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Huge enhancement of optical nonlinearity in conjugated polyenes

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A huge enhancement is predicted for the nonlinear optical response of conjugated polyenes, where the scaling dependence of the hyperpolarizability γ on the chain length N ($\gamma \propto N^{\eta}$, valid for small N) undergoes a dramatic change with the electron correlation strength. Such a change is a collective effect of the ground state and the excited states. This finding not only provides a clue for maximizing the nonlinear optical effect, but also presents an interesting topic for experiments.

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Reduced dimensionality often yields many exotic physical properties. Investigations along this line are rewarding not only because such physical properties are readily described at a high theoretical level, but also because theoretical predictions can be readily tested experimentally. Such a close interaction between theory and experiment substantially improves our understanding of physical phenomena. One example is conjugated polymers, where experiments show a reverse ordering between the one and two-photon-allowed states,[1] which has been subsequently proved by the correlated theory.[2] This confirmation is often quoted as the first evidence showing the importance of electron correlation in conjugated polymers. Also due to the electron correlation, the ground state in the extended Hubbard model undergoes a phase transition from a spin-density wave to a charge-density wave (CDW) for a ratio of intersite and on-site interactions V/U of over 0.5.[3,4] A similar sharp change was recently reported in the excited-state transition moments,[5] where the dependence of the moment on the chain length changes dramatically with the ratio. The experimental verification of these well-established theoretical predictions is of great interest, but has not yet been performed.

In this paper, we report that, as a direct consequence of electron correlation, a strong enhancement is achieved in the nonlinear optical response. Our results demonstrate that the scaling behavior of the hyperpolarizability γ undergoes a dramatic change. For a smaller ratio $V/U < 0.3$, the increase of γ with the chain length N is moderate; a sharp increase of γ with N appears for V/U larger than 0.4. An enhancement of nearly four orders of magnitude in γ is found along the transition border line. Such an observation presents a guideline to maximize the nonlinear optical response, and raises an interesting topic for experiments.

The conjugated polyene is described by the generic Peierls-extended Hubbard model,[6,7]

$$\hat{H} = -t \sum_{i,\sigma} [1 + (-1)^i \delta](c^{\dagger}_{i+1,\sigma} c_{i,\sigma} + \text{H.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_i n_i n_{i+1}, \tag{1}$$

where $c^{\dagger}_{i,\sigma}(c_{i,\sigma})$ is the electron creation (annihilation) operator with the spin orientation $\sigma(=\uparrow,\downarrow)$ at site i and $n_{i,\sigma} = c^{\dagger}_{i,\sigma} c_{i,\sigma}$. Hereafter the on-site and intersite interactions U and V are in units of the hopping integral t; t is chosen to be 1 and $\delta = 0.07$. Other parameters will be specified later. The half-filling case is considered. Since the model contains electron correlation, a theoretical calculation for a large system is not straightforward: the large Hamiltonian matrix immediately exhausts standard computational resources. In the meantime, approximate schemes may lead to inconclusive results and blur the real physical pictures. The theoretical situation was not improved much until the advent of the technique known as the density-matrix renormalization-group (DMRG),[8] which is best suited for the ground-state calculation. For the excited states, the Lanczos-based DMRG (LDMRG)[6,9] is the method of choice because of its accuracy and simplicity.[5,6,10] This was demonstrated in a very recent calculation of the whole spectrum of the susceptibility in polyacetylene,[11] where both the calculated relative intensity and peak positions are strongly consistent with two different sets of experimental measurements.[12] The essence of the LDMRG success is due to the preselection of targeted states by the Lanczos method, which consequently avoids targeting catastrophes. Details of the method were presented elsewhere.[6,10,11] In the present work, 230 states are kept in the density matrices, and the truncation error is below 10^{-9}.

We first investigate the effects of the on-site interaction U and intersite interaction V on the static hyperpolarizability γ for a fixed chain length $N = 20$.[13] In Fig. 1, we show the dependence of γ on U with V fixed at 1.4. Here γ is in the same but arbitrary units.[14] We note that with the increase of U, γ is reduced sharply, which can be nicely fitted to $\gamma \propto \mathrm{e}^{-0.72U}$. This is not surprising, since U enlarges the excitation gap, which is detrimental to γ. Note that such reduction in γ is missing in the Hartree-Fock (HF) limit, where U only rigidly shifts the bands. This indicates that the essential property of U is beyond a simple HF approach, and requires a higher level of theory.

