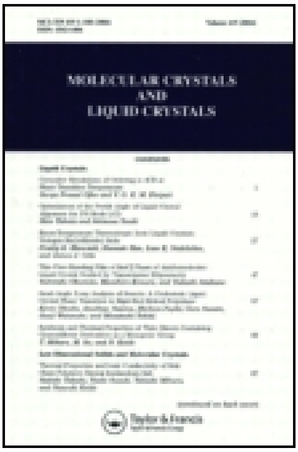

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Dimerization and Peierls Instability in Polyacetylene

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π-Electron excitations of conjugated polymers reflect both electron–phonon (e–p) and electron–electron (e–e) contributions. The Pariser–Parr–Pople (PPP) model with molecular e–p and e–e parameters is shown to give the polyacetylene (PA) dimerization, backbone vibrations, and optical gap. Both self-polarization and potential-energy contributions increase the effective e–p coupling in mean-field theory, while full inclusion of e–e correlations is important for low-lying electronic excitations. Correlation contributions to the Peierls instability are distinguished from changes in the dimerization amplitude. The demonstration of closely related microscopic parameters for conjugated molecules and polymers confirms chemical intuition and supports widespread transferability of model parameters among conjugated systems.

I. Microscopic Parameters for Conjugated Molecules and Polymers

Conjugated molecules hibit rich structural variety within the confines of essentially identical sp^2 centers. Their electronic structure has consequently been of central importance to theoretical chemistry.[1] Their longer cousins, conjugated polymers, achieve high conductivity on doping and have strong nonlinear susceptibilities.[2] These novel phenomena involve no bond angle or bond length changes with increasing size. Even the backbone vibrations and π-π* excitations of the polymers are consistent with the extrapolation to very long molecules.[3] General π-electron theories must clearly incorporate such systematics, which strongly suggest relations among microscopic parameters of conjugated molecules and polymers. Both electron–electron (e–e) and electron–phonon (e–p) interactions are important in finite polyenes.[4] The Pariser–Parr–Pople (PPP) model for interacting π-electrons provides a consistent, but approximate, molecular description.[3]

The Su-Schrieffer-Heeger (SSH)[5] model for polyacetylene (PA) retains e–p interactions for noninteracting π-electrons and focuses on ground and excited state geometries. However, negative spin densities imply e–e contributions, as do the different excitation energies for neutral and charged solitons.[2,3] Hubbard models generalize the SSH model to on-site interactions, while PPP models have a long-range potential $V(R)$. Only the PPP choice is viable for both polymers and molecules, although its application to PA has been difficult. We examine here the Peierls instability[6] and dimerization of PA using molecular PPP parameters, as an essential starting point for demonstrating that similar microscopic parameters apply to conjugated molecules and polymers.

The PA ground state energy per site $\epsilon_T(u)$ is sketched in Figure 1 for alternating bond-lengths $R_0 \pm u$, in the Born-Oppenheimer approximation. The uniform ($u = 0$) array is unstable, and dimerization to $\pm u_0 \sim 0.04$ Å is observed.[7] For trans PA, $\epsilon_T(u)$ is an even function by symmetry. In benzene, C_6H_6, the backbone is hexagonal, with $u = 0$ and $R_0 = 1.397$ Å. The ground state is nondegenerate even at $u = 0$ and leads to finite $\pi \rightarrow \pi^*$ excitation energies. But cyclobutadiene, C_4H_4, is rectangular[8] and has u_0 comparable to PA due to a Jahn-Teller distortion. The Peierls instability associated with the half-filled π-band in PA simply requires a negative curvature, or $\epsilon_T''(0) < 0$ in Figure 1. The PA dimerization $u_0 \sim 0.04$ Å, on the other hand, reflects σ-electron contributions also encountered in C_6H_6, C_4H_4, and many others conjugated molecules.

