

Coupled Oscillator Representation of Many-Body Effects in Ultrafast Optical Response

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Abstract

A theory for the nonlinear optical response of an assembly of four level atoms representing an s-p transition with dipole-dipole interactions is developed. Simulation results for two pulse ultrafast four wave mixing measurements in neat atomic clusters and in liquids demonstrate that the electronic density of states can be obtained by combining linear absorption and four wave mixing measurements. We show that by reversing the pulse time ordering in a photon echo sequence we obtain a sensitive direct probe for interatomic interactions and correlations.

The interpretation of nonlinear optical measurements such as photon echo and pump-probe spectroscopy of a system of dilute chromophores in the condensed phase (e. g. doped crystals and dye solutions at low concentrations) is traditionally made using the optical Bloch equations. Homogeneous and inhomogeneous dephasing (T_2 processes) can be easily incorporated in these equations. The tremendous success of these equations in the interpretation of nonlinear optical measurements involving simple few level systems makes it tempting to apply them to more complex many body systems such as neat liquids and semiconductors. In these applications all many body effects are lumped into a frequency dependent dephasing rate. However, mapping a complex many body system into an effective two level system makes it very hard to develop physical intuition. Photon echoes, for example, are traditionally analyzed using the optical Bloch equations, but as the broadening of the linear absorption line for a neat cluster or a liquid is caused entirely by the intermolecular interactions among chromophores (rather than by the interactions with optically inactive bath molecules) this model does not apply. An alternative approach is based on a quasiparticle representation where the many-body system is mapped onto a set of coupled anharmonic (exciton) oscillators. This direct generalization of the Drude (harmonic oscillator) model for linear response [1,2] provides a completely different framework for analyzing such spectroscopies in terms of spectral densities. Nonlinear signals for ordered nanostructures of two level atoms were calculated using this approach [3,4]. Both frequency domain and time domain techniques have been investigated.

We consider a system of four-level atoms interacting via dipole-dipole interactions. The model can represent small clusters as well as liquids. Each atom has a ground state and a triply degenerate excited p state, separated by an optical transition frequency Ω . We chose this as a simple model for describing many-body effects in assemblies of polarizable atoms including exciton dynamics. Whenever needed we use parameters of Ar. We assume the following Hamiltonian [5]

$$H = \sum_{n\alpha} \Omega B_{n\alpha}^\dagger B_{n\alpha} + \sum_{n<m, \alpha\beta} J_{n\alpha, m\beta}(\mathbf{r}_{nm}) (B_{m\beta}^\dagger B_{n\alpha} + B_{n\alpha}^\dagger B_{m\beta}) + H_{\text{nucl}} - \sum_{n\alpha} \mu_n E_{n\alpha} P_{n\alpha} \quad (1)$$

Here B^\dagger and B are creation and annihilation operators for the s-p system at atom m . The index n runs over the atoms and α runs over the internal degrees of freedom, $\alpha = x, y, z$. $B_{n\alpha}^\dagger$ changes the state of atom n from the ground s to the excited state p_α . J represents the interatomic dipole-dipole interaction

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$$J_{n\alpha, m\beta}(r_{nm}) = -\mu^2 \left[\frac{3r_{nm, \alpha} r_{nm, \beta}}{r_{nm}^5} - \delta_{\alpha, \beta} \frac{1}{r_{nm}^3} \right] (1 - \delta_{n, m}) ,$$

where δ is the Kronecker delta, and μ is the magnitude of the transition dipole moment. The dipole coupling in Eq. (1) conserves the number of excitons (The Heitler London approximation). H_{nucl} represents the nuclear motions

$$H_{\text{nucl}} = \sum_n \frac{p_n^2}{2m_n} + \sum_{n < m} V_{\text{exc}}(r_{nm}) .$$

Finally the last term in Eq. (1) represents the interaction of the electric field at r_n which is polarized in the α direction ($E_{n, \alpha}$) with the electronic polarization operator $P_{n\alpha}$.

