results are discussed in terms of "exponential-decay theory." The general results presented here have direct bearing in areas such as surface vibrational spectroscopy of adsorbed molecules, metal-hydride spectroscopy, and surface chemical-reactivity theory.

I. INTRODUCTION

When viewed from a field-theoretic point of view, the basic structure and mathematical content of theory on a broad spectrum of superficially unrelated physical phenomena in condensed matter, chemical, and nuclear physics are often times quite similar. Consequently, mastery of the basic theoretical ideas should enable one to more easily access relevant points for ones own specialized work from research in other areas. However, a danger presents itself since field-theoretic formulations of problems frequently tend to obscure the inherent physical simplicity of the model being worked upon.

For reasons to be detailed later, the focus of inquiry here is on the dynamically coupled system consisting of a localized vibrating massive particle (atom or molecule) and the electronic excitations of an infinitely (or semi-infinitely) extended Fermi liquid, within (or upon) which the particle is embedded (or adsorbed). For present purposes, the Fermi liquid will always be a metal, adequately thought of as a free-electron gas, in which case the valence-electron excited states consist of a discrete collective plasmon (or surface plasmon) with eigenenergy typically in the 5–15-eV range and a continuum of lower-energy electron-hole pair excitations within the range $0 < \omega(k) < k v_F$, where k is the pair wave vector and v_F the Fermi velocity.[1] Such a division is meaningful provided the wave number of the excitations is less than some k_c, roughly of order of the average inverse interelectron separation within the electron gas. Since the effects studied here do not depend upon the interparticle Coulomb interactions, the final results apply as well to neutral Fermi systems.

More specifically, the localized particle is imagined to undergo harmonic oscillations characterized by a "bare" frequency or energy $\epsilon_0 = \hbar \omega_0 \lesssim 0.25$ eV.[2] Owing to the significant mismatch between the vibrational and plasmon energies, coupling of the particle motion to the electron-hole pair excitations is expected to provide the dominant dynamic effect. Regarding the oscillator as a quantized boson field, the problem is then one of a spin-$\frac{1}{2}$ fermion field coupled to a boson field by some prescribed, physically meaningful interaction. Depending upon the details of the interaction which can often be taken as a linear function of some field variable for each field, this problem then shows up in many different contexts such as electron-phonon related phenomena in the solid state (Refs. 1, 3, and 4), ^{3}He-^{4}He mixtures,[5] radiationless transitions in chemical physics,[6] and meson-mediated interactions in nuclear matter.[7]

For the electron gas treated within the random-phase approximation (RPA), the linearly coupled field problem possesses a particularly simple mathematical structure which is exactly soluble (equivalent to a normal-mode analysis) and which provides clear insights into the physical significance and origins of the interaction-induced features of the coupled fields.[7] This can be seen upon consideration of the physical content of the RPA which is basically a semiclassical theory in the sense that those elementary excitations of the electron gas retained in the theory correspond to density fluctuations, either single particle-hole pairs or coherent superpositions of pairs to form

the collective plasmon mode.[1,8] The individual particle nature of an electron or hole does not appear in the theory and any interactions are between density fluctuations rather than particles. Consequently those interaction terms in the interacting electron-gas Hamiltonian which involve four fermion operations

$$H_{int} = \sum_{1,2,3,4} V_{1234} a_1^\dagger a_2^\dagger a_3 a_4$$

are replaced by a bilinear coupling between density fluctuations

$$H_{int}^{eff} \simeq \sum_{1,2} \Lambda_{12} \rho_1^\dagger \rho_2 .$$

In this form $i\dot\rho_i = [\rho_i, H]$, the equation of motion for the density fluctuations is linear in ρ, and thus the eigenvalues are obtained by a normal-mode analysis[8,9] where it is found that the excited eigenstates correspond to harmonic density oscillations about the mean electron density. This correspondence has prompted explicit modeling of the RPA electron gas in terms of quantized Tomonaga oscillators[8-11] satisfying the usual boson conditions, and has led to the view of the excited solid as a weakly interacting gas of boson excitations, hence the descriptive name bosonized electron gas.[12-14] What this means for us is that the problem of a localized oscillator linearly coupled to the excited states of the electron gas is equivalent to a problem of coupled harmonic oscillators and thus is also exactly soluble.

One specific feature of the present problem deserves some additional comment. As mentioned earlier, the low-frequency localized oscillator is expected to be dynamically coupled most strongly to the continuum of extended electron-hole pair excitations of the solid, and as such bears a formal similarity to other phenomena involving discrete state mixing with degenerate continua such as the Anderson model for magnetic impurities,[15] the Fano configuration-interaction approach to autoionization,[16] the Bixon-Jortner model for intramolecular radiationless transitions,[17] substitutional mass-defect vibrational modes,[18,19] polaron effects in mixed-valence materials,[20] incomplete relaxation in photoelectron-Auger–x-ray emission spectroscopy,[21] and chemisorption theory.[22] As emphasized in the review article by Elliot, Krumhansl, and Leith, "... model Hamiltonians ... show that to a good approximation electron, phonon, magnon, and exciton problems reduce to the same formulation. ... we have noticed considerable duplication in the timing and content of ideas put forth by specialists in these particular topics, and hope by our presentation to supply the reader with a basis for comparing

the literature of random systems no matter what the context."[19] It is in this spirit that this paper is presented.

The structure of this paper is the following. In Sec. II, the model Hamiltonian for the system of localized oscillator and a free-electron gas coupled via an interaction linear in both oscillator displacement and electron-gas density fluctuations is established. In a manner similar to that used by Dover,[7] the exact equations of motion for the field variables are constructed in Sec. III along with their RPA reduction. Within this model, the formal equivalence to a system of coupled harmonic oscillators is stressed.[3,7,23] The eigenvalues, normal modes, and local spectral properties are obtained in Sec. IV. Both quasilocalized resonances as well as truly localized modes are discussed. Section V is devoted to a further reduction of the spectral functions with a "constant matrix element" or electron-hole pair density-of-states limit. Parametric calculations are presented in Sec. VI. General discussion is offered in Sec. VII.

Specific detailed applications are reserved in order to minimize obscuring the general features of the model with the parochial interests of the writer. Nonetheless we note that[24] the model is applied to problems associated with infrared[25] and electron-energy-loss[26] vibrational line shapes for adsorbates carrying a net electronic charge as well as for dipole line shapes, hydrogen vibrational line shapes in metal hydrides,[27] and surface-enhanced chemical reactivity theory.[23,28]

II. MODEL

We consider a theory in which the coupled system of electron gas and localized oscillator is described by the Hamiltonian

$$H = \sum_{\vec{k},\sigma} \epsilon_{\vec{k}} a_{\vec{k}}^\dagger a_{\vec{k}} + \hbar\omega_0 B^\dagger B + H_{int} , \qquad (1)$$

where the symbols have the usual meaning[1,3]; a's and B's are Fermi (electron) and Boson (oscillator) operators satisfying anticommutation and commutation relations, respectively, $\epsilon_{\vec{k}} = \hbar^2 k^2 / 2m$ is the free-electron eigenvalue, ω_0 is the localized oscillator frequency, and the coupling term H_{int} is to be discussed. Since spin effects do not appear explicitly in our considerations, their indices will be suppressed henceforth.

