



Absence or existence of intrinsic optical bistability of coupled ion pairs in solids

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Abstract

There has been a number of papers [2–4,8] published which deal with the prediction of intrinsic optical bistability of coupled ion pairs in a coherent radiation field. This coupling can be different, either electromagnetic near-field coupling of the transition dipoles or other more general interactions. In the last year Malyshev et al. published a paper in which the authors deny the existence of this bistability. In this paper the reason is discussed for this discrepancy, which seems to be due to different approaches of introducing the external phase destroying perturbations. The bistability is based on an inversion-dependent resonance frequency of coupled ions which can generally be important for phase-sensitive effects. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

There are two formalisms to treat open systems which are in dissipative contact with another energy accepting or spending system generally called a heat bath.

1. Rate equations: they connect the populations of different states of a system by incoherent transition probabilities. They can describe the dynamics of a system on a time scale which is long compared to the quantum mechanical coherence times of the states involved. Rate equations are useful, e.g., to describe the phonon-assisted transfer of excitation energy between rare-earth ions in solids. The short lifetimes of the phonons always guarantee an incoherent process on the time scale of the metastable electronic states.
2. Density matrix: this formalism bases on a quantum mechanical description of the dynamics of a system under the influence of its reversible internal and external interactions. In addition it allows to introduce dissipative interactions with an external heat bath by appropriate relaxation terms. The details of the dissipative relaxations do not matter and different interactions can be subsumed into the same relaxation rate. But the phenomenologically introduced relaxation rates have to represent in a realistic way the physical processes of interaction between the quantum mechanical system

and the heat bath. There are no problems with simple systems, as e.g., two-level systems in contact with the phonon field of a crystal. In this case, the relaxation terms are obvious. But the situation becomes less obvious for more complex systems and the problem is that the choice of the relaxation terms and of the wave functions can significantly influence the result of the calculations. For this reason, one has to keep in mind that the relaxation rates represent physical interactions, which determine the choice of the proper wave functions in the same way as the explicit Hamiltonian. So, in the case of coupled ion pairs in a coherent radiation field, the calculations can give contradicting results, the absence or presence of an intrinsic optical bistability (IOB), an interesting bistability which works without external feedback and offers very short switching times.

In this paper both methods of calculation will be discussed and the reason for the different results will be shown.

2. Hamiltonian

For reasons of simplicity we treat the ion pair as two coupled two-level systems as shown in Fig. 1 together with the Hamiltonian \mathbf{H} . \mathbf{H}_0 is the Hamiltonian of the two isolated ions, $\mathbf{H}(1,2)$ the ion–ion interaction, and \mathbf{H}_{RF} is the interaction of the ions with the incident classical

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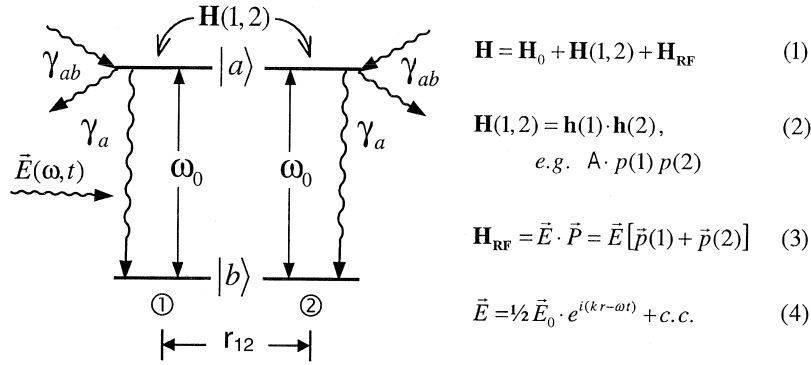


Fig. 1. Scheme of the two interacting two-level systems. \mathbf{H}_0 is the Hamiltonian of the two noninteracting ions, $\mathbf{H}(1,2)$ their mutual interaction, and \mathbf{H}_{RF} their interaction with the electromagnetic field $\mathbf{E}(\omega, t)$ by their dipole moments p_i . γ_a and γ_{ab} are the relaxation rates of the population and of the phase correlation, respectively.

