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Effect of nonadiabaticity and disorder on nonlinear optical susceptibilities

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The effect of nonadiabaticity on optical linear polarizability (α) and third-order polarizability (γ) is investigated numerically for a Holstein-Hubbard finite chain system. The variations of α and γ are studied as a function of the nonadiabaticity parameter, electron-phonon coupling strength and electron-electron interactions. For a specific range of values of each of these parameters, α and γ are significantly enhanced. Disorder in either electronic or phonon degrees of freedom is also found to enhance optical nonlinearity.
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Broken-symmetry ground states in currently studied complex electronic materials are sensitively dependent on competitions between electron-electron and electron-lattice interactions, on dimensionality, disorder, and chemical doping, as well as external fields.[1] These ground states are responsible for semiconductorlike gaps in the electronic spectrum. Consequently most applications rely on controlling these gaps and their melting to metallic phases or between broken-symmetry phases, as functions of the above parameters. In this regard it is very important to understand the multi-time-scale and energy-scale effects, i.e., ''nonadiabatic'' effects, inherent in the competitions for ground states.

The purpose of this work is to study the consequences of relaxing the adiabatic approximations on optical polarizabilities (linear, α, and nonlinear, γ). We do so for a Holstein-Hubbard finite chain model that includes electron-electron (e-e) correlations and electron-phonon (e-ph) coupling. This model is frequently adopted for low-dimensional conjugated polymers, charge-transfer salts and inorganic semiconductors. In higher dimensions, the same model (and issues) are relevant to many prototypical systems, e.g., perovskite oxides, organic charge-transfer and spin-Peierls compounds. Not surprisingly, the greatest sensitivities in our model are found near crossovers between spin-density-wave (SDW) and charge-density-wave (CDW) ground states where broken symmetries are soft, when the lattice frequencies are resonant with charge or spin frequencies, or when disorder length scales become relevant. In these regimes we find significant enhancements of both α and γ.

For typical systems with both strong e-e correlation and e-ph couplings, a direct investigation into the role of nonadiabaticity has been very difficult for various perturbative or variational schemes, and no systematic methods have been developed to solve for the nonadiabatic optical susceptibilities of such systems. The difficulty first lies in the lack of a direct approach to solve for the eigenspectrum of a full quantum mechanical problem with sufficient excited-state information, mainly because the phonon Hilbert space is intrinsically infinite. Along with recent progress in numerically exact solutions of many-fermion systems,[2] a few studies have gradually approached this nonadiabatic problem of quantum phonons.[3,4] For example, the quantum polaron problem[3,5] and the optimization of the density-matrix–renormalization-group (DMRG) method have been extensively examined. However, an efficient method that is able to yield sufficient excited-state information is still not available. In another recent study, direct evidence of quantum breathers and breather-exciton bound states have been revealed for e-ph coupled systems with appropriate strengths of nonadiabaticity.[6]

Another difficulty in solving a quantum phonon problem is how to utilize information from the usually incomplete solution of the eigenproblem so as to directly calculate the various observable susceptibilities. Simple diagonal correlation functions can be calculated through the moment method or the projective Lanczos method.[7] However, they cannot easily be applied to the problem of high-order nondiagonal correlation functions. In Ref. 8, this goal has been achieved for a fermion system: an extended Hubbard model system is solved via a DMRG method, while the static γ is calculated through the correction vector method.[9] In the present study, along with the two schemes in Refs. 6 and 8, we develop a numerical nonperturbative approach to investigate the nonadiabatic problem of a fully quantum e-ph system.

