Collective charge density fluctuations and nonlinear optical response of C_{60}

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The absolute magnitude of the optical susceptibility $\chi^{(3)}$ for C_{60} and its frequency dispersion are calculated using the Pariser–Parr–Pople (PPP) model by deriving equations of motion for the single electron density matrix and solving them using the time-dependent Hartree–Fock procedure. Collective charge density fluctuations induced by the radiation fields are shown to provide the mechanism for the linear and the nonlinear optical response. The insight provided by the present real space picture allows the direct comparison with linear conjugated polyenes.

C_{60} is a molecule with unique symmetry [1]. Recently, it has attracted much attention because of its interesting structure and physical properties such as superconductivity at high temperatures [2] and ferromagnetism [3].

Several authors have measured and reported relatively large values of the third-order susceptibility of C_{60} [4–8]. Harigaya and Abe calculated the dispersion of third harmonic generation (THG) using the Hückel model which neglects the Coulomb interactions between π electrons [9]. However, it is widely known that these interactions are crucial for the structure [10] and nonlinear optical properties [11] of linear polyenes. Matsuzawa and Dixon used the semiempirical MNDO model which takes the Coulomb interaction into account [12], to calculate the static nonlinear polarizabilities. In the molecular approach used in these studies, nonlinear susceptibilities are calculated by multiple summations over excited states [13]. These calculations are very tedious for systems of the size of C_{60}, and provide very little insight on the origin of nonlinearities. The problem is particularly severe for off resonant response, which is most important for optical material applications, where the number of excited states contributing to the optical response is prohibitively large.

In this article we adopt a fundamentally different,

semiconductor like, approach [14] and calculate the optical response by deriving equations of motion for the π electron single particle reduced density matrix which maps the problem onto the dynamics of coupled anharmonic oscillators. We thus avoid the tedious calculation of global molecular eigenstates and focus directly on the collective motions [15] which are responsible for the linear and the nonlinear optical response. Coulomb interactions are naturally included in this approach. The equations of motion are closed using the TDHF approximation [16]. Our method is particularly suitable for the large molecules whose optical response is dominated by collective motions.

The PPP Hamiltonian for the π electrons includes short and long range Coulomb interactions and reproduces many important properties of conjugated polyenes [10]. In this model each carbon atom has a single p orbital. We introduce the following set of binary electron operators: $\hat{\rho}^{\sigma}_{n,m} = \hat{c}^{\dagger}_{m,\sigma}\hat{c}_{n,\sigma}$, where $\hat{c}^{\dagger}_{n,\sigma}$ ($\hat{c}_{n,\sigma}$) creates (annihilates) an electron of spin σ at the nth carbon atom and they satisfy the Fermi anti-commutation relation $\{\hat{c}^{\dagger}_{m,\sigma}, \hat{c}_{n,\sigma'}\} = \delta_{m,n}\delta_{\sigma,\sigma'}$. The PPP Hamiltonian [10] is given by

$$H = \sum_{n,m,\sigma} t_{m,n}\hat{\rho}^{\sigma}_{n,m} + \sum_{n} U\hat{\rho}^{\uparrow}_{n,n}\hat{\rho}^{\downarrow}_{n,n}$$

$$+ \frac{1}{2}\sum_{n,m,\sigma,\sigma'}^{n \neq m} V_{n,m}\hat{\rho}^{\sigma}_{n,n}\hat{\rho}^{\sigma'}_{m,m} - E(t)\hat{P} . \tag{1}$$