electromagnetic field $\mathbf{E}(\omega, t)$. Since the distance between the ions is very small ($\sim 5 \text{ \AA}$) as compared to the wavelength of light ($\sim 5000 \text{ \AA}$), we can set the spatial phase difference of the light wave between both ions $kr_{12} \cong 0$. With this long-wavelength approximation the interaction Hamiltonian between the electromagnetic field and the ion pair simplifies to:

$$\mathbf{H}_{\text{RF}} = \frac{1}{2} \vec{E}_0 e^{-i\omega t} [\vec{p}(1) + \vec{p}(2)] + c.c. \quad (5)$$

For the interaction Hamiltonian $\mathbf{H}(1,2)$ we choose for reasons of simplicity a product form (2). It can be realized e.g. by the near-field dipole–dipole interaction between the ions. Furthermore, we assume that $\mathbf{h}(i)$ has only non-diagonal matrix elements in the wavefunctions of ion i .

Looking now at the full Hamiltonian (1,2,5) we see that it shows permutation symmetry with respect to interchange of ions 1 and 2

$$\mathbf{P}_{12} \mathbf{H} = \mathbf{H} \quad (6)$$

The symmetry-adapted wavefunctions of the pair are

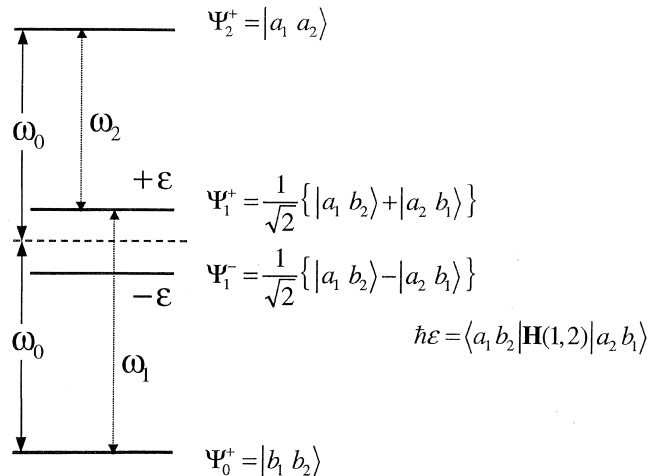


Fig. 2. Energy-level scheme of the pair coupled by the interaction $\mathbf{H}(1,2)$. 2ϵ is the resonance splitting.

therefore the well-known Dicke functions [5] given in Fig. 2 together with the resulting energy level scheme. The resonance splitting between the symmetric and antimetric singly excited states Ψ_1^+ and Ψ_1^- is twice the interaction matrix element

$$\hbar \epsilon = \langle a_1 b_2 | \mathbf{H}(1,2) | a_2 b_1 \rangle \quad (7)$$

Since both interaction Hamiltonians have positive parity under ion permutation

$$\mathbf{H}_{\text{RF}} = \mathbf{H}_{\text{RF}}^+, \quad \mathbf{H}(1,2) = \mathbf{H}(1,2)^+, \quad (8)$$

they can connect only states with the same parity. So, the Hilbert space of the pair reduces to three states excluding the antimetric singly excited state Ψ_1^- .

3. Relaxation terms

The equation of motion is given by the von Neumann equation including the relaxation terms (\mathbf{RT})

$$\dot{\rho} = -\frac{i}{\hbar} [\mathbf{H}, \rho] + \mathbf{RT} \quad (9)$$

In the chosen basis set of wavefunctions it has the matrix form

$$\dot{\rho}_{k,l} = -\frac{i}{\hbar} \langle k | [\mathbf{H}, \rho] | l \rangle - \alpha_{kl} \rho_{kl} \quad (10)$$

with $k, l = 0^+, 1^+, 2^+$

These are the equations of motion as given by Malyshev et al. [1]. They have the following properties:

1. The Hamiltonian and the relaxations connect only the symmetric Dicke states. In order to satisfy this condition, the interactions with the heat bath have to be symmetric under the exchange symmetry of the ions 1 and 2 like the Hamiltonian. This is a severe restriction to the relaxation processes, which is realized e.g. for spontaneous photon emission. But it is not fulfilled for ion–phonon interaction as will be discussed later on.

