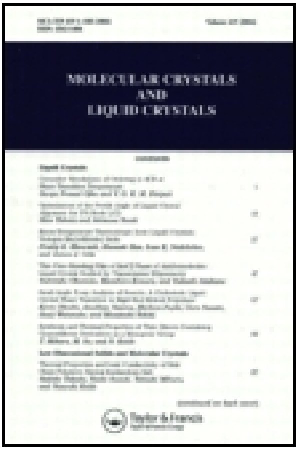

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I. D. L. Albert [a] & S. Ramasesha [a]

[a] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, 560 012

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Numerically Exact Study of Polarizabilities and Hyperpolarizabilities of Correlated Conjugated Organic Models†

I. D. L. ALBERT and S. RAMASESHA
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012

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Polarizabilities and Hyperpolarizabilities of conjugated organic chains are calculated using correlated model Hamiltonians. While correlations reduce the Polarizabilities and extend the range of linear response, the Hyperpolarizabilities essentially are unaffected by the same. This explains the apparently large Hyperpolarizabilities of conjugated electronic systems.

Keywords: polarizability, hyperpolarizability, correlated models, conjugated organic systems.

I. Introduction

One of the technologically important properties of conjugated organic systems such as polydiacetylenes is the observation of large nonlinear optical susceptibilities.[1] While the origin of this large nonlinearity is not yet clear, it has been convincingly demonstrated in these systems that the electron correlations are indeed strong.[2] The manifest properties due to strong electron-electron interactions are, the large excitation gaps introduced for dipole allowed transitions,[3] existence of dipole forbidden states below the lowest dipole allowed state,[4] reduced (compared to the noninteracting value) oscillator strengths for the dipole transitions,[5] introduction of negative spin densities in radicals[6,7] *etc.* In this short paper we explore the effect of correlations on the polarizabilities and hyperpolarizabilities of conjugated systems. We present numerically exact calculations of polarizabilities and hyperpolarizabilities of correlated one-dimensional model systems aimed at understanding the large hyperpolarizabilities of the quasi one-dimensional organic systems.

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II. Computational Method

The model exact calculation of polarizabilities via a sum over states (SOS) perturbation expression for the polarizability[1,8]

$$= 2 \sum_{i} \left\langle i|d|j \right\rangle \left\langle j|d|i \right\rangle / (E_i^0 - E_j^0) \tag{1}$$

(where d is the dipole moment operator) involves, besides calculation of the excited state wave functions and energies, the computation of all the transition matrix elements. For hyperpolarizability calculations this method would be even more tedious since multiple summations would occur in their expressions derived from perturbation theory.[8] In the case of correlated systems, this would amount to diagonalizing the entire configuration interaction (CI) matrix, which, even for small systems with full symmetry adoptation, would correspond to order of the matrices running into several thousands. Instead, it would be advantageous to compute the polarizabilities and hyperpolarizabilities directly by the finite field method (FFM).[9] In FFM, the polarization developed in the ground state (or any excited state) in response to the external field, E, is directly computed by solving only for the ground state (or the particular excited state) eigen function of the Hamiltonian with the external field term. The polarization can be expanded in a power series

$$p_i(E_j) = p_{i0} + \alpha_{ij} E_j + \frac{1}{2!} \beta_{ijk} E_j E_k + \frac{1}{3!} \gamma_{ijkl} E_j E_k E_l + \ldots.. \tag{2}$$

the quantities α, β, γ etc. can now be computed as successive partial derivatives of components of p with respect to appropriate components of E. Thus, this method bypasses computation of transition matrix elements and the subsequent summing over of states. However, the order of the CI matrix that needs to be solved in the presence of an external field is large compared to the field free CI matrix, since the application of an external field destroys some of the symmetries present in the latter case. Typically, for a linear chain of N electrons on N identical atoms, the symmetries destroyed are the electron-hole symmetry and the spatial symmetry corresponding to reflection about the center of the chain, for a field applied along the chain length. However, spin related symmetries are still conserved by the Hamiltonian in the external electric field. Therefore, we employ the valence bond (VB) technique for solving the model Hamiltonian in an external field.[10]

