Electron-lattice and electron-electron coupling in conjugated polymers: Minimum total-energy calculations on the Hubbard-Peierls Hamiltonian

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Minimum total-energy calculations, which account for both electron-lattice and electron-electron interactions in conjugated polymers, are performed for chains with up to eight carbon atoms. These calculations are motivated in part by recent experimental results on the spectroscopy of polyenes and conjugated polymers and they shed light on the long-standing question of the relative importance of electron-lattice vs electron-electron interactions in determining the properties of these systems.

A large amount of experimental evidence[1] regarding conjugated polymers can be understood in terms of independent-electron theories that account for electron-lattice (*e-l*) coupling and σ-bond compressibility.[2,3] However, there exists a considerable body of spectroscopic results, concerning especially the ordering of excited states,[4-9] which cannot be explained without invoking electron-electron (*e-e*) correlations. Since such different experimental results are usually rationalized in terms of models that describe adequately only either the *e-l* or the *e-e* interaction, different groups of researchers have been led to emphasize in these systems the importance of one of the two effects at the expense of the other.

Here, the results of a set of minimum-total-energy calculations that fully include both interactions are presented. There are several reasons to pursue this goal. From a theoretical standpoint it is natural to assume that the transfer integrals depend on the distance between carbon sites and that there is an energy cost involved in stretching a carbon-carbon bond.[2] It is also not surprising to find manifestations of *e-e* interactions which are not accounted for by models implying complete screening such as those of Refs. 2 and 3. On the experimental side there is a growing amount of evidence indicating that the ordering of excited states depends on the specific polymer and in some instances it appears that different probing techniques lead to different results in this regard.[4-9] In particular, recent observations in short thiophene oligomers[6] and in poly (*p*-phenylene-vinylene)[7] show that in these systems the ordering of the two lowest excited states is reversed compared to that observed in polyenes.[4,5] Within the context of the Su-Schrieffer-Heeger (SSH) model[3] it is natural to interpret this reversal in terms of lack of ground-state degeneracy in the systems of Refs. 6 and 7. This is because, upon excitation of one electron from the highest occupied to the lowest unoccupied molecular orbital, lack of ground-state degeneracy leads to two separate bipolaron levels as opposed to a pair of degenerate soliton levels. *e-e* repulsion favors the $2\,^1A_g$ over the $1\,^1B_u$ level,[10] and the results of Refs. 6 and 7 suggest that this latter effect is not strong enough to overcome the energy difference between bipolaron lev-

els in these systems. These qualitative considerations hint to the possibility that important physical effects may be overlooked if the spectroscopic results are interpreted without fully accounting for *e-l* interactions.

Minimum-total-energy calculations based on the SSH description were presented in Refs. 10 and 11. For a *trans*-polyacetylene chain with N carbon atoms, the starting point is the Hamiltonian for the π-electron system:

$$H = -\sum_{n,s}[t_0 - \alpha(u_{n+1} - u_n)](c^\dagger_{n+1,s}c_{n,s} + c^\dagger_{n,s}c_{n+1,s})$$
$$+ \frac{K}{2}\sum_n(u_{n+1} - u_n)^2 . \tag{1}$$

Here $c^\dagger_{n,s}$ and $c_{n,s}$ are creation and annihilation operators for an electron of spin s on site n; u_n is the displacement of the nth ion from its equilibrium position, so that $(u_{n+1} - u_n)$ is the deviation of the length of the nth bond from its equilibrium length. The first sum describes hopping with transfer depending linearly on bond length. The energy associated with σ-bond compressibility is described by the second term, K being an elastic spring constant. The Hamiltonian of Eq. (1) can be rescaled and rewritten in terms of the dimensionless coordinates $\beta_n = \alpha(u_{n+1} - u_n)/t_0$ as

$$\frac{H}{t_0} = -\sum_{n,s}(1 - \beta_n)(c^\dagger_{n+1,s}c_{n,s} + c^\dagger_{n,s}c_{n+1,s}) + \gamma\sum_n\beta_n^2 , \tag{2}$$