- They are exactly linear in the matrix elements of the density operator since the Hamilton operator, the commutator operation and the relaxation terms are all linear by themselves. The system does not contain any non-linearity necessary for an IOB as discussed in more detail by Malyshev et al. [1]. Increasing the intensity of the coherent radiation field, the pairs show a simple saturation behaviour [1].

The situation becomes different if the ion pair is embedded in a dense environment as in a crystal. In this case the dominating relaxation mechanism is the ion–phonon interaction. This interaction has the following properties:

- Since the phonons have wavelengths comparable with the ion–ion distance, the long-wavelength approximation $\vec{k} \cdot \vec{r} \approx 0$ valid for photons does not hold for phonons. The spatial phonon phase is different at both ions and there is no permutation symmetry between the ions anymore. Thus the ion–phonon interaction does not have a definite parity and can, in principle, connect all four Dicke states of the pair. Consequently, the problem does not stay three-dimensional in Hilbert space as suggested by the Hamiltonian, but becomes four-dimensional due to the relaxation processes between the ions and the phonons.
- The ion–phonon interaction is dominated by the interaction of the ion with the next ligands. The ion–ion interaction in the dimer generally extends over a larger distance with one or more ligands between them. Although this interaction is a resonant one, it is generally not to be expected that it can definitely dominate the ion–phonon interaction. Therefore, both interactions have to be simultaneously introduced into the calculations as competing interactions together with the interaction with the radiation field: The ion–ion interaction and the radiation field tend to bring the phases of the ions into the ones of the Dicke states, whereas the ion–phonon interaction tends to scramble them in a stochastic way.
- The optical energy gap $\hbar\omega_0$ is of the order of 20 000 cm^{-1} , the phonon energies usually range up to about 1000 cm^{-1} . So, it is obvious that the ion–phonon interaction does not significantly contribute to the relaxations over the optical gap. These relaxations are expected to be mainly due to spontaneous emission of radiation and/or other spontaneous processes.
- It is known from coherent-transient experiments on rare-earth ions in solids, e.g. Pr^{+3} in LaCl_3 [6,7], that already at liquid helium temperatures the phase relaxation time t_2 is orders of magnitude shorter than the lifetime t_1 of the excited state, i.e.

$$\gamma_{ab} \gg \gamma_a \quad (11)$$

This means that the contribution of t_1 to the phase

relaxation can be neglected. The phase relaxation is dominated by elastic phonon scattering including as intermediate states also nearby crystal-field levels not explicitly given in Fig. 1. Since the phonons have different wavelengths and different directions relative to the pair axis, the phase relaxations at both ions of the dimer can be assumed to be stochastic and uncorrelated in good approximation.

4. Calculations

For reasons of mathematical simplicity the calculations [4] were carried out in the 4-dimensional product space $(a_1, b_1) \times (a_2, b_2)$ (Fig. 1).

This allows to use the symmetry between the ions 1 and 2 and to introduce the identical but uncorrelated relaxations at both ions in a simple and adequate way.

The calculations could be done also in the basis of all four Dicke states introducing the relaxations in a proper way and introducing simultaneously all three external interactions, the ion–ion, the ion–phonon and the interaction with the radiation field. The result is expected to be the same since the product states and the Dicke states are related one to another by a unitary transformation.

In the course of the calculations the following additional approximations were made:

- The density operator $\rho(1,2)$ of the pair is taken in the product form

$$\rho(1,2) = \rho(1) \cdot \rho(2) \quad (12)$$

This approximation neglects fluctuations of the form

$$\mathbf{H}_r = (\mathbf{h}(1) - \langle \mathbf{h}(1) \rangle)(\mathbf{h}(2) - \langle \mathbf{h}(2) \rangle) \quad (13)$$

but it allows to reduce the 4×4 density matrix of the pair into two coupled 2×2 matrices of the single ions [4].

- The well-known rotating wave approximation (RWA) was used.