$$P_{n\alpha} \equiv (B_{n\alpha}^\dagger + B_{n\alpha}) .$$

The commutation relations for the B operators can be found by studying the action of the B's on the basis $|s\rangle$, $|p_x\rangle$, $|p_y\rangle$, and $|p_z\rangle$. We immediately find that $B_x^\dagger |p_\alpha\rangle = 0$, and, using this, also that $B_x B_y^\dagger = 0$. We then have

$$[B_{n\alpha}, B_{m\beta}^\dagger] = \delta_{nm}(\delta_{\alpha\beta} - B_{n\beta}^\dagger B_{n\alpha} - \delta_{\alpha\beta} N_n) , \quad (2)$$

where $N_n \equiv \sum_\alpha B_{n\alpha}^\dagger B_{n\alpha}$ counts the number of excitations at atom n (0 or 1). For $n \neq m$ they commute and behave as bosons. The second and third terms on the right hand side represent deviations from a boson character. The second ($B^\dagger B$) term corresponds to a collection of three two level atoms on the same atoms. Eq. (2) shows that an s-p atom is not identical to a collection of three two level atoms on the same site, but contains an additional nonlinearity since each atom can carry only one excitation. This additional nonlinearity is given by the N_n term in Eq. (2) and contributes to the nonlinear response. It can be probed, e.g. through the dependence of the signal on the polarization of the incoming beams.

To calculate the third order nonlinear polarization

$$P_n^{(3)}(t) = \mu_n [\langle B_n(t) \rangle^{(3)} + \langle B_n^\dagger(t) \rangle^{(3)}] ,$$

we used the Heisenberg equation of motion for an operator $A(t)$, $\hbar dA(t)/dt = i[A, H]$. The calculation requires the dynamics of single exciton states represented by B as well as of two exciton variables BB . Terms of normally ordered products of three and four B's are irrelevant for the third order response. We finally obtain the following closed set of equations

$$\frac{1}{i} \frac{d}{dt} \langle B_{n\alpha} \rangle^{(1)} = -(\Omega_n - i\gamma) \langle B_{n\alpha} \rangle^{(1)} - \sum_{m\beta} J_{n\alpha, m\beta}(t) \langle B_{m\beta} \rangle^{(1)} + \frac{\mu_n}{\hbar} E_{n\alpha}(t) . \quad (3a)$$

$$\begin{aligned} \frac{1}{i} \frac{d}{dt} \langle B_{n\alpha} B_{m\beta} \rangle^{(2)} &= -(\Omega_n + \Omega_m - 2i\gamma) \langle B_{n\alpha} B_{m\beta} \rangle^{(2)} \\ &- (1 - \delta_{n, m}) \sum_{i\gamma} J_{n\alpha, i\gamma}(t) \langle B_{i\gamma} B_{m\beta} \rangle^{(2)} - (1 - \delta_{n, m}) \sum_{i\gamma} J_{m\beta, i\gamma}(t) \langle B_{n\alpha} B_{i\gamma} \rangle^{(2)} \\ &+ (1 - \delta_{n, m}) \frac{\mu_n}{\hbar} E_{n\alpha}(t) \langle B_{m\beta} \rangle^{(1)} + (1 - \delta_{n, m}) \frac{\mu_m}{\hbar} E_{m\beta}(t) \langle B_{n\alpha} \rangle^{(1)} , \end{aligned} \quad (3b)$$

$$\begin{aligned} \frac{1}{i} \frac{d}{dt} \langle B_{n\alpha} \rangle^{(3)} &= -(\Omega_n - i\gamma) \langle B_{n\alpha} \rangle^{(3)} - \sum_{m\beta} J_{n\alpha, m\beta}(t) \langle B_{m\beta} \rangle^{(3)} \frac{\mu_n}{\hbar} E_{n\alpha}(t) \\ &- \frac{\mu_n}{\hbar} \sum_{\beta} [E_{n\beta}(t) \langle B_{n\beta}^\dagger \rangle^{(1)} \langle B_{n\alpha} \rangle^{(1)} + E_{n\alpha}(t) \langle B_{n\beta}^\dagger \rangle^{(1)} \langle B_{n\beta} \rangle^{(1)}] \\ &+ \sum_{m\beta\gamma} J_{n\gamma, m\beta}(t) \langle B_{n\gamma}^\dagger \rangle^{(1)} \langle B_{n\alpha} B_{m\beta} \rangle^{(2)} J_{n\alpha, m\beta}(t) \langle B_{n\alpha}^\dagger \rangle^{(1)} \langle B_{n\gamma} B_{m\beta} \rangle^{(2)} . \end{aligned} \quad (3c)$$

2γ is the exciton decay rate (inverse lifetime), which is introduced here phenomenologically and $\langle \dots \rangle$ denotes the quantum average

