RELAXED EXCITED STATE GEOMETRIES
IN A PEIERLS-HUBBARD MODEL FOR POLYENES

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ABSTRACT
Using parameter values relevant to polyacetylene and its finite polyene analogs, we determine, via exact finite size diagonalization of a 1D Peierls-Hubbard model, the relaxed geometry and optical absorption spectra of several states of interest in optical experiments (the singlet (1\(^{1}\)A\(_g\)) and triplet (1\(^{3}\)B\(_u\)) ground states, the singlet one (n\(^{1}\)B\(_u\)) and two (2\(^{1}\)A\(_g\)) photon gaps, and the triplet one (n\(^{3}\)A\(_g\)) photon gap) in order to examine the question of how well this simple model can really capture the behavior of this simple material.

INTRODUCTION
Recent experimental and theoretical work have established for the whole class of exciting novel reduced dimensional materials, including the high-temperature superconducting copper oxides, “heavy-fermion” systems, organic synthetic metals including conducting polymers, organic superconductors, and charge transfer salts, and halogen-bridged transition-metal chains, that it is essential to include both the electron-electron (e-e) and electron-phonon (e-p) interactions if we are to truly understand the properties of these materials. By carrying through detailed comparison of model calculations with real materials, we hope to achieve our modest goal: to gain an enhanced understanding of the nature of the competition between these two basic interactions of condensed matter physics. The hope of achieving our goal is greatest, of course, when the material and model are as simple as possible while still retaining the essence of the competition between the e-e and e-p interactions. Thus, studying a linear chain material of simple atomic constituents should be ideal. In fact, polyacetylene, or (CH)\(_x\), has previously been touted as the “hydrogen atom of the conducting polymers.”

No interpretation of dynamics of finite polyenes and conducting polymers can be considered complete unless it correctly captures the important role of the triplet and other excited states in these systems. Triplet states in (derivatives of) finite polyenes are known to be of considerable importance in the processes of vision [1] and of photosynthesis [2], in that they control certain crucial relaxation paths after electronic excitation. In conducting polymers, triplets appear essential to the understanding of the nature of long-lived excited states and specifically of the spectra observed in photoinduced photoabsorption. From a theoretical perspective, knowledge of excited states and their properties
can provide additional insight into the relative importance of electron-electron and electron phonon interactions and can help determine the parameters in the theoretical models of these materials.

**MODEL**

In the context of conducting polymers, the one-dimensional Peierls-extended Hubbard Hamiltonian [3] provides a theoretical framework capable of treating both electron-phonon (e-p) and electron-electron (e-e) interactions of arbitrary strengths. We focus on the one-dimensional Peierls-extended Hubbard Hamiltonian (1-D PHH) in the context of trans-polyacetylene (trans-(CH)$_x$). The 1-D PHH is

$$H = \sum_{\ell} (-t_0 + \alpha \delta_{\ell}) \sum_{\sigma} (c_{\ell \sigma}^\dagger c_{\ell+1 \sigma} + c_{\ell+1 \sigma}^\dagger c_{\ell \sigma}^\dagger) + U \sum_{\ell} n_{\ell \uparrow} n_{\ell \downarrow} + V \sum_{\ell} n_{\ell \uparrow} n_{\ell+1 \uparrow} + \frac{1}{2} K \sum_{\ell} (\delta_{\ell} - a_0)^2 \quad (1)$$

where the general features of this Hamiltonian have been described elsewhere [3]. Our studies here are a continuation of the work described in Ref.s [4], [5], and [6] as to its specific applicability to polyacetylene. We now can incorporate additional excited state information.