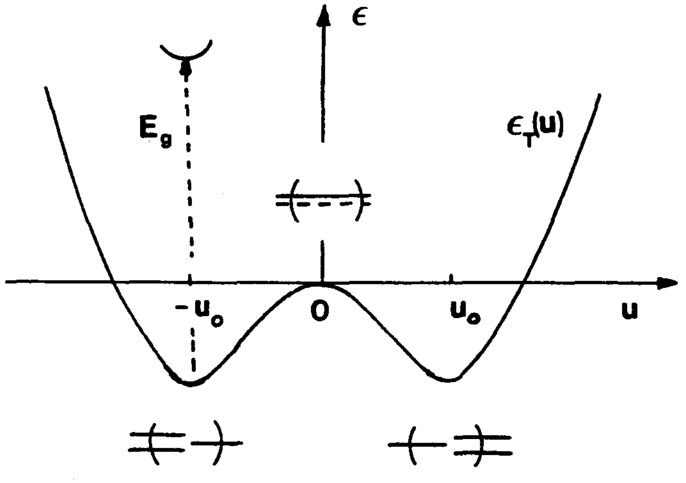

FIGURE 1 Schematic representation of the PA ground-state energy per site $\epsilon_T(u)$ for alternating bond lengths $R_0 \pm u$. The lowest dipole-allowed excitation defines the band gap E_g.

Although σ-π separability is certainly an approximation, it has implicitly been invoked for PA and $\epsilon_T(u)$ is written as

$$\epsilon_T(u) = \epsilon(u) + Ku^2/2 \tag{1}$$

Here $\epsilon(u)$ is the π-electron ground-state energy per site. At this stage, the exact π-electron Hamiltonian has yet to be specified, including the form of the e–e and e–p interactions. The σ-electron contribution is assumed to be harmonic in (1), with force constant K, although anharmonic corrections are important in polyenes.[4] And a single lattice degree of freedom, the dimerization amplitude u, is retained. More realistic analyses[9,10] retain additional in-plane degrees of freedom of $(CH)_x$. The alternation of transfer integrals $t(1 \pm \delta)$ is related to u via $\alpha u = t\delta$ for linear e–p coupling α. The simplifications in (1) focus attention on $\epsilon(u)$ and are characteristic of π-electron theories.

Direct observations on PA are restricted to the equilibrium geometry, since equal bond lengths have not been induced in neutral samples. In addition to $u_0 \sim 0.04$Å, resonance Raman spectra in the C–C stretching region reflect the curvature $\epsilon_T''(u_0)$, and optical spectra give the π-π^* excitation, $E_g \sim 1.8$ ev, and other low-lying states.[2,3] Such data may be obtained for other conjugated systems, quite independently of any ground-state degeneracy.

Theoretical models for $\epsilon_T(u)$ provide a connection between an instability at $u = 0$ and the equilibrium dimerization u_0 in systems with degenerate ground-states. Longuet-Higgins and Salem[11] showed that $\epsilon_0(\delta)$ goes as $\delta^2 \ln\delta$ for noninteracting electrons and alternating $t(1 \pm \delta)$. Hückel or SSH theory leads to a $\ln\delta$ divergence for $\epsilon_0''(\delta)$, which clearly gives $\epsilon_T''(0) < 0$ for finite K in (1).

Within a given theoretical model the minimum number of microscopic parameters is the σ-electron force constant K, the e–p coupling constant $\alpha = t\delta/u$, the transfer integral t at $u = 0$ which is usually taken as the C_6H_6 value, and a π-electron potential $V(R)$. The SSH parameters[5] in Table I were originally chosen to fit E_g and u_0 with essentially molecular values. Subsequent analysis of infrared data, or $\epsilon_T''(u_0)$, led to the Vanderbilt-Mele[12] choices in Table I, still for noninteracting π-electrons. Since the bandwidth of $4|t| \sim 10$ ev is generally accepted, α and K are adjustable and now deviate significantly from the molecular (PPP) choices in Table I. These rather old values are based[3,13] on small molecules and a long-range potential with $V(0) = U = 11.13$ ev obtained from gas-phase carbon data. The natural question, whether the PA data can be fit, is discussed in

TABLE I

Microscopic parameters for π-electron models: transfer integral t at $R = R_0$, linear e–p coupling constant α, harmonic σ-electron force constant K, and e–e potential $V(R)$ fixed at $U = V(0)$ in PPP models.