The first term is the Hückel Hamiltonian, where $t_{m,n}$ is the hopping integral between the nth and mth atoms. This integral has an exponential dependence on the interatomic distance and we assume that an electron can hop only between nearest-neighbour atoms. Thus when the nth and mth atoms are nearest-neighbours with bond length $r_{n,m}$, we set $t_{m,n} = \beta_0 \times \exp[\mu(r_0 - r_{m,n})]$, otherwise $t_{m,n} = 0$, with $\beta_0 = -2.0419$ eV, $\mu = 1.2518$ Å^{-1}, and $r_0 = 1.536$ Å. We have used the experimentally observed bond lengths: $r_{m,n} = 1.45$ Å for the bonds of the pentagons, and $r_{m,n} = 1.40$ Å for the bonds connecting the pentagons [17]. The second term contains electron–electron Coulomb interactions. An on-site Hubbard repulsion U is given by $U = U_0/\epsilon$, and a repulsion between the nth and mth atoms $V_{n,m}$ is given by the Ohno formula $V_{n,m} = U/\sqrt{1 + (r_{n,m}/a_0)^2}$, where $U_0 = 11.13$ eV is the unscreened on-site repulsion, ϵ is the dielectric constant, and $a_0 = 1.2935$ Å. We have used these parameters appropriate to polyenes without any adjustment. However, since the dielectric constant describing screening by σ electrons depends on the density of carbon atoms, the value appropriate to linear polyenes cannot be used for C_{60}. Thus we have taken $\epsilon = 6$ which yields an energy gap of 2.92 eV, very close to the experimental value of 2.85 eV [5]. The third term represents the dipole interaction between the π electrons and the uniform external electric field $E(t)$. The total polarization operator is given by $\hat{P} = -e \sum_{n,\sigma} z(n) \hat{\rho}_{n,n}^\sigma$, where $-e$ is the electron charge and $z(n)$ is the z coordinate of nth atom. The electric field is polarized along the z direction and we set the origin at the center of the C_{60} molecule. For simplicity, we assumed that the electric field is vertical to one of the pentagons. However, since the molecule is almost spherical, the results should not strongly depend on this configuration.

We have calculated the 60×60 matrix $\rho_{n,m}^\sigma(t) = \langle \Psi(t) | \hat{\rho}_{n,m}^\sigma | \Psi(t) \rangle$ which can be interpreted as the single electron density matrix, and whose diagonal elements give the charge density required for calculating the polarization. Using the Schrödinger equation, we obtained the equations of motion $i\hbar \dot{\rho}_{n,m}^\sigma(t) = \langle \Psi(t) | [H, \hat{\rho}_{n,m}^\sigma] | \Psi(t) \rangle$. These equations are exact but they are not closed since the rhs contains expectation values of products of two $\hat{\rho}_{n,m}^\sigma$ operators. To close the equations, we invoke the TDHF approximation and assume that the wave-function $| \Psi(t) \rangle$ can be represented by a single Slater determinant at all times. This results in a proper factorization of higher order products and yields,

$$i\hbar \dot{\rho}^\sigma(t) + i\Gamma\{\rho^\sigma(t) - \bar{\rho}^\sigma\} = [h^\sigma(t) + f(t), \rho^\sigma(t)].$$
$$(2)$$

Here $h^\sigma(t)$ and $f(t)$ are the Fock operator matrices of the present Hamiltonian with spin σ, and are zeroth and first order in the external field, respectively, Γ is a phenomenological relaxation rate which represents line broadening, and $\bar{\rho}^\sigma$ is the density matrix of the zeroth-order solution in the external field. We assumed $\Gamma = 0.1$ eV in this Letter.

Eq. (2) can be solved as follows: we first find the zeroth-order solution which is taken to be the stationary Hartree–Fock (HF) solution, and is calculated numerically by iterative diagonalization. We next solve the TDHF equation by expanding the single electron density matrix in powers of the external field as $\rho(t) = \bar{\rho} + \rho^{(1)}(t) + \rho^{(2)}(t) + \rho^{(3)}(t) + ...$, where $\rho^{(q)}(t)$ is the qth-order contribution. Since both the total Hamiltonian and the stationary HF solution are symmetric with regard to spin exchange, the TDHF solution also has that symmetry; hereafter we thus omit the spin index. Substituting the expansion into eq. (2), we obtain the first-, second- and third-order equations of motions. These equations are linear, and we have solved them numerically in the frequency domain. To first order, the present approximation is equivalent to the random phase approximation (RPA), which describes small amplitude collective quantum fluctuations very well [16]. Thus the linear absorption spectrum, which is obtained from the first-order density matrix in our method, is equivalent to the RPA [18]. This is not the case, however, for optical nonlinearities. The present approach takes into account the anharmonic coupling between the RPA fluctuations in the higher orders, and therefore incorporates certain correlation effects beyond the RPA. Consequently, the resulting nonlinear optical susceptibilities are quite different from those obtained by the sum over RPA excited states [19]. The second RPA [20] provides an alternative route for incorporating correlation effects beyond the RPA. However, this method requires the diagonalization of an $N^4 \times N^4$ matrix ($N = 60$ is the number of sites) which makes it hard to implement for large systems. The local density ap-

proximation describes correlation effects well. It is applied to C_{60} and related materials, and the linear absorption spectrum by this method is in good agreement with excrement [21].

