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EQUATION-OF-MOTION CALCULATIONS ON AN ISOLATED CHAIN OF POLYACETYLENE

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Abstract An equation-of-motion (EOM) method for calculating the excited states of one-dimensional systems is discussed. This method is similar to configuration-interaction theory except the ground state is constrained to remain the Hartree-Fock ground state. Issues relating to the size-consistency of the method are briefly discussed. EOM calculations are performed using the semi-empirical Hamiltonian appropriate for gas-phase polyenes. In these calculations, electrons and holes are created on the Hartree-Fock ground state. In the low energy states, the electrons and holes get bound together by Coulomb forces into many-body excitations, or effective particles. These effective particles are delocalized over the entire polymer, but there is limited separation between the electrons and holes within the particle. The effective particles may have significant contributions from both single and double electron-hole pair configurations. It is speculated that dielectric screening may be much weaker for states with small electron-hole pair separations than for states with large electron-hole pair separations. The effective particles present in the low-energy highly-correlated states may then remain essentially intact; while at the same time, dielectric screening may significantly lower the energy of the free electron-hole pair, charge-separated states.

INTRODUCTION

While conjugated polymers can be viewed as one-dimensional semiconductors, much of the physics present in these materials is distinctly different from that of inorganic semiconductors such as GaAs. The most obvious distinction is the nearly one-dimensional delocalization of electrons along the polymer backbone.[1] There are also large structural distortions associated with the self-trapped excitations — solitons, polarons and bipolarons — created by either chemical doping or photo-excitation.[2] Another unusual characteristic, and the one we will concentrate on in this paper, is the possibly large effects that arise from electron correlation. One of the most well-known such effects is the presence of a highly-correlated 2^1A_g electronic state below the 1^1B_u state in polyenes.[3–5] Most of what we know about this 2^1A_g state comes from calculations on short chains, and the extrapolation of these results to long chains is not straightforward.[6,7] In this paper we consider a simplified model of electron correlation, but obtain results directly in the polymeric limit. In creating an excited state, we create electrons and holes on top of the Hartree-Fock ground state. These electrons and holes then interact through Coulomb forces. A more accurate description of the excited states will require the creation of electrons and holes on a correlated ground state. This will lead to "dressed" electrons and holes, and these dressed electrons and holes may interact in ways considerably more complex than those seen here. Nevertheless, it is useful to first consider how undressed electrons and holes interact. The calculations presented here also ignore the geometric relaxation of the excited states and the

effects of dielectric screening. We will discuss such effects briefly in the *discussion* section.

Our approach is motivated by the results of singles-configuration interaction (S-CI) theory.[8,9] In S-CI theory, a single electron-hole (e^--h^+) pair is created on top of the Hartree-Fock ground state and there is Coulomb attraction between the electron and hole. We can make an analogy between the states obtained in S-CI theory and the states of an electron and proton in a box. In the low energy states, a hydrogen atom is delocalized throughout the box. In the high energy states, the electron and proton dissociate and the electron and proton are separately delocalized throughout the box. In polymers, the hydrogen atom corresponds to a bound e^--h^+ pair, or exciton, and the dissociated states correspond to unbound e^--h^+ pair states. The energetics of the excitons may be quite different from that in inorganic semiconductors. For example, in CdS it takes about 2.5eV to create an unbound e^--h^+ pair and the binding energy between the electron and hole in the lowest-energy exciton state is less than 0.04eV.[10] When using an unscreened Coulomb interaction, such as that used in gas-phase calculations of polyenes, the exciton binding energy is quite large, about half the energy needed to create a free e^--h^+ pair. Given this strong interaction between a single electron and a single hole, we might also expect to find strong interactions between two electrons and two holes. In order to investigate these interactions, we will use the equation-of-motion formalism discussed below.

THE EQUATION OF MOTION FORMALISM

In the theories we will consider, the excited states are written

$$|\text{excited state}\rangle = \Omega^\dagger|\text{HF}\rangle, \tag{1}$$

where $|\text{HF}\rangle$ is the Hartree-Fock ground state and $\Omega^\dagger$ is a linear combination of e^--h^+ pair creation operators. For an undistorted polymer with periodic boundary conditions, we can write $\Omega^\dagger$ as

