

An Effective Hamiltonian for Giant Polaritons in Highly Excited Molecular Crystals

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Abstract

Within the Random Phase Approximation and by using the exact trilinear commutation relations for Frenkel exciton operators an effective Hamiltonian is constructed for a coupled exciton–photon system in highly excited molecular crystals. The polariton dispersion relations derived from the Hamiltonian is explicitly dependent on the excitation level.

1. Introduction

At low excitation levels only a few of excitons exist in the crystal which can be treated as ideal bosons. The Hamiltonian describing a coupled exciton–photon system may easily be diagonalized yielding new quasi-particles named polaritons [1–4]. But under strong excitations a many-exciton system will be established. In such a system excitons interact with each other dynamically via a residue of Coulomb forces and, furthermore, being transformed from r -space into K -space by unitary (but not canonical) transformations, their operators in K -space obey an opened set of commutation relations (see [5] for example) which make them to be neither bosons, fermions nor paulions. The Hamiltonian of the system of many excitons interacting with electromagnetic radiation can not be straightforward diagonalized as in the low excitation case and one has to restudy the polariton concept for this situation [6–9]. Using classical amplitudes for both photon and exciton operators, in [6] a polariton-like solution for excitons at high densities was obtained which then was referred to as giant polariton. In [7] a formalism was developed to build an effective Hamiltonian for giant polaritons. However, as will be shown in this paper, it is not self-consistent. The authors of [8] investigated the density-dependent shift of the two branches of giant polariton energy near the point $K = 0$ using Green function technique. Yet, their results were quite hasted. Here we are attempting to overcome the inconsistencies met in [7, 8]. In [9] the giant polariton energy spectrum, by the way, has been determined from the pole of the expression for the exciton total number but not from the effective Hamiltonian and the main subject of [9] has dealt with the effect of optical bistability.

2. Low excitations: Usual polaritons

For simplicity, consider a three-dimensional molecular crystal with one molecule in a unit cell and let us restrict ourselves only to the study of the lowest excited state of the molecule. For low exciton densities: $L \ll N$ (L is the number of excited molecules and N is that of unit cells) the Hamiltonian H_l for the exciton–photon system in the K -representation can be derived and it is of the form (In what follows we are going to work in the unit system with Plank’s constant and the light

velocity equal to unity: $\hbar = c = 1$):

$$H_l = \sum_K \{ E_K a_K^\dagger a_K + \omega_K c_K^\dagger c_K + \frac{1}{2} B_K (2c_K^\dagger c_K + c_K c_{-K} + c_K^\dagger c_{-K}^\dagger) + g_K (a_K^\dagger - a_{-K}) (c_K + c_{-K}^\dagger) \} \quad (1)$$

where a_K and c_K are bosonic operators for excitons and photons, resp.. Their energies corresponding to the momentum K are denoted by E_K and ω_K . $B_K = \omega_0^2/2\omega_K$ with ω_0 being the plasma frequency that stems from the A^2 -type term of the light-matter interaction. Finally, $g_K = -i (2\pi N/V\omega_K)^{1/2} E_K P_K$ with V being the volume of the sample and P_K – the dipole photon–exciton transition matrix element. Antiresonant terms in (1) are necessary to get the correct polariton dispersion near the point $K = 0$ while for $K \neq 0$ their affect on the spectrum is not essential (see [10] and also [4]). Now and later in Section 3 we for a close comparison with the results of [7] neglect all the antiresonant contributions in writing the equations of motion for a_K and c_K which are:

$$\frac{da_K}{dt} = \dot{a}_K = -iE_K a_K - ig_K c_K \quad (2)$$

$$\frac{dc_K}{dt} = \dot{c}_K = -i(\omega_K + B_K)c_K + ig_K a_K \quad (3)$$

By means of Bogolubov transformations H_l with antiresonant terms ignored may exactly be cast into the following diagonalized form:

$$H_l = \sum_{K,v} \Omega_{vK} \alpha_{vK}^\dagger \alpha_{vK}; \quad v = 1, 2. \quad (4)$$

where α_{vK} – the polariton operators and $\Omega_{1K}(\Omega_{2K})$ – the lower – (upper) branch polariton energy:

$$\Omega_{vK} = \frac{1}{2} \{ E_K + \omega_K + B_K + (-1)^v [(E_K - \omega_K - B_K)^2 + 4|g_K|^2]^{1/2} \} \quad (5)$$

