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INVESTIGATION OF MODEL SYSTEMS WITH NON-ADIABATIC ELECTRON-PHONON INTERACTION

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Abstract - We consider the eigenvalue problem of an electronic two site system with intersite coupling interacting locally with two vibrational modes. By operator transformations the eigenvalue problem is reduced to that of an electronic two level system coupled to a single vibrational mode via dispersive and transitive couplings. The eigensolutions are determined numerically using scalar and matrix continued fraction methods.

I - INTRODUCTION

The interaction between electronic and vibrational degrees of freedom is of importance in many fields of solid state physics. It plays a crucial role in determining e.g. optical and ESR line shapes and their temperature dependence /1,2/, vibrational relaxations and non-radiative transitions /3,4/, phonon assisted tunneling processes /5,6/ as well as energy transfer mechanisms or charge transport problems /7,8/.

For the treatment of this kind of problems many approximation schemes have been developed /9-12/ which are valid in limiting cases in which a perturbational expansion in powers of a small parameter is possible. However, if all relevant coupling parameters are of the same order of magnitude, none of these approximations can be used.

Recently we have investigated such a situation for an electronic two-level system which is coupled to one vibrational mode. This simple but non-trivial coupling was used by many authors, e.g. /13,14/, for the discussion of different theoretical approaches, such as static and adiabatic decoupling procedures or transformation techniques. Recently, for special parameter combinations isolated exact solutions could be found by a treatment using Bargman's Hilbert space /15/. In our treatment we have used scalar as well as matrix continued fraction methods and showed that exact numerical eigensolutions for this system may be obtained without too much effort and that previous analytical approximations /11,12/ may be rederived and improved in a systematic manner.

II - MODEL HAMILTONIAN AND NUMERICAL PROCEDURE

The total Hamiltonian of our theoretical model system is given by

$$H_{\text{tot}} = \bar{\epsilon}(A_2^+A_2 - A_1^+A_1) + T(A_1^+A_2 + A_2^+A_1) + \sum_n B_n^+B_n + \sum_n g(B_n^+ + B_n)A_n^+A_n. \quad (\text{II.1})$$

A_n^+ and A_n are creation and annihilation operators, respectively, for electrons at site n and B_n^+ and B_n are Bose operators for vibrational quanta of an oscillator localized at site n . $\bar{\epsilon}_n$ describes the energy difference of the electron between sites 1 and 2, T its transfer matrix element between these sites, and g is the coupling strength between electrons and vibrations. All quantities are measured in units of the vibrational energy quantum.

The relation $\sum_n A_n^+A_n = 1$ holds, because we are considering only one electron either on site 1 or on site 2. To simplify the Hamiltonian we introduce new operators for the vibrations

$$B_1 = 2^{-\frac{1}{2}}(b_1 - b_2), \quad B_2 = 2^{-\frac{1}{2}}(b_1 + b_2) \quad (\text{II.2})$$

and for the electrons

$$A_1 = A_+ \sin\vartheta + A_- \cos\vartheta, \quad A_2 = A_+ \cos\vartheta - A_- \sin\vartheta. \quad (\text{II.3})$$

It is furthermore convenient to express the Hamiltonian in terms of spin $\frac{1}{2}$ operators satisfying the usual commutation relations ($[\sigma_x, \sigma_y] = i\sigma_z$; $[\sigma_x, \sigma_y]_+ \equiv 0$) and being defined by

$$\sigma_x = \frac{1}{2}(A_+^+A_- + A_-^+A_+), \quad \sigma_y = \frac{1}{2i}(A_+^+A_- - A_-^+A_+) \quad (\text{II.4})$$

$$\sigma_z = \frac{1}{2}(A_+^+A_+ - A_-^+A_-).$$

With these transformations the Hamiltonian then splits into two parts, $H = H_1 + H_2$, with H_1 containing only vibrational degrees of freedom, $H_1 = b_1^+b_2 + \hat{g}(b_1^+ + b_1)$, and describing a displaced harmonic oscillator. The interesting part H_2 is given by ($b \equiv b_2$)

$$H_2 = \epsilon\sigma_z + \Delta\sigma_x(b^+ + b) + D\sigma_z(b^+ + b) + b^+b. \quad (\text{II.5})$$