Due to space limitations, we refer the reader to Ref.s [4] and [5] for our determination of polyene parameters using ground state data and to Ref. [6] for initial studies of excited geometries using conventional polyacetylene parameters. We found that, since the bandwidth is partly due to e-e and partly e-p interactions, the hopping integral is less than the conventional $t_0 = 2.5$ eV value, but the parameter ratios remain roughly the same. Our best fits were obtained with $t_0=1–1.5$ eV, $\alpha=3.5–4.5$ eV/Å, $U=3–6$ eV, $V=0–2$ eV (with the fit roughly depending only on $U–2V$), and $K=40–60$ eV/Å$^2$. A typical absorption using parameters in this range showing agreement with triplet and soliton absorptions was shown in Fig. 3 of Ref. [5].

**EXCITED STATES**

Using the method for extracting excited states described in the appendix, we use the Lanczös method to determine the energies and wavefunctions of the ground state and several important excited states: the lowest triplet state ($1^3B_u$), the second singlet “$A_g$” state ($2^1A_g$) which determines the two-photon gap, and the “optical states” which determine the singlet optical gap ($n^1B_u$) and triplet optical gap ($n^3A_g$) [7]. Initial studies using conventional polyacetylene parameters and a fixed uniformly dimerized geometry were reported in Ref. [6]. Initial relaxed studies of only the triplet geometry were also reported in that paper. We have now obtained relaxed geometry information for all these excited states. Both conventional polyacetylene parameters and our new set given above have roughly $U/t_0=3$ and $\alpha \delta/t_0=0.1$, where $\delta$ is the average dimerization in the ground state [8]. The relaxed geometries for this (dimensionless) parameter set are shown in Fig. 1 for a 12-site system using open boundary conditions. Rather than the raw distortion, we have plotted the distortions order parameter $\pm (-1)^n \delta_n$ (with the sign being chosen so that a short bond at the chain end is positive) so that the deviation from uniform distortion is more apparent. We also plot the total energy for each of these states at each of these geometries to show the expected luminescence shifts, as well as check that our numerical procedure converged to the lowest energy configuration and not a higher lying local minimum. Unfortunately, for this small an electron-phonon coupling, it is difficult to analyze the geometry dependence as it is so weak. Thus, following Ref. [9], we increase the electron-phonon coupling until $\alpha \delta/t_0=0.5$. The results are shown in Fig. 2. Note that the singlet gap at the relaxed geometry of the optical state is approximately half its value at the ground state geometry. We also show in Fig. 3 the size dependence of the relaxed geometries for these same parameters. The state labeled “$2^1A_g$” is higher in energy than the state labeled “$2^1A_g$” on small systems ($N=8,10$) but becomes lower in energy on larger systems ($N=12$). Note that in the ground state geometry, the $2^1A_g$ lies roughly twice as far above the ground
Fig. 1 (left). Relaxed geometry and total energy of the various ground and excited states discussed in the text for $U/t_0=3$ and $\alpha \delta/t_0=0.1$.

Fig. 2 (right). Same as Fig. 1, but for $\alpha \delta/t_0=0.5$. For this electron-phonon coupling, a higher lying $2^1A_g$ geometry can also be found.

state as does the $1^3B_u$ state. This strongly hints that the $2^1A_g$ state is in some sense composed of two triplets, as suggested also by the work of Tavan and Schulten [10]. From Fig. 3 we see that the $1^3B_u$ state has the lattice distortion appropriate to two neutral solitons, and the $2^1A_g$ prefers a 4-soliton configuration at $N=12$. Does this mean that one should view the $2^1A_g$ state as composed of four solitons? Such an interpretation was proposed in the renormalization group studies of Hayden and Mele [11] but is explicitly contradicted in the configuration interaction studies [10] and (at least apparently) in combined experimental/theoretical studies on octatetraene [12]. Unfortunately, it is difficult to determine a definitive answer to this question (see Ref.s [3] and [6] for a more thorough discussion). At present, our data on the fully relaxed geometry and energy of the $2^1A_g$ state on the largest systems ($N = 12,14$) are not sufficient to determine the resolution of this question unambiguously. This difficulty arises in part because the $2^1A_g$ state is not the lowest singlet state of $A_g$ symmetry and thus must be extracted from the Lanczös data with considerable care. However, to date our Lanczös results are most consistent with the “4-soliton” viewpoint for long polyenes, and not inconsistent with the experiment showing a different geometry for octatetraene.