The qth-order density matrix induced by optical electric field $E(t) = E_0 \cos(\Omega t)$ can be written as

$$p^{(q)}(t) = \frac{1}{\sqrt{2\pi}} \{ \text{Re}[\tilde{p}^{(q)}(q\Omega)] \cos(q\Omega t)$$

$$+ \text{Im}[\tilde{p}^{(q)}(q\Omega)] \sin(q\Omega t) + ... \} , \quad (3)$$

In the present calculations we focus on THG. Thus we keep only the frequency components contributing to THG in eq. (3). Using the amplitudes $\tilde{p}^{(q)}$ we have,

$$\alpha(\Omega) = -\frac{1}{E_0} \frac{4e}{\sqrt{2\pi}} \sum_n z(n) \tilde{p}_{n,n}^{(1)}(\Omega) , \quad (4a)$$

$$\gamma(-3\Omega; \Omega, \Omega, \Omega) = -\frac{1}{E_0^3} \frac{4e}{\sqrt{2\pi}} \sum_n z(n) \tilde{p}_{n,n}^{(3)}(3\Omega) , \quad (4b)$$

where $\alpha(\Omega)$ is the linear polarizability and $\gamma(-3\Omega; \Omega, \Omega, \Omega)$ is the nonlinear polarizability responsible for THG. Other polarizabilities can be obtained in the same way.

In fig. 1, we compare the absorption lineshape $(\text{Im}[\alpha(\Omega)])$ with $|\gamma(-3\Omega; \Omega, \Omega, \Omega)|$ which is proportional to the square root of the THG signal. We
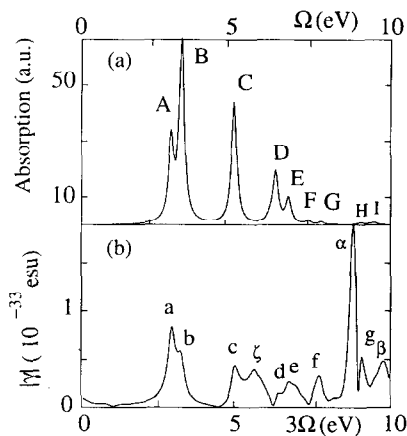
denoted the resonances in absorption by A, B, ..., G and the resonances of $|\gamma(-3\Omega; \Omega, \Omega, \Omega)|$ by a, b, ..., g, α, β and ζ. We note the following: (i) a, b, ... and g are three-photon resonances of the transitions corresponding to the absorption peaks A, B, ... and G, respectively; (ii) α and β are one-photon resonances corresponding to the A and B transitions, respectively; (iii) ζ is a two-photon resonance.

Meth, Vanherzeele and Wang have measured the absorption and the dispersed THG spectra of C_{60} in thin films [5]. They found two closely lying resonances in linear absorption in the frequency range $1.5 < \Omega < 4$ eV; the resonance with the higher frequency being more intense. In the dispersed THG studied in the frequency range $1.5 < 3\Omega < 4$ eV, they found a resonance at one-third the lower frequency but no resonance at one-third the higher frequency. These features are reproduced very well in our calculations.