	$t(R_0)$, ev	α, ev/Å	K, ev/Å^2	U = V(0), ev
SSH	2.5	4.1	21.0	—
PPP/molecular	2.40	3.21	24.6	11.26
Vanderbilt-Mele	3.0	8.0	68.6	—

Section III by combining separate previous analyses of E_g and of u_0 and $\epsilon''_T(u_0)$.

Recent approaches[14–22] to e–e contributions in PA fix t, α and K while turning on some potential $V(R)$. The equilibrium dimerization u_0 from (1) is

$$K = -\frac{1}{u_0}\left[\frac{d\epsilon}{du}\right]_{u_0} \tag{2}$$

and is a functional of $V(R)$. For noninteracting electrons and $\alpha u = t\delta$ we have

$$\frac{t}{\alpha^2}K = -\frac{1}{\delta_0 t}\left[\frac{d\epsilon_0}{d\delta}\right]_{\delta_0} = \frac{4}{\pi q^2}[K(q) - E(q)] \tag{3}$$

with $q^2 = 1 - \delta_0^2$ and complete elliptic integrals K and E. In the usual application of (2) and (3), $d\epsilon_0/du$ changes as $V(R)$ is turned on and $u_0[V(R)]$ may be compared with u_0 for the same t, α, and K. Then correlations enhance or suppress dimerization for $u_0[V(R)]/u_0 > 1$ or < 1, respectively. Alternatively, (2) and (3) can be used to compare $K[V(R)]$ needed to match the value of u_0 for noninteracting electrons. If we plot tK/α^2, or equivalently $-\epsilon'(\delta_0)/\delta_0 t$, against δ_0 for various $V(R)$ we could compare either δ_0 at fixed K, or K at fixed δ_0, for the different $V(R)$. This is done in Figure 2 and discussed in Section III. Hubbard,[14–17] PPP,[20] and other choices[18–19] for $V(R)$ have been considered, with $\epsilon(u = \delta t/\alpha)$ approximated by various self-consistent field,[20] variational,[16,19] and perturbative schemes[18,21] or by exact,[14] Monte Carlo,[15] or renormalization group[17] results on finite systems. The resulting $u_0[V(R)]/u_0$ curves may suffice for equilibrium considerations, but, as shown in Section II, hardly help with $\epsilon''(\delta)$ near $\delta \rightarrow 0$ where (3) diverges.

