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ON A CLASS OF SQUEEZED EXCITED STATES IN EXCITON–PHONON AND JAHN–TELLER SYSTEMS ('EXOTIC STATES')

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Abstract. By employing the Fulton–Gouterman (FG) transformation recently a nonconventional type of excited ('exotic') states in exciton–phonon systems was found, which is characterized by a stiffening of the phonon subsystem. It is shown that the phonon part for these nonconventional exciton–phonon states is well described by squeezed oscillatory functional forms. This can be understood analytically by subjecting the FG Hamiltonian to a Fröhlich-type unitary transformation. By applying the adiabatic approximation it is shown that the nonconventional states correspond to the solutions which pertain to the upper adiabatic potential. The accuracy of the adiabatic approximation, however, is remarkably below that of the Fröhlich-type and variational approaches.

Key words: exciton–phonon coupling, squeezed states.

1. INTRODUCTION

In a previous work excited exciton–phonon states of a new type ('exotic states') have been found numerically [1]. The most pronounced feature of these solutions with regard to the vibrational part $\phi(Q)$ of the wave function (Q = vibrational coordinates) is their compressed, practically undisplaced form ('squeezed states') indicating a liberation of the exciton from its tendency to self-trapping.

The frame of the present work is the Fulton–Gouterman transformation [2, 3], which exactly diagonalizes the original Hamiltonian in the excitonic subspace. The evolving Schrödinger-like equations (FG equations) for the oscillatory part of wave functions are subsequently handled by two alternate sequences of two unitary transformations, respectively.

In the first of these two alternate approaches, a variational ansatz is constructed by means of a unitary product transformation which aims to simulate the two dominant antagonistic tendencies [1] in the Fulton–Gouterman Hamiltonian. In the second approach, a Fröhlich–type transformation [4] is used for a further transcription of the FG Hamiltonian which then explicitly displays a stiffening of the effective oscillatory potential. By means of this, direct analytical evidence is given that squeezed oscillatory solutions pertain to this transformed Hamiltonian.

These two approaches are compared with the adiabatic approximation. We find that they yield remarkably better results than the adiabatic approximation, where nonconventional states are described by the solutions pertaining to the upper adiabatic potential.

2. THE FULTON–GOUTERMAN TRANSFORMATION

The archetype exciton–phonon model (dimer),

$$H = \frac{\Omega}{2}\{(P^2+Q^2) - T(|l\rangle\langle r| + |r\rangle\langle l|) + DQ(|l\rangle\langle l| - |r\rangle\langle r|)\}, \quad (1)$$

describes a two-level exciton system interacting linearly with a harmonic oscillator of frequency Ω. T denotes the excitonic transfer and D, the exciton–phonon coupling constant. We introduce the reflection operator R

$$R^{-1} = R^{\dagger}, \quad R^{\dagger} = R, \quad R = R_x R_Q,$$
$$R_x|l\rangle = |r\rangle, \quad R_x|r\rangle = |l\rangle, \quad (2)$$
$$R_Q Q = -QR_Q, \quad R_Q P = -PR_Q,$$

where R_x is the excitonic and R_Q, the oscillatory reflection operator. By means of the unitary operator

$$U_{FG} = \frac{1}{\sqrt{2}}\{|l\rangle\langle l| + |l\rangle\langle r| + (|r\rangle\langle l| - |r\rangle\langle r|)R_Q\} \quad (3)$$

Hamiltonian (1) is diagonalized in the excitonic subspace (Fulton–Gouterman transformation (FGT))

$$U_{FG}^{\dagger} H U_{FG} = |l\rangle\langle l| H_{FG}^{(p=+1)} + |r\rangle\langle r| H_{FG}^{(p=-1)}. \quad (4)$$

In this manner the problem is reduced to the solution of purely oscillatory Schrödinger-like equations (FG equations) of the form $H_{FG}^{(p)}\phi^{(p)} = E^{(p)}\phi^{(p)}$ or

$$\frac{\Omega}{2}\{(P^2+Q^2)+\underbrace{DQ}_{\substack{\text{self-trapping}\\ \text{tendency}}}-\underbrace{pTR_Q}_{\substack{\text{anti-self-trapping}\\ \text{tendency}}}\}\phi_n^{(p)}(Q)=E_n^{(p)}\phi_n^{(p)}(Q). \quad (5)$$