Closer ties with physical models are possible if the Hamiltonian is expressed in the representation of electron-density fluctuations and oscillator displacements. In terms of the electron operators, pair creation operators are

$$\rho_{\vec{k}\vec{q}}^{\dagger} = a_{\vec{k}+\vec{q}}^{\dagger} a_{\vec{k}} \tag{2}$$

and density-fluctuation operators

$$\rho_q^{\dagger} = \sum_{\vec{k}} a_{\vec{k}+\vec{q}}^{\dagger} a_{\vec{k}} = \sum_{\vec{k}} \rho_{\vec{k}\vec{q}}^{\dagger} \tag{3}$$

from which it can be seen that a density fluctuation of wave vector $\vec{q}$ is a coherent superposition of electron-hole pairs. In the case of the localized oscillator, the canonically conjugate momenta and displacement are given by[3,1]

$$P = i \left(\frac{\hbar M \omega_0}{2} \right)^{1/2} (B^{\dagger} - B) \tag{4a}$$

and

$$Q = \left(\frac{\hbar}{2M\omega_0} \right)^{1/2} (B^{\dagger} + B) \tag{4b}$$

with M the "mass" of the oscillating particle. The simplest physically significant coupling between fields varies linearly in both oscillator displacements and density fluctuations and has the virtue of presenting an exactly soluble model within RPA.[7] This is expressed as

$$H_{int} = \sum_{\vec{q}} \lambda_{\vec{q}} Q \rho_{\vec{q}}^{\dagger}, \tag{5}$$

where $\lambda_{\vec{q}}$ is the "coupling constant" depending upon the specifics of the system in question. This will be discussed at an appropriate time. Within the (Q, ρ) representation, Eqs. (1)–(5) give the model Hamiltonian:

$$H = \sum_{\vec{k}} \epsilon_{\vec{k}} \rho_{\vec{k}0}^{\dagger} + \frac{1}{2} \left(\frac{P^2}{M} + M\omega_0^2 Q^2 \right) + \sum_{\vec{q}} \lambda_{\vec{q}} Q \rho_{\vec{q}}^{\dagger}. \tag{6}$$

With $\rho_{\vec{k}0}^{\dagger} = a_{\vec{k}}^{\dagger} a_{\vec{k}}$ or equivalently, in the (a, B) representation:

$$H = \sum_{\vec{k}} \epsilon_{\vec{k}} a_{\vec{k}}^{\dagger} a_{\vec{k}} + \hbar\omega_0 B^{\dagger} B$$

$$+ \sum_{\vec{k}, \vec{q}} \lambda_{\vec{q}} \left(\frac{\hbar}{2M\omega_0} \right)^{1/2} (B^{\dagger} + B) a_{\vec{k}+\vec{q}}^{\dagger} a_{\vec{k}}. \tag{7}$$

Equations (6) or (7) characterize the model with which we will work.

III. EQUATIONS OF MOTION

Having established the relevant Hamiltonian we now can proceed to the equations of motion governing the system dynamics. The Heisenberg equation for the time-dependent pair operator is, with Eq. (6),

$$i\hbar\dot{\rho}_{\vec{k}\vec{q}}^{\dagger} = [\rho_{\vec{k}\vec{q}}^{\dagger}, H] = \sum_{\vec{k}'} \epsilon_{\vec{k}'} [\rho_{\vec{k}\vec{q}}^{\dagger}, \rho_{\vec{k}'0}^{\dagger}] + \sum_{\vec{k}'} \lambda_{\vec{k}'} Q [\rho_{\vec{k}\vec{q}}^{\dagger}, \rho_{\vec{k}'}^{\dagger}]. \tag{8}$$

Expressing the pair- and density-fluctuation operators in terms of Fermi operators as in Eqs. (2) and (3) and evaluating the commutators using the anticommutation relations

$$\{a_{\vec{k}}, a_{\vec{k}'}^{\dagger}\} = \delta_{\vec{k}, \vec{k}'}, \quad \{a_{\vec{k}}^{\dagger}, a_{\vec{k}'}^{\dagger}\} = \{a_{\vec{k}}, a_{\vec{k}'}\} = 0,$$

Eq. (8) can be cast into the form

$$i\dot{\rho}_{\vec{k}\vec{q}}^{\dagger} = -\omega_{\vec{k}\vec{q}}^{0} \rho_{\vec{k}\vec{q}}^{\dagger} - \sum_{\vec{k}'} \frac{\lambda_{\vec{k}'} Q}{\hbar} (\rho_{\vec{k}, \vec{k}'+\vec{q}}^{\dagger} - \rho_{\vec{k}-\vec{k}', \vec{k}'+\vec{q}}^{\dagger}), \tag{9}$$

where $\hbar\omega_{\vec{k}\vec{q}}^{0} = \epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}$ is the unperturbed electron-hole pair energy . Since $Q = Q(t)$ in Eq. (9), an oscillator equation is also required. The Hamilton equations $\dot{Q} = \partial H/\partial P$ and $\dot{P} = -\partial H/\partial Q$, with H given by Eq. (6), provide

$$\ddot{Q} + \omega_0^2 Q = -\frac{1}{M} \sum_{\vec{k}'} \lambda_{\vec{k}'} \rho_{\vec{k}'}^{\dagger} = -\frac{1}{M} \sum_{\vec{k}, \vec{k}'} \lambda_{\vec{k}'} \rho_{\vec{k}, \vec{k}'}^{\dagger}, \tag{10}$$

which shows how the oscillator displacement depends upon the pair dynamics through $\rho_{\vec{k}, \vec{k}'}^{\dagger} = \rho_{\vec{k}, \vec{k}'}^{\dagger}(t)$. At this stage, Eqs. (9) and (10) are exact for the linear coupling of Eq. (5). A general solution of these coupled equations is difficult. However, a very useful approximate solution can be obtained by suitably restricting the type of density fluctuations which one considers. The RPA represents one exactly soluble model resulting from an appropriate set of restrictions.

There exist a variety of representations and derivations for the properties of the RPA electron gas, all of which must have identical physical content in spite of their apparent mathematical dissimilarities.[1,3,7-9] Here we choose that picture which emphasizes the analogies between the properties of the density fluctuations and those of a harmonically oscillating system, thus facilitating contact between the bosonized electron gas and simple mechanical harmonic oscillators.[7-14]

Within the present context, the RPA is introduced in the following way: From Eqs. (2) and (3) it is noted that $\vec{k}$ and $\vec{q}$ can take on any values. The RPA places a restriction on the allowed values by retaining only those terms in the unrestricted $\vec{k}$ sum of Eq. (3) which correspond to creation of a hole within (outside) and of an electron outside (within) the Fermi sphere. The scattering of an electron or hole from one state to another, both states being outside (within), are not considered. Thus the RPA version of the density-fluctuation operator, Eq. (3), is written as

$$\rho_{\vec{q}}^{\dagger} \approx \sum_{\substack{|\vec{k}| < P_F \\ |\vec{k}+\vec{q}| > P_F}} a_{\vec{k}+\vec{q}}^{\dagger} a_{\vec{k}} + \sum_{\substack{|\vec{k}| > P_F \\ |\vec{k}+\vec{q}| < P_F}} a_{\vec{k}+\vec{q}}^{\dagger} a_{\vec{k}}. \tag{11}$$

The second ingredient of the RPA is the assumption that the pair states [Eq. (2)] can be regarded as

distinct entities obeying boson commutation relations

$$[\rho_{\vec{k}\vec{q}}, \rho_{\vec{k}'\vec{q}'}^{\dagger}] = \delta_{\vec{k}', \vec{k}'}\, \delta_{\vec{q}', \vec{q}'} ,$$

$$[\rho_{\vec{k}\vec{q}}, \rho_{\vec{k}'\vec{q}'}] = [\rho_{\vec{k}\vec{q}}^{\dagger}, \rho_{\vec{k}'\vec{q}'}^{\dagger}] = 0. \tag{12}$$

Physically this implies that an electron-hole pair propagates as a unit and does not exchange electrons or holes with other pairs. Although the Pauli principle is mildly violated by this assumption, this will not lead to any significant consequences as long as the number of pair excitations is small relative to the number of states within the Fermi sphere. This is always so whenever the interaction energy responsible for the pair excitations is small relative to the Fermi energy. Note that it is this step of bosonizing the pairs, and thus density fluctuations, which permits replacement of interaction terms containing four Fermion operators by effective perturbations with two boson operators, thus reducing the problem to that of a normal-mode analysis.[7-9]