where $\gamma = (Kt_0)/(2\alpha^2)$ accounts for the strength of the *e-l* coupling (small γ corresponds to strong coupling). A diagonalization of the first term in the right-hand side of Eq. (2) gives the single-particle electronic energy levels $\epsilon_{m,s}(\{\beta_n\})$. For a given set of occupation numbers $v_{m,s}$, it is possible to determine the values of the coordinates β_n (i.e., of the hopping constants) which minimize the total energy

$$E_T(\{\beta_n\}) = \sum_{m,s}v_{m,s}\epsilon_{m,s}(\{\beta_n\}) + \gamma\sum_i\beta_i^2 \tag{3}$$

for a given γ. Here the first sum runs over the possible

single-particle energy levels; the second is a sum over the $(N-1)$ bonds. It is through such a minimization procedure that the models of Refs. 2 and 3 account for e-l interactions. In the ground state of the half-filled system this procedure leads to Peierls dimerization.[10]

Within the framework outlined above, the first ^1B_u excited state is obtained moving one of the two electrons occupying the Nth level to the $(N+1)$th level. In a long chain (even $N\rightarrow\infty$) the set of bond lengths (i.e., the set of values of β_n) which minimizes $E_T(\{\beta_n\})$ for this electronic configuration displays two kinks; these delimit a central portion of chain where the dimerization is inverted.[10] Corresponding to this bond geometry the Nth and $(N+1)$th levels are degenerate and are found at the center of the Peierls gap. Similar drastic distortions of the ground-state bond geometry with inverted dimerization in the middle of the chain occur for short chains; however, finite-size effects modify the kink bond geometry and break the degeneracy of Nth and $(N+1)$th levels. In all cases the total energy corresponding to the optimized bond geometry is substantially smaller than the energy that the system would have for the same electronic configuration in the ground-state bond geometry. From the Franck-Condon principle it should be expected that absorption experiments probe the situation where bond lengths are held to their ground-state values while fluorescence experiments probe the spectrum found by optimizing the bond geometry.

Similar considerations hold for higher electronic excited states. Indeed, for realistic values of γ, if one allows bond geometry relaxation, the lowest ^1A_g excited state corresponds to moving both the Nth level electrons to the $(N+1)$th level: in the $N\rightarrow\infty$ limit both the total energy and the bond geometry corresponding to this situation are the same as those of the first ^1B_u excited state.[12] However, if the bond geometry of the ground state is kept fixed, the electronic configuration which gives the lowest excited ^1A_g state is different: it corresponds to moving one of the Nth-level electrons to the $(N+2)$th level.[10]

The rest of this paper is devoted to studying how adding Hubbard terms of the form

$$\frac{h}{t_0}=+v_0\sum_m n_{m,\uparrow}n_{m,\downarrow}+v_1\sum_m n_m n_{m+1} \qquad (4)$$

to the Hamiltonian of Eq. (2) modifies the picture presented above. Here, as usual, v_0 and v_1 describe on-site and nearest-neighbor e-e repulsion, n_m is the number operator for electrons on site m, and $n_{m,\uparrow}$ ($n_{m,\downarrow}$) is the number of spin up (down) electrons. The distinguishing feature of the treatment presented here resides in the way the Hamiltonian [sum of (2) and (4)] is dealt with. The fermionic part of the Hamiltonian is diagonalized to give the (many-body) energy levels $E_m(\{\beta_n\},v_0,v_1)$. Then the set of values of the coordinates β_n which minimize the total energy

$$E_{T,m}(\{\beta_n\},v_0,v_1)=E_m(\{\beta_n\},v_0,v_1)+\gamma\sum_i\beta_i^2 \qquad (5)$$

associated with the mth (many-body) level can be deter-

mined for given values of γ, v_0, and v_1. This procedure is the natural extension of that of Refs. 2 and 3. The hopping constants (bond lengths) are not forced into configurations which cease to be optimal when e-e interactions are turned on.

