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Reply to "Comment on 'Electronic properties of polymeric silicon hydrides'"

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The question raised by Teramae is related to that of the capability of Hartree-Fock or local-density calculations in describing the orbitals around the Fermi level correctly. Both types of calculations suffer from severe problems in this context. For polysilene, however, it is here argued that an adequate modification of the local-density bands will not change the ordering of the conduction bands. This indicates that polysilene is metallic. Furthermore, a number of other studies on Si-containing materials have demonstrated Si *d* functions to be important for orbitals just above the Fermi level in contradiction with the results of Teramae.

The main disagreement between my results[1] and those of Teramae[2] concerns the relative positions of the bands around the Fermi level and whether polysilene $(SiH)_x$ is metallic. A part of the former question is related to that of the importance of Si *d* functions in describing the bands around the Fermi level, whereas the last question is of ultimate importance for a number of properties of the material, including transport and optical properties. Despite the differences it is pleasing to observe fair agreement between structural parameters as obtained with the two different parameter-free methods. Thus, I found Si—H bond lengths of 2.89 a.u. and Si—Si—Si bond angles of 119°, whereas Teramae found 2.79 a.u. and 124°, respectively. Teramae allowed the Si—Si bond lengths to alternate, whereas I focused mainly on structures with constant lengths and only considered alternating bond lengths peripherally. However, his bond lengths (4.09 and 4.34 a.u., giving an average of 4.22 a.u.) agree well with mine (4.15 a.u.).

Returning to the main difference between our results, one should be aware of the fact that neither local-density nor Hartree-Fock calculations are the best starting point for exploring the size (and existence) of the gap between occupied and unoccupied orbitals. The former underestimate the gap and may even predict systems to be metallic that should not be (see, e.g., Ref. 3), whereas the latter overestimate the gap and are in principle not able to describe metallic systems (see, e.g., Ref. 4).

In order to improve the agreement between the single-particle eigenvalues as calculated with density-functional methods and electronic excitation energies one may calculate the so-called quasiparticle energies as, e.g., done by Hybertsen and Louie[5] for crystalline Si. Their results indicated a close connection between the quasiparticle energies and the eigenvalues to the Kohn-Sham equations with a local approximation, such that the latter were to be modified by one additive constant for the valence bands and another additive constant for the conduction bands in order to arrive at the former. Assuming the same to hold for polysilene, this indicates that both bands that I find to cross the Fermi level will experience the same modifications. Thereby, the relative ordering of the orbitals around the Fermi level will not be altered, and polysilene will remain metallic with two bands crossing the Fermi level.

Instead of holding the underlying methods responsible for the disagreement, Teramae concludes that my suggestion of the importance of Si *d* functions is not correct. One reason for Teramae's result might be that since he studies a single, isolated chain and since he finds the unoccupied σ bands to have positive energies, these orbitals might be close to being free-electron-like and thus be described better by more delocalized *s* and *p* functions than by localized *d* functions.

His result is at variance with those of other theoretical studies on Si-based systems. Bose, Winer, and Andersen[6] found in their density-functional studies on crystalline Si that Si *d* functions contribute with about 50% of the total density of states for the lowest conduction orbitals. Furthermore, according to the semiempirical calculations of Takeda, Matsumoto, and Fukuchi,[7] the band gap of polysilane $(SiH_2)_x$ is reduced by more than 2 eV upon inclusion of *d* functions.

The Si—Si bond in Si_2H_4 should resemble that in polysilene. For this molecule Davis Curtis[8] argued that *d* functions are not important for the ground state but that they increase the bonding capabilities in the excited states significantly. Passing to the polysilene polymer one may accordingly suggest these *d* functions to become partially occupied in order to strengthen the chemical bonds between the Si_2H_2 units—in agreement with my results. Furthermore, Jones[9] has shown that Si *d* functions are required in order to explain the structure of the Si_3 molecule.

Finally, one may solve the Kohn-Sham equations numerically for one isolated atom. Doing so for an isolated Si atom it turned out that the atom with one 3*s* electron excited to a 3*p* orbital and that with one 3*p* electron excited to a 3*d* orbital had comparable total energies and that the excitation energies were similar to those required for exciting one 2*s* electron to a 2*p* orbital for an isolated C atom. This may be considered a further indication of the importance of virtual Si *d* functions for Si-containing systems.

In conclusion I have attempted to present arguments in favor of my results. But, one should be aware of the problems related to studying the band gap with density-functional or Hartree-Fock methods. I am not convinced that the question of the existence and/or size of a gap in polysilene can be solved by further theoretical studies of those kinds, but believe we should await the (hopefully) successful synthesis of this material.

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