With regards to the linear coupling, incorporation of Eqs. (11) and (12) in Eq. (5) yields the RPA interaction between the localized oscillator and the host electron-hole pairs:

$$H_{\rm int}^{\rm RPA} \simeq \sum_{\substack{|\vec{k}|<P_F \\ |\vec{k}+\vec{q}|>P_F}} \lambda_{\vec{q}}\, Q(\rho_{\vec{k}\vec{q}}^{\dagger} + \rho_{-\vec{k}-\vec{q}}) . \tag{13}$$

Bookkeeping is made easier by introducing the operator

$$A_{\vec{k}\vec{q}}^{\dagger} = \rho_{\vec{k}\vec{q}}^{\dagger} + \rho_{-\vec{k}-\vec{q}} \tag{14}$$

and rescaling the oscillator displacement through $Q \equiv \bar{x}_0 \phi$ and $\lambda_{\vec{q}} \equiv \hbar \bar{\lambda}_{\vec{q}}/\bar{x}_0$ where $\bar{x}_0 \equiv (\hbar/M\omega)^{1/2}$. Equations (9) and (10), with the RPA interaction of Eq. (13), are then easily manipulated into the form

$$\ddot{A}_{\vec{k}\vec{q}}^{\dagger} + \omega_{\vec{k}\vec{q}}^{0,2} A_{\vec{k}\vec{q}}^{\dagger} = -2\bar{\lambda}_{\vec{q}} \omega_{\vec{k}\vec{q}}^{0}\, \varphi \tag{15a}$$

and

$$\ddot{\varphi} + \omega_0^2 \varphi = -\omega_0 \sum_{\substack{|\vec{k}|<P_F \\ |\vec{k}+\vec{q}|>P_F}} \bar{\lambda}_{\vec{q}}\, A_{\vec{k}\vec{q}}^{\dagger} \tag{15b}$$

which are just a set of coupled harmonic oscillator equations. In obtaining Eq. (15), we have used the fact that $\ddot{A}_{\vec{k}\vec{q}}^{\dagger} = \ddot{\rho}_{\vec{k}\vec{q}}^{\dagger} + \ddot{\rho}_{-\vec{k}-\vec{q}}$ together with the Heisenberg equation $i\hbar\dot{\rho} = [\rho, H]$ and $\dot{\rho}$ given by Eqs. (9) and (13). The physical picture represented by Eq. (15a) is one in which the initially uncoupled pair oscillators are driven by a force that is proportional to the displacement of a localized discrete oscillator. However, from Eq. (15b), the displacement of the localized oscillator depends upon the force due to all the electron-hole pairs and it is through the mediation by the

localized oscillator that the original independent electron-hole pairs couple. Nonetheless, the linear interaction permits diagonalization of the set of Eqs. (15a) and (15b), in terms of delocalized normal modes composed of an admixture of electron-hole pairs and localized oscillations, with the degree of relative admixture varying with energy of the normal modes in a way yet to be determined. Visually we can imagine a localized oscillator dressed by a cloud of virtual pairs to form a distinct eigenstate, very similar to a polaron, but with pairs rather than phonons as the virtual bosons. The eigenvalues and local spectral characteristics must now be determined.

IV. SOLUTION

Analysis of the eigenstates of a system consisting of a localized discrete state interacting with a continuum has been carried out within several different contexts.[15-22] A common feature of all problems of this type is that two forms of eigenstates obtain. The discrete state is displaced down in energy (red shift) by interaction with higher-lying unperturbed continuum states and up (blue shift) by the lower-lying continuum states. Depending upon the net effect, new eigenstates may be pushed above or below the continuum if either the continuum or the coupling constant $\bar{\lambda}_{\vec{q}}$ is bounded. Under these circumstances truly localized states (of the Koster-Slater type[29]) for the coupled system are possible. More germane for present purposes are the cases in which the discrete state remains degenerate with the perturbed continuum, in which case resonance "states" are formed. The discrete state appears to be shifted and broadened into a narrow band due to the coupling with the continuum.

The acquisition of a "width" is frequently (and somewhat misleadingly) interpreted as a manifestation of an energy decay process between approximate system eigenstates. For a true decay process, energy must be transferred from the system undergoing the transition to another body, heat sink, or some other field. In the case of resonance states, the eigenstates are delocalized over the entire normalization volume of the system with some states having greater amplitude than others in the vicinity of the localized perturbation. The local density of states or spectral function is a measure of the relative amplitudes of system states at the localized center. In its most simple form, this function will be a bell-shaped curve such as a Lorentzian (for unbounded continua and uniform coupling constants[30]), peaked near the unperturbed discrete-state energy. However, the width is not a measure of a decay time

between "eigenstates"; rather it is a measure of the distribution of eigenstates required to form a localized wave packet on the scattering center. One can view a localized resonance as consisting of an initially coherent superposition of a little bit of many states. From this point of view, the width then relates to the timescale over which this spatial coherence is lost. For the *pure harmonic system* which we have considered, an initial localized disturbance will at first spread throughout the system. However, if the system is finite in extent (as all real systems are), eventually the initial state will be restored, at which time the cycle repeats itself. In practice, this recurrence time is usually so much larger than all other relevant time scales that any possible manifestations of the recurrence are neglected in approximate theoretical treatments. The omitting of recurrences together with the inclusion of anharmonic effects, present in nature but not in our model, are required if truly irreversible decay is to be handled within the model. In other words, discrete-state coupling with a continuum by itself does not necessarily imply the irreversible behavior commonly associated with energy decay.[31,32] In order to clearly differentiate between truly irreversible energy decay and cyclic energy migration throughout a complicated but nonetheless harmonic system, we have chosen to present the theory of the discrete oscillator coupled to host electron-hole pair excitations in terms of exactly soluble normal modes.

The solution will now be obtained in the spirit of Mahan's discussion[33] of Fano theory.[16] The pair operators and oscillator displacements are written as normal-mode expansions

$$A^\dagger_{\vec{k}\vec{q}}(t) = \sum_l a_{\vec{k}\vec{q},l} e^{i\omega_l t} \tag{16a}$$

and

$$\varphi(t) = \sum_l b_l e^{i\omega_l t} . \tag{16b}$$

Insertion of Eqs. (16) in (15) generates a set of l coupled algebraic equations for the coefficients $a_{\vec{k}\vec{q},l}$ and b_l:

$$a_{\vec{k}\vec{q},l}(-\omega_l^2 + \omega_{\vec{k}\vec{q}}^{02}) = -2\tilde{\lambda}_{\vec{q}}\omega_{\vec{k}\vec{q}}^0 b_l \tag{17a}$$

and

$$b_l(-\omega_l^2 + \omega_0^2) = -\omega_0 \sum_{\vec{k},\vec{q}}' \tilde{\lambda}_{\vec{q}} a_{\vec{k}\vec{q},l} , \tag{17b}$$

where the prime on the summation of Eq. (17b) represents the restricted sum $|\vec{k}| < P_F$, $|\vec{k}+\vec{q}| > P_F$. From Eq. (17a),

$$a_{\vec{k}\vec{q},l} = \frac{2\tilde{\lambda}_{\vec{q}}\omega_{\vec{k}\vec{q}}^0 b_l}{\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}} \tag{18}$$

which with Eq. (17b) yields the formal result

$$(\omega_l^2 - \omega_0^2) = \omega_0 \sum_{\vec{k},\vec{q}}' \frac{|\tilde{\lambda}_{\vec{q}}|^2 2\omega_{\vec{k}\vec{q}}^0}{\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}} . \tag{19}$$