To explore the mechanism and the electronic dynamics underlying the nonlinear optical response, we examined the charge density created by the external electric field. The total dipole moment (and hence the linear and nonlinear polarizabilities) is determined from the diagonal elements $\tilde{p}_{n,n}^{(q)}$, that is, the charge density oscillation amplitude induced by the external field at the nth atom. The charge densities have a term oscillating in phase (out of phase) with the external electric field. Their amplitudes are $\text{Re}[\tilde{p}_{n,n}^{(q)}]$ $(\text{Im}[\tilde{p}_{n,n}^{(q)}])$ and they contribute to the real (imaginary) parts of the linear and nonlinear polarizabilities as seen from eqs. (4). With our choice of z axis, the atoms lie in eight planes defined by $z = \pm3.3, \pm2.6, \pm1.8, \pm0.6$ Å. The number of atoms in each plane is 5, 5, 10, 10, respectively. By symmetry, all atoms in a given plane have the same $\tilde{p}_{n,n}^{(q)}$. The contribution of the z plane to the dipole moment is given by $\tilde{p}_{n,n}^{(q)}$ multiplied by the number of atoms in the plane. We define that product, that is, the charge density oscillation amplitude of the plane as $\tilde{d}_z^{(q)}$. The z dependence of $\tilde{d}_z^{(q)}$ is shown in figs. 2 and 3 at four frequencies: 0.34, 0.98, 1.85 and 2.92 eV. There is no peak in absorption and in THG at $\Omega = 0.34$ eV, no peak in absorption but a three-photon resonance peak a in THG at $\Omega = 0.98$ eV, no peak in absorption but a two-photon resonance peak ζ in THG at $\Omega = 1.85$ eV, a peak A in absorption and a large peak α in THG at $\Omega = 2.92$ eV. The figures
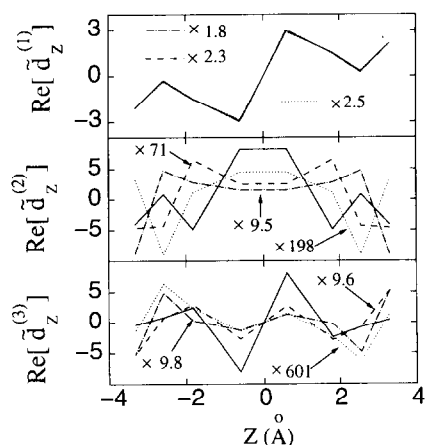

Fig. 1. (a) The linear absorption spectrum $\text{Im}[\alpha(\Omega)]$ is plotted versus Ω. (b) The hyperpolarizability $|\gamma(-3\Omega; \Omega, \Omega, \Omega)|$ connected to THG is plotted versus 3Ω.

Fig. 2. The z dependence of charge density oscillation amplitudes $\mathrm{Re}[\tilde{d}_z^{(q)}]$ for $q=1$–3. The solid, dash-dotted, dashed and dotted lines show the results at the frequency $\Omega=2.92$, 1.85, 0.98 and 0.34 eV, respectively. The solid lines are always shown in unit magnification. The amplitude of each of the other lines has been magnified with the degree of magnification indicated in the figure. The applied external electric field is $E_0=10^8$ V/m.
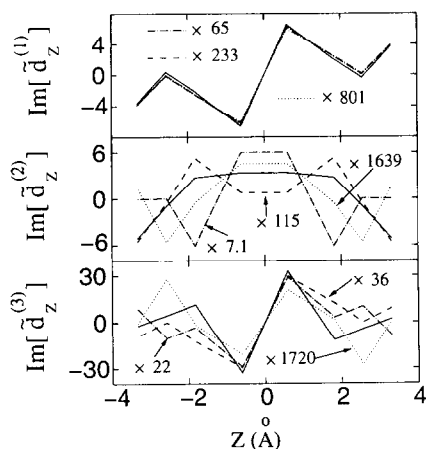

Fig. 3. The z dependence of $\mathrm{Im}[\tilde{d}_z^{(q)}]$. All the parameters are the same as in fig. 2.

show that the charge density oscillates in a very similar pattern at all the frequencies in a given order, which indicates that this characteristic collective motion dominates the optical response. In first order, both the real and the imaginary parts clearly show a pair of opposite charges coupled by Coulomb interactions. This excitation thus closely resemble charge transfer excitons [22]; one exciton has opposite charges at $z=\pm0.6$ Å and the other one has opposite charges at $z=\pm3.3$ Å. These two excitons have parallel dipole moments. The spatial profile of