We consider a Holstein-Hubbard (HH) model Hamiltonian of a finite one-dimenisonal e-ph coupled system:

$$H_e=\sum_{i\sigma} -t_0(c_{i\sigma}^{\dagger}c_{i+1,\sigma}+\text{H.c.})+\sum_i U n_{i\uparrow}n_{i\downarrow} + \sum_{i\sigma\sigma'} V n_{i\sigma}n_{i+1\sigma'}+\sum_i \hbar\omega_0(b_i^{\dagger}b_i+\tfrac{1}{2}) - \sum_{i\sigma}\lambda(b_i^{\dagger}+b_i)n_{i\sigma}. \quad (1)$$

Here, $c_{i\sigma}^{\dagger}(c_{i\sigma})$ and $b_i^{\dagger}(b_i)$ are the creation (annihilation) operators of electrons and phonons, respectively, and they obey the normal commutation relations. t_0, U, and V are the electron kinetic energy, and the on-site and nearest-neighbor

Coulomb repulsions; $\hbar\omega_0$ is the bare phonon energy. The form of the e-ph coupling (λ term) is that used in the Holstein model.[10] Throughout this study, we consider electronically half-filled systems with periodic boundary conditions. Lengths of chains simulated range from 2 to 6 sites due to computational limitation. The ratio of bare phonon and electronic energies, $\hbar\omega_0/t_0$, serves well as an indication of the adiabaticity of this e-ph system. When $\hbar\omega_0/t_0 \to 0$, an adiabatic approximation cannot be justified.

To solve this nonadiabatic problem for a finite e-ph system, our numerical approach consists of two major steps: First, we use the exact diagonalization method[5] to solve for the ground state eigenvalue and eigenfunction of the system Hamiltonian matrix represented in the Hilbert space defined by appropriately selected basis functions. We deal fully with nonadiabaticity and e-e correlations; the only approximation involves the truncation of the infinite phonon Hilbert space. The effect of the truncation is evaluated through various distribution functions.[11] Physical convergence is generally achieved through addition of phonon basis states and confining the calculation to finite system sizes and suitable parameter regions. We find that convergence is more easily reached for parameter sets with more nonadiabatic and stronger e-e correlated systems. High-quality numerical convergence is maintained through an efficient exact diagonalization method, such as a modified Davidson method, which can also deliver higher excited states to examine the convergence of the ground state.[5] However, finite-size effects remain to be systematically studied.

Second, we use the correction vector method to calculate α and γ. The main merits of this method are that (i) the nondiagonal correlation functions are calculated without knowledge of the entire excited-state eigenspectrum and only useful information within the optically involved states is extracted and accounted for, and (ii) it is unnecessary to calculate even the individual eigenstates of the optically active states; instead, only a few linear combinations of such states are solved for the purpose of the total susceptibility calculation. Such linear combinations, ''correction vectors,''[9] are defined as

$$(H-\mathcal{E}_g+\hbar\Omega_1+i\Gamma)|\boldsymbol{\phi}^{(1)}(\Omega_1)\rangle=\boldsymbol{J}|\Psi_g\rangle, \tag{2}$$

$$(H-\mathcal{E}_g+\hbar\Omega_2+i\Gamma)|\vec{\phi}^{(2)}(\Omega_1,\Omega_2)\rangle=\boldsymbol{J}|\phi^{(1)}(\Omega_1)\rangle, \tag{3}$$

for a typical third-order optical process. Here H is the system Hamiltonian (1), $\mathcal{E}_g$ and $|\Psi_g\rangle$ are the ground-state eigenvalue and eigenfunction, respectively; $\hbar\Omega_1$ and $\hbar\Omega_2$ stand for the energies of the incident photons, and Γ is a phenomenological optical damping factor. $\boldsymbol{J}$ is the current operator (within the electric dipole approximation):

$$\boldsymbol{J}=-\imath\boldsymbol{e}_x\sum_{i\sigma} t_0[a+l(b_{i+1}^{\dagger}+b_{i+1}-b_i^{\dagger}-b_i)(c_{i\sigma}^{\dagger}c_{i+1\sigma} - c_{i+1\sigma}^{\dagger}c_{i\sigma})]+\imath\boldsymbol{e}_x\sum_i \hbar\omega_0 l(b_i^{\dagger}-b_i)\left(Z_i-\sum_\sigma c_{i\sigma}^{\dagger}c_{i\sigma}\right), \tag{4}$$