The correlated model Hamiltonians considered in the calculation are the Hubbard model

$$H_{\mathrm{Hub}} = t \sum_{i,\sigma} (a_{i\sigma}^{*} a_{i+1\sigma} + \mathrm{HC}) + U \sum_{i} n_i \uparrow , n_i \downarrow \tag{3}$$

and the Pariser-Parr-Pople model given by

$$H_{\mathrm{PPP}} = H_{\mathrm{Hub}} + \sum_{i,j} V(r_{ij}) (n_i - 1)(n_j - 1) \tag{4}$$

where $v(r_{ij})$ is parametrised using the Ohno parametrisation[11] such that the potential $V(r_{ij} = U$ for $r_{ij} = 0$ and the potential is e^2/r_{ij} for r_{ij}. While the PPP model is appropriate for correlated organic systems which are essentially insulating in the extended condensed phase, the Hubbard model, by its simplicity affords a physical understanding of the variation in the properties as the correlations are gradually turned on. The potential due to an external electric field is given by

$$V_{\text{ext}} = e\, E_{\text{ext}} \sum_i r_i\, (n_i - 1) \tag{5}$$

where E_{ext} is the external electric field.

The actual computation involves, setting up of the full CI matrix which is nonsymmetric in the VB formalism we have chosen (due to nonorthogonality of the VB basis) and solving for the lowest left eigen state (which is identical to the eigen state of a symmetric CI matrix in the VB basis) of the matrix using Rettrup's algorithm.[12] The dipole moment in the ground state is calculated by transforming the eigen state of the full CI matrix into a VB representation in which the overlap matrix of the VB basis is block-diagonal with blocks of equal size being identical.[2] This property of the VB basis emerges from the charge orthogonality of the VB functions. The polarization is calculated as the ground state expectation value of the dipole moment operator. The VB function being an eigen function of the dipole moment operator, this procedure is straight forward once the overlap matrix is known. The polarizabilities and hyperpolarizabilities are calculated from the following relations

$$\alpha_{ij} = [p_i(E_j) - p_i(-E_j)]/2E_j; \qquad \gamma_{iiii} = [3(p_i(5E_i) - p_i(-5E_i)) \tag{6}$$

$$- 39(p_i(3E_i)\, p_i(-3E_i)) + 102(p_i(E_i) - p_i(-E_i))]/1152\, E_i^3 \tag{7}$$

These are accurate to order (E^3) and (E^7) respectively. The check on calculation is obtained from SOS calculations for small system sizes as well as considering checks such as the necessity for symmetry related components of $\alpha(\gamma)$ to be equal. These checks are well satisfied for α as well as γ. The hyperpolarizability also remains constant over a reasonably wide range of field values near the critical field.

III. Results and Discussion

The typical p vs. E diagrams for a noninteracting (U = 0 in Eq. 2) model and an interacting model are shown in Figures 1a and 1b. The behavior of p vs. E is linear at low electric fields and becomes nonlinear at higher electric fields, and saturates at the highest fields. The limiting polarization in the large E limit is given by the dipole moment of the configuration in which all the atoms on one part of the chain are doubly occupied while those on the other part are empty. This would correspond to the lowest energy eigen state of the operator H_{ext}. The saturation polarization is the same for the correlated models and the uncorrelated models, although as

