Utilization of Canonical Transformations for the Vibronic Self-Energies of Coupled Impurity Centers

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The self-energies of a system of two electronically coupled impurity centers, one of which interacts with the vibrations of the surrounding crystal (Fano system), are derived by use of non-linear canonical transformations. The regions of applicability of this method are discussed and the results compared with those derived by Green's function techniques in an earlier paper of one of the authors (N. N. K.). The self-energies calculated up to second order have a very simple form and exhibit the correct behaviour also in regions where the results of the Green's function method are no longer valid.

1. Introduction

Optical spectra are one of the main tools for the investigation of atomistic single or many-body systems. A peculiar case of these spectra is the so-called Fano effect[1]. If there is an interaction of a discrete excited state with a continuous background, there will be interference in the optical response, and a drastic deviation of the line shape from a simple superposition can be expected. In particular there is the characteristic appearence of an asymmetric peak or a dip.

In the case of solid state spectra this effect is also wellknown. But because of the presence of phonons the theory of Fano must be reformulated. Recently some investigations were done by Shibatani and Toyozawa[2], Onodera[3], Cho[4] and one of the authors (N. N. K.)[5,6].

In the present article we will show the possibility to derive the vibronic self-energies of a system of interacting impurity centers by use of canonical transformations. The model of our calculations is a system of two electronically coupled impurity centers, one of which interacts with the vibrations of the surrounding crystal. Examples of such a situation are found in the optical spectrum of V^{2+} in octahedral fluoride coordination[7,8].

Our system is described by a Hamiltonian of the form[5]

$$H = \varepsilon_1 a_1^+ a_1 + \varepsilon_2 a_2^+ a_2 + V(a_1^+ a_2 + a_2^+ a_1)$$
$$+ a_1^+ a_1 \sum_j S_j(b_j^+ + b_j) + \sum_j \omega_j b_j^+ b_j , \quad (1)$$

where b_j^+, b_j are phonon creation- and annihilation operators (commutation), whereas the a_i^+, a_i $(i = 1, 2)$ pertain to the (high-energy) electronic states (anti-commutation). V is a measure for the electron-electron coupling strength and S_j is the electron-phonon coupling parameter[6].

The method of nonlinear canonical transformations has been used by two of the authors (M. W.)[9], (E. S. and M. W.)[10] and (U. G. and M. W.)[11] in earlier works. The calculations there were done for systems very similar to the one here, namely for Jahn-Teller systems. There the main result consisted in a specific resonance behaviour in the optical absorption spectra.

2. The Transformation

The electronic and nuclear motions (vibrational) of a many-body system are usually handled as being independent (Born-Oppenheimer approximation). This procedure is highly inadeqaute for electronic states, the energy separation of which is of the same order as the elementary excitations in the nuclear system. In this case there will be dynamical mixing effects. Such a situation occurs for degenerate or nearly degenerate electronic states (Jahn-Teller and Pseudo-Jahn-Teller effect)[9-11], and it is well-known that here the procedure of the ordinary perturbation theory breaks down[12].

To resolve these difficulties in the present article we will make use of the method of canonical transformations. All operators and wavefunctions will be transformed and we consider no longer real particles

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(electrons) or quasi-particles (phonons). Instead we are handling „dressed" particles[13]. The results of the transformation method will be compared with those of Ref.[6], which were obtained by Green's function techniques.

a) *Nonlinear Canonical Transformations after a Pure Electronic Pre- Transformation*

The aim of our calculations will be the diagonalisation of the initial Hamiltonian (1). In Ref.[6] one of us has shown that the pure electronic part of the

Hamiltonian can be diagonalized exactly. This is achieved by a *linear* unitary transformation of the form

$$a_1 = c_1 A_1 + c_2 A_2, \quad a_2 = -c_2 A_1 + c_1 A_2, \tag{2}$$

where $A_i{}^+$, A_i obey the old anti-commutation relations. The transformed Hamiltonian has the form

$$H = \sum_{i=1}^{2} A_i{}^+ A_i \{\varepsilon_i + c_i{}^2 \sum_j S_j (b_j + b_j{}^+)\} + c_1 c_2 (A_1{}^+ A_2 + A_2{}^+ A_1) \sum_j S_j (b_j + b_j{}^+) + \sum_j \omega_j b_j{}^+ b_j \tag{3}$$

with the reformalized energies

$$\varepsilon_{1/2} = \tfrac{1}{2} (\varepsilon_1 + \varepsilon_2) \mp \tfrac{1}{2} \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4 V^2} \tag{4}$$

and the coefficients

$$c_1 = -\alpha (1 + \alpha^2)^{-1/2}, \quad c_2 = -(1 + \alpha^2)^{-1/2}, \tag{5}$$

where

$$\alpha = (1/2 V) [\varepsilon_2 - \varepsilon_1 + \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + 4 V^2}]. \tag{6}$$

