

Dynamical Nonlinear Optic Coefficients from the Symmetrized Density Matrix Renormalization Group Method

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We extend the symmetrized density matrix renormalization group (SDMRG) method to compute the dynamic nonlinear optic coefficients for long chains. By computing correction vectors in the appropriate symmetry subspace we obtain the dynamic polarizabilities, $\alpha_{ij}(\omega)$, and third-order polarizabilities $\gamma_{ijkl}(\omega, \omega, \omega)$ of the Hubbard and "U - V" chains in an *all - trans* polyacetylene geometry, with and without dimerization. We rationalize the behavior of $\bar{\alpha}$ and $\bar{\gamma}$ on the basis of the low-lying excitation gaps in the system. This is the first study of the dynamics of a fermionic system within the DMRG framework.

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The dynamic linear and nonlinear response functions of finite interacting systems have most commonly been obtained from an explicit computation of the eigenstates of the Hamiltonian and the matrix elements of the appropriate operators in the basis of these eigenstates [1]. This has been the most widely used method, particularly in the computation of the dynamic Nonlinear Optic (NLO) coefficients of molecular systems and is known as the sum-over-states (SOS) method. In the case of model Hamiltonians, the method that has been widely used to study dynamics is the Lanczos method [2,3]. The spectral intensity corresponding to an operator \hat{O} is given by

$$I(\omega) = -\frac{1}{\pi} \text{Im} \left[\langle G | \hat{O}^\dagger \frac{1}{(E_0 + z - \hat{H})} \hat{O} | G \rangle \right] \quad (1)$$

where $|G\rangle$ is the ground state eigenvector of the Hamiltonian with eigenvalue E_0 , $z = \omega + i\epsilon$, ω is the frequency at which the response is sought, ϵ is the mean life time parameter and \hat{H} is the Hamiltonian. In the Lanczos method, $I(\omega)$ is computed as a continued fraction,

$$I(\omega) = -\frac{1}{\pi} \text{Im} \left[\frac{\langle G | \hat{O}^\dagger \hat{O} | G \rangle}{z - a_0 - \frac{b_1^2}{z - a_1 - \frac{b_2^2}{z - a_2 - \dots}}} \right] \quad (2)$$

wherein the coefficients a_i and b_i are respectively the diagonal and the off-diagonal matrix elements in the tridiagonal matrix representation of the Hamiltonian obtained in the Lanczos procedure. In this method, there

is an implicit truncation of the Hilbert space due to the smaller size of the tridiagonal matrix compared with the total dimensionality of the space spanned by the Hamiltonian [3]. Therefore, the dynamic quantities computed by this technique are approximate even though the ground state obtained is exact.

In the context of NLO properties [4–6] of the Hubbard and extended Hubbard Models it was shown by Soos and Ramasesha that the model exact dynamical NLO coefficients could be obtained by solving for correction vectors [7]. If we define the correction vector $\phi^{(1)}(\omega)$ by the equation

$$(\hat{H} - E_0 - z)\phi^{(1)}(\omega) = -\hat{O}|G\rangle, \quad (3)$$

then the spectral function, $I(\omega)$, can be expressed as

$$I(\omega) = -\frac{1}{\pi} \text{Im} \langle G | \hat{O}^\dagger | \phi^{(1)}(\omega) \rangle \quad (4)$$

The correction vector is solved for in the basis of the configuration functions, which is also the basis in which the Hamiltonian matrix is set-up for obtaining the ground state. Given the ground state and the correction vector, it is straightforward to compute the spectral function. This method is quite general and has been employed in the computations of dynamic NLO coefficients of a wide variety of Hamiltonians [8]. The inhomogeneous linear algebraic equations encountered in this method involve large sparse matrices and an iterative small matrix algorithm, which runs parallel to the Davidson algorithm for eigenvalue problems, gives rapid convergence for the solution of the system of equations [9].