$$\Omega^\dagger = \sum_{n=1}^{N} e^{iKn}\Omega_n^\dagger, \tag{2}$$

where $\Omega_n^\dagger$ creates e^--h^+ pairs centered on the n^{th} unit cell, and N is the total number of unit cells. Due to translational symmetry, the form of the operator $\Omega_n^\dagger$ is the same on each unit cell. What we have done in eq. 2 is separate the overall "center-of-mass" motion of the electrons and holes, which are delocalized with wavevector K, from the relative motion of the electrons and holes, which is contained in the form of the operator $\Omega_n^\dagger$. Many properties are consequences of the overall delocalization of the particles created by $\Omega_n^\dagger$. For instance, as the length of the polymer increases, low-energy states will fill in the band edge, leading to red-shifted absorption. The size of the red-shift and the chain length at which the red-shift saturates are both indications of the degree of delocalization; however, neither provides direct information on the form of the particle being delocalized.

SINGLES-CONFIGURATION INTERACTION (S-CI) THEORY

Within S-CI theory,[8,9] the excitation operator $\Omega_n^\dagger$ is written as a linear combination of single e^--h^+ pair creation operators:

$$\Omega_n^\dagger = \sum_{\Delta} c_\Delta a_{n+\Delta}^\dagger b_n^\dagger \tag{3}$$

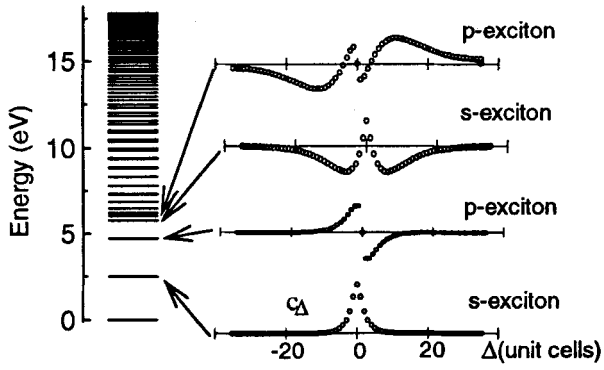

Figure 1: Energy levels and wavefunctions from a S-CI calculation on an isolated polyacetylene chain with 71 unit cells, using the PPP Hamiltonian with Ohno parameterization[4,8]. Only K=0 energy levels are shown. c_Δ gives the dependence of the wavefunction on Δ, the separation between the electron and hole in unit cells. The states above about 6eV contain unbound e-h pairs and form a continuum on an infinitely long polymer.

where $a_n^\dagger$ creates an electron in the conduction-band Wannier function on the n^{th} site and $b_n^\dagger$ creates a hole in the valence-band Wannier function on the n^{th} site.[10,8] $\Omega_n^\dagger$ can then be viewed as the creation operator for an exciton centered on the n^{th} unit cell. The structure of the exciton is contained in c_Δ, the amplitude for finding the electron and hole separated by Δ unit cells. Physically, the presence of an electron on a unit cell indicates a negative charge on that unit cell, and the presence of a hole indicates a positive charge. c_Δ then gives the amplitude for charge transfer over a distance of Δ unit cells. The primary distinction between S-CI and uncorrelated theories is that S-CI theory limits the amount of charge transfer present in the low-energy excited states. In uncorrelated theories, the low energy states contain unbound e^--h^+ pairs, which implies that charge transfer between remote positions of the polymer is just as likely as charge transfer between adjacent unit cells.

Figure 1 shows S-CI results for an isolated chain of polyacetylene, calculated within the Ohno parameterization of the Pariser-Parr-Pople (PPP) π-electron model.[4,8] The binding energy between the electron and hole measured relative to the free e^--h^+ pair states is quite large, about 3.5eV in the lowest excited state. The resulting exciton is correspondingly small, with an average e^--h^+ pair separation of a few unit cells. The form of the excitons, c_Δ of eq. 3, is shown for the lowest excited states. c_Δ gives the dependence of the wavefunction on the separation between the electron and hole. For the lowest-energy excited state, $c_\Delta = c_{-\Delta}$, and states with this property will be referred to as s-exciton states, by analogy to s atomic orbitals. In the next highest state $c_\Delta = -c_{-\Delta}$, and these states will be referred to as p-exciton states.