Special attention must be given to those pair states in the summation for which the energy denominator vanishes. Following Dirac,[34] we introduce a yet-to-be-determined quantity $Z(\omega_l)$ through the replacement

$$\frac{1}{\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}} = \mathcal{P}\left(\frac{1}{\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}}\right) + i\pi Z(\omega_l)\delta(\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}) \tag{20}$$

in Eq. (19), where $\mathcal{P}$ represents a principal-part integration and $Z(\omega_l)$, related to the residue at the pole, may be complex. In anticipation of the final result, the suggestive definitions of level shift and broadening functions

$$\Lambda(\omega_l) \equiv \mathcal{P}\left(\sum_{\vec{k},\vec{q}}' \frac{|\tilde{\lambda}_{\vec{q}}|^2 2\omega_{\vec{k}\vec{q}}^0}{\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}}\right) \tag{21a}$$

and

$$\Delta(\omega_l) \equiv \pi \sum_{\vec{k},\vec{q}}' |\tilde{\lambda}_{\vec{q}}|^2 2\omega_{\vec{k}\vec{q}}^0 \delta(\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}) \tag{21b}$$

combined with Eqs. (19) and (20), and solved for $Z(\omega_l)$, give

$$Z(\omega_l) = \frac{\omega_l^2 - \omega_0^2 - \omega_0\Lambda(\omega_l)}{\omega_0\Delta(\omega_l)} . \tag{22}$$

This object can be related to physical quantities by consideration of the eigenvectors or normal modes, formed as linear combinations of localized oscillator displacements and pair fluctuations

$$\xi_l(t) = \eta_l\left(b_l e^{i\omega_l t} + \sum_{\vec{k},\vec{q}}' a_{\vec{k}\vec{q},l} e^{i\omega_l t}\right) , \tag{23}$$

where b_l and $a_{\vec{k}\vec{q},l}$ are the contributions of the oscillators and pairs, respectively, to the lth normal mode, and η_l is an appropriate normalization. Normalizing the eigenvectors "per unit energy," orthogonality and Eq. (23) yield

$$\langle \xi_l | \xi_{l'} \rangle = \delta(\omega_l - \omega_{l'})$$

$$= \eta_l^* \eta_{l'}\left(b_l^* b_{l'} + \sum_{\vec{k},\vec{q}}' a_{\vec{k}\vec{q},l}^* a_{\vec{k}\vec{q},l'}\right) \tag{24}$$

using also the orthogonality of pair states. Equations (18), (20), and (24) can be written as

$$\delta(\omega_l - \omega_{l'}) = \eta_l^* \eta_{l'} b_l^* b_{l'} \left\{ 1 + \sum_{\vec{k},\vec{q}}' |\tilde{\lambda}_{\vec{q}}|^2 4\omega_{\vec{k}\vec{q}}^{02} \left[\mathcal{O}\left(\frac{1}{\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}}\right) - i\pi Z^*(\omega_l) \delta(\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}) \right] \right.$$

$$\left. \times \left[\mathcal{O}\left(\frac{1}{\omega_{l'}^2 - \omega_{\vec{k}\vec{q}}^{02}}\right) + i\pi Z(\omega_l) \delta(\omega_{l'}^2 - \omega_{\vec{k}\vec{q}}^{02}) \right] \right\} \tag{25}$$

which is well behaved except for the double singularity associated with the product of the two principal-part terms. This is dealt with by using the identity[35]

$$\mathcal{O}\left(\frac{1}{\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}}\right) \mathcal{O}\left(\frac{1}{\omega_{l'}^2 - \omega_{\vec{k}\vec{q}}^{02}}\right) = \mathcal{O}\left(\frac{1}{\omega_l^2 - \omega_{l'}^2}\right) \left[\mathcal{O}\left(\frac{1}{\omega_{l'}^2 - \omega_{\vec{k}\vec{q}}^{02}}\right) - \mathcal{O}\left(\frac{1}{\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}}\right) \right] + \pi^2 \delta(\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}) \delta(\omega_{l'}^2 - \omega_{\vec{k}\vec{q}}^{02}) \tag{26}$$

and the equivalence

$$\sum_{\vec{k}\vec{q}}' f(\vec{k}\vec{q}) \delta(\omega_l^2 - \omega_{\vec{k}\vec{q}}^{02}) \delta(\omega_{l'}^2 - \omega_{\vec{k}\vec{q}}^{02})$$

$$= \sum_{\vec{k}\vec{q}}' f(\vec{k}\vec{q}) \delta(\omega_l^2 - \omega_{l'}^2) \delta(\omega_l^2 - \omega_{kq}^{02}) . \tag{27}$$

Use of Eqs. (21b), (26), and (27) in (25) with $\omega_l = \omega_{l'}$, (i.e., keeping terms proportional to the delta function) gives

$$|b_l|^2 = \left(\frac{\pi}{|\eta_l|^2} [1 + |Z(\omega_l)|^2] \Delta(\omega_l) \right)^{-1} . \tag{28}$$

Requiring

$$\int_0^\infty |b_l|^2 d\omega = 1 \, (|\eta_l|^2 = 2)$$

and placing Eq. (22) in Eq. (28) produces the final expression for the local vibrational spectrum of the quasilocalized oscillator resonance:

$$|b_l|^2 = \frac{2}{\pi} \frac{\omega_0^2 \Delta(\omega_l)}{[\omega_l^2 - \omega_0^2 - \omega_0 \Lambda(\omega_l)]^2 + [\omega_0 \Delta(\omega_l)]^2} \equiv \rho_{osc}(\omega_l) \tag{29}$$

with $\Lambda(\omega_l)$ and $\Delta(\omega_l)$ given by Eqs. (21a) and (21b).

As already noted, truly localized states can also form. The signature for these states is that $\Delta(\omega_l) \to 0$ in the energy region in which $\omega_l^2 \approx \omega_0^2 + \omega_0 \Lambda(\omega_l)$. The first of these conditions is met, from Eq. (21b), if either the coupling constant $\tilde{\lambda}_{\vec{q}}$ vanishes for states in which $\omega_l^2 \approx \omega_{\vec{k}\vec{q}}^{02}$ or if the continuum is bounded such that the sum on $\vec{k}, \vec{q}$ does not extend into this region. Whether such a state forms then depends upon the proximity of ω_0 to ω_l or upon the strength of the coupling and thus level shift $\Lambda(\omega_l)$. The spectral weight for the localized state is determined by rewriting Eq. (29) as

$$|b_l^{loc}|^2 = \frac{\omega_0}{\pi} \lim_{\Delta(\omega_l) \to 0}$$

$$\times \text{Im}\left(\frac{1}{f(\omega_l) - i\omega_0 \Delta(\omega_l)} - \frac{1}{f(\omega_l) + i\omega_0 \Delta(\omega_l)} \right)$$

with $f(\omega_l) \equiv \omega_l^2 - \omega_0^2 - \omega_0 \Lambda(\omega_l)$. The pole terms give

$$|b_l^{loc}|^2 = 2\omega_0 \delta(f(\omega_l))$$

$$= \left(\frac{2\omega_0 \delta(\omega_l - \omega_p)}{\left| \frac{df(\omega_l)}{d\omega_l} \right|} \right)_{f(\omega_l = \omega_p) = 0} ,$$

or explicitly

$$|b_l^{loc}|^2 = \frac{\omega_0}{\omega_l} \left(1 - \frac{\omega_0}{2\omega_l} \frac{d\Lambda(\omega_l)}{d\omega_l} \right)^{-1}$$

$$\times \delta(\omega_l - [\omega_0^2 + \omega_0 \Lambda(\omega_l)]^{1/2}) , \tag{30}$$

where the transcendental equation for $f(\omega_l) = 0$ must be solved in some convenient manner after the specifics of the mixing interaction are set. For our purposes, Eqs. (21), (29), and (30) constitute the formal solution to the problem.