for the Hamiltonian (1). Here, a stands for the lattice constant and $l=\sqrt{\hbar/2M\omega_0}$ is the length scale of lattice vibration (assumed as $l=10^{-3}$ throughout this study). $\vec{e}_x$ is the unit direction vector along the chain. Z_i is the core charge of site i (assumed as $Z_i=1$ for half-filled systems). It is appropriate to use the current operator rather than the dipole operator in the presence of periodic boundary conditions. Equations (2,3) are solved through an iterative linear system solver, a modified generalized minimal residual method.[12] This method is more efficient when applied to the linear equation, systems (2) and (3), because the latter are not necessarily positively definite. Furthermore, the optical susceptibilities can be expressed as the products of these correction vectors and the matrix elements of the current operator.[8] Within this study, only static susceptibilities of the first and third orders [i.e., $\alpha(\Omega\to 0)$ and $\gamma(\Omega_1,\Omega_2\to 0)$] are evaluated (the second-order susceptibility is zero due to the symmetry requirement). We also calculated the dynamic linear susceptibility for the full frequency range using the projective Lanczos method.[6,7] Note that both methods of eigenvalue solver and linear equations solver are subspace iterative methods, and they scale linearly with the dimension of the Hilbert space. It is also only necessary to design and apply the operation of matrix-vector multiplication such as $|\Psi\rangle=\hat{\mathrm{O}}|\Psi\rangle$

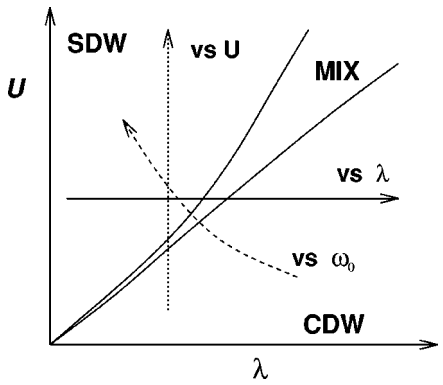

FIG. 1. Schematic phase diagram for the HH model.

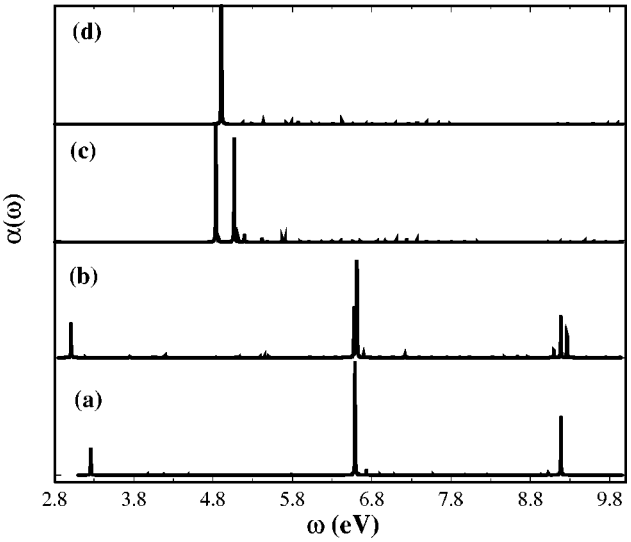

FIG. 2. Optical absorption of a six-site Holstein-Hubbard chain with $t_0=1.00$, $\lambda=0.35$, $U=5.13$, $V=2.75$, $M_{\mathrm{ph}}=4$, and $\mathcal{M}=1\,638\,400$. (a) $\hbar\omega_0=0.10$, (b) $\hbar\omega_0=0.15$, (c) $\hbar\omega_0=0.40$, (d) $\hbar\omega_0=0.80$ (M_{ph} and $\mathcal{M}$ stand for phonon truncation and the total dimension of the matrix). Energy units are in eV.

