

Comment on "Electron Correlation and Bond Alternation in Polymers"

There has been considerable discussion (and even confusion) in the physics community about the effect of electron-electron (e - e) interactions and the effect of electron correlation (i.e., when going beyond the restricted Hartree-Fock limit) on the magnitude of bond alternation in polymers such as *trans*-polyacetylene.¹⁻³ For instance, the results of extended Hubbard calculations³ imply that weak e - e interactions enhance bond dimerization in contrast to results inferred from the addition of bond charge repulsion in the Hubbard model.¹ Recently, Wu, Sun, and Nasu⁴ have reported calculations combining the effects of both e - e interaction and electron correlation in *trans*-polyacetylene. Their results indicate that for short-range (screened) e - e repulsion, bond alternation actually decreases with increasing e - e interaction strength (even in the weak interaction limit). On the other hand, they find that bond alternation increases when long-range e - e repulsion is considered.

In this Comment, we distinguish the effects of e - e interaction and electron correlation and focus on the influence of the latter on bond alternation.

Paldus and co-workers⁵ have treated the case of large polyene rings (mimicking polyacetylene) using a Pariser-Parr-Pople (PPP) Hamiltonian with unscreened e - e repulsion and exchange. For values of the parameters suitable to polyacetylene, they obtain at the PPP-RHF level a bond alternation on the order of 0.10 Å.^{5(a)} From the Hamiltonian, it can be estimated that the contribution of the electron-lattice term to the bond alternation is much smaller, on the order of 0.01 Å. Therefore, the work of Paldus and Chin^{5(a)} demonstrates that long-range e - e interaction increases bond alternation, in agreement with the results of Wu *et al.*⁴ We note that the PPP bond alternation value is on the same order as that derived at the Hückel Su-Schrieffer-Heeger Hamiltonian level.⁶ This points to the fact that the physical origin of bond alternation is very different at the Hückel and PPP levels.

Using either delocalized Bloch functions^{5(b)-5(d)} or localized Wannier functions^{5(e),5(f)} Paldus and co-workers have then introduced electron correlation effects by following different approaches: (i) the unrestricted Hartree-Fock method;^{5(b)} (ii) the alternant molecular-orbital technique;^{5(c)} (iii) many-body perturbation theory up to fourth order;^{5(d),5(e)} and (iv) the coupled-cluster approach.^{5(f)} In all cases, they find that the effect of electron correlation is to depress bond dimerization; the stronger the e - e interaction (at the RHF level), the larger the reduction. For physical values of the parameters, the effect of electron correlation is to decrease the bond dimerization only slightly to 0.09 Å (down from the 0.10-Å RHF value). The reason is that for weak to intermediate e - e interaction strength, the correlation energy is calculated to be almost constant for bond dimerizations ranging between 0.00 and 0.15 Å.^{5(f)}

Brédas, Dory, and André⁷ have obtained similar results with the PPP Hamiltonian on long polyene chains. Inclusion of electron correlation via configuration interaction results in a slight lowering of bond alternation and, for fixed magnitude of dimerization, in a reduction of the single-particle gap. Suhai⁸ has performed *ab initio* quantum-chemical calculations with an extended basis set on an infinite chain of *trans*-polyacetylene. Geometry optimizations lead to a 0.103-Å bond dimerization at the *ab initio* RHF limit. Again, this value is lowered to 0.084 Å by electron correlation introduced via an approach estimated to recover at least 75% of the total correlation energy.

All these results indicate that *electron correlation always tends to depress bond dimerization*. For values of the parameters appropriate to polyacetylene, the effect of electron correlation is to reduce the absolute value of bond dimerization by an amount on the order of (10-20)% relative to the value obtained including all e - e interactions at the RHF level limit.

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J. L. Brédas^(a) and A. J. Heeger

Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, California 93106

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^(a)Permanent address: Service de Chimie des Matériaux Nouveaux, Université de Mons, B-7000 Mons, Belgium.

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