The total wave function of the original Hamiltonian then reads

$$|\psi_n^{(p)}\rangle=\frac{1}{\sqrt{2}}\left[\,|l\rangle\phi_n^{(p)}(Q)+p\,|r\rangle R_Q\phi_n^{(p)}(Q)\,\right]. \quad (6)$$

The Fulton–Gouterman Hamiltonian exhibits two antagonistic tendencies ('displacement' and 'reflection' or likewise 'self-trapping' and 'anti-self-trapping') which in their counteraction generate different species of wave functions in different energy regions. This is exemplified in Fig. 1, in which the numerically found solutions of the FG equation for $p=-1$ are displayed. For low energies we find a species of FG wave functions with an effective broadening in Q space, tantamount to a softening of the phonon subspace. Each of these wave functions is separated into two spatial parts which are mirror images of each other with different weight. In addition to these 'conventional' types of states there is another species which makes its appearance at higher energies only ($n=54$, 57 in Fig. 1). For these states the interplay of the antagonistic tendencies is such that there is only a very small self-trapping combined with a narrowing of the spatial extension of the wave functions. This leads to a hardening of the phonon subsystem. We may denote these nonconventional states as 'exotic' or as squeezed. As described in [1], the existence of these states provides a good basis for the explanation of the retarded luminescence phenomenon. Specifically the lowest states of this sequence for each parity adopts the role of a bottleneck for the time evolution of luminescence.

3. SQUEEZED DISPLACED TRIAL FUNCTION

The shape of the lowest nonconventional state in Fig. 1 suggests a trial ansatz, which is a displaced and squeezed version of the ground state wave function of the harmonic oscillator $\phi_0(Q)=\pi^{-1/4}\exp(-Q^2/2)$. It can be constructed by a product of two unitary operators

$$U_d=\exp(idP),\quad U_s=\exp[-is(PQ+QP)] \quad (7)$$

such that

$$\phi(Q)=U_sU_d\phi_0(Q). \quad (8)$$

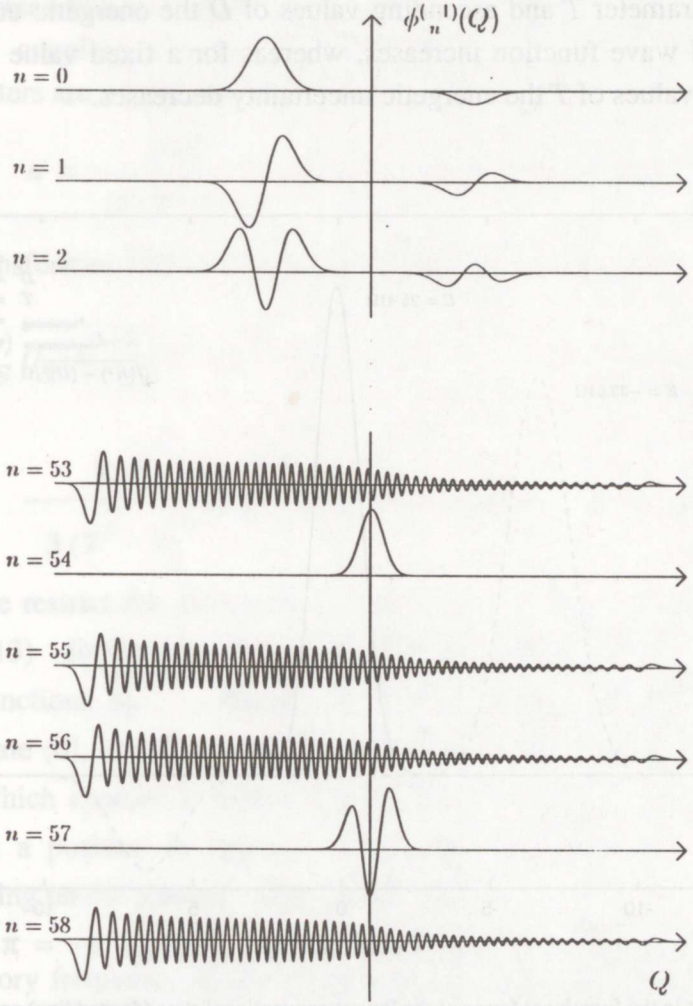

Fig. 1. Eigenfunctions of FG equation (5) for $p = -1$, $D = 15$, $T = 50$. All functions below $n = 54$ display an odd number of nodes, whereas the eigenfunctions $n = 54$ and $n = 57$ display an even number of nodes. For $p = +1$ the situation is reversed.