SINGLES-DOUBLES EQUATION-OF-MOTION (SD-EOM) THEORY

S-CI theory constrains the excited states to contain exactly one electron and one hole. We can relax this constraint by including doubly excited configurations in the basis set for

the excitation operator:

$$\Omega_n^\dagger = \sum_\Delta c_\Delta a_{n+\Delta}^\dagger b_n^\dagger + \sum_{h_1,e_1,e_2} c_{h_1}^{e_1,e_2} a_{n+e_1}^\dagger a_{n+e_2}^\dagger b_{n+h_1}^\dagger b_n^\dagger \tag{4}$$

Note that this is not equivalent to configuration-interaction (CI) theory. In CI theory, single and double excitations are allowed to mix into the ground state, and the resulting description of dynamic correlation is not size consistent. Here, the ground state is constrained to be the Hartree-Fock ground state. The operator $\Omega^\dagger$ is used strictly to define the difference between the ground and excited states, not to modify the ground state itself. This technique fits within the equation-of-motion formalism discussed by Rowe,[11] so we choose to call this method SD-EOM theory (equation-of motion theory with single and double excitations).[a] The matrix that is diagonalized in SD-EOM theory to determine $\Omega^\dagger$ is identical to the SD-CI matrix except that matrix elements connecting the Hartree-Fock ground state to doubly-excited configurations have been removed. Since, by Brillouin's theorem, there are no matrix elements between the Hartree-Fock ground state and singly-excited configurations, S-CI theory can also be viewed as an equation-of-motion method[11] and could just as well be labeled S-EOM theory.

We are currently investigating the size-consistency of the SD-EOM approach. The SD-EOM method is size consistent in the following sense. Consider the excited states obtained on application of SD-EOM theory to two separate systems, A and B. These same excited states will be obtained when SD-EOM theory is applied to a supersystem consisting of two *non-interacting* subsystems A and B.[b] This appears to guarantee that the energy of the excited states will scale linearly with chain length in the polymeric limit. From a more physical perspective, consider an infinitely long polymer. S-CI theory can describe the creation of a single exciton on this polymer in a size consistent manner. On an infinite polymer, there should be states containing two essentially noninteracting excitons. But if we were to use SD-CI theory to describe these states, the double e^--h^+ pair configurations would mix with the Hartree-Fock ground state. $\Omega^\dagger$ would not only be used to create the excitons but would modify the ground state itself. The equation-of-motion formalism prevents such a modification of the ground state, making it possible to describe a state containing two excitons in the same exact manner as S-CI theory describes a state containing a single exciton.[c]

Our results from SD-EOM calculations on polyacetylene are shown in Figure 2. The addition of double excitations to the basis set for $\Omega_n^\dagger$ increases the number of linear parameters to be determined from N to N^3 (see eq. 4). To make calculations tractable, we use local approximations. Consider first the use of local approximations in S-CI theory. In the low energy states, c_Δ goes to zero for large e^--h^+ pair separations (Figure 1). The left panel of Figure 2 shows S-CI calculations performed using only those basis functions with e^--h^+ pair separations smaller than some cutoff distance. Comparison with the wavefunctions of Figure 1 shows that the size of the basis needed to give a converged energy provides a good measure of the size of the exciton in that state. The right panel of Figure 2 shows results from truncated SD-EOM calculations. These calculations include all singly-excited

[a]The requirement that $\Omega^\dagger$ not modify the Hartree-Fock ground state is equivalent to the more general requirement of EOM theories, $\Omega|GS>=0$. This latter constraint may be viewed as a requirement that the excitation created by $\Omega^\dagger$ must not be present in the ground state

[b]This is true of S-EOM and SD-EOM theory, but not SDT-EOM theory.

[c]Addition of triple excitations in SDT-EOM theory will lead to size-consistency problems because states containing a single exciton will mix with states containing three excitons, since these are doubly excited configurations with respect to the single exciton state.

