RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 8 15 MARCH 1987-I

Local-density-functional results for the dimerization of *trans*-polyacetylene: Relationship to the band-gap problem

J. W. Mintmire and C. T. White
Naval Research Laboratory, Washington, D.C. 20375-5000

(Received 12 November 1986)

We report the results of a computational study of the dimerization of the all-*trans*-polyacetylene chain within the local-density-functional formalism employing the Gáspár-Kohn-Sham exchange-correlation potential. Our calculated bond alternation at equilibrium is less than experimentally implied by roughly a factor of 3. Evidence is presented that suggests that this underestimation of dimerization is closely connected with the much discussed band-gap problem in local-density-functional theory.

Several conflicting local-density-functional studies of the total energy of the prototypical semiconducting polymer all-*trans*-polyacetylene as a function of geometry have recently appeared. We have reported calculations[1] for a periodic all-*trans*-polyacetylene chain using a linear-combination-of-atomic-orbitals local-density-functional (LCAO-LDF) approach that employs a Gáspár-Kohn-Sham potential.[2,3] Our calculated equilibrium geometry with alternating carbon-carbon bond lengths of 1.377 and 1.434 Å corresponds to somewhat less dimerization than the experimentally suggested[4,5] bond alternation of 1.36 and 1.45 Å. However, our calculated energy of stabilization (minimum energy for the dimerized conformation minus the minimum energy of the undimerized conformation) was close in magnitude to that expected from the Su-Schrieffer-Heeger (SSH)[6] model. More recent work by Springborg[7] using linearized muffin-tin orbital techniques yielded alternate bond lengths in agreement with experiment, but with an energy of stabilization roughly an order of magnitude greater than ours. On the other hand, very recent work using general potential linearized augmented-plane-wave (LAPW) techniques on crystalline polyacetylene systems[8] yields equilibrium dimerizations and stabilization energies much less in magnitude than our earlier reported results. The LAPW work also suggests that the total energies may be sensitive to the numerical treatment of the Brillouin zone (BZ).

These conflicting results together with improved experimental data have led us to examine in detail the dimerization process in all-*trans*-polyacetylene within the local-density-functional model. In this study we have improved significantly on the accuracy of our earlier work. Our new results show that accurate local-density-functional calculations predict rather less dimerization at equilibrium for single polyacetylene chains than experimentally implied, with a stabilization energy much less than that suggested by SSH.[6] As we shall see, the origin of this disagreement appears intimately associated with the well-known result that local-density-functional methods underestimate band gaps in insulators and semiconductors.[9]

The computational methods used here are described in Ref. 1. Two basis sets have been employed: a $7s3p/3s$ orbital basis set identical to that used in Ref. 1, and a $9s5p/4s1p$ basis set also chosen from van Duijneveldt[10] with a unit exponent p function added to the hydrogen basis set. The fitting basis sets differ from those of Ref. 1 by the addition of p-type fitting functions for both types of auxiliary basis sets. No major basis-set effects on either the calculated equilibrium position or the stabilization energy were found. Therefore, only the $9s5p/4s1p$ basis-set results are reported.

We used a discrete set of evenly spaced points in the one-dimensional Brillouin zone for calculating the band energies and one-electron wave functions. Total-energy calculations were carried out for ten pairs of alternating bond distances (i.e., ten independent conformations); all bond angles were fixed at 120° and the carbon-hydrogen bond distance was fixed at 1.08 Å. For each separate conformation, independent self-consistent calculations have been performed using 10, 20, and 40 points in the Brillouin zone. The alternate bond lengths obtained at equilibrium were 1.386 and 1.443 Å using 10 points, 1.394 and 1.435 Å using 20 points, and 1.399 and 1.430 Å using 40 points. The stabilization energies using 10, 20, and 40 points were, respectively, 0.0212, 0.0075, and 0.0030 eV per CH unit. For all treatments of the Brillouin zone with the $9s5p/4s1p$ basis set, the minimum-energy undimerized conformation occurred for equal bond lengths of 1.415 Å.

Results for the equilibrium conformations were obtained by fitting the total energies calculated at the ten independent conformations to a two-dimensional quadratic function and solving for the minimum fitted energy. Stabilization energies were calculated as the difference between the total energy estimated at the fitted minimum and the total energy estimated for the minimum energy undimerized conformation using a one-dimensional quadratic fit.

