Optical nonlinearity in a system of coupled atoms

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A chain of two-level atoms is considered in which the wave functions of the excited electron states of neighboring atoms overlap. The intensity threshold for optical nonlinearity in such systems is lower than for isolated atoms. A mechanism is discussed which accounts for the large optical nonlinearities observed during resonant formation of excitons.

The interatomic distances in many compounds are such that appreciable overlapping can occur only between the wave functions of excited electron states in neighboring atoms—the overlaps between excited and unexcited states or between two unexcited states can be neglected. Because of the overlap of the excited wave functions, the energy required to excite an atom with at least one excited neighbor is quite different from the excitation energy required for an atom with unexcited neighbors. Thus an incident electromagnetic wave of frequency resonant for an atom with unexcited neighbors cannot resonantly excite atoms with excited neighbors. In other words, the effect of the wave is such that two adjacent atoms cannot both be excited. Optical nonlinearities in polyatomic systems of this type therefore show up at lower incident intensities than is the case for isolated atoms.

In this paper we consider a closed chain of N identical, periodically spaced, two-level atoms in which the wave functions of the excited electron states overlap for neighboring atoms. We analyze the behavior of the system in an intense radiation field whose frequency ω is resonant for an atom with unexcited neighbors.

The Hamiltonian is given by

$$\hat{H}=\sum_{n=1}^{N}\{E(a_n{}^+a_n+b_n{}^+b_n)-\lambda(a_n{}^+b_n{}^+e^{-i\omega t}+b_na_ne^{i\omega t})+Ta_n{}^+a_n\overset{+}{a}_{n+1}a_{n+1}\},$$

$$E={}^1/_2(E_1-E_0),\quad \lambda={}^1/_2\mathbf{d}_{10}\vec{\mathscr{E}}_0. \tag{1}$$

Here $a_n{}^+$ is the creation operator for an electron in the excited state of atom n, and b_n is the hole creation operator (electron annihilation operator) for a ground-state hole of atom n; a_n and b_n annihilate excited electrons and ground-state holes in atom n, respectively, and E_0 and E_1 are the energies of the ground and excited states of an atom with unexcited neighbors; $\mathbf{d}_{10}$ is the matrix element for the dipole transition; $\vec{\mathscr{E}}_0$ is the electric field amplitude of the wave (we may take λ real without loss of generality); T determines the interaction between adjacent excited atoms due to overlapping of the excited electron wave functions. Since the chain is closed, $a_{N+1}{}^+a_{N+1}=a_1{}^+a_1$. We neglect possible resonant energy transfer from one atom to another.

Since in our case

$$|2E-\hbar\omega|\sim|\lambda|\ll T,\ \hbar\omega \tag{2}$$

the wave interacts resonantly with atoms having unexcited neighbors and nonresonantly otherwise.

In the resonance approximation the nonresonant terms in the Hamiltonian (1) are discarded. We assume that all the atoms are in the ground state when no electromagnetic wave is present, so that no two neighboring atoms can be simultaneously excited after the wave interaction is turned on. This circumstance permits us to adopt the following formalism to determine the form of the resonant part of the Hamiltonian. If we define the operator

$$\hat{G}_n=a_{n-1}\overset{+}{a}_{n-1}a_{n+1}\overset{+}{a}_{n+1}, \tag{3}$$

the familiar anticommutation relations for Fermi operators show readily that the eigenvalue of $\hat{G}_n$ is equal to 1 only if atoms $n-1$ and $n+1$ are unexcited; in all other cases it vanishes. We can use $\hat{G}_n$ to rewrite the Hamiltonian as

$$\hat{H}_r=\sum_{n=1}^{N}\{E(a_n{}^+a_n+b_n{}^+b_n)-\lambda(a_n{}^+b_n{}^+e^{-i\omega t}+b_na_ne^{i\omega t})\hat{G}_n\}, \tag{4}$$

in which only the resonant contribution appears. The operator $\hat{G}_n$ in (4) ensures that atom n will not interact resonantly with the wave provided at least one neighbor is excited, because the eigenvalue of $\hat{G}_n$ then vanishes.

The unitary transformation

$$U(t)=\exp\left\{-\frac{i\omega t}{2}\sum_{n=1}^{N}(a_n{}^+a_n+b_n{}^+b_n)\right\} \tag{5}$$

leads to the time-independent expression

$$\hat{H}_{r0}=\sum_{n=1}^{N}\{\varepsilon(a_n{}^+a_n+b_n{}^+b_n)-\lambda(a_n{}^+b_n{}^++b_na_n)\hat{G}_n\},$$

$$\varepsilon=E-{}^1/_2\hbar\omega, \tag{6}$$

for the Hamiltonian (4).