In contrast to Expr. (1) the Hamiltonian (3) has no off-diagonal terms of pure electronic nature. To diagonalize also the electron-phonon interaction part we apply a further canonical transformation which now is nonlinear and defined by

$$\tilde{H} = \exp(-\hat{S}) H \exp(\hat{S}) = H + [H, \hat{S}] + (1/2!) [[H, \hat{S}], \hat{S}] + \cdots. \tag{7}$$

For our system the exponent $\hat{S}$ has the form[14]

$$\hat{S}_a = \sum_{i-1}^{2} c_i{}^2 A_i{}^+ A_i (\sum_j (S_j/\omega_j) (b_j - b_j{}^+))$$

$$- c_1 c_2 \sum_j \frac{S_j}{[(\varepsilon_1 - \varepsilon_2)^2 - \omega_j{}^2]} \{(\varepsilon_1 - \varepsilon_2) (A_1{}^+ A_2 - A_2{}^+ A_1) (b_j + b_j{}^+) + \omega_j (A_1{}^+ A_2 + A_2{}^+ A_1) (b_j - b_j{}^+)\}. \tag{8}$$

This choice of $\hat{S}$ guarantees that in the transformed Hamiltonian no off-diagonal terms of order S_j appear, which is evident from the fact that

$$[H_0, \hat{S}] = -H_I. \tag{9}$$

Here H_0 is the unperturbed diagonal-part of the Hamiltonian, H_I the nondiagonal interaction part of order S_j. An expansion of the commutator-series (7) up to quadratic order in the electron-phonon coupling parameter leads to the Hamiltonian

$$\tilde{H}_a = \left(\bar\varepsilon_1 - c_1{}^4 \sum_j \frac{S_j{}^2}{\omega_j} + c_1{}^2 c_2{}^2 \sum_j \frac{S_j{}^2}{[(\bar\varepsilon_1 - \bar\varepsilon_2)^2 - \omega_j{}^2]} \omega_j \right) A_1{}^+ A_1$$

$$+ \left(\bar\varepsilon_2 - c_2{}^4 \sum_j \frac{S_j{}^2}{\omega_j} + c_1{}^2 c_2{}^2 \sum_j \frac{S_j{}^2}{[(\bar\varepsilon_1 - \bar\varepsilon_2)^2 - \omega_j{}^2]} \omega_j \right) A_2{}^+ A_2 + \sum_j \omega_j b_j{}^+ b_j$$

$$- \tfrac{1}{2} c_1 c_2 (\bar\varepsilon_1 - \bar\varepsilon_2) - (c_1{}^2 - c_2{}^2) (A_1{}^+ A_2 + A_2{}^+ A_1) \sum_j S_j (b_j + b_j{}^+) \sum_i \frac{S_i}{[(\bar\varepsilon_1 - \bar\varepsilon_2)^2 - \omega_i{}^2]} (b_i + b_i{}^2)$$

$$- \tfrac{1}{2} c_1 c_2 (c_1{}^2 c_2{}^2) (A_1{}^+ A_2 - A_2{}^+ A_1) \sum_j S_j (b_j + b_j{}^+) \sum_i \frac{S_i}{[(\bar\varepsilon_1 - \bar\varepsilon_2)^2 - \omega_i{}^2]} \omega_i (b_i - b_i{}^+)$$

$$- c_1 c_2 \sum_j \frac{S_j{}^2}{[(\bar\varepsilon_1 - \bar\varepsilon_2)^2 - \omega_j{}^2]} \omega_j (c_1{}^2 A_1{}^+ A_2 + c_2{}^2 A_2{}^+ A_1)$$

$$- \tfrac{1}{2} c_1 c_2 (c_1{}^2 - c_2{}^2)(A_1{}^+ A_2 - A_2{}^+ A_1) \sum_j S_j (b_j + b_j{}^+) \sum_i (S_i/\omega_i)(b_i - b_i{}^+)$$