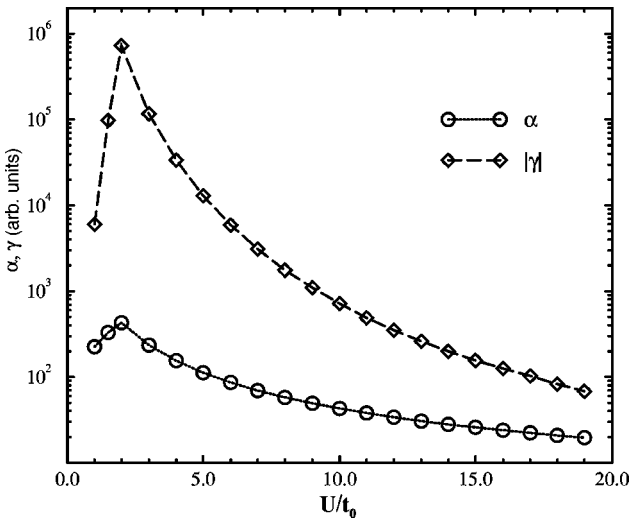

FIG. 3. Effects of e-e correlations (U/t_0) on α and γ (see text). The system is a six-site Holstein-Hubbard chain with $t_0=1.00$, $\lambda=0.37$, $\hbar\omega_0=0.21$, $V=0.123$, $M_{\rm ph}=10$, and $\mathcal{M}=1\,638\,400$, and various U/t_0.

for the cases where the multimillion-dimensional matrix H is involved.

We first present a schematic phase diagram in the U–λ plane in Fig. 1 for the HH model. For relatively large λ and small U, the ground state is in a phase with strong charge fluctuations (charge-density waves, labeled CDW's, in the mean-field sense). In contrast, for large U and small λ the ground state is in a phase with strong spin fluctuations (spin-density waves, labeled by SDW's). In mean-field arguments,[13] we expect an intermediate phase where an increase in nonadiabaticity ($\hbar\omega_0/t_0$) corresponds to moving from the CDW state into the intermediate region and then into the SDW phase.

Figure 2 depicts optical absorption for different optical phonon frequencies, i.e., as a function of nonadiabaticity. For $\hbar\omega_0=0.10t_0$ there are two main peaks at $\sim 3.2t_0$ and $\sim 5.5t_0$

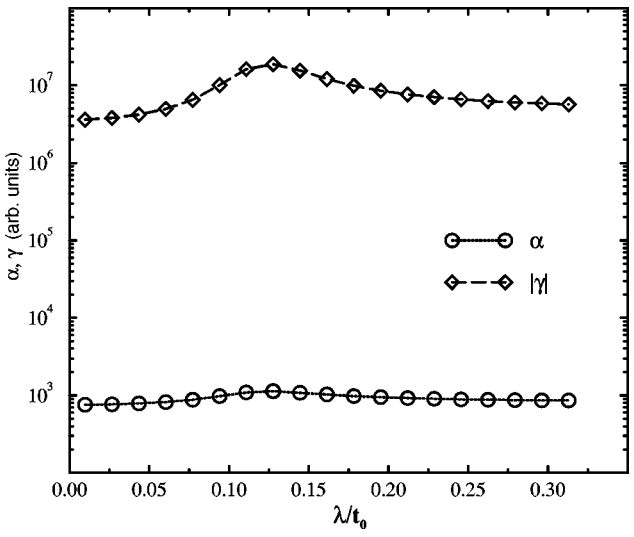

FIG. 4. Effects of e-ph coupling strength (λ/t_0) on α and γ (see text). The system is a 4-site Holstein-Hubbard chain with $t_0=1.00$, $\hbar\omega_0=0.15$, $U=1.50$, $V=0.323$, $M_{\rm ph}=10$, and $\mathcal{M}=360\,000$, and various λ/t_0.