We carried out simulations to explore the possible formation of an echo in clusters of s-p atoms. We used the Lennard-Jones form for the interaction potential $V(r) = 4\epsilon[(r/\sigma)^{-12} - \epsilon[(r/\sigma)^{-6}]$. All fields are assumed to be linearly polarized along the same

direction, and nuclear motions were not included in the following calculations. The natural timescale of our model is \hbar/J with $J \equiv \mu^2/\sigma^3$. For Argon this timescale is ~ 5 fs. We studied an ensemble of clusters and a liquid at a temperature $T^* \equiv k_B T/\epsilon = 0.2$, (corresponding to 16K for Ar). The ensemble of configurations were created using a molecular dynamics program where after a short thermalization period, a "box potential" was slowly turned off. The temperature was controlled by monitoring the average kinetic energies, and scaling the velocity if needed. Liquid simulations were done by a single run of a thermalized sample. The system interacts with two pulses (the first with wavevector \mathbf{k}_1 and the second with wavevector \mathbf{k}_2) separated by a delay τ . The photon echo signal is related to the third order polarization with wavevector $\mathbf{k}_s = 2\mathbf{k}_2 - \mathbf{k}_1$, and is proportional to $|P^{(3)}(\mathbf{k}_s, t)|^2$.

We have found the following physical interpretation for our simulations. The linear absorption spectrum is given by

$$I(\omega) = \sum_j \langle \delta(\omega_j - \omega) | \langle k=0 | \psi_j \rangle |^2 \rangle ,$$

where ω_j is the energy of mode j , $|\psi_j\rangle$ is its eigenfunction and $|k\rangle = \sum_i B_i^\dagger |0\rangle$, and $\langle k=0 | \psi_j |0\rangle$ represents the transition dipole of the j 'th electronic state.

Let us consider the Fourier transform of the echo polarization for a given delay time τ

$$\psi(\omega) \equiv \int dt P^{(3)}(\mathbf{k}_s, t) \exp(i\omega t) .$$

Using standard expressions [2,4] we can always recast $\psi(\omega)$ in terms of sums over all global (electronic plus nuclear) states of the system. Such expressions are not practical for actual computations since the number of terms is very large and a complete calculation of all the states is a formidable task. Nevertheless they are still useful to gain some insight. Each term in the sum requires four interactions with the electric field. As an echo setup requires an exact rephasing, it is plausible that the levels can be considered independent for the dominant contribution. To test this idea we consider the following quantity

$$H(\omega) = \sum_j \langle \delta(\omega_j - \omega) | \langle k=0 | \psi_j \rangle |^4 \rangle .$$

This is the density of states scaled by the transition dipole moment to the fourth power. We argue that $H(\omega)$ should be at least qualitatively similar to $\psi(\omega)$. In Figure 1 we compare $H(\omega)$ with $\psi(\omega)$ for a s-p liquid. The striking similarity confirms our conjecture. Is this a viable way to obtain the density of (electronic) states using purely spectroscopic experiments? To answer this question we performed simulations for $I^2(\omega)/H(\omega)$, the results for a small cluster with 7 atoms are presented in Figure 2 and for a liquid in Figure 3. If our conjecture holds, this quantity should be proportional to the density of states. As is obvious from the figures this is perfectly realized for a liquid, and is a very good approximation for a cluster.

When the order of the two pulses in the echo experiment is reversed (i.e. pulse 2 is first and we set $\tau < 0$) the nature of the signal completely changes [6]. When applied to a simple multilevel system (e.g. s-p atom) we find that it can no longer show an echo. For an isolated two level system the signal vanishes identically within the rotating wave approximation (RWA). For these reasons this particular pulse sequence is much less common and it does not even have a name! Simulation results for $\tau < 0$ are presented in Figure 4. What makes this technique particularly interesting is the fact that the entire signal is induced by intermolecular interactions. This could form an important new means for probing intermolecular motions in liquids. A detailed microscopic interpretation of the signal remains to be developed.

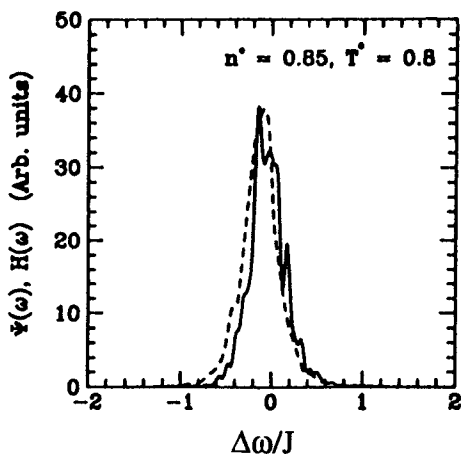


Figure 1

Solid: The Fourier transform of the echo amplitude $\psi(\omega)$ for a liquid at $T^*=0.2$ and one particular delay ($J\tau = 20$) compared to the “hyperabsorption spectrum” $H(\omega)$, (dashed).