$$+ c_1 c_2 (c_1{}^2 A_2{}^+ A_1 + c_2{}^2 A_1{}^+ A_2) \sum_j (S_j{}^2/\omega_j)$$

$$+ c_1{}^2 c_2{}^2 (\bar{\varepsilon}_1 - \bar{\varepsilon}_2)(A_1{}^+ A_1 - A_2{}^+ A_2) \sum_j S_j (b_j + b_j{}^+) \sum_i \frac{S_i}{[(\bar{\varepsilon}_1 - \bar{\varepsilon}_2)^2 - \omega_i{}^2]} (b_i + b_i{}^+) + \cdots . \tag{10}$$

b) *Direct Transformation without Electronic Pre-Transformation*

In this section we will try to diagonalize the initial Hamiltonian (1) by *one single nonlinear* canonical transformation. To this end we again search the exponent $\hat{S}$ of the transformation in such a form that relation (9) is satisfied. We get

$$\hat{S}_b = - \frac{V}{(\varepsilon_1 - \varepsilon_2)}(a_1{}^+ a_2 - a_2{}^+ a_1) + a_1{}^+ a_1 \sum_j \frac{S_j}{\omega_j}(b_j - b_j{}^+) . \tag{11}$$

This operator is much simpler than the one we have used in the previous section. We will see, however, that in the lower terms of the commutator-expansion series (7) the self-energies of section a) are more accurate than the one here. Also, the applicability region of the simpler form (11) is more restricted. For the new Hamiltonian we get

$$\tilde{H}_b = a_1{}^+ a_1 \left(\varepsilon_1 - \sum_j \frac{S_j{}^2}{\omega_j} + \frac{V^2}{\varepsilon_1 - \varepsilon_2}\right) + a_2{}^+ a_2 \left(\varepsilon_2 - \frac{V^2}{\varepsilon_1 - \varepsilon_2}\right) + \sum_j \omega_j b_j{}^+ b_j$$

$$- \frac{V}{2}\left\{(a_1{}^+ a_2 - a_2{}^+ a_1) \sum_j \frac{S_j}{\omega_j}(b_j - b_j{}^+) + \frac{a_1{}^+ a_2 + a_2{}^+ a_1}{\varepsilon_1 - \varepsilon_2} \sum_j S_j(b_j + b_j{}^+)\right\} + \cdots . \tag{12}$$

We will now investigate the behaviour of the transformation (11) in various limiting cases. First we assume that the electron-phonon coupling is negligible, e.g. $S_j \to 0$ for all j. The Hamiltonian (1) then becomes

$$H = \varepsilon_1 a_1{}^+ a_1 + \varepsilon_2 a_2{}^+ a_2 + V(a_1{}^+ a_2 + a_2{}^+ a_1) + \sum_j \omega_j b_j{}^+ b_j$$

and the transformation (11) is given by

$$\hat{S} = - [V/(\varepsilon_1 - \varepsilon_2)](a_1{}^+ a_2 - a_2{}^+ a_1) .$$

After some elementary calculations the expansion (7) can be summed up and we arrive at

$$\tilde{H}_b = \varepsilon_1 a_1{}^+ a_1 + \varepsilon_2 a_2{}^+ a_2 + (a_1{}^+ a_1 - a_2{}^+ a_2) V \left\{\sin\left(2\frac{V}{\varepsilon_1 - \varepsilon_2}\right)\right.$$

$$\left. + 1/(2 V/\varepsilon_1 - \varepsilon_2)\cos\left(2\frac{V}{\varepsilon_1 - \varepsilon_2}\right) - \frac{1}{\left(2\frac{V}{\varepsilon_1 - \varepsilon_2}\right)}\right\}$$

$$+ (a_1{}^+ a_2 + a_2{}^+ a_1) V \left\{\cos\left(2\frac{V}{\varepsilon_1 - \varepsilon_2}\right) - \left[\frac{1}{\left(2\frac{V}{\varepsilon_1 - \varepsilon_2}\right)}\right]\sin\left(2\frac{V}{\varepsilon_1 - \varepsilon_2}\right)\right\} . \tag{13}$$

