

Missing Bond-Charge Repulsion

Until recently the debate about the role of electron-electron interactions in conjugated polymers turned around the size of Hubbard's parameter U , the contribution of long-range Coulomb interactions [as in Pariser-Parr-Pople (PPP) parametrizations], and the relative size of U and the nearest-neighbor Coulomb term V . Models of this type have been successfully used for decades to describe organic molecules and polyenes. Therefore, the assertion of Kivelson, Su, Schrieffer, and Heeger (KSSH)¹ that important terms have been missed so far comes as a surprise.

We agree that there are, in principle, contributions like the nearest-neighbor exchange and the "hybrid integral,"² which correspond to W and X , respectively, in the notation of KSSH. We also agree that a finite W tends to reduce bond alternation. The real question is how large the different couplings are. KSSH use a very unrealistic δ -function potential in order to estimate these numbers and find $X > V = W$. On the other hand, for a Coulomb potential one expects V to be larger than W . Explicit calculations for benzene, using Slater orbitals for the π electrons, give $U = 16.93$ eV, $V = 9.027$ eV, $W = 0.923$ eV, and $X = 3.313$ eV.³ The nearest-neighbor exchange term W is an order of magnitude smaller than the nearest-neighbor Coulomb term V . Since it is hard to imagine that the relative size of these numbers should be very different for polyacetylene, the crucial assumption of KSSH that $V - 3W < 0$ cannot be sustained.

The expression of KSSH for the first-order contribution to the energy should be slightly modified. Expanding their Eq. (12) up to second order one finds

$$\Delta E(z) = (2/\pi^2)(3W - V)z^2 [\ln(4/z) - \frac{3}{2}]^2$$

which is about a factor of 2 smaller, for a typical value $z = 0.18$, than their Eq. (13). But the important point is that with "realistic" values for V and W this contribution is negative and favors bond alternation. Since it is now generally agreed that correlation effects, especially those originating from the large U term, further stabilize the dimerization,⁴ our conclusion is opposite to that of KSSH. We believe that old-fashioned models like PPP, Hubbard, or extended Hubbard keep making sense and provide useful parametrizations.

Recently several experiments have shown that conjugated polymers are not so dissimilar to finite polyenes where the importance of Coulomb correlations has been clearly demonstrated.⁵ Optical absorption involving neutral and charged solitons,⁶ a determination of the oscillator strength for π - π^* transitions in polyacetylene,⁷ and the observation of triplet excitons in polydiacetylene⁸ consistently indicate that the effective U comes close to

the π bandwidth. New electron-nuclear double-resonance experiments on oriented samples of polyacetylene⁹ give a ratio of negative and positive spin densities of 0.43, in striking agreement with theoretical predictions using standard PPP parameters.¹⁰ The large size of the Coulomb interaction (together with the small value of the electron-phonon coupling) puts the conjugated polymers into a regime where the bond alternation and the optical gap are mainly determined by correlation effects.¹¹

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