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Ground State of trans-Polyacetylene and the Peierls Mechanism - Ashkenazi et al. reply

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Ashkenazi *et al.* Reply: The Peierls energy [Eq. (1)] plotted in Fig. 1 of our recent Letter¹ was scaled incorrectly, as noted by Mintmire and White² (MW). A corrected Fig. 1 has been presented in an Erratum.³ This change, which does not affect our calculated energy differences, is relevant to our interpretation of the cancellation of the nonanalytic Peierls energy by a similar "strain" term, a result which followed from our demonstration on quite general grounds (using formal linear-response arguments) that a similar nonanalytic term occurs in it as well as the band-energy term.

The first point raised by MW concerns our fit¹

$$\delta E_{\text{tot}} = (W/2)[a_1 + a_2\Delta^2 + a_3\Delta^2 \ln\Delta + a_4\Delta^4 + a_5\Delta^6] \quad (1)$$

to the calculated energy change due to distortion (Δ is proportional to the gap). MW report two alternative representations (fits). The first, similar to several we have obtained and discarded, we would reject for at least three reasons: (i) the result contains large canceling terms which are larger than the variation of the large terms in the energy itself (such as the eigenvalue sum and the Coulomb energy) and much larger than the net change in energy, while the purpose of the parametrization is to characterize the small, net energy variation; (ii) their $\Delta^2 \ln\Delta$ coefficient has the Peierls sign but is an order of magnitude larger, suggesting the strain term itself would lead to a distortion, a highly questionable result; (iii) the Δ^6 term is unreasonably large, so it would dominate the behavior at distortions 2–4 times larger than the very small values we calculated. We have produced, and rejected, a variety of related (and unacceptable) fits, which come about (as suggested by MW) because of the similarity of the Δ^2 and $\Delta^2 \ln\Delta$ functions in this range if a simple least-squares fit is demanded.

Our published fit was obtained by beginning with small values of three of the terms (others zeroed), iterating with a nonlinear (Levenberg-Marquardt) method to a point where improvement was negligible in comparison to the uncertainty of the "data" points, and then adding another term and repeating. The Δ^6 term was only checked to ensure that it would not alter the fit obtained up to that point. The fit we reported indicated that the $\Delta^2 \ln\Delta$ and Δ^4 terms were individually small and comparable, and were the only important terms. [Since a rescaling of Δ , $\Delta^2 \ln\Delta \rightarrow (\Delta/\Delta_0)^2 (\ln\Delta - \ln\Delta_0)$, will change the coefficient of the Δ^2 term, the absence of this term in our fit has limited physical implication. Note that such a scaling does not affect the sign of the $\Delta^2 \ln\Delta$ term.]

In checking the points raised by MW, we have obtained another satisfactory fit (mathematically and physically) containing primarily Δ^2 and Δ^4 terms (both positive and of comparable size), which provides information on the uncertainty of the constants a_2 , a_3 , a_4 , and suggests that a_2 may not necessarily vanish. The second fit MW report, in which the coefficient of the nonanalytic term is fixed at the Peierls value (modulo a spin-

degeneracy factor), also confirms that reasonable fits may lead to differing values of a_2 , a_3 , and a_4 so we agree that definite conclusions about cancellations of analytic terms cannot be drawn.

MW further contend that their results,⁴ which via extrapolation to dense sampling of states led to a dimerization energy of 0.13 mRy = 20 K per CH unit and a magnitude of distortion that was one-third of the experimental value, is a verification of the Peierls mechanism within the local-density approximation (LDA). Although their calculations are consistent with ours, we contended, and remain convinced, that such a minimum is meaningless. Since $(\text{CH})_x$ remains dimerized well above room temperature, corresponding to several mRy, and the inferred distortion from a total-energy curve assuming static nuclei will be strongly decreased by fluctuations in quasi-one-dimensional systems, the true minimum from a total-energy calculation must be at least a factor of 20 deeper than that reported by MW.

To summarize our conclusions: (i) using formal methods we established that the strain energy in 1D systems contains a nonanalytic term identical in form to the nonanalytic Peierls term; (ii) the theoretical energy change due to dimerization in crystalline $(\text{CH})_x$ (on which the measurements are done) is indistinguishable from that in isolated linear chains, at least within LDA; (iii) no appreciable minimum due to dimerization (i.e., on the scale required to account for experimental data) exists in the energy curve within LDA. It will be necessary to go "beyond LDA" in some manner to learn the physics (mechanism) of the dimerization of $(\text{CH})_x$. Since LDA contains the ingredients of the Peierls mechanism, we conclude (quite independently of details of fitted parameters) that the conventional Peierls mechanism is not driving dimerization in $(\text{CH})_x$.

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³J. Ashkenazi *et al.*, Phys. Rev. Lett. **63**, 1539(E) (1989).

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