V. DENSITY-OF-STATES LIMIT

A particularly neat explicit solution to the problem follows when the coupling constant (or matrix element) can be replaced by some angle-averaged value in which the $\vec{q}$ dependence is approximately dealt with by mapping $\tilde{\lambda}_{\vec{q}}$ onto some energy dependent $\tilde{\lambda}(\omega)$. The usual prescription is to take $\tilde{\lambda}(\omega \leq \omega_c) = \tilde{\lambda}$, a constant, and $\tilde{\lambda}(\omega > \omega_c) = 0$, where ω_c is a cutoff energy estimated from the range and/or strength of the interaction, provided $\hbar\omega_c \lesssim \epsilon_F$ (Refs. 12, 33, and 35) where ϵ_F is the Fermi energy. In addition, for pair states with excitation energy less than $\approx \epsilon_F$, the $\vec{k}, \vec{q}$ sums in Eq. (21) can be replaced by frequency integrals, that is

$$\sum_{\vec{k},\vec{q}}' f(\omega_{\vec{k}\vec{q}}^0) \simeq \int f(\omega) \rho(\omega) d\omega , \tag{31}$$

where $\rho(\omega) = \sum_{\vec{k},\vec{q}}' \delta(\omega - \omega_{\vec{k}\vec{q}}^0)$ is the pair excitation density of states. As detailed elsewhere,[12] for $\omega \lesssim \omega_F$, $\rho(\omega)$ is well represented by

$$\rho(\omega) \simeq \hbar \rho_{\epsilon_F}^2 \omega , \tag{32}$$

where ρ_{ϵ_F} is the Fermi-level electron density of states in units of states per eV per atom, and $\rho(\omega)$ is in units of states per frequency per atom.

Within the framework just outlined, $\tilde{\lambda}_{\vec{q}}$ appearing in Eqs. (21a) and (21b) can be pulled out of the

summation. Then Eqs. (21b), (31), and (32) combine to give for the level-width function

$$\Delta(\omega_l) \simeq 2\pi \, |\tilde{\lambda}|^2 \int_0^{\omega_c} \rho(\omega)\omega\delta(\omega_l^2 - \omega^2)\, d\omega$$

$$= \begin{cases} \pi\hbar^2\rho_{\epsilon_F}^2 \, |\tilde{\lambda}|^2\omega_l\,, & \omega_l \leqslant \omega_c \\ 0\,, & \omega_l > \omega_c \end{cases}\,. \qquad (33)$$

Similarly, the level-shift function is

$$\Lambda(\omega_l) \simeq 2|\tilde{\lambda}|^2 P\left(\int_0^{\omega_c} \frac{\rho(\omega)\omega}{\omega_l^2 - \omega^2}\, d\omega \right)$$

$$= 2\hbar^2\rho_{\epsilon_F}^2 \, |\tilde{\lambda}|^2 \omega_c \left(-1 + \frac{1}{2}\frac{\omega_l}{\omega_c}\ln\left|\frac{\omega_c + \omega_l}{\omega_c - \omega_l}\right| \right), \qquad (34)$$

valid for all ω_l except in the vicinity of the $\omega_l \simeq \omega_c$ singularity, which is a sharp-cutoff artifact.

It is instructive to consider some qualitative features of the spectral distribution for the quasi-localized resonance which follow from Eqs. (29), (33), and (34). The situation is shown in Fig. 1, where the cutoff continuum with linear density of states representing the pair excitations, interacts with the discrete state at ω_0 to form the local spectral distribution on the right. Typically, $\hbar\omega_0 \lesssim 0.2$ eV, whereas $\omega_c \sim 1$–10 eV. Thus the net downward repulsion of continuum states in the range $\omega_0 < \omega < \omega_c$ dominates over the upward push from the $0 < \omega < \omega_0$ states. Consequently, the resonance peak is depressed or red shifted from its noninteracting value and this would appear as a softening of vibrational frequencies. In any event, near the resonance $\omega_l \sim \omega_0 + \delta\omega$ with $\delta\omega \ll \omega_0$ so the quantity $x \equiv \omega_l/\omega_c \approx \omega_0/\omega_c \ll 1$. Performing a small-$x$ expansion on $\Lambda(\omega_l)$, given by Eq. (34), one obtains

$$\lim_{x\to 0} \Lambda(\omega_l) \simeq \frac{2}{\pi}C\omega_c\left(-1 + \frac{\omega_l^2}{\omega_c^2} + \cdots \right) \qquad (35a)$$

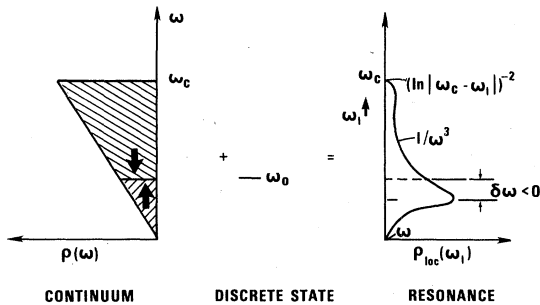FIG. 1. Schematic display of a localized state with frequency ω_0 interacting with a bounded continuum $(0 \leqslant \omega \leqslant \omega_c)$ whose density of states varies linearly with ω. As shown, the continuum states $\omega > \omega_0$ $(\omega < \omega_0)$ red shift (blue shift) the discrete state. The resulting local spectral function for the discrete state is shown on the right where various qualitative features of the perturbed state are labeled.

and

$$\Delta(\omega_l) = C\omega_l \approx \frac{\pi}{2}\frac{\omega_l}{\omega_c}\Lambda \qquad (35b)$$

with $C \equiv \pi\hbar^2\rho_{\epsilon_F}^2 \, |\tilde{\lambda}|^2$. From Eq. (35a), note that $\Lambda(\omega_l)$ is always negative for $\omega_l/\omega_c \ll 1$ and that the *width* Δ is of order ω_l/ω_c (typically ~ 0.1 to ~ 0.01) *smaller* than the "level *shift*." Equations (29), (33), and (34) [(or 35a) and (35b)] also show the following qualitative features:

$$\rho_{\text{osc}}(\omega_l) \sim \begin{cases} \omega_l\,, & \omega_l \to 0 \\ 1/\omega_l^3\,, & \omega_0 \lesssim \omega_l \ll \omega_c \\ \left(\ln\left|\dfrac{1}{\omega_l - \omega_c}\right|\right)^{-2}, & \omega_l \to \omega_c \end{cases}$$

which are indicated in Fig. 1. While this line shape is far from Lorentzian, many of the interesting departures appear in the wings which is that part of the spectrum usually obscured by "background" in an actual experiment. One may then wonder, to what extent naive application of "exponential-decay perturbation theory" produces an acceptable line shape. The standard Lorentzian result follows from the following steps. First the physically significant RPA interaction, Eq. (13), which varies linearly with oscillator and pair displacement is replaced by the simpler transfer interaction

$$H_{\text{int}}^{\text{Lor}} \simeq \sum_{\vec{k},\vec{q}}{}' \tilde{\lambda}_{\vec{q}}(B\rho_{\vec{k}\vec{q}}^\dagger + B^\dagger \rho_{-\vec{k}-\vec{q}})$$

in which products of two creation or annihilation operators are neglected. Standard Anderson-model analysis[15] then yields the local density of states

$$\rho_{\text{Lor}}(\omega_l) = \frac{1}{\pi}\frac{\Delta_L(\omega_l)}{[\omega_l - \omega_0 - \Lambda_L(\omega_l)]^2 + \Delta_L^2(\omega_l)} \qquad (36a)$$

with

$$\Lambda_L(\omega_l) = \mathcal{P}\left(\sum_{\vec{k},\vec{q}}{}' \frac{|\lambda_{\vec{q}}|^2}{\omega_l - \omega_{\vec{k}\vec{q}}^0} \right) \qquad (36b)$$