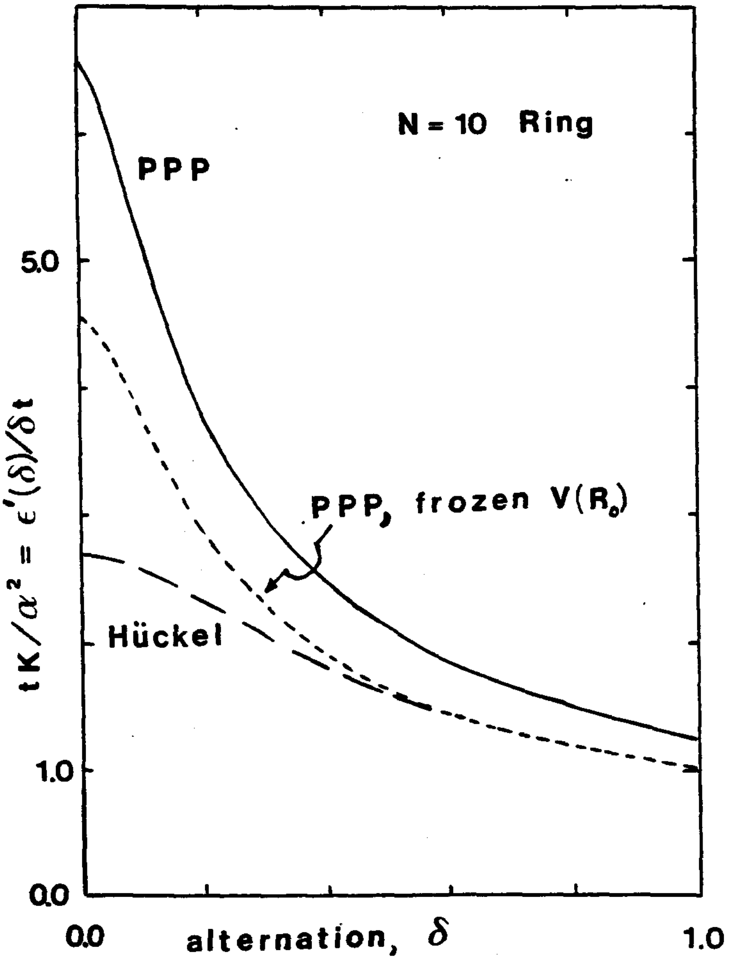

FIGURE 2 Lattice force constant Kt/α^2 in eq. (10) for equilibrium dimerization $\delta = \alpha u/t$ in an $N = 10$ Hückel ring, $N = 10$ PPP ring with frozen potential at $u = 0$, and $N = 10$ PPP ring with $V(R)$ from eq. (5) and Table I. The equilibrium restoring force for finite $4n + 2$ Hückel rings does not diverge as $\delta \to 0$.

$V(R)$ does not depend on u in either Hückel or Hubbard models. Then u_0 in (2) reflects kinetic-energy changes due to $t(1 \pm \delta)$. For more general $V(R)$, the Hellmann-Feynman theorem also gives a $\langle \partial V/\partial u \rangle$ term in (2). Such contributions are shown in Section III to be vital for reconciling the molecular α in Table I with the infrared data without resorting to the large Vanderbilt-Mele α.

II. DIMERIZATION VS. PEIERLS INSTABILITY IN HUBBARD MODELS

Mazumdar and Dixit,[14] Hirsch,[15] and Baeriswyl and Maki[16] take different approaches for finding $\epsilon(u)$ in half-filled Hubbard models. They all find on-site interactions $V(0) = U$ to enhance dimerization up to $U \sim 4|t|$. Dimerization is suppressed for $U > 4|t|$ and vanishes altogether as $U/|t| \rightarrow \infty$. Thus $u_0(U)/u_0$ has a maximum at $U \sim 4|t|$ and vanishes as $U \rightarrow \infty$. Similar results are expected in PPP models,[23] which also reduce to localized spins on increasing $V(0)$ and merely change the excitation energies of virtual ionic states.

What about e–e contributions to the Peierls instability? For large U and fixed $J = 2t^2/U$, the half-filled Hubbard model reduces to a linear spin-½ Heisenberg antiferromagnet. Linear e–p coupling $\alpha u = J\delta$ now produces a spin-Peierls instability.[24] Black and Emery[25] show $\epsilon(\delta)$ to go as $\delta^{4/3} \ln\delta$, a form consistent with finite-size extrapolations.[26] Bozonization[27] leads to $\delta^{4/3}$ behavior for the linearized problem. Either form is stronger than the $\epsilon_0(\delta) \sim \delta^2 \ln\delta$ behavior at $U = 0$ for free fermions. The Peierls instability for $U >> 4|t|$ is consequently stronger than at $U = 0$, even though the dimerization $u_0(U)$ for fixed t, α, and K is then infinitesimal.

The discrepancy has to do with a change in the electronic energy, from order t at $U = 0$ to t^2/U as $U \rightarrow \infty$. No such change occurs in the XXZ spin-½ chain,

$$H(\delta, \Delta) = \sum_n [1 - (-1)^n\delta](S_n^+ S_{n+1}^- + S_n^- S_{n+1}^+ + 2\Delta S_{nz} S_{n+1z}) \tag{4}$$

with $J = 1$. We have a half-filled band of noninteracting spinless fermions at $\Delta = 0$, with $\epsilon_0(\delta, 0) \sim \delta^2 \ln\delta$. The Heisenberg case corresponds to $\Delta = 1$. Direct analysis[28] of finite XXZ chains shows the dimerization amplitude to increase between $\Delta = 0$ and 1, to have a maximum around 1, and to decrease for $\Delta > 1$ when an Ising-like spin system and finite gap at $\delta = 0$ are found. In the $\Delta \rightarrow \infty$ limit of (4), $\epsilon(\delta)$ is readily seen to be independent of δ in the Neél ground state, $\cdots\alpha\beta\alpha\beta\cdots$, while $\epsilon(\delta, \Delta)$ goes[29] as $\delta^{4/3}$ without logarithmic corrections for $0.5 < \Delta < 0.09$. The maximum spin-Peierls distortion at $\Delta = 1$ nevertheless corresponds to the vanishing Peierls distortion at $U >> 4|t|$. Here the reduced energy scale with increasing U completely obscures the correlation contribution. A simple alternative, to use $\epsilon(0) - \epsilon(1)$ as the constant unit of energy, regains the qualitative features of (4). Now $u_0(U)$ increases[30] monotonically with U, has a point of inflection around $U \sim 4|t|$ in $(4n + 2)$-site rings, and becomes constant in the Heisenberg regime $U >> 4|t|$.