We find the ground-state wave function by the variational technique by writing

$$|\Psi\rangle=\prod_{n=1}^{N}y_n(1+x_na_n{}^+b_n{}^+\hat{G}_n)|0\rangle, \tag{7}$$

where x_n and y_n are the variational parameters and $|0\rangle$ is the ground state of the system. The role of $\hat{G}_n$ in (7) is to rule out states with two adjacent excited atoms. This permits us to derive an expression for functions of the type $\langle\Psi|\hat{f}|\Psi\rangle$ in terms of determinants. The normalization condition is

$$\langle\Psi|\Psi\rangle=S\prod_{n=1}^{N}y_n{}^2=1, \tag{8}$$

where

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$$S=\begin{vmatrix} 1 & ix_{N-1} & & & & & ix_N \\ ix_{N-1} & 1 & ix_{N-2} & & & 0 & \\ & ix_{N-2} & 1 & \ddots & & & \\ & & & \ddots & ix_3 & & \\ & 0 & & ix_3 & 1 & ix_2 & \\ & & & & ix_2 & 1 & ix_1 \\ ix_N & & & & & ix_1 & 1 \end{vmatrix}$$

$$+2(-i)^N \prod_{n=1}^{N} x_n. \tag{9}$$

Formula (9) implies that S is a sum of terms containing different combinations of the factors $x_n{}^2$ $(n=1, 2, \ldots, N)$. If a term contains $x_n{}^2$ then it cannot contain $x_{n-1}{}^2$ or $x_{n+1}{}^2$.

Similar expressions hold for the matrix elements needed to calculate $\langle\Psi|\hat{H}_{r0}|\Psi\rangle$:

$$W=\langle\Psi|\hat{H}_{p0}|\Psi\rangle+\mu\langle\Psi|\Psi\rangle$$

$$=x_n\langle\Psi|b_n a_n \hat{G}_n|\Psi\rangle=x_n{}^2\frac{\partial S}{\partial x_n{}^2}\prod_{m=1}^{N} y_m{}^2. \tag{10}$$

We thus minimize the function

$$W=\langle\Psi|\hat{H}_{p0}|\Psi\rangle+\mu\langle\Psi|\Psi\rangle$$

$$=\left\{\sum_{n=1}^{N}[2\varepsilon x_n{}^2-2\lambda x_n]\frac{\partial S}{\partial x_n{}^2}+\mu S\right\}\prod_{m=1}^{N} y_m{}^2; \tag{11}$$

where μ is a Lagrange multiplier.

Since the atoms are all identical, we must have

$$x_1=x_2=\ldots=x_N=x, \quad y_1=y_2=\ldots=y_N=y \tag{12}$$

at the minimum point. This simplifies the calculations considerably by reducing the problem to evaluating nth order determinants of the form

$$D_n(x)=\begin{vmatrix} 1 & ix & & & & \\ ix & 1 & ix & & 0 & \\ & ix & 1 & \ddots & & \\ & & & \ddots & & \\ & & & 1 & ix & \\ & 0 & & ix & 1 & ix \\ & & & & ix & 1 \end{vmatrix} \tag{13}$$

It is easy to see that the D_n satisfy the recursion relation

$$D_n(x)=D_{n-1}(x)+x^2D_{n-2}(x). \tag{14}$$

The substitution $D_n=(2z)^{-n}D_n{}'$, where $z=1/2ix$, yields a new recursion formula for the $D_n{}'$ which coincides with the one for Chebyshev polynomials.[1] Since $D_1=1$ and $D_2=1+x^2$, we thus get

$$D_n(x)=\frac{1}{2(^1/_4+x^2)^{1/2}}\left\{\left[\frac{1}{2}+\left(\frac{1}{4}+x^2\right)^{1/2}\right]^{n+1}\right.$$
$$\left.-\left[\frac{1}{2}-\left(\frac{1}{4}+x^2\right)^{1/2}\right]^{n+1}\right\}. \tag{15}$$

The extremum equations for W contain functions which for $x_1=x_2=\ldots=x_N=x$ can be expressed in terms of the D_n (x) as follows:

$$S=D_N(x)+x^2D_{N-2}(x), \tag{16}$$

$$\partial S/\partial x_n{}^2=D_{N-2}(x), \tag{17}$$

$$\frac{\partial^2 S}{\partial x_m{}^2\partial x_n{}^2}=\begin{cases} 0, & m=n,\ n\pm 1 \\ D_{N-4}(x), & m=n\pm 2 \\ D_{n-m-2}(x)D_{N+m-n-2}(x), & 1\leqslant m\leqslant n-3 \\ D_{m-n-2}(x)D_{N+n-m-2}(x), & n+3\leqslant m\leqslant N \end{cases} \tag{18}$$