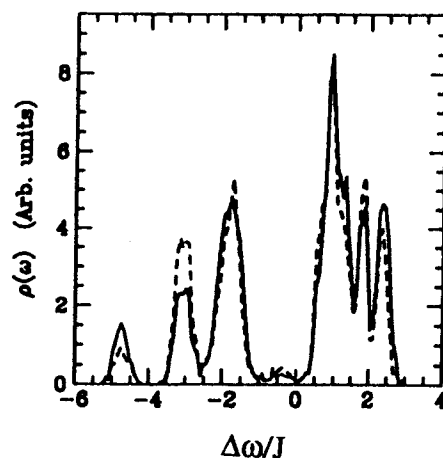


Figure 2

The density states for a cluster with 7 s-p atoms and Lennard-Jones interactions $T^*=0.2$ (solid) compared to spectroscopic observable $I^2(\omega)/H(\omega)$ (dashed).

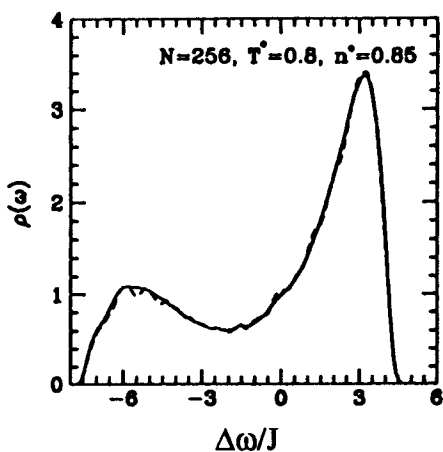


Figure 3

The density of states for a $N = 256$ liquid at $T = 0.8$, $n = 0.85$ (solid) compared to spectroscopic observable $I^2(\omega)/H(\omega)$ (dashed) of the same state point.

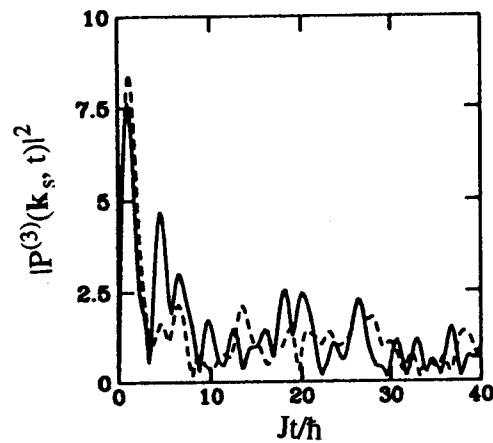


Figure 4

Two pulse four wave mixing signal for negative delays for two delays, $J\tau = -5$ (solid) and $J\tau = -20$ (dashed) at $\mathbf{k}_s = 2\mathbf{k}_2 - \mathbf{k}_1$ when pulse 2 comes first.

Nonlinear ultrafast spectra of molecular and semiconductor materials are remarkably similar. Yet, for historical reasons, their theoretical modeling is done using a completely different language and physical picture. Quantum chemists base their thinking for the most part on the global (many body) electronic eigenstates of molecular systems. It is then common to express the optical response using sums over states. Ultrafast spectroscopy of semiconductors is calculated using a quasiparticle electron hole picture. Since the methods for calculating eigenstates vary among disciplines it is very hard to compare systems with localized and delocalized electron states. It is possible to bridge the gap between these approaches by developing a systematic procedure that starts with the microscopic hamiltonian and maps the system onto a collection of coupled anharmonic oscillators. This way, the analysis and differences become more transparent and a direct comparison is possible. The present formulation can be generalized to various types of materials. (1) Molecular materials and assemblies can be represented as excitonic oscillators; This case was illustrated here (2) In off resonant spectroscopy in liquids, nuclear motions can be treated as oscillators [7,8]; (3) In semiconductors the oscillators describe electron hole pairs and Wannier excitons; and (4) Conjugated polyenes are intermediate between molecular and semiconductor materials and can be modeled as charge transfer exciton oscillators [9].

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