Correlation contributions to the Peierls instability are far more difficult to estimate than the dimerization amplitude. The Heisenberg results show the instability at $u = 0$ in Figure 1 to be stronger at $U >> 4|t|$ than at $U = 0$, and the behavior is probably monotonic. The dimerization amplitude is nevertheless far smaller in spin-Peierls than in Peierls systems with comparable α and K, and spin-Peierls systems are rare.[24] Quite aside from detecting infinitesimal dimerization, weak interchain interactions may become dominant as $T \rightarrow 0$ K. Such theoretical questions about Hubbard or PPP models with arbitrary parameters are quite different from those associated with the dimerized PA ground state.

III. PPP ANALYSIS OF PA

Correlations in finite polyenes rationalize the order of the two-photon 2^1A_g and dipole-allowed $1^1B_u(E_g)$ excitations.[3,4,23] Molecular PPP parameters from Table I lead to satisfactory agreement for both neutral and ionic species, as summarized in Table II. The same parameters account for the low-lying states of naphthalene,[31] including the fine-structure constants and spin densities in 1^3B_{2u}. Such approximate agreement has made PPP theory the accepted choice among π-electron models. However, all-electron calculations will undoubtedly prove to be superior as they become practical in larger systems.

Extrapolations of experimental E_g data for polyenes against N^{-1}, where $(N - 1)R_0$ is the conjugation length, suggests $E_g \sim 2$ ev for PA, in good agreement with the 1.8–2.0 ev maximum absorption in trans and cis PA, respectively. The PPP results from Table II extrapolate to $E_g \sim 2.8$ ev. The gas-phase value is red shifted by some ~0.5 ev in a polarizable medium, as shown explicitly for finite polyenes.[4,32] Some solid-state reduction of $V(R)$ is likely, although 10% changes in Table I hardly warrant complete reparametrization. The key to satisfactory E_g results in PPP theory is to include all correlations, or to solve the model exactly.

The results in Table II are based on the Ohno interpolation[33]

$$V(R) = U[1 + U^2R^2/e^4]^{-1/2} \tag{5}$$

between $V(0) = U = 11.13$ ev and e^2/R at large R. Takahashi and Paldus[10] use similar PPP parameters to study u_0 and $\epsilon''(u_0)$ via several

TABLE II

Optical gap E_g and two-photon excitation energy of gas phase polyenes with N carbons, N_e π-electrons, and alternation δ. The PPP results are for all-trans geometry and molecular parameters. (from ref. 23.)

N	N_e	δ	E_g (ev) PPP	E_g (ev) expt	2^1A_g (ev) PPP	2^1A_g (ev) expt
molecules[a]						
8	8	0.07	4.561	4.40	3.775	3.59
10	10	0.07	4.234	4.02	3.404	3.10
12	12	0.07	4.001	3.65		2.73
anions[b]						
5	6	0.0	3.456	3.42		
7	8	0.0	2.799	2.88		
cations[c]						
5	4	0.0	3.456	3.13		
7	6	0.0	2.789	2.64		
9	8	0.0	2.343	2.25		
11	10	0.0	2.009	1.98		

[a] expt.—Table 2, B. S. Hudson, B. E. Kohler, and K. Schulten, *Excited States*, **6**, 1 (1982) (ed. E. Lim, Academic, New York).

[b] expt.—A. H. Zimmerman, R. Gygax, and J. I. Brauman, *J. Amer. Chem. Soc.*, **100**, 5595 (1978).