and

$$\Delta_L(\omega_l) = \pi \sum_{\vec{k},\vec{q}}{}' |\tilde{\lambda}_{\vec{q}}|^2 \delta(\omega_l - \omega_{\vec{k}\vec{q}}^0) \qquad (36c)$$

which is Lorentzian if the frequency dependence of $\Lambda_L(\omega_l)$ and $\Delta(\omega_l)$ can be neglected. Furthermore, in the density-of-states limit,

$$\Lambda_L(\omega_l) = \hbar^2\rho_{\epsilon_F}^2 \, |\tilde{\lambda}|^2\omega_c\left(-1 + \frac{\omega_l}{\omega_c}\ln\left|\frac{\omega_l - \omega_c}{\omega_l}\right| \right),$$

$$\Delta_L(\omega_l) = \begin{cases} \pi\hbar^2\rho_{\epsilon_F}^2 \, |\tilde{\lambda}|^2\omega_l\,, & \omega_l \leqslant \omega_c \\ 0\,, & \omega_l > \omega_c \end{cases},$$

which for small $x = \omega_l/\omega_c \approx \omega_0/\omega_c$, become

$\lim_{x\to 0} \Lambda_L(\omega_l) \approx \frac{1}{2} \Lambda(\omega_l) = C\omega_c/\pi$ and $\Delta_L(\omega_l) = \Delta(\omega_l)$ from Eqs. (35a) and (35b). Thus the Lorentzian peak is shifted by $\Lambda(\omega_l)/2$ from the unperturbed frequency. For comparison, the exact peak position (for constant Λ and Δ) from Eq. (29) occurs at

$$\omega_l = \omega_0[1 + \Lambda(\omega_l)/\omega_0]^{1/2}$$

$$= \omega_0[1 + \tfrac{1}{2}\Lambda(\omega_l)/\omega_0 - \tfrac{1}{8}\Lambda^2(\omega_l)/\omega_0^2 + \cdots],$$

which is identical to leading order in Λ. The full width at half maximum (FWHM) from Eq. (29) is $\Delta_{FWHM} = \Delta(\omega_l)[1 - \Lambda(\omega_l)/2\omega_0 + \cdots]$ which is only slightly more narrow than the Lorentzian width $\Delta_L(\omega_l)$. This exercise suggests that for weak-interaction phenomenon which do not depend strongly on the details of the line shape other than peak position and width, exponential-decay theory should provide an adequate algebraic if not physical representation.[36]

VI. NUMERICAL RESULTS

At this point it seems worthwhile to explore the nature of the numerical consequences of the model presented here. The basic quantity which is of interest is the spectral function, Eq. (29), which is in one-to-one correspondence with line shapes measured in vibrational spectroscopy. We will restrict considerations to the density-of-states limited model so that the level-width and -shift functions are given by Eqs. (33) and (34), respectively. In Sec. VI A, the problem will be set up for numerical evaluation and a rough argument providing a connection between the coupling constant and physical properties of the system will be given. Section VI B pertains both to line shapes evaluated with parameters in the range likely to be relevant for vibrational spectroscopy of molecular oscillators in or on real metals, as well as line shapes over a broader range of parameters chosen to illustrate the variety of solutions possible.

A. Generalities

For numerical studies, it is most convenient to express the spectral function and frequency variables in dimensionless form. Introducing the quantities

$$x \equiv \omega_l/\omega_c, \tag{37a}$$

$$y \equiv \omega_0/\omega_c, \tag{37b}$$

$$C \equiv \pi\hbar^2\rho_{\epsilon_F}^2 |\tilde{\lambda}|^2, \tag{37c}$$

and

$$\rho_0 \equiv 2/\pi\omega_c, \tag{37d}$$

the width and shift functions [Eqs. (33) and (34)] are

$$\Delta(\omega_l) = C\omega_c x \tag{38a}$$

and

$$\Lambda(\omega_l) = \frac{2}{\pi}C\omega_c f(x) = \frac{2\Delta(\omega_l)}{\pi x} f(x) \tag{38b}$$

with

$$f(x) = -1 + \frac{x}{2}\ln\left|\frac{1+x}{1-x}\right|,$$

where the continuum falls in the range $0 \le x \le 1$ and truly localized states [Eq. (30)] occur only for $x > 1$. In terms of Eqs. (37) and (38), the quasilocalized oscillator spectral functions, Eq. (29) is written as

$$R \equiv \frac{\rho_{osc}(x;y,C)}{\rho_0} = \frac{Cx}{\left(\dfrac{x^2}{y} - y - \dfrac{2}{\pi}cf(x)\right)^2 + C^2 x^2}$$

$$(0 \le x \le 1) \tag{39}$$

where x is the frequency variable and the parameters y and C specify the unperturbed oscillator frequency and coupling strengths, respectively.

The frequency variation of the level-shift operator is given by $f(x)$ which is plotted in Fig. 2. Note that for $x < 0.83$, the shift is negative. As already mentioned, the divergence at $x = 1$ is an artifact which would be replaced by a large but finite functional form if the sharp cutoff was softened. The asymptotic $\lim_{x \gg 1} x^2 f(x) = 3$ just reflects the fact that high-frequency oscillators $(\omega_0 \gg \omega_c)$ basically see the pair continuum as a static entity and thus the level-shift function becomes frequency independent as it approaches zero.

One condition for sharp structure to appear in the local spectral function is for the approximate eigenvalue condition $x^2/y - y - (2/\pi)cf(x) = 0$ in Eq. (39) to be satisfied. Defining $g(x;y,C) \equiv (\pi/2C) \times (x^2/y - y)$, this is equivalent to $f(x) = g(x;y,C)$. The quantity $(2C/\pi)g(x;y,C)$ is also drawn in Fig. 2 for various values of y. In the special case in which $C = \pi/2$, the intersections of these curves with $f(x)$ denote the positions of possible resonances or true localized states if $x_{int} > 1$. With arbitrary C, the $g(x;y,C)$ curves must be rescaled.

A semiquantitative feel for the numerical range of coupling constants in physically significant situations is easily arrived at. As it now stands, the coupling constant is

$$\tilde{\lambda} = \frac{1}{\hbar}\left(\frac{\hbar}{M\omega_0}\right)^{1/2}\lambda, \tag{40}$$

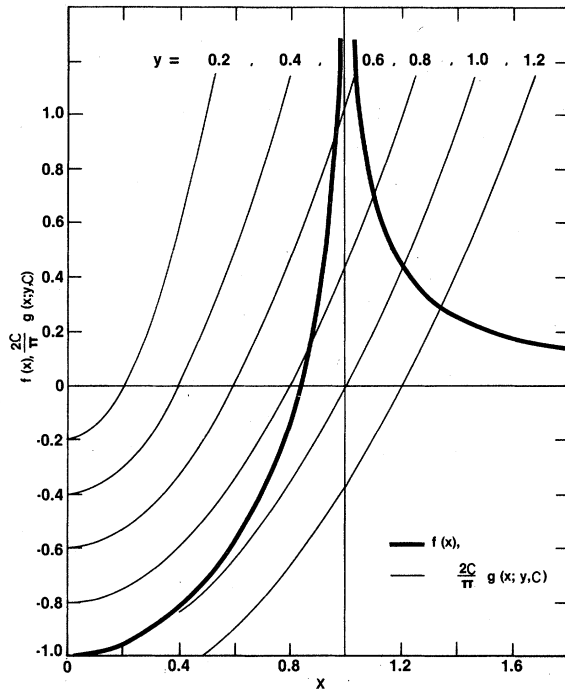where $(\hbar/M\omega_0)^{1/2} \equiv \bar{x}_0$ is the rms zero-point local-