With

$$U_d f(Q) = f(Q+d), \quad U_s f(Q) = e^{-s} f(e^{-2s} Q) \tag{9}$$

the variational ansatz in Q space assumes the form

$$\phi(Q) = \pi^{-1/4} e^{-s} \exp[-(e^{-2s} Q + d)^2/2] \equiv \phi(d, s) . \tag{10}$$

The two trial parameters, d and s, are calculated by minimalizing the energy uncertainty, $\delta(\langle H^2 \rangle - \langle H \rangle^2) = 0$. If this is done, the wave function assumes the form which is depicted in Fig. 2. Within the drawing discernibility the result coincides with the numerically exact result for the chosen model parameters $D = 15$ and $T = 50$. The energetic uncertainty

of the trial state is $\sqrt{\langle H^2\rangle - \langle H\rangle^2} = 0.04\ \Omega$. For a fixed value of the transfer parameter T and ascending values of D the energetic uncertainty of the trial wave function increases, whereas for a fixed value of D and ascending values of T the energetic uncertainty decreases.

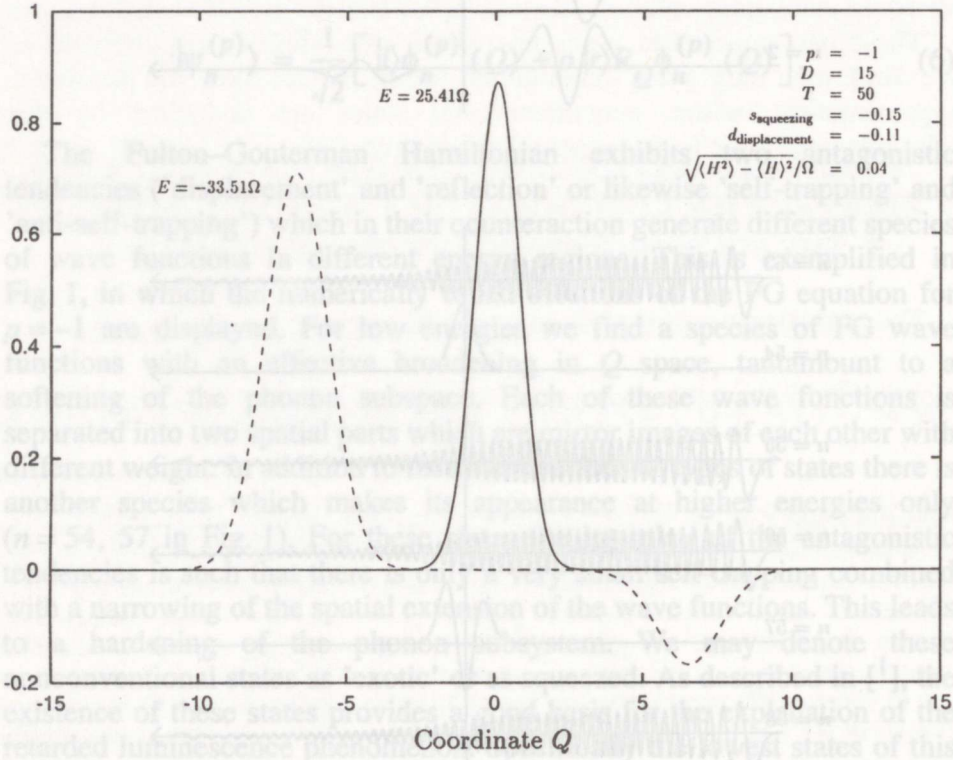

Fig. 2. Contrast in the functional forms of the lowest conventional state (dashed line) and the lowest nonconventional state ('exotic', solid line), represented by optimized trial wave function (10), which practically coincides with the numerically exact result. Parameter set: $p = -1$, $D = 15$, $T = 50$.