[c] expt.—T. Sorenson, *J. Amer. Chem. Soc.*, **87**, 5075 (1965). $(CH_3)_2C(CH)_{N-2}C(CH_3)_2^+$ in concentrated H_2SO_4; slightly higher energies are reported for N = 7, 9, and 11 in heptafluorobutyric acid.

different self-consistent schemes. Instead of (4), they use the Mataga-Nishimoto interpolation[34]

$$V_1(R) = U[1 + RU/e^2]^{-1} \tag{6}$$

and adopt a slightly more complicated, anharmonic σ-potential in (1). As also found by Mele and Rice,[9] realistic modeling of PA vibrations requires a C—C—C bond angle and different single and double bonds, with fixed total length $r_1 + r_2 = 2R_0$. CH vibrations and nonplanar models are not considered. Takahashi and Paldus fix the σ-potential in (1) by forcing agreement with the a_{1g} and b_{2u} vibrations of benzene, C_6H_6, and consider higher $(CH)_{4n+2}$ rings. With increasing $n(\sim n = 10)$, u_0 saturates around 0.05 Å and the calculated ir frequencies agree with cis and trans PA data. A more realistic force field, slightly different potentials (5) or (6), and corrections to SCF must all be considered in further refinements.

The important point is that PPP analysis of PA accounts for E_g, u_0, and $\epsilon''(u_0)$ without significant changes of the microscopic parameters in Table I. In the SSH model, the gap is $4\alpha u$, whereas in the

PPP model a major portion of E_g is due to electron correlations. Correlations also enhance u_0. Smaller values of α and K are sufficient and reflect renormalization within single particle (SCF) descriptions. SCF suffices for the ground-state potential in Figure 1, but extensive configuration interaction is required for the π-π^* excitations.

PPP theory uses the zero-differential-overlap (ZDO) approximation to restrict $V(R)$ to two-center contributions.[1] The merits of ZDO for molecules or solids have been extensively discussed and physically motivated corrections[1,18,19] involving bond charges are conceptually important. Consistent inclusion of all corrections to ZDO is difficult, however, and additional effort may better be directed at relaxing the σ-π separability invoked in (1). Intersite contributions to $V(R)$ reduce in the ZDO approximation to

$$H_{rs} = V(R_{rs})z_r z_s \tag{7}$$

where $V(R)$ is given by (5) or (6) and $z_r = 1 - n_r$ is the charge operator for the rth carbon. We have $z_r = 1$ at C^+ sites missing a π-electron, $z = 0$ at $\dot{\mathrm{C}}$ sites with $n = 1$, and $z = 2$ at doubly-occupied C^- sites.

The intersite distance R_{rs} is independent of the dimerization u when r and s are separated by an even number of bonds. All $\langle \partial V/\partial u\rangle$ contributions to (2) then involve sites separated by an odd number of bonds, with R_{rs} increasing or decreasing by u. The largest $V'(R)$ contribution occurs at R_0. Moreover, ground-state charge correlations $\langle z_r z_s\rangle$ decay rapidly in neutral systems with electron-hole symmetry. We may safely restrict $\langle \partial V/\partial u\rangle$ contributions to $s = r \pm 1$ terms in (7). Linear e–p coupling $\alpha u = \delta t$ and cyclic boundry conditions then lead, in lowest order, to

$$\langle \partial V/\partial \delta\rangle = -\frac{|t|N}{2\alpha} V'(R_0)\,\langle z_2(z_1 - z_3)\rangle \tag{8}$$

for transfer integral $t(1 + \delta)$ between sites 1 and 2 and $t(1 - \delta)$ between 2 and 3. The next contribution, the $V''(R_0)\delta$ term, goes as $\langle z_2(z_1 + z_3)\rangle$ and is small.[30]

The mobile π-electron bond-order[35] p_{rs} is $(\partial\epsilon/\partial t_{rs})/2$. We define $p(\delta)$ with $\delta > 0$ for transfer integral $t(1 + \delta)$

$$p(\delta) = \langle \sum_{\sigma} (a_{1\sigma}^{+}a_{2\sigma} + a_{2\sigma}^{+}a_{1\sigma})\rangle/2 \tag{9}$$

The bond-order for sites 2 and 3 is $p(-\delta)$. It follows that $0 \leq p(\delta) \leq 1$ and that $p(-1) = 0$ for a chain of noninteracting dimers. The Hückel result (3) reduces to the bond-order change, $\Delta p_0(\delta) = p_0(\delta) - p_0(-\delta)$, and $\Delta p_0(\delta)/\delta$ diverges logarithmically as $\delta \to 0$.