FIG. 2. Plot of the level-shift function $f(x) = \pi \Lambda(x)/2C\omega_c$ as a function of x (heavy line). The continuum lies in the range $0 \le x \le 1$. Also shown are the curves $2Cg(x;y,C)/\pi$ treating y parametrically. For the case in which $C = \pi/2$, the intersection of g and f occurs at the discrete-state eigenenergy.

ized oscillator amplitude and

$$\lambda \simeq \frac{\delta}{\delta\rho}\left(\frac{\partial V}{\partial Q}\right), \tag{41}$$

where $V(Q;[\rho])$ is the self-consistently screened Coulomb interaction between the oscillating particle and the density fluctuations.[37] As written above, Eq. (40) has dimensions of angular frequency. For the simplest case of an oscillating "atom" carrying a net charge $=fe$ and with an effective radius R_c for the screening charge ($\simeq$valence-shell radius for atoms with unfilled shells, $\simeq$radius of lowest unoccupied shell for closed-shell atoms[38]), the metallically screened interaction is[39]

$$V \simeq \frac{(fe)^2 \kappa_s}{2}\left[1 - \frac{2}{\pi}\tan^{-1}\left(\frac{2\kappa_s R_c}{\pi}\right)\right]$$

$$\simeq \frac{(fe)^2}{2R_c}\left[1 - \frac{1}{12}\left(\frac{\pi}{\kappa_s R_c}\right)^2 + \cdots\right], \tag{42}$$

where $\kappa_s = 2.95/r_s^{1/2}$ Å^{-1} is the Fermi-Thomas screening parameter. With $\partial V/\partial Q \approx (fe)^2/2R_c^2$, Eqs. (40)–(42) yield

$$\lambda \approx \frac{1}{\hbar}f\left(\frac{x_0}{R_c}\right)\frac{e}{2R_c} \tag{43}$$

which with $f = 1$, $\bar{x}_0 \approx 0.1$ Å, and $R_c \approx 1$ Å gives $\bar{\lambda} \sim 0.735$ eV/$\hbar$, which is a reasonable upper limit. Use of this estimate in Eq. (37c) gives an upper limit $C_{upper} \simeq 1.7\rho_{\epsilon_F}^2$ with ρ_{ϵ_F} in units of states per atom per eV. The Fermi-level density of states has variations between 0.27 eV^{-1} for Ag, ~0.4 eV^{-1} for Al and other free-electronlike materials, and up to ~4.06 eV^{-1} for Ni and other transition metals.[40] Thus depending upon the host material, C_{upper} could fall within the range $0.1 \lesssim C_{upper} \lesssim 30$, all things other than the Fermi-level density of states being equal.

In fact, this substantial variation could provide the experimental means for ascertaining the importance of electron-hole pair coupling to localized oscillators. In alloy systems showing strong changes in Fermi-level electronic structure as a result of modest compositional changes, vibrational spectroscopy line-shape analysis of implanted oscillators as a function of matrix composition seems to be a promising direction. Finally, a cautionary flag must be raised concerning the actual values for coupling constants. The numbers just obtained are maximum possible values within the realm of physical intuition or simple modeling, under ideal (although not outlandish) circumstances. Values appropriate to experimentally realized situations could be much smaller. Since quantitatively meaningful calculation of these quantities is unlikely, the most profitable direction for data analysis is in the answering of questions such as those of self-consistency between observed level shifts and linewidths,[41] both dependent on the same coupling mechanism (if the proposed pair scheme dominates). Model theory such as the present one provides the links between shifts, widths, and general line shapes.

B. Results

Examples of some spectral distributions given by Eqs. (38) and (39) choosing a range of parameters likely to apply to conventional vibrational spectroscopy are shown in Figs. 3 and 4. In both cases, the interaction parameter C is sufficiently small that the curves are well represented by a two-parameter bell-shaped function. Of course the parameters are functions of the interaction strength, as shown in the insets. Both the peak displacement $\Delta\omega$ and the FWHM were determined numerically. No significant departure from the linear relation $\Gamma_{1/2} \propto C$ was noted and $\Delta\omega$ broke off from a linear dependence only as the value of C approached and exceeded that of y. Significant frequency red shifts $\Delta x/y = \Delta\omega/\omega_0$ of the order 1–10% were obtained as a result of the discrete oscillator state (with frequency near the bottom
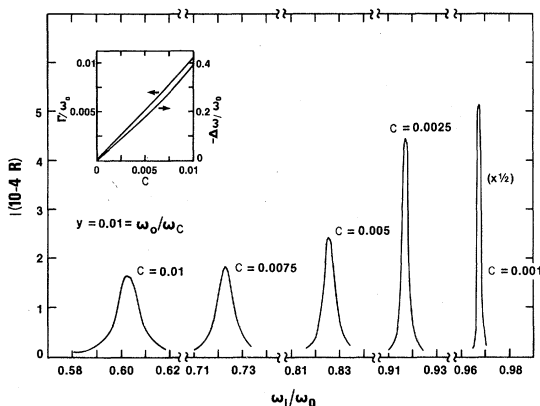
FIG. 3. Localized spectral function, from Eqs. (38) and (39), for parameters within the domain of conventional vibrational spectroscopy. Here $y = 0.01$. The inset shows the level shift and width as a function of the interaction parameter $C = \pi \hbar^2 \rho_{\epsilon_F}^2 |\tilde{\lambda}|^2$. Note the breaks in the x axis.

of the linearly varying continuum) mixing with the electron-hole pair continuum. This conclusion is reasonably general, independent of specific parameter values, and should have a good deal of relevance in the interpretation of vibrational spectra of adsorbed or embedded molecules.

In actual practice, orthodox vibrational spectroscopy typically shows a linewidth[42] $\Delta \sim 1$–5 meV which implies from Eqs. (37a) and (38a), that $C \sim \Delta/\omega_0 \sim 0.01$–0.1, with $\hbar\omega_0 \sim 0.1$ eV. In addition, frequency decreases by as much as 50 meV are observed for some modes.[42] If for the sake of this exercise we assume that the pair mechanism is responsible for this behavior, then the shift $\sim \Lambda/2 \approx C \omega_c / \pi \approx 50$ meV requires a cutoff falling in the range 1.5 eV $\lesssim \hbar\omega_c \lesssim 15$ eV using the values of C implied by the width. Certainly the values
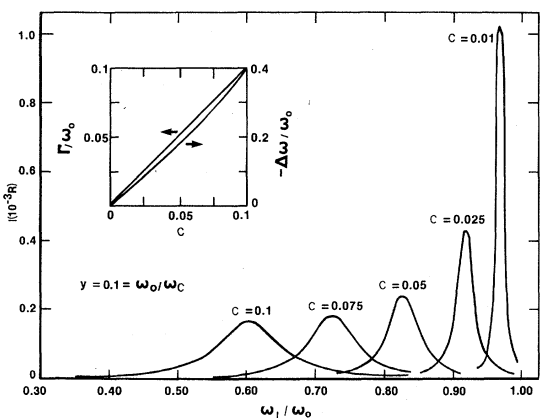

FIG. 4. Same as Fig. 3 but with $y = 0.1$.

for C inferred from Eqs. (37c) and (43) and for $\hbar\omega_c$ given by the conditions of the model, fall within the highly acceptable range required for compatibility with experimentally observed line shapes. Thus at least the present model is internally self-consistent in that it produces line shapes with the correct combinations of shifts and widths, based on a choice of parameters expected from a physically reasonable model.

