

Moments and absorption line shape of an antiresonant electron-phonon system in the strong-coupling limit

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A two-center antiresonant electron-phonon system is calculated in the strong-coupling limit. Expressions for the moments and the optical-absorption line shape are given in an analytic form. The result shows the characteristic behavior of resonant systems.

In recent years the behavior of nonadiabatically coupled electron-phonon systems has been the object of much interest. A peculiar case is the antiresonant electron-phonon system, in which discrete excited electron states interact with a continuous background of vibration modes.¹ I confine myself here to a system of two electronically coupled impurity centers (labeled 1 and 2), one of which interacts with the vibrations of the surrounding crystal.^{2,3} Examples of such a situation are found in the optical spectrum of V^{2+} in octahedral fluoride coordination.⁴ They are characterized by the Hamiltonian ($\hbar=1$)

$$H = \epsilon_1 a_1^\dagger a_1 + \epsilon_2 a_2^\dagger a_2 + v(a_1^\dagger a_2 + a_2^\dagger a_1) + a_1^\dagger a_1 \sum_j S_j (b_j^\dagger + b_j) + \sum_j \omega_j b_j^\dagger b_j, \quad (1)$$

where the a 's and b 's are, respectively, fermion and boson creation and annihilation operators. v is a measure of the electron-electron coupling strength, and S_j of the electron-phonon coupling strength.

This system is studied under the influence of an external light field, which may be polarized in such a way that it affects only center 1. In the strong-coupling region [$\epsilon_1, \epsilon_2, \omega_j \ll v, (\sum_j S_j^k)^{1/2}$], one is able to derive the moments of the absorption spectrum and to calculate the absorption line shape in a closed analytic form.

In the following, I refer to the notation in a paper by Wagner,⁵ where the formula for the moments in the strong-coupling limit is given by

$$\mu_m = \langle 0 a_1^\dagger | \left(v(a_1^\dagger a_2 + a_2^\dagger a_1) + a_1^\dagger a_1 \sum_j S_j (b_j^\dagger + b_j) \right)^m | a_1^\dagger 0 \rangle, \quad (2)$$

where for simplicity I have confined myself to the temperature $T=0^\circ\text{K}$. Furthermore, the external light field is polarized in the x_1 direction and is coupled only to center 1. The integration over the

electronic coordinates can be done by combinatorial calculations:

$$\mu_m = \sum_{\alpha=0}^m \binom{m+\alpha}{2\alpha} v^{2(m-\alpha)} \times \langle 0 | \left(\sum_j S_j (b_j^\dagger + b_j) \right)^{2\alpha} | 0 \rangle. \quad (3)$$

At this point the calculation can be simplified considerably if the number N of coupled phonon oscillators is large enough to satisfy the relation

$$\sum_{j=1}^N S_j^2 \gg \sum_{j=1}^N S_j^4.$$

Then double excitations of the single oscillators may be neglected. This assumption is not restrictive, since the essential result can also be obtained, if only one single oscillator is employed.^{6,7} This provides for the treatment of the phonon matrix elements, and with

$$\langle 0 | \left(\sum_j S_j (b_j^\dagger + b_j) \right)^{2\alpha} | 0 \rangle = \frac{(2\alpha)!}{\alpha!} \left(\frac{1}{2} \right)^\alpha \left(\sum_j S_j^2 \right)^\alpha, \quad (4)$$

one arrives at

$$\mu_{2m} = v^{2m} \left(\frac{2Z}{\pi} \right)^{1/2} e^Z K_{m+1/2}(Z), \quad (5)$$

where

$$Z = v^2 / \sum_j S_j^2. \quad (6)$$

All odd moments vanish, and $K_{m+1/2}(Z)$ is a function of the family of Bessel functions and is defined by (see, e.g., Ref. 8, p.967)

$$K_{m+1/2}(Z) = \left(\frac{\pi}{2Z} \right)^{1/2} e^{-Z} \sum_{\alpha=0}^m \frac{(m+\alpha)!}{\alpha!(m-\alpha)!} = \int_0^\infty e^{-Z \cosh t} \cosh[(m+\frac{1}{2})t] dt. \quad (7)$$

Knowing the moments in the strong-coupling limit, the optical-absorption line shape can be handled in the same coupling region. Using the definition of the moments, the optical response function reads

$$\tilde{G}(t) = e^{-i\epsilon_1 t} \sum_{m=0}^{\infty} \frac{1}{m!} \mu_m (-it)^m, \quad (8)$$

and with Eq. (5),

$$\begin{aligned} \tilde{G}(t) &= e^{-i\epsilon_1 t} \left(\frac{2Z}{\pi} \right)^{1/2} e^Z \\ &\times \sum_{m=0}^{\infty} \frac{(-1)^m}{(2m)!} (vt)^{2m} K_{m+1/2}(Z). \end{aligned} \quad (9)$$

The integral definition (7) of the Bessel function $K_{m+1/2}(Z)$ leads, after some lengthy calculations, to

$$\begin{aligned} \tilde{G}(t) &= \left(\frac{2Z}{\pi} \right)^{1/2} e^Z e^{-i\epsilon_1 t} \int_{-\infty}^{+\infty} \exp \left[-\frac{Z}{2} \left(u^2 + \frac{1}{u^2} \right) \right] \\ &\times \cos(ugt) du. \end{aligned} \quad (10)$$

This expression can easily be Fourier transformed:

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{G}(t) e^{i\omega t} dt.$$

The integration over u also can be done. As a result, the optical function has the form

$$\begin{aligned} G(\omega) &= \left(\frac{2}{\pi} \frac{v^2}{\sum_j S_j^2} \right)^{1/2} \exp \left(\frac{v^2}{\sum_j S_j^2} \right) \\ &\times \exp \left[-\frac{1}{2} \frac{v^2}{\sum_j S_j^2} \left(\frac{(\omega - \epsilon_1)^2}{v^2} + \frac{v^2}{(\omega - \epsilon_1)^2} \right) \right]. \end{aligned} \quad (11)$$

The absorption line shape is shown in Fig. 1.

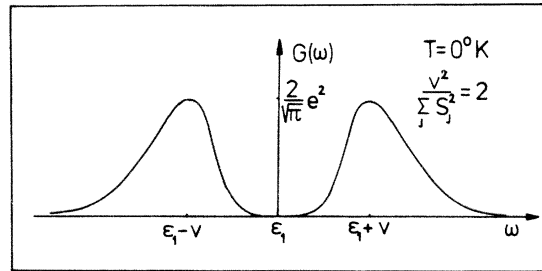


FIG. 1. Optical-absorption line shape of a two-center antiresonant electron-phonon system. $G(\omega)$ is the intensity of the absorption, and ω is a measure of the energy. (For other parameters see text.)

The absorption spectrum is highly symmetric with respect to the energy value ϵ_1 , the excitation energy of center 1. At this point the spectrum shows a broad antiresonant dip, whereas the maximum values of the peaks are located at the energies $\epsilon_1 \pm v$. In the strong-coupling limit, this means that the positions of these peaks are independent of the electron-phonon coupling. On the other hand, the height of the peaks and the broadening of the whole spectrum are highly dependent on both coupling parameters. Since only the strong-coupling limit has been considered, a quantitative comparison with experimental results is not possible. Qualitatively, however, one may compare the result with the investigations of Sturge *et al.*,⁴ in which the absorption spectrum of $\text{KMgF}_3:\text{V}^{2+}$ (${}^4A_2 - {}^2T_2$ transition) exhibits an antiresonant dip in the center of the spectrum and seems to be in agreement with the present calculations.

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