Acknowledgements. This work would have been impossible without the close collaboration of E.Y. Loh, Jr., S. Mazumdar and B. Kohler. We also wish to thank A.R. Bishop, J. Bronzan, R. Friend, and V. Vardeny, among others, for many useful discussions. JTG was supported by a NRC/NRaD Research Associateship through a grant from ONR. Computational support was provided by the ACL, CMS, and CNLS at LANL.
Fig. 3. Size dependence of the relaxed geometries for the parameters of Fig. 2. For $N=8,10$ the configuration labeled $2^1A_g^*$ is preferred, but at $N=12$ the configuration labeled $2^1A_g$ becomes lower in energy.

APPENDIX: NUMERICAL METHOD FOR OBTAINING EXCITED WAVEFUNCTIONS

Our “exact” diagonalizations were performed using a standard Lanczös algorithm which in essence involves expressing the Hamiltonian in a cleverly chosen basis, in which it is tridiagonal. Only the electronic part of the Hamiltonian was treated exactly; the adiabatic approximation was used for the phonons. Our formulation of the standard Lanczös procedure and method for extracting ground state relaxed geometry and optical absorption information, including our averaging technique for enhancing the finite-size results, has been previously described (Ref. [13]).

While the standard Lanczös method is useful for projecting out ground states, we are typically interested in several states which are important for, e.g., optical experiments: the $1^1A_g$ (ground state), $2^1A_g$ (two-photon singlet gap), $n^1B_u$ (singlet optical gap, $1^1B_u$ for small $U$), $1^3B_u$ (triplet ground state), and $n^3A_g$ (triplet gap, $1^3A_g$ for small $U$). While the standard Lanczös method allows us to get the singlet and triplet (by working in the $S_z=1$ subspace) ground state wavefunctions and energies, it allows us to find only the energy of the one and two photon gap states, and not the wavefunctions of these excited states, and hence we cannot investigate, e.g., questions of geometry relaxation upon excitation and corresponding luminescence spectra. However, by slightly modifying the Hamiltonian and procedure, we can indeed obtain such information, though some care must be taken as occasionally the numerical procedure fails and so one must test that the resultant states are indeed eigenfunctions of the original Hamiltonian with the desired symmetry. Once they have been found, evaluation of correlation functions (such as the bond-charge, which determines the self-consistent relaxed geometry) proceeds as for the ground state. Though we describe here the method only for a single boundary condition, the generalization to our ”boundary condition averaged” scheme, described in Ref. [13] is straightforward.

The first step [14] is to note that the starting Hamiltonian, Eq. 1, commutes with several symmetry (parity) operators, especially if the distortion has some symmetry. Assuming there are equal numbers
of up and down spin electrons and that the distortion is symmetric about some bond (or site), call it the $n$-th one, then we can add the following terms to the Hamiltonian without changing the eigenfunctions:

$$H_1 = \lambda_F F + \lambda_R R + \lambda_S S^2$$

Where $S$ is the total spin, $R$ is the parity operator which inverts about the $n$-th bond (site), and $F$ flips every spin. When $H = H_0 + H_1$ is applied to a wavefunction, one finds

| state   | Energy                                      |
|---------|---------------------------------------------|
| $^1A_g$ | $E_0(^1A_g) + \lambda_F + \lambda_R$      |
| $^1B_u$ | $E_0(^1B_u) + \lambda_F - \lambda_R$      |
| $^3B_u$ | $E_0(^3B_u) - \lambda_F - \lambda_R + 2\lambda_S$ |
| $^3A_g$ | $E_0(^3A_g) - \lambda_F + \lambda_R + 2\lambda_S$ |