The full density matrix can be reduced by taking the trace over one of the ions

$$\text{Tr}_1 \rho(1,2) = \rho(2) \text{Tr}_1 \rho(1) = \rho(2) \quad (14)$$

Doing the same for the equation of motion

$$\dot{\rho}(1,2) = -\frac{i}{\hbar} [\mathbf{H}, \rho(1,2)] + \mathbf{RT} \quad (15)$$

one finds the equation of motion of one ion under the influence of the other one.

$$\dot{\rho}(2) = \frac{i}{\hbar} \text{Tr}_1 [\mathbf{H}, \rho(1,2)] + \mathbf{RT}$$

$$= -\frac{i}{\hbar} [\mathbf{H}_{\text{eff}}(2), \rho(2)] + \mathbf{RT}$$

$$\mathbf{H}_{\text{eff}}(2) = \mathbf{H}_0(2) + \mathbf{H}_{\text{RF}}(2) + \mathbf{h}(2) \text{Tr}_1 (\mathbf{h}(1) \rho(1))$$

$$\mathbf{RT} = -\gamma_a \cdot \rho_{aa} - \gamma_{ab} \cdot \rho_{ab} \quad (16)$$

for the diagonal and non-diagonal matrix element, respectively.

The last term in the effective Hamiltonian represents the coupling between both ions depending on the current status of the other one. This term already points at a mutual feedback between both ions responsible for the IOB. The stationary solution was found under the condition that both ions are excited identically. This is justified by the long-wave approximation which states that the coherent electromagnetic field is identical in phase and amplitude at both ions. The result is an inversion-dependent resonance frequency of the pairs based on the mutual status-dependent interaction. For the absorbed energy we find the proportionality [4]

$$W_{\text{abs}} \sim \frac{-\langle \mathbf{E}_0 \cdot \vec{\mathbf{p}} \rangle^2 n}{1 + \left[\frac{\omega_0 - \omega - \varepsilon n}{\gamma_{\text{ab}}} \right]^2}, \quad n = \rho_{\text{aa}} - \rho_{\text{bb}} \quad (17)$$

This equation is of third order in the inversion n and therefore a bistable behaviour of the pairs can be expected for certain parameters γ_{ab} and ε . The strongly nonlinear dependence of the excited-state population ρ_{aa} as function of a normalized intensity σ of the radiation field [4] is shown in Fig. 3. It demonstrates that for ‘resonant’ excitation $\omega = \omega_0$ bistable behaviour starts from $\varepsilon/\gamma_{\text{ab}} \cong 5$ and becomes more pronounced for greater values. For the negative slopes of $\rho_{\text{aa}}(\sigma)$ the system is unstable and jumps at the turning points to the stable branch with the same value of σ as indicated by the arrows. The very pronounced bistability and the fast switching time, expected to be of the order of the phase-relaxation time γ_{ab}^{-1} , look very promising for application as e.g. for optical computers. But there is a serious drawback. The bistability reacts quite sensitively and in an asymmetric way to deviations between the frequency of the electromagnetic field ω and the

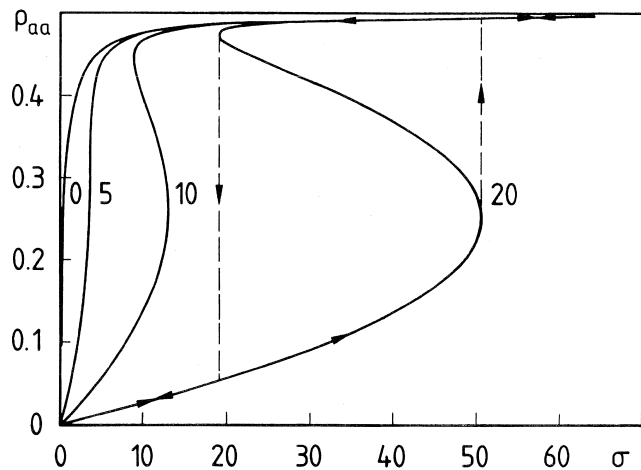


Fig. 3. Intrinsic optical bistability (IOB) for certain parameters $\varepsilon/\gamma_{\text{ab}}$. ρ_{aa} =population of the excited state, σ =normalized intensity of the electromagnetic field [4]. ‘Resonant’ excitation: $\omega = \omega_0$.