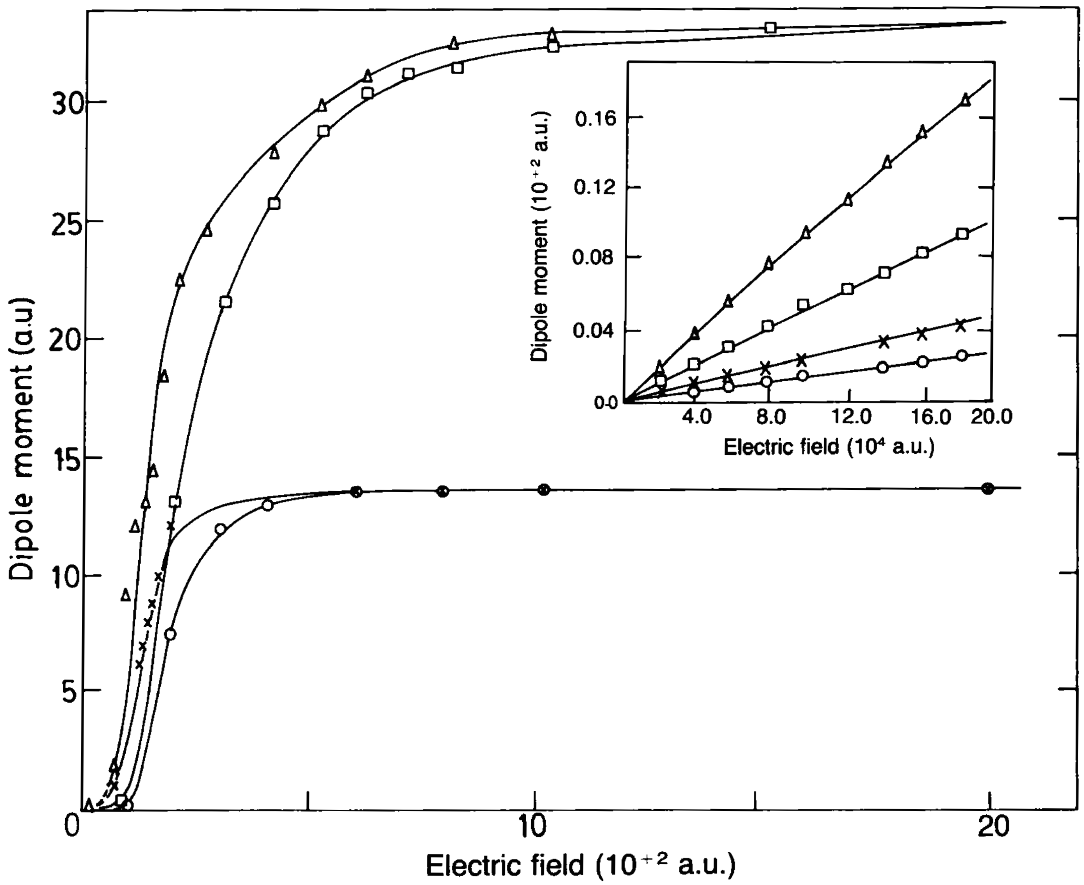

FIGURE 1a Induced dipole moment Vs electric field for a Huckel chain of eight. The upper curves are for p_z and the lower curves for p_x. The inset shows the linear behavior for low fields.