3. High Excitations

3.1. Effective Hamiltonian

The situation will change if one investigates the crystal by the use of an intense light beam. For a given light intensity the system may be in a highly excited stationary state which is in general non-equilibrium, single- or multi-stable [9]. For the steady regime, there are two, among other things, important features – which one has to handle very carefully. Firstly, the dynamic exciton–exciton interaction will come into play (Note that this interexciton coupling was not taken into account in [7]). And, secondly, excitons, as mentioned in the introduction, can no longer be simply considered as ideal

bosons as at low excitation levels. The Hamiltonian H_h of the system in the high excitation case must differ from H_l . According to [8, 9], we have:

$$H_h = \sum_{\mathbf{K}} \left\{ E_{\mathbf{K}} a_{\mathbf{K}}^{\dagger} a_{\mathbf{K}} + \frac{N}{4} F_{\mathbf{K}} \rho_{\mathbf{K}} \rho_{-\mathbf{K}} + \omega_{\mathbf{K}} c_{\mathbf{K}}^{\dagger} c_{\mathbf{K}} + \frac{B_{\mathbf{K}}}{2} (2c_{\mathbf{K}}^{\dagger} c_{\mathbf{K}} + c_{\mathbf{K}} c_{-\mathbf{K}} + c_{\mathbf{K}}^{\dagger} c_{-\mathbf{K}}^{\dagger}) + g_{\mathbf{K}} (a_{\mathbf{K}}^{\dagger} - a_{-\mathbf{K}}) (c_{\mathbf{K}} + c_{\mathbf{K}}^{\dagger}) \right\} \quad (6)$$

$$\rho_{\mathbf{K}} = \frac{2}{N} \sum_q a_{\mathbf{K}+q}^{\dagger} a_q \quad (7)$$

In (6) $F_{\mathbf{K}}$ are the Fourier components of the coupling constants between excitons whose concrete expressions are not specified here. As distinct from (1), the exciton operators $a_{\mathbf{K}}$ and $a_{\mathbf{K}}^{\dagger}$ in (6) do not satisfy a closed set of commutation relations for bosons that makes a great difficulty for the theoretical study of physical phenomena involving many excitons. To deal with the exciton non-boson characteristics in [11, 12] was found a rigorous presentation of a real exciton operator in terms of an infinite series in ideal boson operators. Nevertheless, working with such an infinite series one often meets some uncertainties in concrete calculations. Namely, one does not know to what order the expansion needs to be confined up and so one has to distinguish limiting cases: the very low density limit and the high density one. A more precise approach to the problem was explored in [13] where a closed and exact set of commutation relations for real exciton operators was built which were trilinear but not bilinear as usual:

$$[[a_{\mathbf{K}}^{\dagger}, a_r], a_q] = -\frac{2}{N} a_f, \mathbf{K} + \mathbf{f} = \mathbf{r} + \mathbf{q} \quad (8)$$

$$[[a_{\mathbf{K}}^{\dagger}, a_r], a_q^{\dagger}] = \frac{2}{N} a_f^{\dagger}, \mathbf{K} + \mathbf{q} = \mathbf{r} + \mathbf{f} \quad (9)$$

$$[a_{\mathbf{K}}, a_r] = [a_{\mathbf{K}}^{\dagger}, a_r^{\dagger}] = 0 \quad (10)$$

The specific commutators (8)–(10) are valid for any density, so they seem to be most useful for the physics of highly excited crystals. Note that the relations (8)–(10) look quite simple for the Frenkel excitons whose operators in r -space are paulionic [13]. In semiconductors the Wannier-Mott exciton operators as a bilinear sum of electron (e) and hole (h) operators $a_{\mathbf{K}} = V^{-1/2} \sum_{\mathbf{P}} f(\mathbf{P} - \beta\mathbf{K}) h_{\mathbf{P}} h_{\mathbf{K}-\mathbf{P}}$ (f the hydrogen-like envelope function and $\beta = m_h/(m_e + m_h)$) with m_h (m_e) the effective hole (electron) mass) lead to very confusing trilinear commutation relations (see e.g., eqs. (10) to (13) in [14]). However, as shown in [14], general results remain the same disregarding what kind of excitons is to be dealt with. Now using (6)–(10) and keeping only resonant terms we again write down the equations of motion of $a_{\mathbf{K}}$ and $c_{\mathbf{K}}$:

$$\dot{a}_{\mathbf{K}} = -iE_{\mathbf{K}} a_{\mathbf{K}} - ig_{\mathbf{K}} c_{\mathbf{K}} + i \sum_r [E_{\mathbf{K}} \rho_{r-\mathbf{K}} a_{\mathbf{K}} + g_r \rho_{r-\mathbf{K}} c_r - \frac{1}{2} F_r (\rho_{-r} a_{\mathbf{K}-r} + \rho_r a_{\mathbf{K}+r})] \quad (11)$$

$$\dot{c}_{\mathbf{K}} = -i(\omega_{\mathbf{K}} + B_{\mathbf{K}}) c_{\mathbf{K}} + ig_{\mathbf{K}} a_{\mathbf{K}} \quad (12)$$