4. FRÖHLICH-TYPE TRANSFORMATION

Perhaps the most famous of all unitary transformations is the Fröhlich transformation [4] with its application in the field of superconductivity, where it is used to establish the BCS Hamiltonian. The transformation can also be applied to our exciton–phonon Hamiltonian (1). In this case the transformation operator is of a mixed exciton–phonon nature. However, it is more favourable to proceed first to the Fulton–Gouterman frame before applying the Fröhlich transformation. For that purpose, the original form of the transformation operator has to be transcribed into the Fulton–Gouterman frame. Its form then pertains only to the phonon subspace:

$$U_F = \exp(S_F), \quad S_F = aQR_Q + ibQ + cPR_Q + idP. \qquad (11)$$

The parameters a to d can be chosen in such a manner that in the transformed Fulton–Gouterman Hamiltonian, $U_F^{\dagger} H_{FG}^{(p)} U_F$, all terms linear in the coupling constant D disappear ('Fröhlich condition'). The parameters are then given by

$$a = -\frac{pTD}{2(T^2-1)}, \quad d = -\frac{D}{2(T^2-1)}, \quad b = c = 0. \tag{12}$$

The transformed Fulton–Gouterman Hamiltonian assumes the form

$$U_F^{\dagger} H_{FG}^{(p)} U_F = \frac{\Omega}{2}\left\{P^2 + Q^2 - pTR_Q + \frac{D^2}{4(T^2-1)} - p\frac{TD^2}{2(T^2-1)}Q^2 R_Q - \right.$$

$$\left. -\frac{TD^3}{3(T^2-1)^2}(TQ^3 + pQR_Q + ipQ^2 PR_Q)\right\} + O(D^4). \tag{13}$$

If we restrict the discussion to the terms up to the second order in D, Expr. (13) displays a reflection symmetry and has parity-ordered eigenfunctions $\tilde{\phi}_F^{(p,\pi)}$, where p as hitherto pertains to the parity of full eigenstate (6), and $\pi = \pm 1$ is the artificial parity of the eigenfunction of (13), which appears if anharmonic terms are neglected. Then the $Q^2 R_Q$ term is a positive or negative correction to the undisturbed Q^2 term, depending on the product of the parities p and π.

For $\pi = -p$, the $Q^2 R_Q$ term in (13) generates an increased effective oscillatory frequency which corresponds to an elastic hardening and to a squeezing of the oscillatory wave functions. This situation pertains to unconventional ('exotic') states.

For $\pi = +p$ on the other hand, the $Q^2 R_Q$ term produces an elastic softening and pertains to the states of conventional nature (broadened in Q space). It is worth noting that in this case the correction term tends to compensate the undisturbed Q^2 term and may produce a harmonic instability. In this range of parameters the functional form of the conventional states turns from a one-peak (anti-squeezed-broadened) form to a one with two peaks (mirror images with different weight).

Thus, for a fixed value of p we find two distinct sequences of eigenstates, depending on their symmetry properties in Q space. For $p = -1$ the symmetric wave functions ($\pi = +1$, even number of nodes) display squeezing and their energetic spacing is increased. The antisymmetric eigenstates ($\pi = -1$, odd number of nodes) are spatially broadened and energetically compressed. For $p = +1$ the situation is reversed.

Neglecting the anharmonic terms in Hamiltonian (13), the lowest state for $p = +1$ is a squeezed oscillatory function

$$\tilde{\phi}_F^{(p=-1,\,\pi=+1)} = (\pi\Omega/\tilde{\Omega})^{-1/4} \exp[-(\tilde{\Omega}/\Omega)\,Q^2/2\,],$$

$$\tilde{\Omega} = \Omega\{1 + [TD^2]/[2\,(T^2-1)]\}^{1/2} \qquad (14)$$

and, reversing the Fröhlich transformation, we find a Fulton–Gouterman wave function which for $D = 15$ and $T = 50$ practically falls onto those drawn in Fig. 2 and cannot be discerned separately. The nondiagonality of this wave function can be estimated by calculating the variance of the terms of (13), which are of the third order in the coupling D. In Fig. 3 we compare the results obtained by different approaches for energy uncertainties.