The treatment outlined above differs from the explanations usually given[13–15] to rationalize the spectroscopic results of Refs. 4–9: these are based on the results of Pariser-Parr-Pople quantum chemical calculations, where the hopping constants are forced into a dimerized configuration fixed from the outset. Within this scheme, lattice relaxations are prevented: i.e., neither the hopping constants for the ground state nor those for the excited states are optimized. Bond lengths are obtained a posteriori from π bond orders. Hayden and Mele[16] addressed the issue of geometry optimization in models including e-e interactions; using a renormalization-group (RG) method they did obtain the optimized ground-state geometry. However, they computed the energy of the excited states using the ground-state geometry; this procedure does not account for the e-l effects underlying the soliton physics.

The program described above has been implemented numerically within the full basis set of singlet states for half-filled systems with up to eight carbon atoms.[17] The valence bond basis of Ref. 18 for the $S=0$ subspace is used as a starting point. A symmetric fermion Hamiltonian is obtained by changing to a new basis of singlet states by Gram-Schmidt orthogonalization; standard algorithms can then be used to find the required eigenvalues.[19] The set of coordinates β_n which minimizes the right-hand side of Eq. (5) must correspond to bond geometries symmetric with respect to the midbond. Therefore for a system of N sites minimization of a function of $N/2$ independent variables is required; the downhill simplex method has been used for this purpose.[20]
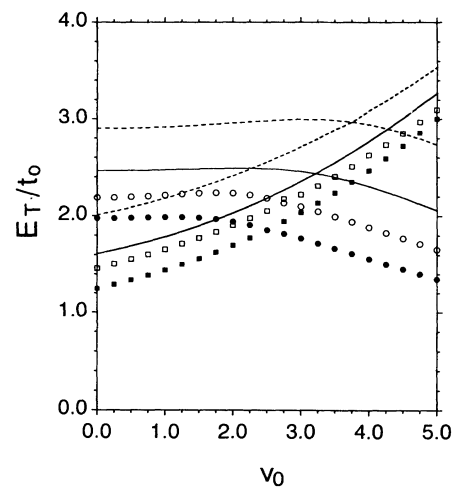

FIG. 1. Energy E_T (in units of t_0), relative to the ground state, of the $1\,^1B_u$ state (empty squares $\gamma=0.9$, filled squares $\gamma=1.2$) and of the $2\,^1A_g$ state (circles $\gamma=0.9$, bullets $\gamma=1.2$). Here $v_1=0$ and $N=8$. The continuous ($\gamma=1.2$) and broken ($\gamma=0.9$) curves show the corresponding results obtained from the fixed ground-state bond lengths.

Figure 1 displays examples of results obtained in this way:[21] it shows the energy (relative to the ground-state energy) of the $1\,^1B_u$ and of the $2\,^1A_g$ states for two different values of γ ($\gamma=0.9$,[22] and $\gamma=1.2$), $N=8$, and $v_1=0$. The energies of $1\,^1B_u$ and $2\,^1A_g$ obtained keeping the ground-state bond geometry fixed are also shown. Note that level crossing[23] between $1\,^1B_u$ and $2\,^1A_g$ occurs at much lower values of v_0 for the optimized excited-state bond geometries than for bond lengths fixed to their ground-state values. Also larger γ's, e.g., smaller e-l interactions, lead to $1\,^1B_u$–$2\,^1A_g$ crossings at lower values of v_0, at least for $N\leq 8$. Including a nearest-neighbor interaction (nonvanishing v_1) does not (for reasonable values of the ratio v_1/v_0) change the qualitative features of these results. In the range $0\leq v_0\leq 5$, the main effect is to increase slightly the $2\,^1A_g$ energy while that of $1\,^1B_u$ is nearly unchanged. As a result, the $1\,^1B_u$–$2\,^1A_g$ crossing occurs at slightly higher values of v_0. Results qualitatively similar to these are found both for $N=6$ and $N=4$. A detailed description of these and of the other numerical results summarized here will appear in a forthcoming publication.

