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Department of Theoretical Chemistry, Jagiellonian University, Cracow, Poland

Exciton-Exciton Interaction Resulting from Phonon-Exciton Coupling

By

ANDRZEJ WITKOWSKI

It is shown using second quantization formalism and treating excitons as bosons that phonon-exciton coupling leads to exciton-exciton interaction. This interaction limits substantially the possibility of exciton condensation.

Es wurde mit Hilfe des Formalismus der zweiten Quantisierung gezeigt, daß die Phonon-Exziton Kopplung zu einer Exziton-Exziton Wechselwirkung führt. Dabei wurden die Exzitonen als Bosonen behandelt. Diese Wechselwirkung begrenzt wesentlich die Möglichkeit einer Kondensation der Exzitonen.

En traitant les excitons comme bosons on a demontré par le formalisme de la deuxième quantisation que le couplage exciton-phonon conduit à l'interaction exciton-exciton. Cette interaction limite sensiblement la possibilité de la condensation des excitons.

1. Introduction

Recent developments in the laser intense light sources, synthesis of molecules forming molecular crystals with exceptionally low laying exciton states (like tetracyanoquinomethantype crystals) create experimental conditions for high exciton concentrations. Interaction between excitons is then a natural question and is now being studied in reference to paramagnetic properties of tetracyanoquinomethantype crystals [*5*] and semiconducting properties [*6*] of molecular crystals.

Coupling of exciton with the nuclear vibrations is a rather well established fact for molecular crystals [*11*]. It seems resonable therefore to suspect that virtual exchange of a phonon between the excitons can lead in a similar fashion to superconductivity theory [*2*], to effective exciton-exciton interaction. It will be shown in this note that indeed the exciton phonon coupling in a three-dimesional molecular crystal leads to exciton-exciton interaction.

Coupling of an exciton with the nuclear vibrations arises from the change of the potential energy for nuclear motions between the ground and excited electronic states of the molecule [*12, 13*].

The Hamiltonian H of the molecular crystal is

$$H = \sum_{n} T_n + \sum_{n} h_n + \tfrac{1}{2} \sum_{n,m} V_{nm} \tag{1}$$

where T_n is nuclear kinetic energy, h_n the electronic Hamiltonian of the molecule n and V_{nm} is the interaction between the molecules which is supposed to depend only on electronic coordinates [*13*]. Denote by φ_n normalized and antisymmetrized electronic wave function of the crystal when molecule n at R_n is electronically excited. Then

$$h_n \varphi_n = [E^0 (Q_n) + \delta E(Q_n)] \varphi_n$$

$$h_m \varphi_n = [E^0 (Q_m)] \varphi_n \tag{2}$$

where in $\delta E(Q_n)$ we retain only the linear term in normal coordinates [*13*]. Introduce the creation and distrution operators $a_n^\dagger$, a_n:

$$\psi = \sum_n a_n \varphi_n \tag{3}$$

and denote by N the number of molecules with periodic boundary conditions.

Exciton operators obey, like spin waves, the Pauli commutation relations [*1*]. Following Dyson's theory of spin-wave interactions [*7*] we will traet them however as bosons. The kinematic interaction *i.e.* the fact that two excitons (like spin waves) can not be localized at the same lattice site is then a purely statistical effect and should appear in the statistical calculations but is supposed not to appear in the dynamics of the exciton interactions in which we are intersted here.

Transform now φ_n to the crystal exciton wave functions

$$\psi_k = N^{-\frac{1}{2}} \sum_n \exp (ik R_n) \varphi_n \tag{4}$$

and introduce in the similar wave the phonon creation and destruction operators $b_w^\dagger$, b_w

$$[b_w, b_{w'}^\dagger] = \delta_{ww'} \, . \tag{5}$$

In this representation the Hamiltonian [*1*] has the form:

$$H = \sum_k \varepsilon_k a_k^\dagger a_k + \omega \sum_w b_w^\dagger b_w + \gamma\omega N^{-\frac{1}{2}} \sum_{k,w} (a_k^\dagger a_{k-w} b_w + a_{k-w}^\dagger a_k b_w^\dagger) \tag{6}$$

where ω is vibrational frequency, $\gamma = - \alpha \left(\frac{m\omega}{2}\right)^{\frac{1}{2}}$ a dimensionless coupling constant and α, defined by $\delta E(Q_n) = - m\omega^2 \alpha Q_n$, is the change of nuclear equilibrium position between the ground and excited molecular states. Similar exciton-phonon Hamiltonian has been used recently by MERRIFIELD [*10*] in his variational treatment of the lowest crystal exciton state. As we are interested here in exciton-exciton interaction resulting from coupling with phonons we are not including in (6), for simplicity, direct exciton-exciton interactions.