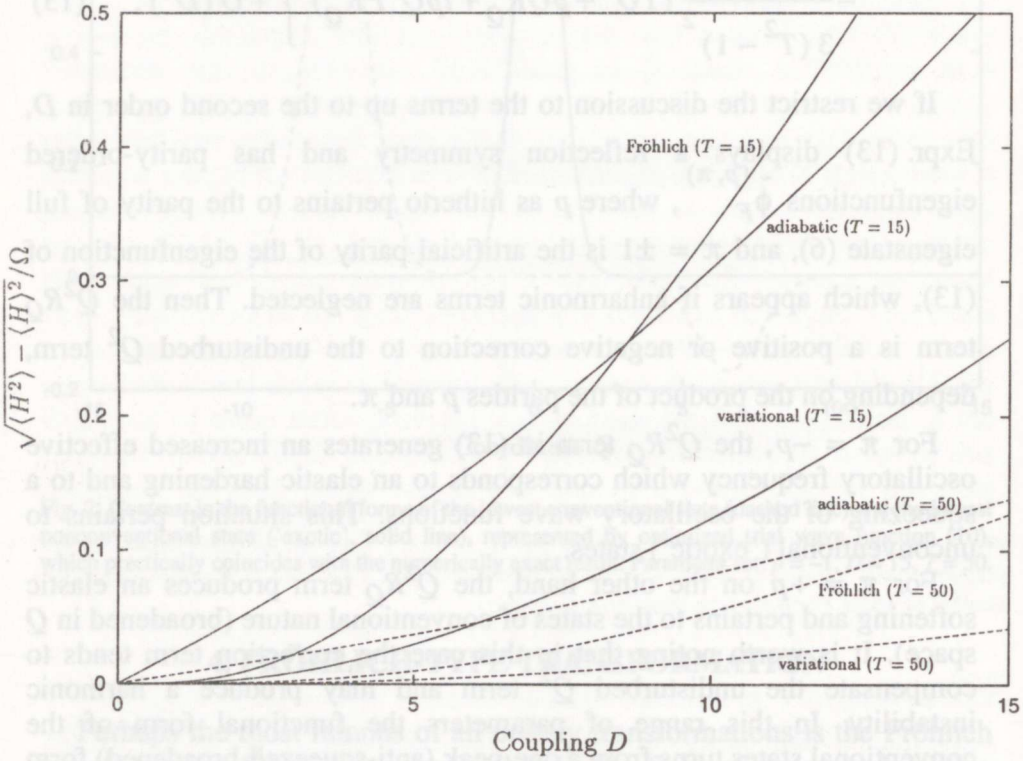

Fig. 3. Energy uncertainty of variational ansatz (10), the approximate wave function deduced by the Fröhlich-type transformation and adiabatic wave function (15) for $p = -1$. Solid line: $T = 15$, dashed line: $T = 50$.

5. ADIABATIC APPROXIMATION

We also demonstrate the description of the 'exotic' states in the frame of adiabatic approximation. In this approach unconventional states appear as solutions pertaining to the upper adiabatic potential.

In the adiabatic approximation the total wave function $|\Psi_{ad}(x, Q)\rangle$ is written as a product of the form

$$|\Psi_{ad}(x, Q)\rangle = |\chi(x, Q)\rangle\,|\Phi(Q)\rangle, \tag{15}$$

where the Q-dependent exciton state $|\chi(x, Q)\rangle$ satisfies the 'adiabatic' eigenvalue equation

$$\frac{\Omega}{2}\left\{-T\left(|l\rangle\langle r| + |r\rangle\langle l|\right) + DQ\left(|l\rangle\langle l| - |r\rangle\langle r|\right)\right\}|\chi(x, Q)\rangle = \\ = W(Q)\,|\chi(x, Q)\rangle. \tag{16}$$

This equation is solved by

$$|\chi_c(x, Q)\rangle = \sin\eta(Q)\cdot|l\rangle + \cos\eta(Q)\cdot|r\rangle, \tag{17}$$

$$|\chi_u(x, Q)\rangle = \cos\eta(Q)\cdot|l\rangle - \sin\eta(Q)\cdot|r\rangle, \tag{18}$$

whereby

$$\sin\eta(Q) = \sqrt{\frac{1}{2} - \frac{DQ}{2\sqrt{T^2 + D^2Q^2}}}, \\ \cos\eta(Q) = \sqrt{\frac{1}{2} + \frac{DQ}{2\sqrt{T^2 + D^2Q^2}}}. \tag{19}$$