In the analysis of vibrational spectra, the state of the chemical environment (bonding sites and/or bonding orbitals) of an adsorbed or embedded molecule is often inferred from observed shifts of the order of 1%. As has been shown here, at least that order of red shift is to be expected from the oscillator interaction with the bounded pair continuum, independent of the chemical effects, suggesting that a proper data analysis must take both effects into account on an equal footing. In fact, one of the more significant general points of this exercise is this realization that the discrete-state-continuum interaction produces such a large shift even when the apparent broadening (or "lifetime decay width") is negligibly small. In other words, when the oscillator frequency lies near the lower edge of a continuum characterized by the linear density of states, as depicted in Fig. 1, the dominant observable effect due to the electron-hole pairs, is a significant softening of the oscillator frequency which, on the 1–10% level, cannot be ignored, even if the vibrational width due to pair interactions is much smaller.

For the sake of completeness, line shapes obtained from Eq. (39) for choices of parameters y and C which yield spectral distributions spread out over a frequency range comparable with the continuum are shown in Figs. 5 and 6. In Fig. 5, the $y = 0.5$ state is still far enough below the $x = 0.83$ point where $\Lambda(x) = 0$ that it sees a basically red-shifting interaction with the continuum that pushes the state down into the small-level-width region $[\Delta(\omega_l) = C\omega_l]$. Consequently, an eyeball analysis of the curves yields a bell shape. Quantitatively this is not so accurate, as illustrated by the nonlinear variations of $\Delta\omega$ and $\Gamma_{1/2}$ in the inset. In addition, we can see the initial linear variation of R vs x for $C = 0.5$, which is certainly not indicative of a Lorentzian. Another aspect is illustrated in Fig. 6 near the upper cutoff of the continuum $x \to 1$. For the weakest interaction shown, that is $C = 0.1$, $R(x)$ monotonically decreases and goes to zero as $[\ln(1/(1-x)]^{-2}$. However, as the interaction and thus C increases, a pileup of states occurs near but within the continuum edge as shown in the $C = 0.25$ curve. As the interaction is further increased, these states push out above the continuum forming the true

localized states given by Eq. (30). The spectral
weight for these states is taken from the within-
band pileup which is relatively reduced for $C = 0.5$
and finally returned to the logarithmic zero for
$C = 0.7$. Both the position and pole strength ob-
tained from Eq. (30) are shown in the inset where
it is seen that the depicted band-edge behavior is
quite consistent with the emergence of localized
states with $x_{loc} > 1$. Not much quantitative sig-
nificance should be attached to these numbers for
the present choice of parameters as they are
strongly influenced by the sharp-cutoff artifacts
leading to the $x = 1$ divergence of $f(x)$ shown in
Fig. 2. Nonetheless, the qualitative aspects are
correct and would survive in a more realistic cut-
off procedure.

It is somewhat problematic to what extent real
systems might be characterized by parameter
values $y \gtrsim 0.1$ as shown in Figs. 5 and 6. At least
for the specific case of an atomic oscillator in-
teracting with a metallic electron gas, $\hbar\omega_l < 0.2$
eV always. If the cutoff is set by a Fermi-energy
parameter, then $\hbar\omega_c \sim 5-10$ eV and thus $y_{max} \approx 0.04$.
On the other hand, if the cutoff is determined by
the bandwidth parameters of a narrow d-band
straddling the Fermi level, then for nearly empty
or full bands, the cutoff might be expected to be
determined by the width of the full or empty por-
tion of the band which could be quite small ($\sim$few
tenths of an eV), in which case $y_{max} \sim 1.0$ could be
realized and these results would then be of more
than academic interest.

VII. SUMMARY

A model has been presented for a system con-
sisting of a localized harmonic oscillator dynam-
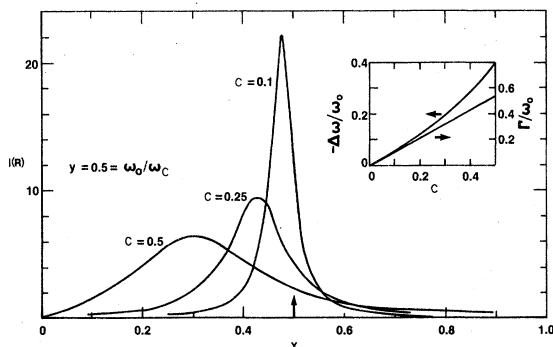ically coupled to the electron-hole pair excitations

FIG. 5. Localized spectral function, from Eqs. (38)
and (39), for parameters which spread the distribution
throughout the continuum, here with $y = 0.5$. The non-
linear variation of shift with C, as shown in the inset,
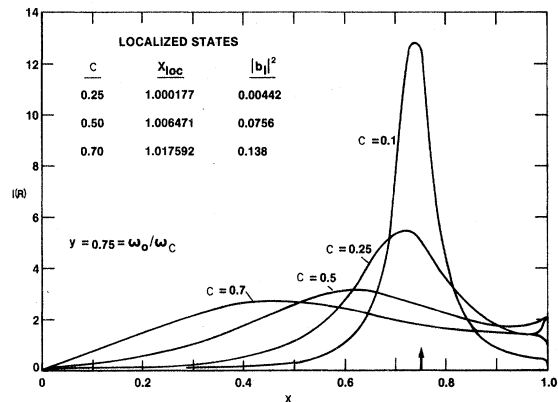is indicative of the breakdown of simple perturbation
theory.

FIG. 6. Same as Fig. 5 but with $y = 0.75$. Special at-
tention is directed towards the emergence of localized
states above the continuum edge at $x = 1$ as labeled.

of a Fermi liquid via an interaction that is linear
in oscillator displacement and Fermi liquid-elec-
tron-gas pair-density fluctuations. For an elec-
tron gas treated within the random-phase approxi-
mation, this model is exactly soluble as a nor-
mal-mode analysis of coupled harmonic oscilla-
tors. For the case investigated here in which one
of the oscillators is spatially localized, the prob-
lem is also one of a discrete state interacting
with a continuum, and when thought of in this con-
text, is related to a number of other physically
realized phenomena.[15-22] The manifestations of
the interaction as revealed in the spectral dis-
tribution of the perturbed localized oscillator,
are the acquisition of a level shift and broadening.
Furthermore, the true line shape is non-Lorent-
zian (although this is often a reasonable approxi-
mation) for a number of reasons.[30] First, in order
for a Lorentzian to be rigorously valid, the con-
tinuum to which the discrete state couples, must
be unbounded or at least broad enough relative to
interaction strengths and unperturbed discrete-
state energies that edge effects are not seen. In
the case of the pair continuum and an atomic or
molecular oscillator, the unperturbed oscillator
lies near the bottom of the continuum and this fact
is responsible for a significant softening of the
apparent oscillator frequency, even when the level
width appears to be small. In the other extreme
in which the unperturbed oscillator is near the
top of the continuum, true localized eigenstates
at energies greater than the continuum cutoff can
form, in addition to nontrivial distortions of the
inband spectral functions. Secondly, since the pair
density of states varies linearly with ω, the local
spectral function $\sim\omega_l$ as $\omega_l \to 0$ and $\sim\omega_l^{-3}$ as $\omega_l \gg \omega_0$,
both being indicative of non-Lorentzian behavior.
Model parametric calculations have been pre-

sented which illustrate these points. While attempts have been made here to place the general results within the context of an experimental world, specific applications of this theory to vibrational spectroscopy of adsorbed atoms and molecules and metallic hydrides and surface reactivity theory have been reserved for a later paper.[24]

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$$B^\dagger = -i(2\hbar M\omega_0)^{-1/2}P + (2M\omega_0/\hbar)^{1/2}Q$$

and

$$B = i(2\hbar M\omega_0)^{-1/2}P + (2M\omega_0/\hbar)^{1/2}Q .$$

Consequently H_{int}^{Lor} depends upon both the displacement and momentum of the oscillator. Specification of $\tilde{\lambda}_{\vec{q}}$ from electrostatic arguments is then impossible. In actual practice, this fundamental problem has been ignored and $\tilde{\lambda}_{\vec{q}}$ is often treated in a manner that is formally inconsistent with the role it plays in the model Hamiltonian.

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