2. The Unitary Transformation of the Exciton-Phonon Hamiltonian

To study the influence of phonons on excitons we will try to separate as far as possible the exciton and phonon variables. For this aim, like in FRÖHLICH's treatment of the superconductivity theory [*8*], we will try by a suitable transformation to get rid of the term linear in phonon variables.

Put

$$U = e^{iS}$$

where

$$S = S^\dagger$$

then U is unitary. Define S by

$$S = \sum_{k,w} \varphi (k, w) a_k^\dagger a_{k-w} b_w + \text{Herm. } c \tag{7}$$

where $\varphi\ (k, w)$ are to be determined. Denote

$$H_0 = \sum_k \varepsilon_k\, a_k^\dagger\, a_k + \omega \sum_w b_w^\dagger\, b_w \tag{8}$$

$$H_1 = \gamma\omega\, N^{-\frac{1}{2}} \sum a_k^\dagger\, a_{k-w}\, b_w + \text{Herm. } c \tag{9}$$

now, as

$$H' = e^{-iS}\, H\, e^{iS} = H + i\,[H, S] - \tfrac{1}{2}\,[[H. S], S] + \dots \tag{10}$$

choose the $\varphi\ (k, w)$ from the condition

$$H_1 + i\,[H_0, S] = 0 \tag{11}$$

what gives

$$\varphi\ (k, w) = i\gamma\omega\, N^{-\frac{1}{2}}\, (\varepsilon_k - \varepsilon_{k-w} - \omega)^{-1}\,. \tag{12}$$

Perform the transformation (10) to the second order in γ and treat vibrations as harmonic (therefore terms quadratic and nondiagonal in $b_w^\dagger$, b_w are neglected). This gives for the transformed Hamiltonian:

$$\begin{aligned} H' = {} & \sum \varepsilon_k\, a_k^\dagger\, a_k + \omega \sum_w \left(1 + \omega\gamma^2\, N^{-1} \sum_k \frac{n_k - n_{k-w}}{\varepsilon_k - \varepsilon_{k-w} - \omega}\right) b_w^\dagger\, b_w + \\ & + \gamma^2\, \omega\, N^{-1} \sum_{k,\, q,\, u} \frac{\omega^2}{(\varepsilon_{k-w} - \varepsilon_k)^2 - \omega^2}\, a_k^\dagger\, a_{k-w}\, a_{q-w}^\dagger\, a_q \end{aligned} \tag{13}$$

where

$$n_k = a_k^\dagger\, a_k\,.$$

3. Discussion

Although the commutation properties of a_k, b_w in the transformed Hamiltonian (13) are the same as in (6) their physical meaning, however is different. The Fourier component of exciton density $\varrho_w = \sum_k a_{k-w}^\dagger\, a_k$ is now $\varrho_w' = U^\dagger\, \varrho_w\, U$ and corresponds to excitons carrying along some molecular distortion. On the other hand b_w are now vibrational amplitudes accompanied by the exciton density oscillations.

In the molecular crystals where overlap of electronic wave functions is small the width of the exciton band, in particular the triplet exciton bands [*9*] is often smaller then the vibrational quantum. Then the third term of (13), describing the exciton-exciton interaction, is negative and all excitons in the band are subject to attractive interaction. As no Bose condensation is possible for bosons with attractive interaction [*4*] the possibility of exciton condensation proposed by Blatt [*3*] seems doubtful in such crystals. For the molecular crystals with strong intermolecular interactions the attractive interaction in the group of exciton states of ω width surrounding the filled exciton level would presumably at low temperatures also limit substantially the possibility of exciton condensation.

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