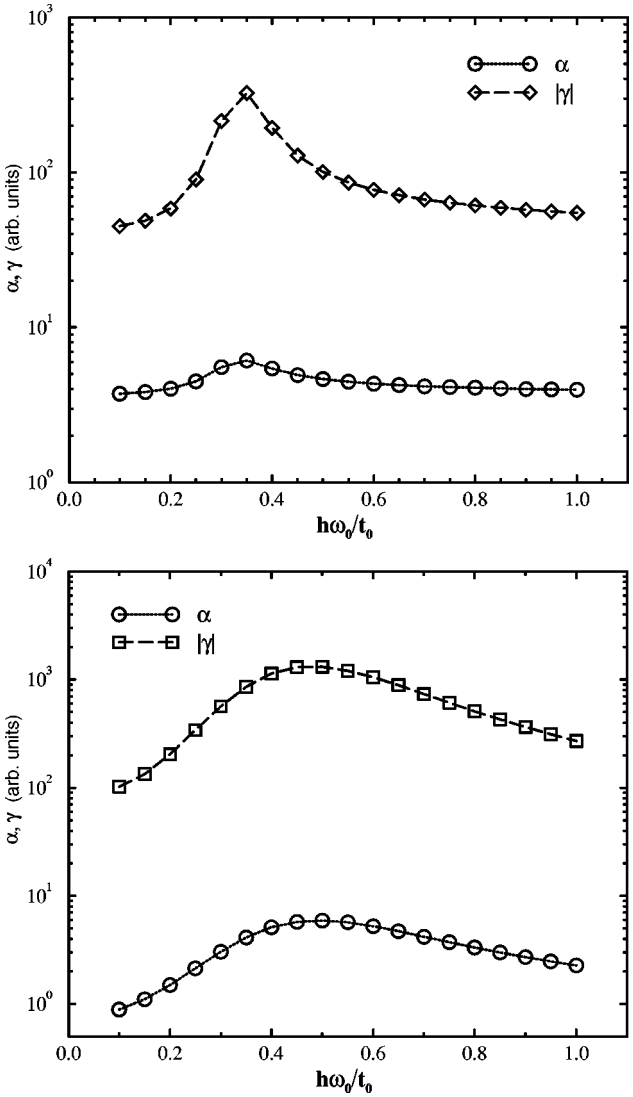

FIG. 5. Effects of nonadiabaticity ($\hbar\omega/t_0$) on α and γ. The system is a six-site Holstein-Hubbard chain (lower panel) with $t_0=1.00$, $\lambda=0.31$, $U=2.39$, $V=1.21$, $M_{\rm ph}=4$, and $\mathcal{M}=1\,638\,400$, and various $\hbar\omega_0/t_0$. For size-consistency, the upper panel shows results for a four-site chain.

associated with the CDW gap and Hubbard gap, respectively. Note that there are some states in the tail of the CDW peak representative of exciton states. As $\hbar\omega_0$ increases to $0.15t_0$, the CDW strength decreases (smaller gap) and the CDW peak moves to a lower energy of ~ 2.9 eV while the Hubbard peak splits into two peaks. For $\hbar\omega_0=0.40t_0$ the system is in a mixed state with a small gap around $4.8t_0$. For $\hbar\omega_0=0.80t_0$ the system is in the SDW state with a spin gap at $4.8t_0$.

Figure 3 shows the change in α and γ with increasing U. There is an initial increase and then a monotonic decrease in the values of these coefficients. As U is increased, the strength of the CDW decreases and the effective gap decreases [see Fig. 1]. This leads to an enhancement in both the linear polarizability (α) and hyperpolarizability (γ). α and γ are largest in the mixed state. As U is further increased, the system ground state changes to a SDW regime with increasing SDW strength (and spin gap). The latter responds optically very weakly whether linearly or nonlinearly. Therefore, a monotonic decrease is observed with further increase in U.

