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The nonlinear optical response of Semiconductor Quantum Wells, Organic Superlattices and Conjugated Polyenes was calculated using collective electronic coordinates, which represent the joint dynamics of electron-hole pairs. The use of femtosecond four-wave mixing spectroscopy to probe the nature of electronic states and Exciton and free-carrier interactions in these systems was explored. The formation and dynamics of quasiparticles involving electrons dressed by nuclear deformations in conjugated polymers was studied. The signatures of charged solitons, neutral solitons, polarons and bipolarons in the resonant and off-resonant optical susceptibilities of conjugated polymers were calculated using the Pariser-Parr-Pople (PPP) model. The optical response was obtained by solving equations of motion for the reduced single-electron density matrix, derived using the time dependent Hartree-Fock (TDHF) approximation. The approach relates the optical signals directly to the dynamics of charges and bond orders (electronic coherences) induced by the radiation field and uses only ground-state information, thus avoiding the explicit calculation of excited states. A Density-Matrix-Electronic-Oscillator representation was employed for calculating the third order nonlinar optical response of semiconductor quantum dots in the limits of weak and strong exciton confinement. The nonlocal electrodynamics of arrays of quantum dots was treated exactly using Green function techniques. The research program included the development of software which uses the newly developed algorithms in the design of new optical materials.

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Nonlinear Optical Response of Confined Excitons in Molecular and Semiconductor Nanostructures

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Executive Summary

Optical spectroscopy of conjugated molecules, semiconductor nanocrystals and organic superlattices was described by using collective electronic coordinates, which represent the joint dynamics of electron-hole pairs. The approach relates the optical signals directly to the dynamics of charges and bond orders (electronic coherences) induced by the radiation field and uses only ground-state information, thus avoiding the explicit calculation of excited molecular states. The resulting real-space picture is reminiscent of the normal-mode analysis of molecular vibrations and offers a unified framework for the treatment of organic and inorganic materials. Spatial coherence displayed in two-dimensional plots of electronic normal modes allows a real-space interpretation of the optical response and provides a useful tool for the design of new optical materials.

People involved in the research were:

L. Belleguie, V. M. Axt, N. Wang, J. A. Leegwater, T. Meier, S. Tretiak, V. Chernyak, S. Yokojima, C. Kowal, A. Law, E, Nagasako, J. Rogers

Publications

1. "Nonlocal Electrodynamics of Arrays of Quantum Dots," L. Belleguie and S. Mukamel, Phys. Rev. B **52**, 1936-1947 (1995)

2. "Anharmonic Oscillator Representation of Nonlinear Optical Susceptibilities of a Charged Soliton, a Neutral Soliton and a Polaron in Conjugated Polymers," A. Takahashi and S. Mukamel, J. Chem. Phys. **103**, 7144-7155 (1995)

3. "Influence of a Phonon Bath on Electronic Correlations and Optical Response in Molecular Aggregates," V. M. Axt and S. Mukamel IMA Volumes in Mathematics and Its Applications, J. Maloney and J. Sipe, Eds. (Springer-Verlag)

4. "Exciton Confinement Effects in Nonlinear Optical Spectroscopy of Interacting Quantum Wires," N. Wang and S. Mukamel, Chem. Phys. Lett. **231**, 373 (1994).

5. "Nonlocal Electrodynamics of Weakly Confined Excitons in Semiconductor Nanostructures," L. Belleguie and S. Mukamel, J. Chem. Phys. **101**, 9719 (1994)

6. "Photon Echoes in Impulsive Optical Spectroscopy of Phonons," J. A. Leegwater and S. Mukamel, J. Chem. Phys. **102**, 2365 (1995)

7. "Electronic-Oscillator Analysis of Femtosecond Four-Wave Mixing in Conjugated Polyenes," T. Meier, S. Tretiak, V. Chernyak, and S. Mukamel, *Phys. Rev. B* . **55**, 4960-4977 (1997)

8. "Density-Matrix-Electronic-Oscillator Representation of Optical Spectroscopy of Semiconductor Nanocrystals," S. Yokojima. T. Meier, and S. Mukamel, *J. Chem. Phys.* **106**, 3837-3853 (1997)

Technical Summary of the Significant Work Accomplished

Electronic-Oscillator Analysis of Femtosecond Four-Wave Mixing in Conjugated Polyenes

Equations of motion which describe the nonlinear optical response of conjugated polyenes using a collective electronic-oscillator representation were derived. Specific signatures of electronic correlations which enter as anharmonicities and scattering between oscillators were predicted in ultrafast resonant four-wave mixing. Only few resonant oscillators need to be considered explicitly; effects of the remaining (off resonant) oscillators were introduced via renormalized anharmonic coupling coefficients. The connection with inorganic semiconductors was established and with organic multiple quantum wells of alternating chemical composition.