It should be noted that three dimensionless parameters (γ, v_0, and v_1) completely determine the ratios between the energies of the electronic states as well as the relative size of the hopping integrals. On the other hand, in order to estimate bond lengths and absolute energies additional phenomenological constants[10] are needed. To avoid introducing other parameters, Table I shows examples of how the hopping constants (rather than the bond lengths) change as e-e interactions are turned on; note that large

TABLE I. Results for the hopping constants ($1-\beta_n$) for chains with $N=8$, $\gamma=0.9$, and $v_1=0$. The nth column gives the nth hopping constant with the outside bond corresponding to $n=1$ and the central bond to $n=4$. N_e is the number of electrons. The last set of data refers to a doped chain.

	$1-\beta_1$	$1-\beta_2$	$1-\beta_3$	$1-\beta_4$
Ground state for $N_e=8$				
$v_0=0.0$	2.041	1.383	1.974	1.412
$v_0=2.0$	2.019	1.363	1.961	1.389
$v_0=4.0$	1.951	1.315	1.911	1.332
$v_0=6.0$	1.839	1.261	1.813	1.270
$1\,^1B_u$ state for $N_e=8$				
$v_0=0.0$	1.829	1.685	1.503	1.856
$v_0=2.0$	1.813	1.662	1.524	1.803
$v_0=4.0$	1.701	1.597	1.479	1.769
$2\,^1A_g$ state for $N_e=8$				
$v_0=0.0$	1.684	1.847	1.172	2.068
$v_0=2.0$	1.607	1.815	1.344	1.883
$v_0=4.0$	1.430	1.742	1.469	1.604
$v_0=6.0$	1.331	1.653	1.404	1.465
Ground state for $N_e=6$				
$v_0=0.0$	1.829	1.685	1.503	1.856
$v_0=2.0$	1.814	1.662	1.524	1.803
$v_0=4.0$	1.768	1.628	1.518	1.740
$v_0=6.0$	1.705	1.592	1.498	1.670

hopping constants correspond to short bonds and vice versa. The experimental values of the energies for the $2\,^1A_g$ and $1\,^1B_u$ states are close in polyenes; i.e., realistic values of v_0 correspond to the $1\,^1B_u$–$2\,^1A_g$ crossing region. It is clear from Table I that the various types of solitonlike bond geometries (and in particular the reversed bond alternation in the chain center) survive at these levels of e-e repulsion.

It seems appropriate at this point to comment on a recent paper by König and Stollhoff[24] which called into question the importance of the Peierls mechanism in determining the ground-state dimerization of trans-polyacetylene. The results of Table I for the half-filled ground state are at variance with the conclusions reached by these authors. These results show that (for realistic[22] values of γ) e-e interactions have little effect on the ground-state hopping constants and are consistent with a picture where the Peierls mechanism is the main reason for dimerization. The results of König and Stollhoff appear due to their failure to fit their ab initio results independently to those obtained from a semiempirical Hamiltonian which does not include correlations.

In order to model systems where ground-state degeneracy is lifted as a consequence of the local molecular structure, an explicitly biased hopping term

$$\frac{H_b}{t_0}=\frac{t_b}{t_0}\sum_{n,s}(-1)^n(c_{n+1,s}^\dagger c_{n,s}+c_{n,s}^\dagger c_{n+1,s})\tag{6}$$