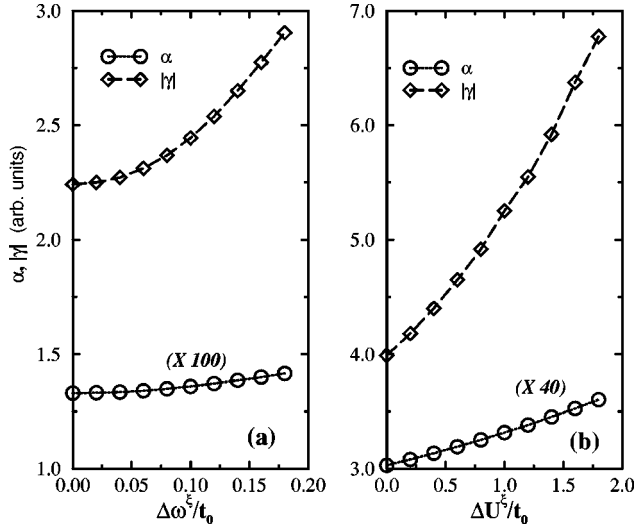

FIG. 6. Effects of disorder strength ($\Delta\hbar\omega^{\xi}/t_0$ and $\Delta U^{\xi}/t_0$) on α and γ. The systems are: (a) a four-site Holstein-Hubbard chain with $t_0=1.00$, $\hbar\omega_0=0.41$, $U=4.67$, $V=0.223$, $\lambda=0.39$, $M_{\rm ph}=10$, and $\mathcal{M}=360\,000$, and various $\Delta\hbar\omega^{\xi}/t_0$. (b) a four-site Holstein-Hubbard chain with $t_0=1.00$, $\hbar\omega_0=0.21$, $U=6.67$, $V=0.223$, $\lambda=0.39$, $M_{\rm ph}=10$, and $\mathcal{M}=360\,000$, and various $\Delta U^{\xi}/t_0$.

The peak is observed at a value of $U\sim 2t_0$. We note that this trend, i.e. the location and the amplitude of the peak, holds for variation in α and γ with other parameters (see below).

In Fig. 4 we show the change in α and γ as a function of the strength of the e-ph coupling (λ). The trend is very similar to that of variation with U. However, the effect is less striking in this case. Initially for small λ the system is in the SDW state (see Fig. 1). As λ increases, the strength of the SDW decreases indicating an enhancement of α and γ. The peak is observed in the mixed state at a value of $\lambda\sim 0.13t_0$. With a further increase in λ the system enters the CDW regime with increasing strength, i.e., the gap increases and thus α and γ diminish.

In Fig. 5 we depict the change in α and γ with increasing nonadiabaticity parameter. As $\hbar\omega_0$ is increased, the system is initially in the CDW state, then moves into the mixed state, eventually entering the SDW regime. We find a peak in both α and γ at a value ~ 0.35 of this parameter which corresponds to the mixed state. In addition, the peak in γ is substantially more pronounced than the peak in α.

Figure 6 depicts variation in α and γ with increasing disorder in electronic (ΔU) and phonon ($\Delta\omega$) degrees of freedom. We have added random disorder according to $U_i=U_0+\Delta U$ and $\hbar\omega_i=\hbar\omega_0+\Delta\hbar\omega$. In both cases, for the parameters used, we find moderate, monotonic increase in α with disorder. The (monotonic) increase in optical nonlinearity (γ) is significantly more pronounced. Either type of disorder causes smearing of the electronic density of states (DOS) because previously optically forbidden states now become optically active.[14] Note that disorder in phonon degrees of freedom affects optics since electronic states are modified via e-ph coupling.

Although we considered only one model system, our approach can be generally applied to other e-ph systems. Only the static susceptibilities are calculated in the present study. However, the method can be straightforwardly applied to dynamic susceptibility calculations, while other methods, such as the kernel polynomial method,[15] can also yield efficient computation, especially for dynamic nonlinear optical responses.[16]

In conclusion, we have studied the effect of nonadiabaticity and disorder in electronic as well as phonon degrees of freedom on first- and third-order optical polarizabilities for the Holstein-Hubbard model of an e-ph coupled finite chain. The nonlinear optical susceptibilities have been calculated at a fully quantum-mechanical level. We find that for a specific parameter range, corresponding to an intermediate phase with mixed spin and charge fluctuations, optical nonlinearity is significantly enhanced. Disorder in electronic and phonon degrees of freedom is also found to increase nonlinear optical response. Our results have implications for understanding accumulating experimental results in ultrafast time-resolved and nonequilibrium measurements.[17]

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