We see that eq. (12) formally coincides with eq. (3). Their only difference is that in Eq. (3) $a_{\mathbf{K}}$ are ideal bosonic operators while in Eq. (12) $a_{\mathbf{K}}$ are specific operators obeying the specific

commutators (8 – 10). At this point, we apply the well-known random phase approximation (RPA) [15] which is most suitable for high densities. Formally, the RPA permits us to regard operators ρ_r in (11) as their averaged values (over the steady nonequilibrium states of the system [9]):

$$\rho_r \rightarrow \rho_r^{\text{RPA}} = \langle \rho_r \rangle = \delta_{r0} \delta_0 = \frac{2L}{N} \delta_{r0} \quad (13)$$

Then (11) becomes:

$$\dot{a}_{\mathbf{K}} = -i[E_{\mathbf{K}}(1 - \rho_0) + F_0 \rho_0] a_{\mathbf{K}} - ig_{\mathbf{K}}(1 - \rho_0) c_{\mathbf{K}} \quad (14)$$

Equation (14) together with eq. (12) exhibit the correct equation set for the physical system under investigation. As seen above, to get the physically correct eqs. (12) and (14), we have to resort to the trilinear commutation relations (8)–(10) which are exact but rather complicated in handling. Therefore, it is preferable if one could still arrive at (12) and (14) avoiding the use of the relations (8)–(10). The matter is to construct an appropriate effective Hamiltonian H_{eff} which would contain only ideal bosonic operators and from which the correct equations (12) and (14) might still be derived directly by using the usual bilinear commutators for bosonic operators. If we succeed in doing so, all the nonbosonic and nonideal characteristics of the real excitons will be hidden in the effective Hamiltonian as a virtual dynamics. It is checkable that we can choose H_{eff} as below:

$$H_{\text{eff}} = \sum_{\mathbf{K}} \{ (\omega_{\mathbf{K}} + B_{\mathbf{K}}) c_{\mathbf{K}}^{\dagger} c_{\mathbf{K}} + [E_{\mathbf{K}} + (F_0 - E_{\mathbf{K}}) \rho_0] a_{\mathbf{K}}^{\dagger} a_{\mathbf{K}} + g_{\mathbf{K}} [(1 - \rho_0) a_{\mathbf{K}}^{\dagger} c_{\mathbf{K}} - c_{\mathbf{K}}^{\dagger} a_{\mathbf{K}}] \} \quad (15)$$

3.2. Giant Polaritons

Applying the usual bosonic commutation relations

$$\left. \begin{aligned} [a_{\mathbf{K}}, a_{\mathbf{K}'}^{\dagger}] &= \delta_{\mathbf{K}\mathbf{K}'} \\ [a_{\mathbf{K}}, a_{\mathbf{K}'}] &= [a_{\mathbf{K}}^{\dagger}, a_{\mathbf{K}'}^{\dagger}] = 0 \end{aligned} \right\} \quad (16)$$

we immediately obtain from (15) the equations of motion for $a_{\mathbf{K}}$ and $c_{\mathbf{K}}$ which are nothing else but (12) and (14). That means we have properly chosen the form of H_{eff} . It is worth to note that H_{eff} is a non-hermitian operator (see (15), it can be so for effective Hamiltonians but not for real physical ones), because the coefficients at the terms $\sim a^{\dagger} c$ and the terms $\sim c^{\dagger} a$ are different. The physical meaning of this difference can be interpreted as follows: The generation of an exciton by the absorption of a photon depends on ρ_0 ; When the highest excitation level is reached ($\rho_0 = 1$), no more excitons can be created because of the saturation effect. On the other hand, the radiative recombination of an exciton will always occur if any excitons exist in the crystal independent of how highly excited it is; The term $\sim c^{\dagger} a$ in H_{eff} , thus, is independent of ρ_0 . Being non-hermitian, H_{eff} can not be simply diagonalized by the linear combination of a and c . To determine the analytic expression for the eigenenergy of the giant polariton we try solving the equation system (12) and (14) by seeking its possible particular stationary solutions as

$$a_{\mathbf{K}} = A_{\mathbf{K}} \exp(-i\Omega_{\mathbf{K}} t), \quad A_{\mathbf{K}} = \text{const.} \quad (17)$$

$$c_{\mathbf{K}} = C_{\mathbf{K}} \exp(-i\Omega_{\mathbf{K}} t), \quad C_{\mathbf{K}} = \text{const.} \quad (18)$$