Figure 1 depicts the total-energy curves as a function of dimerization (maintaining an average bond length of 1.415 Å) for calculations using 10, 20, and 40 points in the Brillouin zone, as well as a total-energy curve extrapolated from our results to a continuum treatment of the Brillouin zone (i.e., an infinite number of points) using a scheme to be described below. We have found that the observed systematic error in total energy as a function of dimerization can be almost totally attributed to effects of the π band in this system. Also we have found that the behavior of the

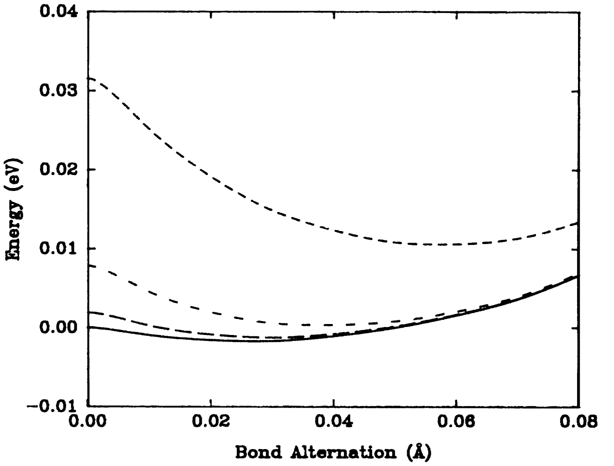

FIG. 1. Relative total energy per CH unit as a function of bond alternation for use of 10, 20, and 40 points in the Brillouin zone (dashed curves from top to bottom, respectively) and for continuum treatment of Brillouin zone (solid line). Bond alternation is defined as difference in lengths of alternate bonds.

error introduced by using a finite number of points N_{BZ} in the Brillouin zone can be adequately described—for purposes of extrapolation—using an algorithm based on a nearest-neighbor tight-binding model. For such a tight-binding π band with average hopping matrix element v_0 and dimerization coordinate Δ, such that alternate hopping matrix elements $v_1, v_2 \equiv v_0(1 \pm \Delta)$, we have shown[11] that the exact expression for the error per site $\delta(N_{BZ})$ caused by summing over N_{BZ} evenly spaced points (rather than integrating) can be approximated to low order as

$$\delta(N_{BZ}) \approx (-1)^{N_{BZ}} \frac{\pi v_0}{3N_{BZ}^2} \exp[-(2N_{BZ}-1)\Delta] \ , \quad (1)$$

for $\Delta \ll 1$ and $N_{BZ} \gg 1$.

Figure 2 depicts our calculated total energies as a function of N_{BZ}. The tight-binding error analysis accurately describes the behavior of the calculated energies in the undimerized conformation (i.e., $\Delta = 0$) for $v_0 = 3$ eV. This value of v_0 is in good agreement with experimentally based estimates of this parameter and will be assumed in the following discussion. The dimerization coordinate Δ can be defined relative to the band gap E_g such that $\Delta \equiv E_g/4v_0$ in the tight-binding model. The second curve in Fig. 2 depicts the π-band error for $\Delta = 0.022$, where we have used our calculated band gap of 0.26 eV in the above definition. We note that the tight-binding model also describes the error in our total energy for dimerized conformations reasonably well, although the dashed line in Fig. 2 suggests that the best value of Δ for Eq. (1) may be larger by roughly 50% than that estimated using $E_g/4v_0$. We have extrapolated our results to the limit of a continuum treatment of the Brillouin zone by adding a correction term based on the tight-binding π-band analysis to the total energy self-consistently calculated for $N_{BZ} = 40$. We estimate any remaining error caused by the approximate treatment of the Brillouin zone to be on the order of 0.0005 eV per CH unit.

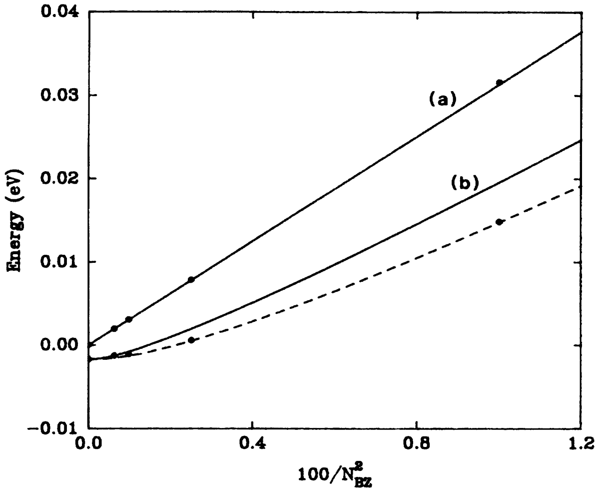

FIG. 2. Relative total energy per CH unit as a function of number of points employed in the Brillouin zone N_{BZ}. Dots represent calculated points for bond alternation of (a) all bond lengths equal to 1.415 Å, and (b) 1.40 and 1.43 Å. Lines represent π-band corrections (for even values of N_{BZ}) relative to extrapolated limits for (a) $\Delta = 0$ and (b) $\Delta = 0.022$ (solid line) and $\Delta = 0.037$ (dashed line).