these excitons can be rationalized as follows: a pair of opposite charges created optically will attempt to minimize its energy. The interaction with the external field favors localizing the charges at the opposite poles $z=\pm3.3$ Å since the dipole moment is the largest in this case. This localization increases the Coulomb repulsion energy. Furthermore, the attractive Coulomb interaction between opposite charges favors exciton confinements. Consequently, the Coulomb interaction confines the opposite charges of the excitons by two different mechanisms: the first one is characteristic of a C_{60} molecule and the second one is general. The confinement stabilizes the exciton near the equator $z=\pm0.6$ Å. The interaction with the external field and the Coulomb interaction compete in our Hamiltonian resulting in these different kinds of excitons. Consequently, the electronic structure of the excitons and the optical response are strongly affected by the Coulomb interaction. In the second order, the first (second) exciton has charges at $z=\pm1.8$–±3.3 Å and opposite charges at $z=\pm0.6$–±1.8 Å. In the third order, one exciton has opposite charges at $z=\pm0.6$ Å and the other one has opposite charges at $z=\pm1.8$–3.3 Å.

The induced charge density amplitude, in particular the imaginary part, strongly depends on the frequency. In the first order, $\mathrm{Im}[\tilde{d}_z^{(1)}]$ at $\Omega=2.92$ eV, which is the only one-photon resonant frequency among the four frequencies calculated, is more than 65 times larger as the other frequencies. On the other hand, $\mathrm{Re}[\tilde{d}_z^{(1)}]$ at $\Omega=2.92$ eV is the largest but still comparable to the other frequencies. In the second order, $\mathrm{Re}[\tilde{d}_z^{(2)}]$ and $\mathrm{Im}[\tilde{d}_z^{(2)}]$ are large at the one-photon resonance frequency, and at the two-photon resonant frequency $\Omega=1.85$ eV; they are more than 7.5 times larger as off resonant or three-photon resonant frequencies. In the third order, $\mathrm{Re}[\tilde{d}_z^{(3)}]$ and $\mathrm{Im}[\tilde{d}_z^{(3)}]$ are also largest at the one-photon resonant frequency, which is the largest peak in THG. They are also large at the two- and three-photon resonance frequencies. The off resonant values are more than 62 times weaker.

We have investigated $\tilde{d}_z^{(q)}$ also at several other frequencies and found that these observations hold at all the frequencies studied, namely, (i) there is a characteristic charge density oscillation pattern in each order and only these collective motions are excited by the external electric field; and (ii) the magnitudes of these collective motion are much larger at

resonant frequencies and are correlated with the magnitude of $|\gamma|$.

The absolute magnitude of polarizability $|\gamma(-3\Omega; \Omega, \Omega, \Omega)| = 9.56 \times 10^{-35}$ esu at $\Omega = 0.02$ eV in the present calculations. It is 31 times smaller as the value 2.93×10^{-33} esu at $\Omega = 0$ reported by Harigaya and Abe, who neglected Coulomb interactions [9]. The difference can be attributed to exciton confinement mentioned before induced by the Coulomb interaction; the confinement reduces the total dipole moment and the polarizability. The third order susceptibility responsible for THG is given by $\chi^{(3)}(-3\Omega; \Omega, \Omega, \Omega) = DL^4\gamma(-3\Omega; \Omega, \Omega, \Omega)$, where $D = 1.38 \times 10^{21}$ cm^{-3} is the density of a C_{60} molecule and $L = \frac{1}{3}(\epsilon+2)$ is the local field factor. We then obtain $|\chi^{(3)}| = 2.56 \times 10^{-12}$ esu at $\Omega = 0.52$ eV. This value is consistent with the experimental value of 2.1×10^{-12} esu at $\Omega = 0.52$ eV by Meth, Vanherzeele and Wang [5]. Hoshi et al. have reported the value of 2×10^{-10} esu at $\Omega = 1.2$ eV [4]. However, this much larger value is not consistent with other experiments [5–7].

In conclusion we note that the nonlinear optical response of linear conjugated polyenes is the subject of intensive effort [23]. The fast scaling of the off resonant optical susceptibility $\chi^{(3)}$ with size ($\sim N^6$) and the crossover to a linear ($\sim N$) dependence at about 20 double bonds were recently shown to correlate with collective charge transfer excitons [24]. The present study establishes a similar physical picture for C_{60}; both systems can be viewed as collections of anharmonic nonlocal exciton oscillators.

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