The Q-dependent eigenvalues $W(Q)$ are given by

$$W_{c,u}(Q) = \mp\frac{\Omega}{2}\sqrt{T^2 + D^2Q^2}, \tag{20}$$

where to the minus sign we assign the subscript c (conventional) and to the plus sign, the subscript u (unconventional). The oscillatory function $|\Phi(Q)\rangle$ is then defined by the equation

$$\left(\frac{\Omega}{2}P^2 + V^{ad}_{c,u}(Q)\right)|\Phi_{c,u}(Q)\rangle = \tilde{E}^{ad}\,|\Phi_{c,u}(Q)\rangle \tag{21}$$

with the adiabatic potential

$$V^{ad}_{c,u}(Q) = \frac{\Omega}{2}Q^2 + W_{c,u}(Q). \tag{22}$$

Due to the inversion symmetry of $V^{ad}_{c,u}(Q)$, Eq. (21) has the parity-ordered eigenfunctions $|\Phi^{(\pi)}_{c,u}(Q)\rangle$;

$$R_Q\,|\Phi^{(\pi)}_{c,u}(Q)\rangle = \pi\,|\Phi^{\pi}_{c,u}(Q)\rangle, \quad \pi = \pm 1. \tag{23}$$

In Fig. 4 the potentials $V_{c,u}^{ad}(Q)$ are depicted for various values of D and a fixed T. It is evident that for $D > 0$ the upper adiabatic potential $V_u^{ad}(Q)$ corresponds to a compressed parabola and its eigenfunctions can be roughly approximated by squeezed versions of harmonic oscillator wave functions.

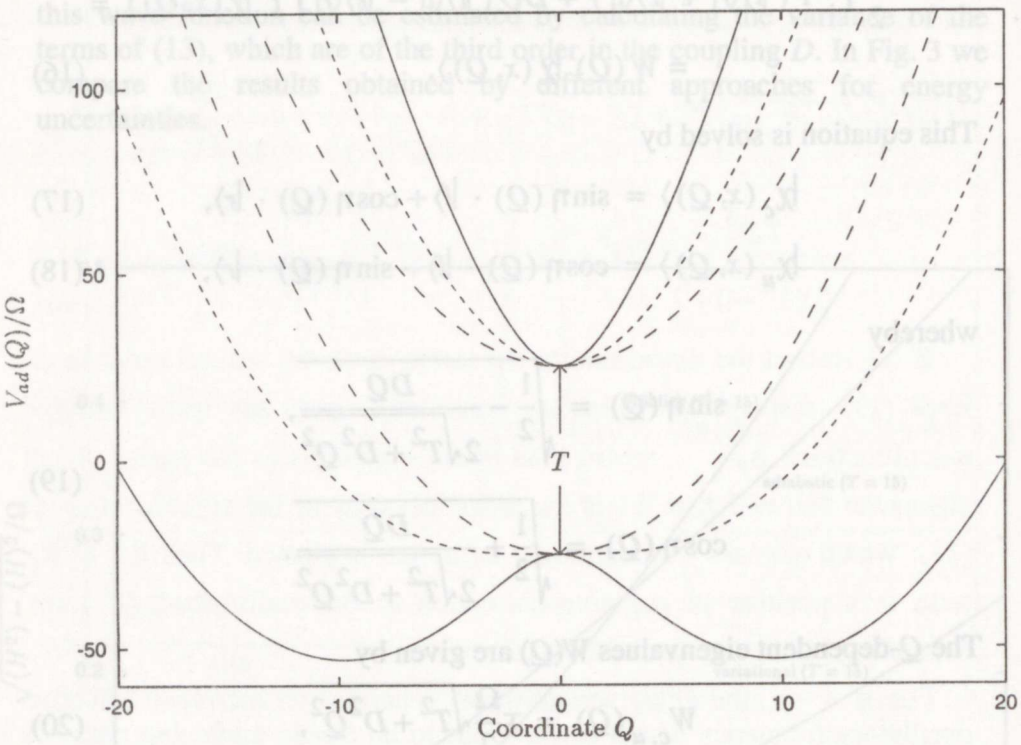

Fig. 4. Adiabatic potentials $V_c^{ad}(Q)$ and $V_u^{ad}(Q)$ (see Eq. (22)) for fixed transfer $T = 50$ and the coupling constants $D = 0$ (long dashes), $D = 10$ (short dashes), $D = 20$ (solid line). For finite D the upper adiabatic potential approximately corresponds to a squeezed parabola and its squeezed eigenstates are connected with nonconventional states.