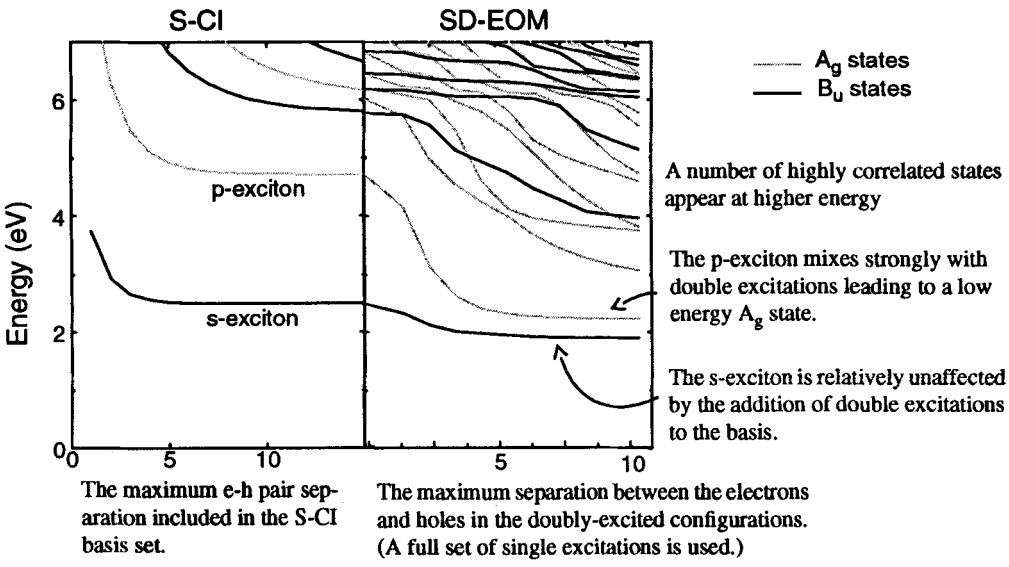

Figure 2: K=0 energy levels from S-CI and SD-EOM calculations using the same parameters as in Figure 1. The size of the basis needed to yield a converged energy indicates the size of the effective particle in that state.

configurations but limit the maximum separation between the electrons and holes in the doubly-excited configurations. The convergence of the low-energy states with respect to the size of the basis indicates that these states contain small, albeit complicated, effective particles.

Note that the size of the effective particles and the chain length at which a measurable property saturates are two entirely different length scales. For example, in S-CI theory, the s-exciton state sets both the band gap and the linear polarizability. (The s-exciton state carries most of the one-photon intensity.) Although the separation between the electron and hole in the s-exciton state is only about 4 unit cells, the band gap and polarizability saturate at much longer chain lengths.[12] Just as in Huckel theory, where the polarizability saturates at some length that has no direct relation to the size of the electron or hole; in S-CI theory, the polarizability saturates at a length that is not directly related to the size of the excitons.

DISCUSSION

The results of SD-EOM theory exhibit many of the features that configuration interaction (CI) calculations on short chains have led us to expect in polyenes.[4,13] CI calculations indicate that the 1^1B_u state is composed primarily of single e^--h^+ pair configurations and is essentially an s-exciton state. In our SD-EOM calculations, the s-exciton state drops from 2.5eV to 2eV, but the mixing with double excitations is small and it remains qualitatively an s-exciton state. Also, CI calculations find a low energy 2^1A_g state that has significant contributions from both singly and doubly excited configurations. Our SD-EOM calculations also find a 2^1A_g state with this character, however, the precise nature of the 2^1A_g

state is probably not well described. For instance, in the limit of large electron repulsion, the ground state takes on spin-density wave character[d] and the 2^1A_g state corresponds to a spin-wave excitation.[3] In SD-EOM theory, the ground state is constrained to be the Hartree-Fock ground state and any tendency towards a spin-density wave is ignored. SD-EOM theory cannot then fully capture the spin-wave excitation character of the 2^1A_g state. An accurate description of the excited states will require the creation of e^--h^+ pairs on a correlated ground state, instead of the Hartree-Fock ground state of eq. 1.

The results obtained here suggest that the low-energy excited states contain effective particles in which electrons and holes are bound tightly together into "local" many-body excitations. These excitations may have single, double, and possibly higher e^--h^+ pair character. The "local" character of these states does not imply the excited states are localized on some region of the polymer; on the contrary, the effective particles are assumed to be delocalized over the entire polymer in eq. 2. The local character refers to the size of the particle that is delocalized.

Both the geometric relaxation of the excited electronic states and the dielectric screening from neighboring polymer chains are ignored in these calculations. In systems with degenerate ground states, such as polyacetylene, lattice relaxation stabilizes the free e^--h^+ pair charge-separated states.[2] Dielectric screening will also strongly favor charge-separated states. In considering the effects of dielectric screening, it may be important to consider the local character of the low-energy excited states. It may be that the effects of dielectric screening increase rapidly with the e^--h^+ pair separation (or charge separation) present in a given state. Such an assumption would allow for the existence of low-energy highly-correlated states, such as the 2^1A_g state obtained here, even in systems where dielectric effects strongly stabilize charge separated states. This assumption could rationalize the existence of both low-energy high-correlated states and the onset of photoconduction near the absorption threshold — two phenomena which at first glance appear to be mutually exclusive. However, these comments are highly speculative and calculations that explicitly include dielectric screening from adjacent chains need to be performed.

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[d]Spin-density wave here refers to a state that in valence bond theory has 100% covalent character.