These computational results indicate that although the LCAO-LDF model predicts that all-*trans*-polyacetylene will dimerize, the model severely underestimates both the equilibrium dimerization (compared to experimental results) and the stabilization energy (compared to that expected from the SSH model assuming experimentally derived parameters). We believe that this underestimation is a general property of local-density-functional methods and is intimately related to the well-known tendency of such models to underestimate band gaps in semiconductors and insulators.[9] To develop this point, consider a general physical model using the same basic assumptions as the SSH model. First, the total energy (E_{tot}) is partitioned into two terms: one term equal to the integrated total electronic energy of the occupied π band (E_π), and a remainder term (the "elastic energy," E_{el}) simulating all other effects in the system via a function quadratic in the dimerization coordinate. Second, the π band is described using a nearest-neighbor tight-binding model with the intersite matrix element equal to a constant plus a term linear in the change of dimerization coordinate. These assumptions imply that E_π and E_{el} have a maximum and minimum, respectively, at zero bond alternation; the equilibrium dimerization will occur where the derivatives of E_π and E_{el} with respect to dimerization coordinate cancel.

We have tested these assumptions with respect to our LCAO-LDF calculations. Figure 3 depicts the decomposition of our calculated total energy as a function of bond alternation into E_π and E_{el} terms. We have calculated the π-band energy by performing a set of self-consistent calculations using $N_{BZ} = 32$ at each conformation, and numerically integrating the π-band energy over the evenly spaced subsets of points containing 8, 16, and 32 total points. The previously described extrapolation scheme[11] was applied

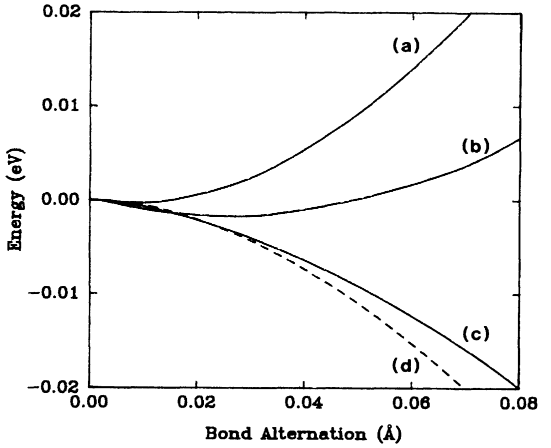

FIG. 3. Change as a function in bond alternation of (a) $E_{\rm el}$, (b) $E_{\rm tot}$, (c) E_π from calculated π bands, and (d) E_π from SSH model. All energies are per CH unit.

using these values to estimate the π-band energy in the continuum limit. We note that $E_{\rm el}$ satisfies to an excellent approximation a quadratic function with an effective bond-stretch spring constant K, using the notation of SSH,[6] of about 24 eV/Å^2. This predicted K is close to the experimentally based estimate of SSH. The dashed line in Fig. 3 depicts the SSH π-band energy in terms of $\Delta \equiv E_g^{\rm LD}/4v_0$. We note the good agreement of our calculated π-band energy with that calculated using the SSH formalism—an agreement consistent with our ability to estimate the total energies of our LCAO-LDF calculations. Thus our LCAO-LDF results, although consistent with the basic assumptions of the SSH model, predict a dimerization much smaller than the experimentally derived value.

The SSH model for the pristine dimerized chain can be expressed in terms of two dimensionless parameters:[12] Δ, a generalized dimerization coordinate, and κ, a stiffness parameter scaled in terms of the π-band parameters. Within the notation of Ref. 6 these parameters can be given as $\Delta = E_g/4v_0$ and $\kappa = Kv_0/\alpha^2$. The dimerization Δ_0 at equilibrium is then given by $\Delta_0 = 4\exp[-(4+\pi\kappa)/4]$.