We compare this result with Hamiltonian (3) by putting $S_j = 0$, $c_1 = 1$ and $c_2 = 0$ [vid. (5) and (6)],

$$\tilde{H}_a = \bar{\varepsilon}_1 A_1{}^+ A_1 + \bar{\varepsilon}_2 A_2{}^+ A_2 + \sum_j \omega_j b_j{}^+ b_j . \tag{14}$$

The eigenvalues of Expr. (13) to the electronically excited states $a_1{}^+|0\rangle$ and $a_2{}^+|0\rangle$ are

$$E_{1/2}^{(b)} = \varepsilon_1 \pm V \left\{\sin\left(2\frac{V}{\varepsilon_1 - \varepsilon_2}\right) + \left[\frac{1}{\left(2\frac{V}{\varepsilon_1 - \varepsilon_2}\right)}\right]\cos\left(2\frac{V}{\varepsilon_1 - \varepsilon_2}\right) - \left[\frac{1}{\left(2\frac{V}{\varepsilon_1 - \varepsilon_2}\right)}\right]\right\} . \tag{15}$$

Assuming V to be very small (in comparison with $|\varepsilon_1 - \varepsilon_2|$) we get

$$E_{1/2}^{(b)} = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \frac{\varepsilon_1 - \varepsilon_2}{2} \cos\left(2\,\frac{V}{\varepsilon_1 - \varepsilon_2}\right). \tag{16b}$$

On the other hand, the eigenvalues of Expr. (14) are given by

$$E_{1/2}^{(a)} = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \frac{\varepsilon_1 - \varepsilon_2}{2} \sqrt{1 + \left(\frac{2\,V}{\varepsilon_1 - \varepsilon_2}\right)^2}. \tag{16a}$$

Since we have assumed $|2\,V/(\varepsilon_1 - \varepsilon_2)| \ll 1$ the Eqs. (16a) and (16b) coincide. This was to be expected, since transformation (11) satisfies relation (9), i.e. the transformation is good both in the region of small electron-electron and small electron-phonon coupling. Second we consider the limiting case, when V asymptotically goes to infinity. From Eq. (15) we get

$$E_{1/2}^{(b)} = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm V \sin\left(2\,\frac{V}{\varepsilon_1 - \varepsilon_2}\right) \pm \frac{\varepsilon_1 - \varepsilon_2}{2} \cos\left(2\,\frac{V}{\varepsilon_1 - \varepsilon_2}\right), \tag{17b}$$

where the second and the last term are of highly fluctuating nature. The energies of the exactly transformed Hamiltonian are given by

$$E_{1/2}^{(a)} = \frac{\varepsilon_1 + \varepsilon_2}{2} \mp V \sqrt{1 + \left(\frac{\varepsilon_1 - \varepsilon_2}{2\,V}\right)^2}. \tag{17a}$$

This expression contains no fluctuating terms. Comparing (17a) and (17b), it is to be seen that transformation (11) leads to wrong results in the limit of strong electron-electron interactions.

Third we neglect the pure electronic interaction ($V \equiv 0$) and deal only with the electron-phonon coupling. In this case the Hamiltonian assumes the simple form

$$H = \varepsilon_1 a_1^+ a_1 + \varepsilon_2 a_2^+ a_2 + a_1^+ a_1 \sum_j S_j (b_j + b_j^+) + \sum_j \omega_j b_j^+ b_j \tag{18}$$

and the transformation operator is given by[15]

$$\hat{S} = a_1^+ a_1 \sum_j (S_j/\omega_j)(b_j - b_j^+). \tag{19}$$

It diagonalizes the Hamiltonian exactly

$$\tilde{H} = a_1^+ a_1 \left(\varepsilon_1 - \sum_j (S_j^2/\omega_j)\right) + \varepsilon_2 a_2^+ a_2 + \sum_j \omega_j b_j^+ b_j. \tag{20}$$

If we look at Eq. (8) under the same assumptions, i.e. if we assume that V goes to 0, c_1 to -1 and c_2 to 0, it will be identical with (19).

This discussion has shown us that the direct transformation (11) can be applied in the regions of small electron-electron coupling both for weak and strong electron-phonon coupling. In the case of strong electron-electron interactions transformation (11) leads to wrong results.