For interacting π-electrons, we obtain[30] from (2) and (8)

$$\frac{t}{\alpha^2}K = -\frac{1}{\delta}\left[\frac{\partial \epsilon}{\partial \delta}\right] = \frac{\Delta p(\delta)}{\delta} + \frac{|t|}{2\alpha\delta} V'(R_0)\langle z_2(z_1 - z_3)\rangle \quad (10)$$

The $\Delta p(\delta)/\delta$ term describes bond-order, or kinetic energy, changes due to alternating transfer integrals. Correlations enter via the exact ground-state expectation values in (2) and (9). The second term in (10) describes potential-energy contributions arising from the distance dependence of $V(R)$. We have $V'(R) < 0$ and $\langle z_2(z_1 - z_3)\rangle < 0$, since $V(R)$ decreases with R and opposite charges are favored on adjacent sites.

For fixed t, α, and K, the dimerization amplitude for noninteracting electrons is $\Delta p_0(\delta)/\delta$ and is explicitly given in (3). The lowest curve in Figure 2 for 10-site rings is $-(d\epsilon/d\delta)/\delta t$ vs. δ for the noninteracting (Hückel) case. The intermediate curve in Figure 2 is associated with the PPP potential (5) frozen at $u = 0$, thereby excluding any $V'(R_0)$ contribution in (10). At fixed K the first two curves demonstrate enhanced bond-order alternation typical[14-17] of Hubbard models with $U < 4|t|$. The largest K, or greatest dimerization at fixed K, in Figure 2 occurs for the full PPP potential (5). As noted by Soos and Ramashesha,[23] $V(R)$ further enhances the dimerization. The Coulomb stabilization of adjacent electron hole pairs is slightly greater in alternating than in regular arrays and the effect is reinforced by the charge correlations in (10). The kinetic and potential contributions are comparable in Figure 2, and both are expected[30] to remain important as $N \to \infty$. Figure 2 explicitly illustrates how correlation and an R-dependent potential enhance dimerization, or the effective K, in the finite system.

The Hückel ground-state is essentially correct for weakly-interacting π-electrons. The charge correlations in (10) then reduce to Coulomb exchange contributions and may be written as

$$\langle z_2(z_1 - z_3)\rangle_0 = -\Delta p_0(\delta)[p_0(\delta) + p_0(-\delta)]/2 \quad (11)$$

The potential also goes as $\Delta p_0(\delta)/\delta$ and thus scales with the kinetic energy. Coulomb exchange contributions (11) remain important for interacting electrons, but additional spin flip contributions like $\langle a^{\dagger}_{1\alpha}a_{2\beta}\rangle$

also occur. The overall behavior of (10) no longer goes as $\Delta p(\delta)/\delta$. The $V''(R_0)$ contributions remain[30] finite as $\delta \rightarrow 0$ and are consequently negligible in discussing the Peierls instability.

Takahashi and Paldus[10] show that, within an SCF approximation to $\epsilon(\delta)$, the renormalization of t and $V'(R_0)$ are both important for fitting the PA vibrations with a molecular α. Our result (10) involves expectation values with respect to the exact ground-state and clearly distinguishes between bond-order (kinetic) and potential energy contributions to the dimerization. Correlation contributions to the Peierls instability await accurate solutions for $\delta \rightarrow 0$. Since both Hubbard and PPP models have electron-hole symmetry, which excludes charge-density waves, their Peierls instabilities are probably similar. The simplicity of the Hubbard model is then advantageous. As has long been known in molecules and has now been shown for PA, however, a longer-range $V(R)$ is needed for a consistent description of the dimerization, backbone vibrations, and electronic excitations. We particularly emphasize the transferability of molecular PPP parameters to conjugated polymers, at least before doping to high conductivity.

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