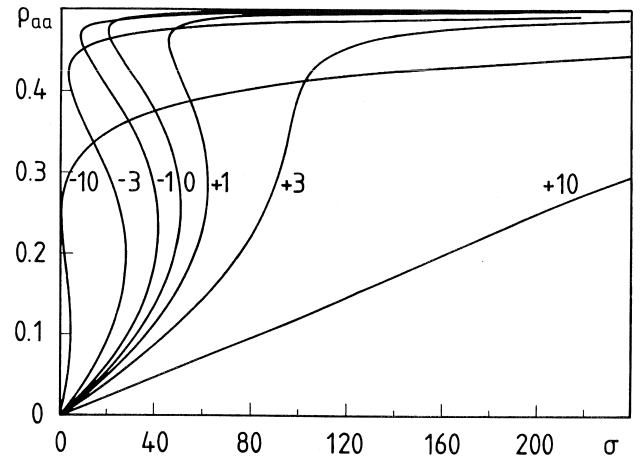


Fig. 4. IOB for the fixed parameter $\varepsilon/\gamma_{\text{ab}} = 20$. ‘Non-resonant’ excitation: $(\omega_0 - \omega)/\gamma_{\text{ab}} = 0, \pm 1, \pm 3, \pm 10$.

resonance frequency of the single ions ω_0 . Fig. 4 shows the dependence of the IOB on the detuning $\omega_0 - \omega$ for a fixed parameter $\varepsilon/\gamma_{\text{ab}}$. It is obvious that detunings $\omega_0 - \omega = \pm \gamma_{\text{ab}}$ are already intolerable for experimental realization and applications.

So, we get as condition for the existence of the IOB the relation

$$\Delta\omega_0 < \gamma_{\text{ab}} \ll \frac{\varepsilon}{5} \quad (18)$$

Whilst γ_{ab} can be adjusted by choosing an appropriate crystal temperature, the condition $\Delta\omega_0 \ll \varepsilon/5$ is hard to realize for crystals doped with rare-earth ions. It needs very small inhomogeneous linewidths because the interaction energy between the rare-earth ions in crystals is typically limited to $\hbar\varepsilon \cong 1 \text{ cm}^{-1}$.

5. Discussion

The results of the calculation can easily be discussed in the product space using Fig. 5. According to (17) the inversion-dependent resonance frequency is given by

$$\omega_{\text{R}} = \omega_0 - \varepsilon n \quad (19)$$

For low intensities of the electromagnetic field $\mathbf{E} \rightarrow 0$ both ions are in the ground state and $n = -1$. This yields for the resonance frequency $\omega_{\text{R}} = \omega_0 + \varepsilon = \omega_1$, i.e. the resonance frequency of the coupled pair as expected from the Dicke wavefunctions for the transition $\Psi_0^+ \rightarrow \Psi_1^+$. Increasing the electromagnetic field $\mathbf{E} = \mathbf{E}(\omega_0)$ the ions show only weak absorption because ω_0 is far out in the wing of the resonance profile. But, by this weak absorption the inversion increases slightly and shifts the resonance frequency ω_{R} of the coupled ions closer to ω_0 further increasing the absorption, the inversion, and the shift of the resonance profile towards ω_0 . By this positive feedback the system becomes unstable and jumps to the stable limit $n = 0$,

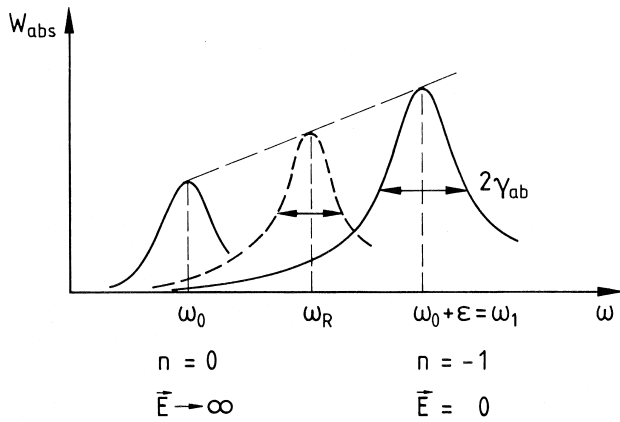


Fig. 5. Discussion of the IOB due to the inversion dependent resonance frequency $\omega_R = \omega_0 - \varepsilon n$; inversion $n = \rho_{aa} - \rho_{bb}$.