The connections between the parameters in (II.5) and those in (II.1) are given by

$$\epsilon = 2(\bar{\epsilon}^2 + T^2)^{1/2}, \quad \Delta = -4\hat{g}T/\epsilon, \quad D = 4\hat{g}\bar{\epsilon}/\epsilon, \quad \hat{g} = \frac{g}{\sqrt{2}} \quad (\text{II.6})$$

and the transformation (II.3) is determined by

$$\sin 2\vartheta = 2T/\epsilon; \quad \cos 2\vartheta = 2\bar{\epsilon}/\epsilon. \quad (\text{II.7})$$

The eigenvectors of the total Hamiltonian factorize into a product of state vectors corresponding to H_1 and H_2 and those of H_2 are represented in terms of eigenstates of σ_z by

$$\psi = \chi_+|+\rangle + \chi_-|-\rangle. \quad (\text{II.8})$$

The expansion coefficients χ_+ and χ_- depend on the vibrational degrees of freedom and are expressed by harmonic oscillator functions

$$\chi_- = \sum_n \beta_n \varphi_n, \quad \chi_+ = \sum_n \gamma_n \varphi_n. \quad (\text{II.9})$$

Introducing the column vectors

$$\psi_n = \begin{pmatrix} \gamma_n \\ \beta_n \end{pmatrix} \quad (\text{II.10})$$

the eigenvalue equation of H_2 may be written in the following form

$$Q_n^- \psi_{n-1} + [Q_n - E I] \psi_n + Q_n^+ \psi_{n+1} = 0. \quad (\text{II.11})$$

E is the eigenvalue, I the 2-dimensional unit matrix, and we have used the notation /16/:

$$Q_n^- = \sqrt{n} (D\sigma_z + \Delta\sigma_x), \quad Q_n = n I + \epsilon\sigma_z, \quad Q_n^+ = \sqrt{n+1} (D\sigma_z + \Delta\sigma_x). \quad (\text{II.12})$$

Introducing the transfer matrices S_n^+ and S_n^- by

$$\psi_{n+1} = S_n^+ \psi_n, \quad \psi_{n-1} = S_n^- \psi_n, \quad (\text{II.13})$$

we end up with the following homogeneous set of equations whose determinant has to vanish in order to guarantee non-trivial eigensolutions:

$$[Q_n^- S_n^- + (Q_n - E I) + Q_n^+ S_n^+] \psi_n = 0. \quad (\text{II.14})$$

To evaluate the determinant the transfer matrices must be known. From (II.11,13) we obtain recurrence relations which allow the following continued fraction representation for S_m^+ , S_m^- :

$$S_m^+ = [EI - Q_{m+1} - Q_{m+1}^+ [EI - Q_{m+2} - Q_{m+2}^+ [EI - Q_{m+3} - Q_{m+3}^+ \dots []^{-1} \dots]^{-1} Q_{m+3}^-]^{-1} Q_{m+2}^-]^{-1} Q_{m+1}^- \quad (\text{II.15})$$

$$S_m^- = [EI - Q_{m-1} - Q_{m-1}^- [EI - Q_{m-2} - Q_{m-2}^- [EI - Q_{m-3} - \dots - Q_1^- [EI - Q_0]^{-1} Q_0^+ \dots]^{-1} Q_{m-3}^+]^{-1} Q_{m-2}^+]^{-1} Q_{m-1}^+ \quad (\text{II.16})$$

Because of the physical structure of our problem (existence of a lowest energy eigenvalue) S_m^- is a finite continued fraction whereas S_m^+ is infinite and has to be approximated by breaking off (II.15) in an appropriate manner. The eigenvalues are then calculated from (II.14) and the eigenvectors from (II.13).