The role of V is opposite to that of U. In the inset of Fig. 1, we plot γ as a function of V/U for U fixed at 3. With an

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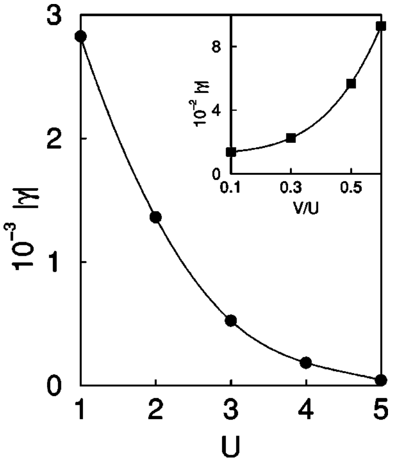

FIG. 1. Effects of the on-site and intersite interactions, U and V, on the hyperpolarizability γ: U monotonically reduces γ, and V increases it.

increase in V, γ is enhanced sharply. An exponential fit shows $\gamma \propto e^{5.8V/U}$. The physical reason for such an increase is that V improves the charge delocalization or the kinetic energy, and shrinks the band gap, which eventually enhances γ. This is clear even in the Hartree-Fock limit, where V contributes an effective kinetic-energy term to the system by $V\Sigma_{i,j,\sigma}\langle c^{\dagger}_{j\sigma}c_{i\sigma}\rangle c^{\dagger}_{i\sigma}c_{j\sigma}$, but explicit dependences can be seen more clearly below.

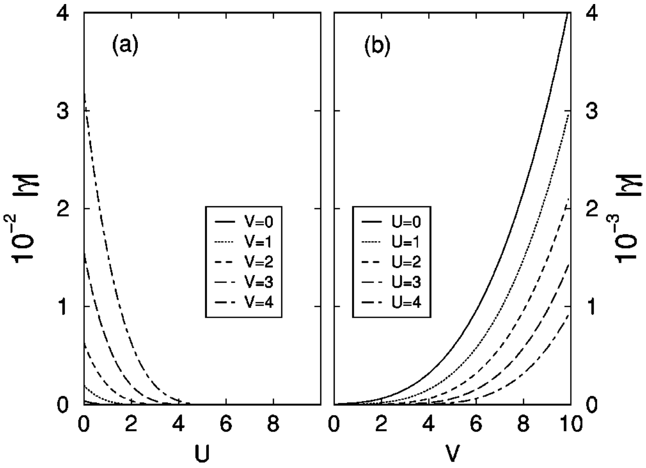

FIG. 2. In a two-site model, the basic features are the same as those for a longer chain (see Fig. 1): U always suppresses γ, while V enhances it. (a) Results are for a series of fixed V. (b) results are for a series of fixed U.

In order to do this, we employ a two-site model, where all the results can be analytically worked out. In the half-filling case, the four basis states are $\phi_1=|\uparrow\downarrow\rangle$, $\phi_2=|\downarrow\uparrow\rangle$, $\phi_3=|\uparrow\downarrow 0\rangle$, and $\phi_4=|0\uparrow\downarrow\rangle$. The eigenvectors and values of the system are

$$\psi_1=\frac{1}{\sqrt{2}}(\phi_1+\phi_2), \quad E_1=V,$$

$$\psi_2=\frac{1}{\sqrt{2}}(\phi_3-\phi_4), \quad E_2=U,$$

$$\psi_{3(4)}=a_{+(-)}\frac{1}{\sqrt{2}}(\phi_1-\phi_2)+b_{+(-)}\frac{1}{\sqrt{2}}(\phi_3+\phi_4),$$

$$E_{3(4)}=\frac{1}{2}(U+V+(-)\sqrt{\Delta}),$$

where $\Delta=(U-V)^2+16t^2$, $a_{+(-)}=2t/\sqrt{4t^2+(E_{3(4)}-V)^2}$, and $b_{+(-)}=(E_{3(4)}-V)/\sqrt{4t^2+(E_{3(4)}-V)^2}$. Since ψ_1 is a dark state, there are only two possible excitation channels, (1) $\psi_4\rightarrow\psi_2\rightarrow\psi_4\rightarrow\psi_2\rightarrow\psi_4$ and (2) $\psi_4\rightarrow\psi_2\rightarrow\psi_3\rightarrow\psi_2\rightarrow\psi_4$, which contribute respectively to the total static second-order hyperpolarizability[14] γ as

$$\gamma=\gamma_1+\gamma_2=-\frac{\langle 4|D|2\rangle^4}{(E_2-E_4)^3}+\frac{\langle 4|D|2\rangle^2\langle 2|D|3\rangle^2}{(E_2-E_4)^2(E_3-E_4)}, \quad (2)$$

where D is the dipole operator, and $\langle i|D|j\rangle$ is the transition matrix element between ψ_i and ψ_j. The asymptotic dependence of γ on U and V for a group of fixed V and U is shown in Fig. 2. One sees that an increase in U indeed reduces the absolute value of γ [see Fig. 2(a)], whereas V enhances it [see Fig. 2(b)]. The physical reason for such a dependence is mainly due to the excitation gap change. Their explicit changes due to U are