$\omega_R = \omega_0$. Reducing now the electromagnetic field the system tries to keep its absorption maximum at the pump frequency ω_0 as long as possible and finally jumps back to $\omega_R \cong \omega_1$ by the same positive feedback effect as before but now in the other direction.

In the Dicke functions the IOB can only be explained by mixing of the symmetric and antimetric singly excited pair states due to the phonon scattering. Accepting this idea, the wavefunction of the coupled pair in the first excited state would be

$$\phi_1 = c^+ \Psi_1^+ + c^- \Psi_1^- \quad (20)$$

with a resonance frequency

$$\begin{aligned} \omega_R &= \frac{1}{\hbar} \langle \phi_1 | \mathbf{H}_0 + \mathbf{H}(1,2) | \phi_1 \rangle \\ &= \omega_0 + \varepsilon (|c^+|^2 - |c^-|^2) \end{aligned} \quad (21)$$

The correlation between this expression for the resonance frequency and the inversion n can be found by means of (19) and the normalization condition for ϕ_1 .

$$|c^+|^2 = \frac{1-n}{2} \quad |c^-|^2 = \frac{1+n}{2} \quad (22)$$

The shift of the resonance frequency from $\omega_0 + \varepsilon$ to ω_0 by increasing the optical pumping is thus represented by a change of the coefficients from $|c^+|^2 = 1$, $|c^-|^2 = 0$ to $|c^+|^2 = |c^-|^2 = 0.5$ for $E \rightarrow \infty$ and $n \rightarrow 0$. The resulting wavefunctions would be

$$\phi_1 = \frac{1}{\sqrt{2}} (\Psi_1^+ \pm \Psi_1^-) = \begin{cases} a_1 b_2 \\ a_2 b_1 \end{cases} \quad (23)$$

This means a complete decoupling of the pairs by the combined interaction of the radiation field and the ion-phonon interaction, a situation which physically seems to be realistic. Furthermore, this is the stable limit as found for the solution in the product space.

A mixed wavefunction as given by (20) can only be

expected introducing the ion-ion and ion-phonon interactions simultaneously as competing effects into the calculations. A subsequent introduction of both interactions prevents this competition. Introducing first $\mathbf{H}(1,2)$ one gets the split states Ψ_1^+ and Ψ_1^- (Fig. 2). Introducing in a second step the electron-phonon interaction, it can only generate inelastic phonon transitions between Ψ_1^+ and Ψ_1^- but not a coherent mixed state as needed for the IOB. The absence of IOB for ion pairs as stated by Malyshev et al. [1] bases just on this subsequent introduction of the ion-ion and ion-phonon interaction. So, the existence of the IOB in a coherent electromagnetic field seems to be realistic for dimers in a solid.

Unfortunately, the experimental situation is not very convincing, yet. In $\text{LaF}_3:\text{Pr}^{3+}$ we could only find strong instabilities of the fluorescence of Pr^{3+} pairs in a coherent laser field which were strongly correlated with the temperature dependence of the dephasing rate of the single Pr^{3+} ions [8]. Bistability could not be found. The reason is probably the inhomogeneous detuning of the monomers which introduces instabilities in addition to the bistability. These instabilities can be described by the same equations of motion as the IOB [8] thus proving the common model so some extend.

The existence of an inversion-dependent resonance frequency of coupled ions as given by (17) has consequences for all phase-sensitive optical effects like coherent transients. It means that the resonance frequency of the ions is slightly shifting during the decay time of the excited states. In [8] it was shown by numerical calculations that the photon echo can strongly be quenched by this effect. This is in accordance with the experimental experience that photon echos can be found only in very diluted doped crystals. Similar quenching can be expected in other coherence experiments as well.

6. Conclusions

1. Theory predicts the existence of IOB for ion pairs in solids if the ion-ion interaction and the dephasing by ion-phonon interaction are introduced simultaneously as competing processes.
2. The experimental realization of the IOB in solids is difficult because of the inhomogeneous line broadening.
3. The inversion-dependent resonance frequency of coupled ions can quench phase-sensitive optical effects.

Acknowledgements

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