III - RESULTS

To solve the eigenvalue problem of H_2 (II.5) numerically /17/ we started from the homogeneous system of equations (II.14) with a fixed index $n = M$. Via (II.12) M defines the matrices Q_M^- , Q_M and Q_M^+ of dimension 2, and it also gives the starting point for the iteration procedure which determines S_M^+ and S_M^- . As mentioned in sec. II., S_M^- is a finite matrix continued fraction (MCF) which can be calculated without approximation (we confined M to values ≤ 20). S_M^+ is an infinite MCF which is approximated by a finite one of length K (by setting $S_{M+K}^+ = 0$). The two integers K and M can be chosen freely. The value of K determines the accuracy of the calculation and the M value defines the "window" in which this numerical procedure allows to determine the eigenvalues most easily. The latter are calculated from the condition

$$F(E) = \text{Det } B(E) = \text{Det}[Q_M^- S_M^- + (Q_M - EI) + Q_M^+ S_M^+] = 0 \quad (\text{III.1})$$

In evaluating (III.1) one has to take care of some numerical facts. For the calculation of S_M^+ and S_M^- numerous matrix summations, multiplications and inversions are

necessary. The multiplications and summations can be treated very accurately and rapidly by a computer. Matrix inversions, however, are more difficult to handle, because from a mathematical point of view a non-singular behaviour of the matrices is required. Nevertheless, if the values of these determinants are $\neq 0$ but very small, the numerical treatment must be controlled carefully to avoid computer overflow.

Fig. 1 - $F(E)$ for $\epsilon = 1$, $\Delta = 2$, $D = 0$, $K = 20$, $M = 1$.

Fig. 2 - $F(E)$ for $\epsilon = 1$, $\Delta = 2$, $D = 0$, $K = 20$, $M = 10$.

Fig. 3 - Energy eigenvalues E for different approximations: (a) MCF: dots (b) approximation of $/12/$:----- (c) numerical diagonalization of a 100by100 matrix: -----. The parameter values are $\epsilon = 4$, $0 < \Delta < 3$, $D = 2/2$, $K = 10$, $M = 0$.

K	E
1	-1.193527083396909
2	-1.494895277023313
4	-1.682490510940550
6	-1.705983490943907
10	-1.707425072193144
15	-1.707425849437712
20	-1.707425849437712
30	-1.707425849437712
50	-1.707425849437712

Table 1 - Lowest energy eigenvalue for $\epsilon = \Delta = 1$ and $D = 2$, using several values for K .

These considerations show that $F(E)$ can be a strongly fluctuating function as can be seen in figs. 1 and 2. In the figures the parameters ϵ , Δ , D and K are the same. We have $M = 1$ in fig. 1 and $M = 10$ in fig. 2. In the behaviour of $F(E)$ different regions can be distinguished. In one region, apart from some poles, $F(E)$ is a continuous function and the energy eigenvalues can be found easily from $F(E) = 0$. In other regions $F(E)$ behaves in an irregular manner, poles and ordinary zeros cannot be separated. Comparing both figures one sees that the region which is favourable for the search of energy eigenvalues is shifting with M . With increasing values of M all eigenvalues of the system can be calculated. The accuracy of the method in dependence of K can be seen in table 1 where the ground state energy is given. The energy value obtained for $K = 10$ coincides up to 10^{-6} with the one determined for $K = 20$. Fig. 3 gives energy eigenvalues as a function of Δ using various approximation schemes.

IV - CONCLUDING REMARKS

We have shown that continued fractions allow to determine numerically exact eigen-solutions in a convenient manner for systems, which cannot be solved analytically. Additional results, especially the comparison with analytic approximations and eigensolutions for an electronic two-level system coupled to two vibrational modes, have been obtained and are contained in more detailed publications /18/.

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