$$\frac{\partial(E_2-E_4)}{\partial U}=\frac{1}{2}[1+\Delta^{-1/2}(U-V)],$$

$$\frac{\partial(E_3-E_4)}{\partial U}=\Delta^{-1/2}(U-V). \quad (3)$$

Since $U>V$, these two derivatives are all positive, meaning that the gaps (E_2-E_4) and (E_3-E_4) increase monotonically with U. The situation for V is just the opposite:

$$\frac{\partial(E_2-E_4)}{\partial V}=-\frac{1}{2}[1+\Delta^{-1/2}(U-V)],$$

$$\frac{\partial(E_3-E_4)}{\partial V}=-\Delta^{-1/2}(U-V). \quad (4)$$

Thus the gaps decrease monotonically with V. Such a decrease is not linear with V due the factor $\Delta^{-1/2}$. Since the gap change plays a decisive role in the nonlinear optical process,[15] from Eqs. (2)–(4) one can readily see a distinctive dependence of γ on U and V. The overall quantitative dependence of γ on U and V can be fitted to $\gamma\propto e^{-\alpha U+\beta V}$, where α and β are positive-valued fitting parameters, which is consistent with the results for a long chain.

Up to now, we have only investigated the effect of the interaction strength on the absolute value of γ, which is already quite involved. Next we embark on a more challenging yet more critical quantity of γ: the *scaling property*. As is known, the initial interest of those conjugated polymers as potential all-optical switching devices is motivated by the power-law increase of γ with the chain length, namely, γ

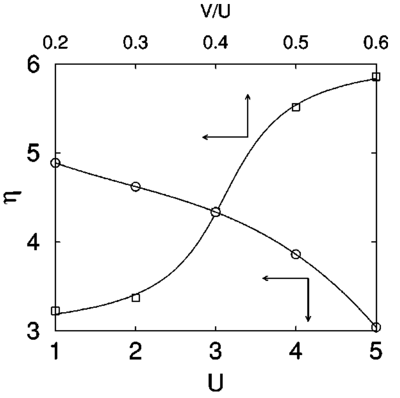

FIG. 3. The scaling dependence of γ on the chain length N is very sensitive to the electron interaction. U strongly suppresses η (○), while V/U greatly enhances it (□). Note that a sharp jump around $V/U=0.4$ signifies a ''phase transition'' in the nonlinear optical process. The change due to V/U can be fit to $\eta(V/U) = a_0\arctan[a_1(V/U-a_2)]+a_3$ (see the text for the parameters).

$\propto N^{\eta}$, valid for small N. As above, we only consider the static γ with N up to 20.[13] A much larger exponent η is of great significance in practice, which naturally attracts many important investigations,[16] but its accurate picture is still unclear. Our results are presented in Fig. 3. Let us look at the effect of U (see the circles). One notes that with an increase in U, the exponent η is reduced sharply. This can be explained as follows. As already noted above, U widens the excitation gap and reduces the electronic kinetic energy. This is more easily seen in the standard Hubbard model, where the kinetic energy $\langle T\rangle$ can be written as,[17]

$$-\langle T\rangle/4Nt \sim (1-0.21358\ U^2/16)/\pi, \quad \text{for} \quad U \ll 1, \tag{5}$$

$$\sim\left[\tfrac{1}{8}\ln 2-\left(\tfrac{3}{64}\right)^2\zeta(3)U^{-2}\right]U^{-1}, \quad \text{for a large } U. \tag{6}$$

One notes that an increase in U reduces $\langle T\rangle$ monotonically, an indication of the enhancement of the charge localization. The optical property is closely connected to the kinetic energy through the well-known f-sum rule,[17] $\int_0^\infty d\omega\sigma(\omega) = -\langle T\rangle/2N$, where $\sigma(\omega)$ is the optical conductivity. With an increase of the chain length, kinetic energy is gained but is quickly reduced by an increase in U [see Eqs. (5) and (6)]. Consequently, this leads to a smaller increase of the hyperpolarizability γ with chain length, or a smaller η.

The effect of the intersite V is intriguing (see the boxes of Fig. 3). The rough trend is that, upon an increase in V, η is enhanced. The reason for this is that the charge delocalization or the kinetic energy is enhanced not only by the chain elongation but also by V, as already mentioned. Such a double enhancement accounts for a much sharper increase in γ, or larger η, and more importantly underlies a huge change in the nonlinear optical responses.