The two correction vectors $\phi_i^{(1)}(\omega_1)$ and $\phi_{ij}^{(2)}(\omega_1, \omega_2)$ encountered in the computation of polarizability and third-order polarizability are solved for from the following linear equations .

$$(H - E_0 + \omega_1 + i\epsilon)|\phi_i^{(1)}(\omega_1)\rangle = \tilde{\mu}_i|G\rangle \quad (5)$$

$$(H - E_0 + \omega_2 + i\epsilon)|\phi_{ij}^{(2)}(\omega_1)\rangle = \tilde{\mu}_i|\phi_j^{(1)}(\omega_1)\rangle \quad (6)$$

where $\tilde{\mu}_i$ s are the *dipole displacement* matrices and other quantities are as defined in eqn.(1). The DMRG method [10,11] as implemented, readily provides us with the

ground state and the Hamiltonian matrix. The matrices of the dipole operators are constructed in the DMRG scheme by renormalizing the matrix representations of the dipole operator corresponding to the left and right parts of the system using the density matrix eigenvector basis in a way which is completely analogous to the corresponding Hamiltonian operators for the fragments. The matrix representation of the dipole operators for the full system are obtained as direct products of the fragment matrices analogous to the way by which the full Hamiltonian matrix is constructed. The dipole displacement matrices are obtained by subtracting the corresponding components of the ground state dipole moments from the diagonal elements of the dipole matrices.

In terms of these correction vectors, the components of the polarizabilities, α_{ij} , and third-order polarizabilities, γ_{ijkl} , can be written as

$$\alpha_{ij}(\omega) = \langle \phi_i^{(1)}(\omega) | \tilde{\mu}_j | G \rangle + \langle \phi_j^{(1)}(-\omega) | \tilde{\mu}_i | G \rangle, \quad (7)$$

$$\gamma_{ijkl}(\omega_1, \omega_2, \omega_3) = \hat{P} \langle \phi_i^{(1)}(\omega_\sigma) | \tilde{\mu}_j | \phi_{kl}^{(2)}(-\omega_1 - \omega_2, -\omega_1) \rangle \quad (8)$$

where the operator \hat{P} generates all the permutations: $(-\omega_\sigma, i)$, (ω_1, j) , (ω_2, k) and (ω_3, l) leading to 24 terms for γ_{ijkl} with $\omega_\sigma = -\omega_1 - \omega_2 - \omega_3$. The tumbling averaged $\bar{\alpha}$ and $\bar{\gamma}$ can be defined as

$$\bar{\alpha} = \frac{1}{3} \sum_{i=1}^3 \alpha_{ii} \quad ; \quad \bar{\gamma} = \frac{1}{15} \sum_{i,j=1}^3 (2\gamma_{iijj} + \gamma_{ijji}) \quad (9)$$

to allow comparison of the calculated NLO response with experiments on systems containing molecules in random orientations [12].

The DMRG method as usually implemented, does not exploit all the symmetries of the system. In the case of model Hamiltonians for polymers, the system possesses total spin symmetry, reflection symmetry about the middle of the chain and in some cases the electron-hole symmetry. These symmetries ensure that a given correction vector spans only a symmetrized subspace and not the entire Hilbert space of the Hamiltonian of the given system. The correction vector lies in the symmetry subspace which is connected to the ground state by the electric dipole operator. For ω values corresponding to resonance between the ground state and eigenstates in that particular symmetry subspace, *lhs* of eqns(5) and (6) become singular for $\epsilon = 0$ and present numerical difficulties even when solving them for reasonable nonzero ϵ values. However, if we do not exploit the symmetries of the Hamiltonian, we encounter singularities in eqns(5) and (6) even for those ω values corresponding to eigenstates of the Hamiltonian found in other symmetry subspaces which are not connected to the ground state by the dipole

operator. Therefore, numerically it would be impossible to obtain the correction vectors at these frequencies and thereby the associated response of the system.

For example, in Hubbard chains at intermediate correlation strengths, a triplet excited state lies below the lowest singlet state in the *ionic* B subspace [13]. The states in the *ionic* B space are connected to the ground state via one-photon transitions. The resonances in polarizability are thus expected only at frequencies corresponding to the energy levels in the *ionic* B space, relative to the ground state. However, we can not solve for the correction vector using equation (5) at an excitation energy corresponding to the energy of the lowest triplet state. Thus the technique of correction vectors will not be able to give the complete dispersion of the polarizabilities upto the first one-photon resonance, unless interferences due to spurious intruders such as the triplet states are eliminated by suitably block-diagonalizing the Hamiltonian matrix. This problem of intruders becomes more severe with increasing system size due to increasing number of intruder states lying below the frequency corresponding to the first "true" resonance.