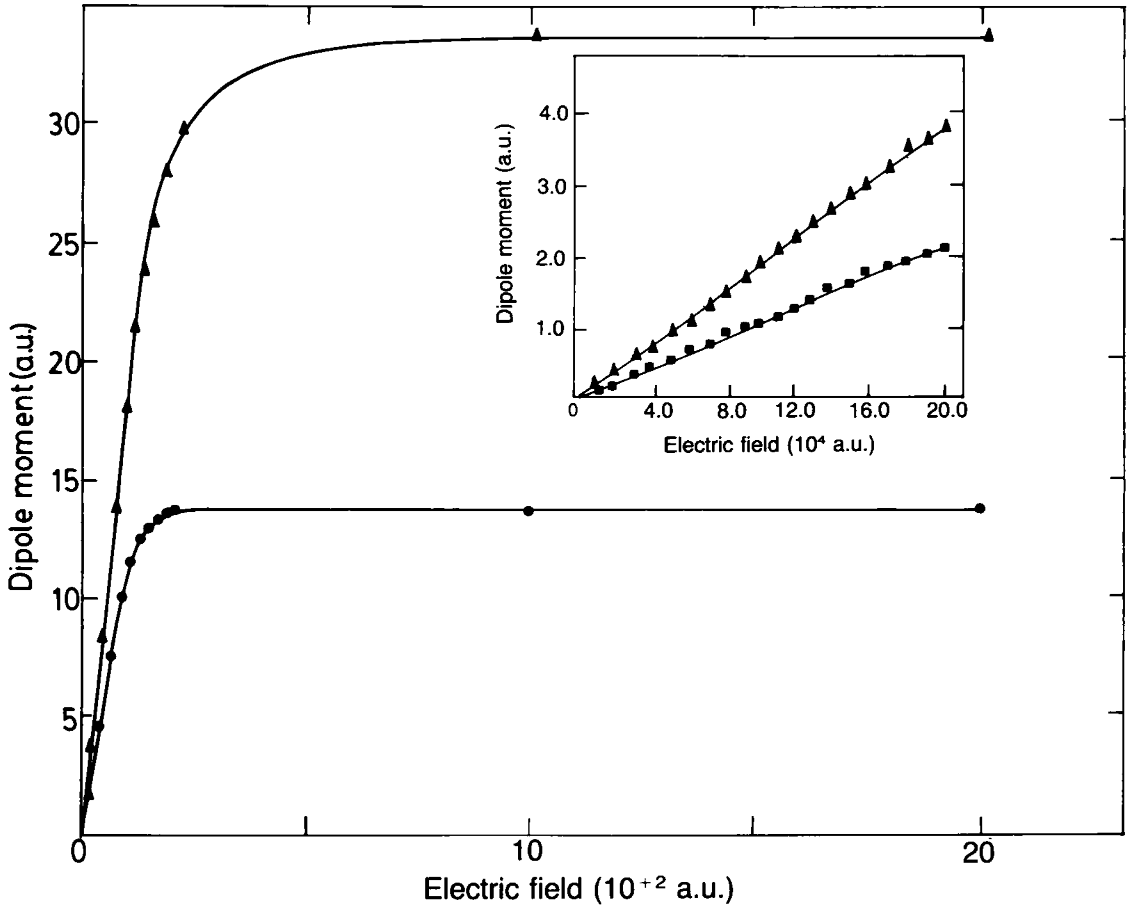

FIGURE 1b Induced Dipole moment Vs electric fields for a Hubbard chain of eight. The upper curves are for p_z and the lower curves are for p_x. The triangles are for U = 4t and squares for U = 6t. The inset shows the linear behavior for low fields.

TABLE I

Polarizabilities and hyperpolarizabilities of a Hubbard chain of eight sites as a function of the on-site correlation U. The polarizability values are in 10^{-8} a.u. The hyperpolarizability values are in 10^{10} a.u.

Hub U	α_{zz}	α_{xz}	α_{xx}	γ_{zzzz}	γ_{xxxx}
0.0	18.731	10.562	27.763	2.933	2.778
2.0	5.659	2.999	2.748	1.372	2.780
4.0	1.027	0.562	0.766	0.479	3.523
6.0	0.276	0.161	0.283	2.053	3.432
8.0	0.109	0.065	0.082	2.099	3.617

we see from the Figures 1a and 1b that the fields at which nonlinearity develops is lower for the uncorrelated model. This is to be expected since the field has to overcome the correlation energy before the saturation effects can appear.

The polarization developed at low fields is also very much smaller in the correlated models than the uncorrelated models. This is once again due to the fact that ionic structures which contribute to polarization are suppressed by electron correlations. Thus it is not surprising to see that the polarizabilities of correlated models systematically reduce as the correlation strength is increased. Table I gives the polarizability of a Hubbard chain of eight sites as the correlation are turned on. For molecular parameters, the polarizability of the PPP model is given for different chain length in Table II. We see from Table II that although polarizabilities are reduced from the Huckel model, the polarizabilities continue to depend strongly on the chain length. The effect of correlations, we find is to reduce the magnitude of polarizability without affecting the size dependence.

In Table III is presented the ratios of polarizabilities as well as hyperpolarizabilities of the correlated PPP models to those of uncorrelated models respectively. While, as already discussed, the polarizability ratio is very much smaller than unity, surprisingly, we see that hyperpolarizabilitity is not affected to the same extent by correlations. This is also seen from the weak dependence of γ on U in Table I. Our calculations implies that the ratio of the polarization developed due to the nonlinear part to that developed due to the linear part in correlated models is much larger than in the uncorrelated models. Thus, it appears that the large hyperpolarizability in the correlated models becomes apparent due to a large reduction in the polarizability from the noninteracting model rather than due to any real enhancement of the hyperpolarizability due to correlations.

TABLE II

Polarizabilities and hyperpolarizabilities of PPP chains with molecular parameters as a function of the chain length N. The polarizability values are in 10^{-8} a.u. The hyperpolarizability values are in 10^{10} a.u.

N	α_{zz}	α_{xz}	α_{xx}	γ_{zzzz}
8	0.232	0.133	0.215	1.349
10	0.436	0.150	0.110	6.742

TABLE III

Ratios of polarizabilities and hyperpolarizabilities of correlated PPP models to those of uncorrelated models.

N	$\alpha^{U}_{zz}/\alpha^{0}_{zz}$	$\alpha^{U}_{xz}/\alpha^{0}_{xz}$	$\alpha^{U}_{xx}/\alpha^{0}_{xx}$	$\gamma^{U}_{zzzz}/\gamma^{0}_{zzzz}$
8	0.0123	0.0125	0.0077	0.5407
10	0.0093	0.0073	0.0117	0.9354

This is reasonable to expect, because the nonlinearity sets in when the field term dominates over the transfer and correlation terms in the Hamiltonian. While the critical field at which the latter two terms become negligible depends upon correlation strength, the actual dependence of the polarization at these fields is insensitive to correlation strengths. Therefore, one should expect the hyperpolarizabilities to be insensitive to correlation while polarizabilities depend strongly on the same. This, we believe explains the large nonlinear optical effects in the strongly correlated conjugated organic systems.

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