

Comments

Comments are short papers which criticize or correct papers of other authors previously published in the *Physical Review*. Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Comment on "Electronic properties of polymeric silicon hydrides"

Hiroyuki Teramae

NTT Basic Research Laboratories, Musashino, Tokyo 180, Japan

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The electronic structure of the polysilene chain is studied by means of the *ab initio* crystal orbital calculations. The electronic structure of polysilene is not metallic at the Hartree-Fock level and the effect of the inclusion of the *d* orbitals on silicon is small. These conclusions are completely different from the recent work of Springborg.

In a recent article, Springborg predicted that polysilene the silicon analog of polyacetylene is metallic.^{1,2} Springborg, using the linear-muffin-tin-orbital method, concluded that the polysilene chain has a one-dimensional overlapping band at the Fermi level, arising from the considerable lowering of the antibonding σ^* to a point below the π^* and the π -like valence band, even in the dimerized geometrical structure (bond alternating form). Because extensive studies of the parent disilene and polysilene oligomers have shown that the orbital ordering is always highest occupied molecular orbital π and lowest unoccupied molecular orbital π^* , we think it is unlikely that the polysilene system would differ so greatly.

Our recent *ab initio* Hartree-Fock crystal orbital calculations are in complete disagreement with Springborg's work. The geometry is optimized at the double-zeta (DZ) basis-set level³ using the energy gradient method.⁴ The final electronic structure is further refined by adding a set of polarization functions on each atom (DZP basis set): *p*-type orbitals on hydrogen and *d*-type orbitals on silicon.³ The lattice summation is taken up to the nearest tenth neighbors with the cellwise cutoff scheme.⁵ 41 *k* points or half the Brillouin zone are taken for the numerical integration of the density-matrix elements.

The optimized geometrical structure obtained here is the dimerized form and the geometrical parameters are $R_{\text{Si-Si}}=4.091$ a.u., $R_{\text{Si-Si}}=4.343$ a.u., $R_{\text{Si-H}}=2.790$ a.u., $\angle\text{SiSiSi}=123.5^\circ$, and $\angle\text{HSiSi}=117.7^\circ$.⁶

Figure 1 shows the electronic band structure of polysilene with DZ and DZP basis sets by the Hartree-Fock method. Although the Hartree-Fock method is not a suitable quantitative method for determining the exact energy levels of the bands of polysilene, the band ordering is reliable. At issue here is whether the σ^* band is the conduction-band bottom or not. The Hartree-Fock method shows that the orbital order for the valence-band

top and conduction-band bottom is π and π^* , respectively. Since the π^* band will always be higher than the π band and the σ^* band remains above π^* , we can conclude, by avoiding any comparison of the energy levels of the bands, that the σ^* band cannot cross the π band. In

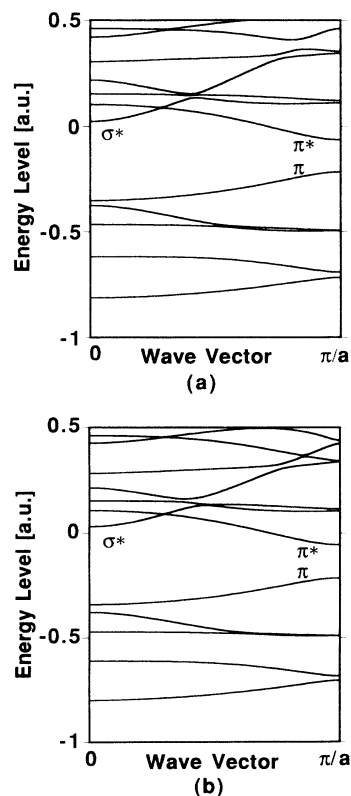


FIG. 1. The energy band structures of the polysilene chain. (a) DZ basis set, (b) DZP basis set.

addition, support for the Hartree-Fock method provided by a first-principles pseudopotential local-density functional (LDF) calculation on bond alternating polysilene by Takeda also shows that the σ^* and π bands do not overlap.⁷ Polysilene should not be metallic.

The Hartree-Fock results also disagree with Springborg's claim of the importance of d -type orbitals for the correct description of polysilene. The contribution of d -type orbitals to the σ^* band is only 1%, and does not effect the band structure as seen in Fig. 1(b).

In conclusion, the electronic structure of polysilene in its dimerized form is not metallic at the *ab initio* Hartree-Fock level. The effect of the inclusion of d orbitals on the silicon is small.

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²K. Takeda and S. Kagoshima, Phys. Rev. B **37**, 6404 (1988).

³T. H. Dunning and P. J. Hay, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer (Plenum, New York, 1977), Vol. 3, p. 1.

⁴H. Teramae, T. Yamabe, and A. Imamura, J. Chem. Phys. **81**, 3654 (1984).

⁵A. Karpfen, Int. J. Quantum Chem. **19**, 1207 (1981).

⁶This is a H-Si=Si angle.

⁷K. Takeda (unpublished).