We have exploited the electron-hole symmetry, the reflection symmetry of the polymers and spin parity to block-diagonalise the Hamiltonian [14]. The electron-hole symmetry divides the Hilbert space into *ionic* and *covalent* spaces. The ground state is in the covalent space while all the dipole allowed excitations from the ground state lie in the *ionic* space. Use of parity conservation divides the Hilbert space of the Hamiltonian into even and odd parity spaces corresponding to even and odd total spin states. We have considered a single excitation frequency in all our calculations ($\omega = \omega_1 = \omega_2 = \omega_3$) and have exploited sparseness of all the matrices to improve upon the computational efficiency. We have employed the finite size DMRG algorithm in some cases to check the convergence of the DMRG results. In these cases, the spatial symmetry is exploited only at the end of the DMRG procedure when the left and the right density matrices correspond to fragments of the same size, i.e., at the end of each finite size iteration.

We have computed the dynamic linear polarizabilities ($\alpha(\omega)$) and third-order polarizabilities ($\gamma(\omega, \omega, \omega)$) corresponding to the third harmonic generation (THG), for the Hubbard and "U-V" chains of upto 20 sites with and without dimerizations, for many values of the parameters of the Hamiltonian,

$$\hat{H} = \sum_{\langle ij \rangle, \sigma} [1 - \delta(-1)^i] [-t(\hat{a}_{i,\sigma}^\dagger \hat{a}_{j,\sigma} + \hat{a}_{j,\sigma}^\dagger \hat{a}_{i,\sigma})] + U \hat{n}_{i\sigma} \hat{n}_{i-\sigma} + \sum_{\langle ij \rangle} [1 - \delta(-1)^i] [V(\hat{n}_i - 1)(\hat{n}_j - 1)] \quad (10)$$

where $\hat{a}_{i,\sigma}^\dagger$ ($\hat{a}_{i,\sigma}$), $\hat{n}_{i\sigma}$, t and U have their usual meaning. V is the nearest neighbour interaction parameter and the

term in V is nonzero only when the nearest neighbours in question are charged, in which case, the interaction is repulsive for like charges and attractive for unlike charges. δ is the dimerization parameter of the system. The geometry of the Hubbard and " $U - V$ " chains required for the computation of the NLO coefficients is chosen to correspond to *all - trans* polyacetylene configuration, with a bond angle of 120° and bondlength of 1\AA , for the uniform chain. Dimerization ($\delta > 0$) leads to proportionate alternation in bond lengths as well as alternation in the t and V parameters. All the computations have been carried out at a single frequency corresponding to an excitation energy of $0.1eV$ and the life-time ϵ is chosen to be $0.001eV$.

We have compared the DMRG results with a cut-off of $m = 200$ (retaining the dominant 200 density matrix eigenvectors in the DMRG scheme) with the *model exact* α and γ values obtained from the correction vector method for chains of upto 12 sites. For the 8-site problem, the DMRG calculation is exact for this cut-off and the DMRG results compare with exact results to numerical accuracy. In the case of the 12 site uniform Hubbard chain with $U/t = 4$, the model exact $\bar{\alpha}$ is $5.343 \times 10^{-24} \text{ esu}$ while the DMRG $\bar{\alpha}$ is $5.293 \times 10^{-24} \text{ esu}$. The model exact $\bar{\gamma}$ value is $598.3 \times 10^{-36} \text{ esu}$ while the DMRG $\bar{\gamma}$ value is $589.3 \times 10^{-36} \text{ esu}$. The error in the dominant α and γ components namely, α_{xx} and γ_{xxxx} is much smaller. The model exact α_{xx} is $14.83 \times 10^{-24} \text{ esu}$ while the DMRG α_{xx} is $14.79 \times 10^{-24} \text{ esu}$. As for γ , the model exact γ_{xxxx} is $2873 \times 10^{-36} \text{ esu}$ while the DMRG γ_{xxxx} is $2870 \times 10^{-36} \text{ esu}$.

In figs.1, we display the dependence of $\bar{\alpha}$ on the chain length for different values of U/t , for uniform (fig. 1a) and dimerized (fig. 1b) Hubbard chains. The polarizability decreases with increasing correlation strength in both the dimerized and the uniform chains. For the same chain length the uniform chains have, as expected [15], higher polarizability than the corresponding dimerized chain at every value of U/t we have studied. For the uniform chain, the average polarizability, $\bar{\alpha}$, for weak correlations exhibits a nice power law dependence on chain length with an exponent of 2.022 ± 0.001 . However, for stronger correlations, the polarizability deviates from a power law dependence and seems to show a size-consistent variation at longer chain lengths. The chain length at which the change over from the power law behavior occurs, systematically reduces with increasing U/t . As the chain dimerizes, the range over which power law behavior is observed decreases (Fig. 1b). Eventually, in the limit $\delta = 1.0$, we would observe only size-consistent dependence as, in this limit the chain breaks down to noninteracting dimers.