Thus we can, e.g., preferentially select the singlet over the triplet ground state by setting $\lambda_F$ to a large number and performing the standard Lanczös procedure. One could also apply a projection operator $P$ which projects out a given total spin. However, this particular operator is (i) computationally expensive and (ii) tends to cause the numerical procedure to fail (through, e.g., loss of orthogonality). Thus we have not employed it. Further, raising or lowering the energy based on the total spin tends to favor zero (singlet) and maximum spin, rather than the singlet and triplet, and flipping the spin has the same singlet/triplet selectivity, thus we have only used the symmetries $F$ and $R$ to project out eigenstates, and tested the resultant state to insure the desired total spin.

To project out the $^1B_u$ is a simple matter of adjusting the $\lambda$ and finding the “ground” state (of $H$, first allowed $^1B_u$ for $H_0$) with the usual Lanczös procedure. However, for large $U$, the $^1B_u$ is not the optical edge [7]. One can get around this problem by a slight modification of the Lanczös procedure. If we assume the ground state $|\phi_0\rangle$ is known, then after we have generated a given basis vector $|\psi_j\rangle$ we also calculate and store $\langle \phi_0 | J | \psi_j \rangle$. Once the storage limit of the computer is reached, instead of selecting the eigenvector with lowest eigenvalue, we select the one with lowest eigenvalue and non-zero $\langle \phi_0 | J | \phi_k \rangle$. (To do this we need only deal with the small matrix which converts a Lanczös basis number to a eigenvector number, thus this step does not add considerably to the time or size of the calculation). We iterate this procedure until the estimate of the $n^1B_u$ energy stops changing, as for the ground state. Note that this (i) only increases the memory requirement by one state, and (ii) only adds one “expensive” step per Lanczös basis state. Of course, the statement “non-zero” above means in practice larger than some cutoff. If too small a cutoff is used, the $^1B_u$, $^2A_g$, triplet ground state, or other lower lying state not of current interest, may be found instead of the desired optically allowed state. We have found a relatively large value of the cutoff (\sim 10^{-2} in units of the matrix element of the optical edge) is required, though this is not as large as it seems, as it is the square which is important for optical absorption. It also means that, e.g., for the triplet ground state geometry, it is not the band edge, but rather the soliton absorption, which is found (unless quite a large value for the cutoff is used, which can be troublesome, or an additional selection requirement that the energy be “near” the value for the uniform geometry, assumed to have been previously calculated, is added).

At the end of this procedure for projecting out a given excited state, it is important to test that the resultant state (i) is an eigenstate of $H_0$, and (ii) has the desired symmetry and total spin, to insure against loss of numerical accuracy. (We have found using $\lambda$ values on the order of the energy separation of interest is usually successful.) Obviously, while straightforward, this excited state projection procedure cannot be used blindly, and it is important to test not only that the “answer” is an eigenstate with correct symmetry and spin (and non-zero $\langle \phi_0 | J | \phi_k \rangle$ if an optically allowed state is
desired) but that comprehensible trends as a function of system size or other parameter are followed, before one can have full confidence that one has indeed calculated what one set out to.

When there are unequal numbers of up and down spin electrons or the distortion has no inversion symmetry, the symmetry operators $F$ or $R$, respectively, cannot be used, though the procedure described above (with obvious modifications) can still be used to project out, e.g., the wavefunction of the first optically allowed state. Also it is clear that one can obtain further excited state information (e.g., second optically allowed state) using these and similar modifications of the basic Lanczos procedure, though at the cost of larger time and storage requirements and (potentially fatal) loss of numerical accuracy. We note that further excited state information, such as the many-body density of states, can also be obtained in a related but somewhat different fashion which essentially involves recursively generating the basis to fill in the necessary matrix element of the correlation function of interest and which does not significantly increase the storage requirements or decrease the numerical accuracy, though it obviously increases the time requirements [15].

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