We find the dependence of x on λ and ε by substituting (16)–(18) into

$$\partial W/\partial x_m{}^2=0, \quad \partial W/\partial y_m{}^2=0. \tag{19}$$

Here the derivatives are evaluated at $x_1=x_2=\ldots=x_N=x, y_1=y_2=\ldots=y_n=y$.

In the limit $N\gg 1$ we have

$$\frac{\lambda}{\varepsilon}=\frac{x[^1/_4(1+3x^2)+{}^1/_2(1+x^2)(^1/_4+x^2)^{1/2}]}{[^1/_8+{}^1/_2(^1/_2-x^2)(^1/_4+x^2)^{1/2}-x^4]}, \tag{20}$$

and the polarization of the atomic chain is

$$\mathbf{P}=\langle\Psi|\mathbf{d}_{10}\sum_{n=1}^{N}(a_n{}^+b_n{}^+e^{-i\omega t}+b_na_ne^{i\omega t})|\Psi\rangle=\mathbf{P}_0\cos\omega t, \tag{21}$$

$$\mathbf{P}_0=\frac{Nd_{10}x}{(^1/_4+x^2)^{1/2}[^1/_2+(^1/_4+x^2)^{1/2}]}.$$

Analysis of Eqs. (20) and (21) reveals that the approximation

$$\mathbf{P}_0/N=\mathbf{d}_{10}\lambda(\varepsilon^2+3\lambda^2)^{-1/2} \tag{22}$$

describes the parametric coupling between $\mathbf{P}_0$ and λ/ε quite accurately (Fig. 1). Formula (22) differs from the one for isolated atoms (see, e.g., Ref. 2) because of the factor 3 multiplying the λ^2 term, which is known to be responsible for the optical nonlinearity. We thus conclude that the intensity threshold for nonlinearity is roughly one-third of the value for isolated atoms.

We note that the decreased nonlinearity threshold should show up to some degree in all polyatomic systems in which the wave functions of the excited electrons overlap for neighboring atoms. Even the simplest case of two coupled atoms ($N=2$) is of interest in this context. If the overlap forbids a resonant transition to a state in which both atoms are excited, the polarization is given by

$$\mathbf{P}_0/2=\mathbf{d}_{10}\lambda(\varepsilon^2+2\lambda^2)^{-1/2}. \tag{23}$$

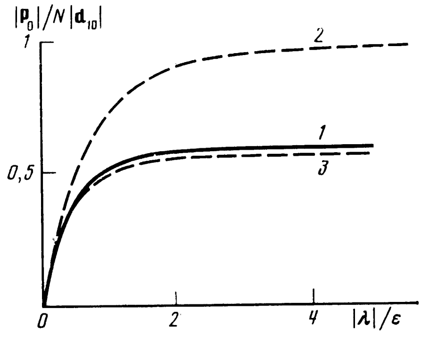

FIG. 1. Parametric dependence of $|P_0|/N$ on λ/ε. The solid curve 1 gives results from Eqs. (20) and (21); curve 2 is for isolated atoms; curve 3 describes the function (22).

We see readily by comparing the results for a chain and for $N = 2$ that the observed nonlinearities should be larger for a coupled-atom chain. This is because each excited atom in the chain prevents its two neighbors from being excited, whereas each atom has only one neighbor for $N = 2$. Large nonlinearities should therefore be observed in materials in which a single excited atom can suppress excitation of many other atoms.

The enhanced nonlinearity may be very important for light interacting coherently with crystals in the exciton region of the spectrum. In particular, if the excitons are strongly coupled, optical nonlinearities should be observed in crystals with a sufficiently strong exciton-exciton interaction. The nonlinearity will be particularly pronounced when weakly coupled excitons are produced resonantly in semiconductors. We conclude from our analysis that excitons generated by an intense electromagnetic wave should be spatially correlated, i.e., their wave functions should not overlap. Because the volume occupied by weakly coupled excitons in semiconductors is greater than the volume of the unit cell, optical nonlinearity in these systems will be observed for relatively weak incident intensities. This mechanism is apparently responsible for the large nonlinearities observed experimentally in Refs. 3 and 4 at exciton frequencies.

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