The transformations of Sect. a) seems to be applicable in all regions. If both coupling parameters are strong, we cannot discuss it in the same way we have done above. But there is some indication that for arbitrary V and S_j it is quasi-exact in the sense of Refs.[9,10]. Therefore we will compare the self-energies derived with this transformation with

the results derived in Ref.[6] by Green's function techniques.

3. Self-Energies

Employing the Hamiltonian (10) we arrive at

$$E_1 = \langle \Omega \rangle_{e1}^{\text{II}} + \sum_j \omega_j n_j, \tag{21a}$$

$$E_2 = \langle \Omega \rangle_{e2}^{\text{II}} + \sum_j \omega_j n_j \tag{21b}$$

with the abbreviations

$$\langle \Omega \rangle_{e1}^{\text{II}} = \varepsilon_1 - c_1^4 \sum_j \frac{S_j^2}{\omega_j} + c_1^2 c_2^2 \sum_j \frac{S_j^2}{(\varepsilon_1 - \varepsilon_2) - \omega_j} \tag{22a}$$

$$\langle \Omega \rangle_{e2}^{II} = \bar{\varepsilon}_2 - c_2{}^4 \sum_j \frac{S_j{}^2}{\omega_j} - c_1{}^2 c_2{}^2 \sum_j \frac{S_j{}^2}{(\bar{\varepsilon}_1 - \bar{\varepsilon}_2) + \omega_j}$$

$$(22\,\mathrm{b})$$

These results are to be compared with the ones derived in Ref.[6] with the help of the Green's function method.

There the Green's function hierarchy has been cut short already in lowest order. The spectral function at $T \equiv 0$ is given by

$$- (I(E)/M_1{}^2) = [E - \varepsilon_2 + p\,V]^2 \,(\varphi(E)/\pi\,D(E)),$$

$$(23)$$

and the singularities of this expression lead to the self-energies of elementary excitations o° the coupled system. $D(E)$ is defined by

$$D(E) = [(E - \bar{\varepsilon}_1)(E - \bar{\varepsilon}_2)$$
$$- f(E)\,[c_1{}^2(E - \bar{\varepsilon}_2) + c_2{}^2(E - \bar{\varepsilon}_1)]]^2 \qquad (24)$$
$$+ \varphi(E)\,[c_1{}^2(E - \bar{\varepsilon}_2) + c_2{}^2(E - \bar{\varepsilon}_1)]^2 .$$

For further definitions see Ref.[6].

We note in agreement with Ref.[6] a phonon-shift of the selfenergies depending on the electronic interaction between the two impurity centres. The analysis of the limiting case of vanishing electron-electron interaction $(V \to 0)$ shows that in this coupling region expression (23) leads not to the correct self-energy shifts. However, these are well-known [see (20)] and with $c_1 = -1$ and $c_2 = 0$ we get the exact results from (22 a) and (22 b) as we have demonstrated earlier. This short-coming of formula (23) is due to the low-order-factorisation of the Green's function hierarchy, where the phonon-shift is only partially accounted for.

More accurate calculations show a further defect of formula (23), consisting in the existence of an energy gap in the absorption spectrum. The gap arises between the absorption line of the vibrationally non-coupled impurity center and the phonon-wings, which will be accumulated to this absorption line via the electronic center-center interaction. This defect does not exist, when the excitation line of the impurity center lies in the continuous part of the spectrum.

As discussed in the previous sections in all these cases the self-energies derived with the canonical-transformation-technique show the correct behaviour.

Summary

The physical arrangement of two electronically coupled impurity centers, one of which interacts with the vibrations of the surrounding crystal, is of great interest, since systems of this sort are Fano systems[1-4, 6] exhibiting resonance or antiresonance behaviour.

One of us (N. N. K.)[6] has calculated this system by use of Green's function techniques, but these results have two shortcomings. First, the self-energy shifts are not correct in the limit of weak electronic center-center interaction, and second, an energy gap exists in the absorption spectrum between the excitation line of the impurity center, which is not coupled to the vibrations, and the phonon part of the spectrum.

Since in our system the adiabatic approximation is not applicable, we have utilized the method of non-linear canonical transformations to calculate the self-energy shifts. The regions of applicability have been obtained by considering two different non-linear transformations and comparing the results of both. We have demonstrated that our method is fairly good in all coupling limits.

The self-energies were calculated up to second order in the coupling parameters and the results were compared with those of the Green's function method. The errors arising in the formula derived by Green's function techniques do not occur in the canonical transformation results.

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