In the extended Hubbard chain, the ground state undergoes a phase transition from a charge-density wave to a spin-density wave with the boundary at about $V/U=0.5$.[3,4] For the excited states, the transition matrix element also exhibits a similar abrupt change at a ratio less than 0.5.[5] As both the ground state and the excited states contribute to the nonlinear optical responses, it is natural to expect that a similar change occurs in the nonlinear processes. This is indeed the case. If one follows the change of the exponent with the ratio V/U, a sharp jump, starting at $V/U=0.4$, can be noted. This indicates that a dramatic change occurs in nonlinear optical processes, where we estimate that γ increases by about four orders of magnitude along the borderline, which is certainly of great significance to experimentalists and future applications. Here two cases should be distinguished: (1) For a small ratio, $V/U<0.3$, many states participate in the nonlinear optical process, and the oscillator strength is rather evenly distributed over a large number of excitation channels, which bring in strong incoherent contributions. Such incoherent effects are destructive, greatly disrupt the charge delocality, and reduce the increase of γ with N, or η. (2) For a larger ratio V/U, the oscillator strength is concentrated on only a few channels. They act more coherently on the nonlinear response and improve the delocalization, in addition to the enhancement due to chain elongation. Consequently, the increase of γ with N, augmented by V, becomes sharper, i.e., larger η. For a much larger ratio, due to the phase-space filling, there is a saturation effect ahead and no additional gain is expected.

Let us discuss this interesting phenomenon in more detail. First of all, we note that the critical ratio on which the sharp increase occurs is smaller than that for the ground-state transition.[18] Understandably, due to the excited nature, for the same ratio, these excited states behave more like a change-density wave than the ground state, namely $\{V/U\}_c$ (excited state)$<\{V/U\}_c$ (ground state).[6] Consequently, the change in the nonlinear optical process occurs at a smaller ratio. Casting the dependence of η on the ratio into an analytic form yields

$$\eta(V/U)=a_0\arctan[a_1(V/U-a_2)]+a_3, \tag{7}$$

where $a_0=1.03236, a_1=16.8739, a_2=0.412078$, and $a_3=4.53216$. Its derivative is

$$\eta'(V/U)=\frac{a_0a_1}{a_1^2(V/U-a_2)^2+1}, \tag{8}$$

which shows that the present change is relatively smooth. This is due to the fact that both the ground state and excited states collectively contribute to the nonlinear optical process. Such a collective contribution brings some incoherent effects into the process, which ultimately leads to a smoother change than that in the ground state.

This finding can be used in practice. Conjugated polymers, as a whole, have very large nonlinear optical responses, but their present performance is still at least two orders of magnitude smaller than the device requirements,[19] such as all-optical switching and data transfer. It is imperative to enhance the nonlinear effect in order to achieve meaningful applications. One important message from the present finding is that the intersite interaction not only enhances the hyperpolarizability but also considerably improves the exponent increase of γ with the chain length. This offers a guideline to optimize the nonlinear optical effect in these conjugated polyenes by V. On the other hand, there is an upper limit on how much one can increase η by changing the ratio V/U. The most sensible range is around $V/U=0.4$, above which no large improvement can be expected. This conclusion should be quite generic since our calculations are performed at the LDMRG level within a generic, model which includes almost all the necessities, such as the electron correlation, of the conjugated polyenes.

Finally, we point out that this prediction presents an interesting topic for experiments. It is well known that the correlation energy E_{corr} roughly obeys the linear dependence on the atomic number Z by $E_{\mathrm{corr}} \propto Z$ $(Z<20)$.[20] By choosing different atoms, in principle, one can alter the interaction strength. Polyenes consisting of these atoms possess different correlation strengths. For instance, a carbon-based polyene, such as polyacetylene, typically has an on-site correlation strength of 10 eV and an intersite interaction strength of 4 eV; a silicon-based polyene, for example, polysilane,[21] has a larger on-site interaction but a smaller intersite interaction. Then we could expect that the increase of the hyperpolarizability in the silicon-based polyenes is weaker than that in the carbon-based ones, which is consistent with the experimental observations. These materials are widely available. At the same time, their nonlinear optical measurements are already quite sophisticated. Thus our prediction provides a challenging yet achievable goal for experiments. In particular, there is very recent experimental work, along a line to ours, which demonstrated how one can manipulate the material properties to achieve a large nonlinear optical response.[22]

In conclusion, we predict that there is a sharp increase in nonlinear optical responses in conjugated polyenes, which is a direct consequence of the double enhancement from the chain elongation and intersite interaction, and reflects the collective effects of the ground state and the excited states. Such a prediction can be used as a guideline to maximize the nonlinear optical response. The results demonstrate that the on-site interaction U suppresses not only γ but also its scaling dependence on the chain length, whereas V does the opposite. Our finding puts forward an interesting paradigm for experiments.

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