Our results imply—within the context of the LCAO-LDF model and using the calculated band gap versus bond alternation to estimate the electron-phonon coupling constant α—an effective value of α of about 3.9 eV/Å. This value of α together with the above estimated value of K and our earlier estimated $v_0 = 3$ eV results in an effective value of $\kappa \approx 4.7$, compared to values computed from experimentally derived parameters of 3.255 (Ref. 12) and 3.123.[6] For this κ the SSH model predicts an estimated equilibrium dimerization coordinate of $\Delta_0 \approx 0.037$ corresponding to a band gap of $E_g \approx 0.4$ eV, in reasonable agreement with our calculated band gap at equilibrium of 0.3 eV. We note that the SSH model implies that an increase in the effective value of α of only 20% would result in an equilibrium band gap of 1.4 eV, close to experiment, and an increase in the amount of equilibrium bond alternation by a factor of 2.7. Such an increase in equilibrium dimerization would represent an increase of our calculated equilibrium bond length difference from 0.03 to 0.08 Å, also close to the experimental value.

The computational results indicate, therefore, that our calculated total energies and π-band electronic structure are—within our numerical accuracy—consistent with the SSH model, except that the effective electron-phonon coupling constant α is smaller than would be expected for parameters derived from experimentally determined values of the band gap and equilibrium dimerization. This diminished effective value of α suggests that the small predicted dimerization and gap are intimately related and probably share common roots with the well-known problem of local-density-functional methods of underestimating band gaps.[9] Such a relationship implies that a proper treatment of the dimerization process of all-*trans*-polyacetylene and distortions in other Peierls distorted systems within a local-density-functional model will have to await a satisfactory and fairly complete solution to the underestimation of band gaps within local-density-functional methods.[13]

Our conclusions are also consistent with Hartree-Fock[14] results for all-*trans*-polyacetylene, which overestimate the band gap and predict equilibrium dimerizations of the order of or larger than the experimentally suggested values. In addition, the work of Suhai[15] in incorporating Møller-Plesset perturbation theory corrections to Hartree-Fock treatments of all-*trans*-polyacetylene indicate that the equilibrium dimerization decreases as the band gap to dimerization ratio decreases.

We thank the Naval Research Laboratory Research Advisory Committee for a grant of computer time on the Naval Research Laboratory Cray-XMP which made this work possible. We also thank Warren Pickett for informing us of his results.

---

[1] J. W. Mintmire and C. T. White, Phys. Rev. Lett. **50**, 101 (1983); Phys. Rev. B **28**, 3283 (1983).

[2] R. Gáspár, Acta Acad. Sci. Hung. **3**, 263 (1954).

[3] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[4] H. Kahlert, O. Leitner, and G. Leising, Synth. Met. (to be published).

[5] C. R. Fincher, C. E. Chen, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. Lett. **48**, 100 (1982).

[6] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).

[7] M. Springborg, Phys. Rev. B **33**, 8475 (1986).

[8] J. Ashkenazi, W. E. Pickett, C. S. Wang, H. Krakauer, and B. M. Klein, Bull. Am. Phys. Soc. **31**, 330 (1986); W. E. Pickett (private communication).

[9] K. Hamrin, G. Johnansson, U. Gelius, C. Nordling, and K. Siegbahn, Phys. Scr. **1**, 277 (1970); S. B. Trickey and J. P. Worth, Int. J. Quantum Chem. **11**, 529 (1977); S. B. Trickey, A. K. Ray, and J. P. Worth, Phys. Status Solidi B **106**, 613

(1981); M. Boring, Int. J. Quantum Chem. **8**, 451 (1974); A. Zunger and A. J. Freeman, Phys. Rev. B **16**, 2901 (1977).

[10] F. B. van Duijneveldt, IBM Report No. RJ945, 1971 (unpublished).

[11] J. W. Mintmire and C. T. White (unpublished).

[12] D. Vanderbilt and E. J. Mele, Phys. Rev. B **22**, 3939 (1980).

[13] See, e.g., J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983); L. J. Sham and M. Schlüter, *ibid.* **51**, 1888 (1983); Phys. Rev. B **32**, 3883 (1985); W. E. Pickett and C. S. Wang, *ibid.* **30**, 4719 (1984); W. E. Pickett, Comments Solid State Phys. **2**, 57 (1986), and references therein.

[14] A. Karpfen and J. Petkov, Solid State Commun. **29**, 251 (1979); Theor. Chim. Acta **53**, 65 (1979).

[15] S. Suhai, Phys. Rev. B **27**, 3506 (1983); Chem. Phys. Lett. **96**, 619 (1983).