Collective Oscillator Representation of Nonlinear Optical Susceptibilities of a Charged Soliton, a Neutral Soliton, and a Polaron in Conjugated Polymers

It is widely accepted that elementary excitations of conjugated polymers are not purely electronic (electrons and holes) but involve nonlinear nuclear motions and deformations such as solitons, polarons and bipolarons. The signatures of a charged soliton, a neutral soliton, and a polaron in the resonant and off-resonant optical susceptibilities of conjugated polymers were calculated using the Pariser-Parr-Pople (PPP) model which induces coulomb interactions. The optical response was obtained by solving equations of motion for the reduced single-electron density matrix, derived using the time dependent Hartree-Fock (TDHF) approximation. The

density matrix clearly shows the electronic structures induced by the external field. The roles of charge density, spin density, bond order and spin bond order waves and how they contribute to the optical response were analyzed. Both charged and neutral solitons show one absorption peak inside the gap of the half-filled case; the frequency of the neutral soliton peak is about 0.7 eV higher than that of a charged soliton. A polaron shows two absorption peaks inside the gap.

The frequency dependence of the linear and nonlinear optical susceptibilities of polyacetylene with charged solitons, neutral solitons or polarons were calculated. By comparing with various nonlinear optical measurements, the types of excitations created in the photoexcitation process of polyacetylene were identified. Significant enhancement of nonlinear susceptibilities can be expected by these defects whose sizes are 10~20 sites. The role of soliton-pair-like lattice fluctuations in enhancing the nonlinear optical susceptibilities was clarified.

Influence of a Phonon Bath on Electronic Correlations and Optical Response in Molecular Aggregates

A generating function algorithm that allows the calculation of the optical response of coupled exciton-phonon systems was developed. For a model of assemblies of three-level molecules coupled via dipole interaction and interacting linearly with nuclear degrees of freedom, we derived a closed set of equations of motion for five generating functions representing the exact response to third order in the external field. These are equivalent to an infinite hierarchy of equations of motion for phonon-assisted variables. Starting with equations for the generating functions, several reduction schemes were derived. By eliminating the phonon degrees of freedom in favor of self-energies, the Haken-Strobel model of relaxation was recovered as a limiting case. A set of time-local equations was presented, extending the Haken-Strobel treatment by keeping the temperature dependence as well as the excitonic signatures of the

phonon self-energies. Finally, we derived equations that interpolate between the coherent and incoherent limits of exciton propagation and properly include the two exciton dynamics.

Density-Matrix-Electronic-Oscillator Representation of Optical Spectroscopy of Semiconductor Nanocrystals

The optical response of CdSe semiconductor nanocrystals was investigated using the reduced single-electron density matrix in real space, calculated by means of the time-depending Hartree-Fock technique. The spectroscopic signatures of exciton confinement were analyzed using the frequency-dependent electronic coherence matrix (off-diagonal density-matrix elements). The effects of Hartree and the Fock (exchange) type Coulomb interactions on the exciton binding energy were discussed. The latter result in almost dark excitons situated energetically below the main transition. Off-diagonal Coulomb matrix elements lead to larger exciton binding energies compared with previous calculations, and result in a better agreement of the size dependence of the lowest optical transition with experiment.

Nonlocal Electrodynamics of Arrays of Quantum Dots

The linear and nonlinear optical responses of an array of quantum dots was analyzed. The model treats the matter-field interaction self-consistently, and includes the nonlocality of the electromagnetic field throughout the system. This procedure addresses the dependence of radiative decay rates as well as of the nonlinear response on size, geometry, and the material, and provides a unified treatment of systems with arbitrary size compared with the optical wavelength. Applications were made to a one-dimensional periodic array of semiconductor quantum dots, where the intradot and interdot exciton motion is of Wannier and Frenkel types, respectively. The optical nonlinearity enhancement of the array was compared with that of a single quantum dot. Geometric confinement gives rise to quantized polariton modes with a finite radiative lifetime. The variation of optical nonlinearities with size, and the role of local field effects were analyzed.