has been added to the Hamiltonian (here t_b is a site-independent phenomenological constant). Figure 2 shows numerical results for this situation when (t_b/t_0)$=0.08$, $\gamma=0.9$, and $v_1=0$. As anticipated the $1\,^1B_u$–$2\,^1A_g$ crossing occurs for higher values of v_0 than before. Again, analog behavior has been obtained for systems with $N=4$ and $N=6$ and the distorted bipolaron-like bond geometry survives in the presence of e-e repulsion. Although these results agree with the qualitative arguments presented at the beginning of this paper, in order to account quantitatively for the findings of Refs. 6
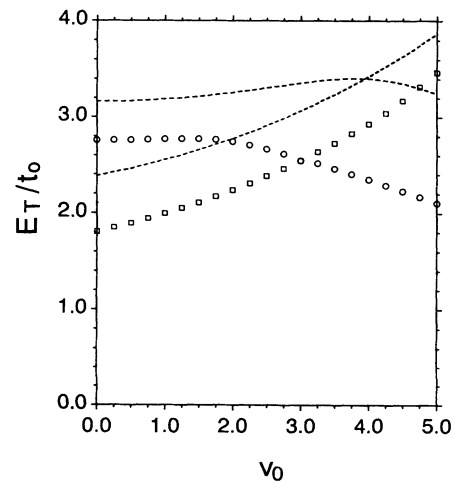

FIG. 2. Same as in Fig. 1 in a system where ground-state degeneracy is broken by a biased hopping term of the form (6), with (t_b/t_0)$=0.08$. Here $\gamma=0.9$, $v_1=0$, and $N=8$.

and 7 computations on larger systems as well as more realistic forms of the terms lifting ground-state degeneracy are needed. It should be stressed, in this regard, that the energies $E_{T,m}$ computed in this paper refer to the semiclassical minima relative to the optimized bond geometries for the mth many-electron level. Spectroscopic experiments, on the other hand, probe the various vibronic levels associated with this electronic state.

The results of Figs. 1 and 2 show that $1\,^1B_u-2\,^1A_g$ crossing occurs for sufficiently high values of v_0 even if the bond geometries are held to their ground-state configurations. However, failure to account for lattice relaxation for the electronic excited states[14,25] amounts to ignoring a physical ingredient which is essential in interpreting the available spectroscopic evidence.

In summary, numerical results from a full many-body description of conjugated chains which includes both e-l and e-e effects have been presented for chains with up to eight carbon sites. These systems are too small to allow reliable extrapolation to $N \to \infty$ of detailed numerical results such as those for the energy of the excited states (for given γ, v_0, and v_1) or for the strength of the e-e repulsion at which $1\,^1B_u-2\,^1A_g$ crossing occurs. However, in view of the results of Refs. 10 and 11, it is natural to expect that for long chains the nonlinear excitations predicted on the basis of the models of Refs. 2 and 3 will continue to correspond to the relaxed (minimum-energy) bond geometries of the excited states when realistic e-e interactions are turned on. Moreover, the effect of such interactions on the electronic excitation spectrum for long chains[12] will be qualitatively similar to that discussed here for smaller systems.

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[17]For a half-filled system with N sites the size P of the full basis for the $S=0$ subspace grows exponentially with N:

$$P = \frac{1}{N+1}\left[\begin{array}{c} N+1 \\ N/2 \end{array}\right]^2 .$$

As a result, in order to deal with N significantly larger than eight, one needs to resort to reduced basis sets (possibly similar to those of Refs. 14 and 15).

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[21]Each point in Fig. 1 involves a few hundred evaluations of the right-hand side of Eq. (5), i.e., diagonalizations of a $P \times P$ matrix with $P = 1764$. A few hours CPU time on a HP 9000/735 workstation are required.

[22]The choice $\gamma = 0.9$ has been used to show that minimum-energy calculations on the SSH Hamiltonian can reproduce within two percentage points *ab initio* results for the bond lengths of 22-carbon polyenes (Ref. 10). For long chains this value of γ yields the accepted kink size in *trans*-polyacetylene.

[23]Further level crossings between $1\,^1B_u$ and higher ^1A_g states occur within the range of v_0 shown in Figs. 1 and 2. The values of β_n which minimize $E_{T,m}$ change continuously with v_0 until a level crossing is reached; in the crossing region the bond geometries are exchanged.

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