Inserting (17, 18) into (12) and (14) we obtain a system of two homogeneous equations for $A_{\mathbf{K}}$ and $C_{\mathbf{K}}$ whose condition

to possess nontrivial roots gives:

$$\begin{aligned} \Omega_K \rightarrow \Omega_{vK}(\rho_0) = & \frac{1}{2} \{E_K + \omega_K + B_K + (F_0 - E_K) \rho_0 \\ & + (-1)^v [(E_K - \omega_K - B_K \\ & + (F_0 - E_K) \rho_0]^2 + 4|g_K|^2(1 - \rho_0)]^{1/2}\} \end{aligned} \quad (19)$$

Ω_{vK} can be treated as the two-branch giant polariton eigenenergy which, in contrast to (5), depends explicitly on the excitation level ρ_0 . For the low density limit (ρ_0 -small), we introduce three quantities such as:

$$\begin{aligned} \delta_v = & \lim_{\rho_0 \rightarrow 0, K \rightarrow 0} [\Omega_{vK}(\rho_0) - \Omega_{vK}(0)] \\ = & \frac{1}{2} \rho_0 \left\{ F_0 - E_0 - (-1)^v \right. \\ & \times \left. \frac{(E_0 - B_0)(E_0 - F_0) + 2|g_0|^2}{[(E_0 - B_0)^2 + 4|g_0|^2]^{1/2}} \right\} \end{aligned} \quad (20)$$

$$\begin{aligned} \Delta = & \lim_{\rho_0 \rightarrow 0, K \rightarrow K_0} \\ & \times \{[\Omega_{2K}(\rho_0) - \Omega_{1K}(\rho_0) - [\Omega_{2K}(0) - \Omega_{1K}(0)]]\} \\ = & \rho_0 [B_{K_0}(E_{K_0}(E_{K_0} - F_0) - 2|g_{K_0}|^2) [B_{K_0}^2 + 4|g_{K_0}|^2]^{-1/2}] \end{aligned} \quad (21)$$

which gain the following physical meanings δ_1 (δ_2) is the density-dependent shift of the polariton lower- (upper-) branch near the point $k = 0$ and Δ describes the density-dependent enlargement of the ‘‘band gap’’ between the two branches near the point k_0 such that $E_{K_0} = \omega_{K_0}$. In reality $E \sim 5\text{eV} > B, |F|, |g|$ so that it immediately follows from (20, 21) that $\delta_2 < 0$ (in agreement with [8]) and $\Delta > 0$ (not yet considered anywhere). The sign of δ_1 , as seen from (20), depends on relative magnitudes of $E_0, |F_0|, B_0$ and $|g_0|$. For the case when $4|g_0|^2 \ll (E_0 - B_0)^2$ we have:

$$\delta_1 \approx \frac{(F_0 - B_0)|g_0|^2 \rho_0}{(E_0 - B_0)^2} \quad (22)$$

which reveals that the lower branch would shift very little and the shift might be up ($F_0 > B_0$) or down ($F_0 < B_0$).

4. Conclusions and Discussions

We have (1) constructed an effective Hamiltonian for the coupled exciton–photon system at high densities which is a non-hermitian one and (2) derived the explicit analytic expression for the eigenenergy of the giant polariton. Both points are in contrast to [7, 8]. H_{eff} in [7], being hermitian, is clearly not self-consistent: eq. (16b) in [7] could not be obtained from the hermitian H_{eff} of [7] (see eq. (17) therein). To be self-consistent, H_{eff} in [7] should also be non-hermitian one. But then the diagonalization procedure could not be performed as misdone in [7]. If H_{eff} in [7] had been correctly

constructed, the density-dependent coefficient of the term $\sim |D_K|^2$ in the expression for Ω_K (see eq. (20) in [7]) would have been $(1 - 2n_0)$ instead of $(1 - 2n_0)^2$. Further, the results of [8] may not be allright, too, because of at least two reasons: (1) eq. (8) in [8] could be valid only for $F_0 > 0$, while in fact F_0 might be positive as well as negative. (2) from $\omega_2^2 > 0$ (we keep the same notations as in [8] where ω_2 stands for the energy lower branch) it obviously does not always follow $\omega_2 > 0$ as it was done in [8]. Then the lower branch near the point $K = 0$ does not shift up as stated in [8] but it may remove to both directions depending on the relative magnitudes of F_0 and B_0 (This paper, Section 3).

Finally, it is noticeable that to fulfil the purpose pursued in [7], i.e., to reproduce the equations of motion, the needed H_{eff} must be non-hermitian as seen from (15). Then, for obtaining the polariton dispersion from such an H_{eff} a numerical diagonalization method developed in [16] should be applied. In this aspect, it would be much easier to have it directly from solving the equations of motion as described from (17) to (19). In [17] another H_{eff} is constructed that is not only hermitian but also allows to obtain both the polariton dispersion and the dependence of exciton density on laser intensity bringing about anomalies of the former.

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