From Eq. (19) we note the symmetry relation $R_Q \sin\eta(Q) = \cos\eta(Q) R_Q$. Then a comparison of total wave function (6) and adiabatic ansatz (15) with (18) reveals that the exact FG wave functions $|\phi^{(p)}\rangle$ for the unconventional states can be approximated by the adiabatic oscillatory wave functions $|\Phi_u^{(\pi)}(Q)\rangle$ via

$$\frac{1}{\sqrt{2}} |\phi^{(p=-\pi)}\rangle \approx \cos\eta(Q) \cdot |\Phi_u^{(\pi)}(Q)\rangle. \qquad (24)$$

The connection between the parity p of the exact total wave function (cf. Eq. (6)) and the parity of the adiabatic oscillatory wave function $|\Phi_u^{(\pi)}(Q)\rangle$ is established by $p = -\pi$. Thus the eigenfunctions of (21) which have an even number of nodes and which pertain to the upper adiabatic potential are approximative forms of the unconventional states with parity $p = -1$.

The lowest of these states is calculated by a numerical diagonalization of Eq. (21). From Fig. 3 we recognize that its energetic uncertainty is remarkably larger than that of optimized variational ansatz (10). Moreover, in the range of the small coupling values D, we find higher accuracy for the Fröhlich-type approach than for the adiabatic one, even for the case of the large transfer parameters T, where the latter approach should work especially well. This becomes lucid if we consider the nonadiabatic potential

$$V_{nad}(Q) = \frac{\Omega}{8} \cdot \left[\frac{TD}{T^2 + D^2 Q^2} \right]^2 . \tag{25}$$

It is centred in the same spatial region as the wave function $\Phi_u^{(\pi)}(Q)$, i.e. for finite coupling constants D the matrix element

$$\int \Phi_u^{(\pi)}(Q)^* V_{nad}(Q) \Phi_u^{(\pi)}(Q) \, dQ \tag{26}$$

always yields a non-negligible value, in contrast to the case of the ground state wave function [5].

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MULJUTUD ERGASTATUD SEISUNDITE KLASSIST EKSITON–FOONON- JA JAHNI–TELLERI SÜSTEEMIDES ("EKSOOTILISED" SEISUNDID)

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Fultoni–Goutermani teisenduse rakendamise abil on leitud eksiton–foonon-süsteemi ebakonventsionaalset tüüpi "eksootilised" ergastatud seisundid, mida iseloomustab foononalamsüsteemi jäikumine. Foonon-seisundid on hästi kirjeldatavad muljutud ostsillaatorfunktsioonide abil.

Analüütiliselt on see mõistetav, kui rakendada hamiltoniaanile Fröhlichi tüüpi teisendust. Adiabaatilise lähenduse kasutamine näitab, et need ebakonventsionaalsed seisundid vastavad lahendeile, mis kuuluvad ülemisele adiabaatilisele potentsiaalile. Adiabaatilise lähenduse täpsus on siiski tunduvalt madalam kui Fröhlichi ja variatsioonlähenduse oma.

О КЛАССЕ СЖАТЫХ ВОЗБУЖДЕННЫХ СОСТОЯНИЙ В ЭКСИТОН-ФОНОННЫХ И ЯН–ТЕЛЛЕРОВСКИХ СИСТЕМАХ ("ЭКЗОТИЧЕСКИЕ СОСТОЯНИЯ")

Матиас СОННЭК, Хуберт АЙЕРМАН, Макс ВАГНЕР

Применением преобразования Фультона–Гутермана найдены неконвенционального типа "экзотические" возбужденные состояния экситон-фононной системы, характеризуемые ростом жесткости фононной подсистемы. Фононные состояния хорошо описываются сжатыми осцилляторными функциями. Аналитически это понятно, если подвергать гамильтониан преобразованию типа Фрелиха. Применение адиабатического приближения показывает, что эти неконвенциональные состояния соответствуют решениям, принадлежащим верхнему адиабатическому потенциалу. Точность адиабатического приближения, однако, значительно ниже точности фрелиховского и вариационного приближений.