In figs.2, we show the log-log plot of average third-order polarizability $\bar{\gamma}$ with the chain length for chains of upto 20 sites with (fig. 2a) zero and (fig. 2b) nonzero bond alternation. The variation of $\bar{\gamma}$ with chainlength

is similar to that found for $\bar{\alpha}$ both in the dimerized and undimerized cases. Nonzero δ leads to a decrease in the $\bar{\gamma}$ value and the decrease is smaller for higher U/t values. An exponent of 5.570 ± 0.001 is found for $\delta = 0.0$ and $U/t = 2.0$, while the exponent is 4.00 ± 0.01 for $\delta = 0.09$ and $U/t = 2.0$. In both these cases, the power-law behavior is observed upto the maximum chain length we have studied. It is interesting to note the strong dependence of the exponent on the dimerization parameter.

In the " $U - V$ " model the dependence of the polarizability on the chain length is very similar to that in the Hubbard model. However, the " $U - V$ " model is more polarizable, for the chosen model parameters and frequency. While the dimerization, δ , decreases the polarizability of the chain, the nearest neighbour interaction, V , increases the same. The exponents for $\bar{\alpha}$, where the power law holds ($U/t = 2.0, V/t = 1.0$) is 2.320 ± 0.001 for the uniform chain and 1.64 ± 0.01 for the dimerized chain ($\delta = 0.09$).

In figs. 3 we present the dependence of $\bar{\gamma}$ on chain length for various values of U/t for the uniform (fig. 3a) and dimerized (fig. 3b) chains, in the " $U - V$ " model with V/t fixed at 1.0. There are some very interesting differences in the variation of $\bar{\gamma}$ between the Hubbard and the " $U - V$ " chains. The dependence of the $\bar{\gamma}$ of the two chains on U are similar for $U > 2V$. In this the *SDW* regime, the third-order polarizability in the " $U - V$ " model is larger than that in the Hubbard model for corresponding chain lengths both with and without dimerization. However, when $U = 2V$, which is the crossover point from the *SDW* to the *CDW* regime, we find that the Hubbard chains have higher third-order polarizability than their counterparts in the " $U - V$ " model. This trend is observed only for $\bar{\gamma}$ and is not seen for the polarizability $\bar{\alpha}$. To understand this behavior we have studied the variation of the *lowest one - photon gap* (fig. 4a) and the *lowest two - photon gap* (fig. 4b) as a function of the chain length in the Hubbard model and the " $U - V$ " model at the *SDW/CDW* transition point. The gap to the lowest one-photon state in the former is higher than that in the latter at all chain lengths, independent of δ . Therefore the polarizabilities of the " $U - V$ " model at the transition point are higher than that of the Hubbard model. The third-order polarizability also has contributions from the two-photon states. The lowest two-photon state in the " $U - V$ " model for these parameters is at a higher energy than in the Hubbard model for all the chain lengths and δ . Consequently, the two-photon contribution to γ is higher for the Hubbard model than for the " $U - V$ " model.

For values of $V/t > U/2t$ (*CDW* regime), the optical gap decreases sharply and the chosen excitation frequency, ω , of $0.1eV$ is above the first three-photon resonance in the system. In this regime, γ is also found to have a negative sign for sufficiently long chains ($N > 10$ sites).

To conclude, we have demonstrated how dynamic NLO responses can be obtained within the DMRG procedure. We have applied the method to Hubbard and "U - V" chains in the *CDW* and *SDW* regimes.

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Figure Captions

Fig.1

Log-Log plot of the average polarizability ($\bar{\alpha}$) in 10^{-24} *esu* versus chain length L in Å for Hubbard chains of upto 20 sites in *all-trans* polyacetylene geometry for (a) $\delta = 0$ and (b) $\delta = 0.09$, for three different values of U/t .

Fig.2

Plot of the log of average third-order polarizability ($\bar{\gamma}$) in 10^{-36} *esu* versus log of the chain length L in Å, for Hubbard chains, with three different values of U/t for (a) $\delta = 0$ and (b) $\delta = 0.09$.

Fig.3

Log-Log plot of the average ($\bar{\gamma}$) in 10^{-36} *esu* versus chain length L in Å for "U - V" chains for three values of U/t and for $V/t = 1$ for (a) $\delta = 0$ and (b) $\delta = 0.09$.

Fig.4

Dependence of (a) one-photon gap (ground state to $1^1B_u^-$) and (b) two-photon gap (ground state to $2^1A_g^+$) on $1/N$. N is the number of sites in the chain.