Local-density-pseudofunction theory of bulk Si

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The pseudofunction implementation of local-density theory for Si is shown to produce the accepted results: a bond length of 2.34 Å, a bulk modulus of $B_0 = 1.03$ Mbar, a pressure derivative of the bulk modulus of $dB_0/dp = 3.44$, and a band structure in agreement with previous calculations and many data.

I. INTRODUCTION

Calculations of electronic structure based on the local-density approximation[1] are known to produce reliable changes in ground-state properties of solids, and are noted for determining equilibrium lattice constants. Local-density calculations for Si, in particular, have been extensive, and therefore a standard has arisen for any new implementation of local-density theory, namely its ability to predict the equilibrium lattice constant of bulk Si.

Kasowski *et al.*[2] have recently proposed the pseudofunction method, which is a version of local-density theory based on a combined localized and extended basis set, and has the merit that it solves the local-density equations for a realistic potential in the bond-charge region, while preserving the advantages for intuitive physical visualization of a real-space representation.

The pseudofunction method is, in principle, numerically superior to other implementations of local-density theory in the following senses: It is computationally faster than the correspondingly rigorous k-space methods, namely the norm-conserving pseudopotential scheme[3] and the linearized augmented-plane-wave (LAPW) method.[4] While of comparable speed with the real-space augmented-spherical-wave[5] (ASW) and linear combina-

tion of muffin-tin orbitals[6] (LMTO) methods, the pseudofunction scheme is more rigorous: It does not approximate the potential in the interstitial regions of the crystal and, in fact, determines both the correct solution of the local-density equations and a realistic potential. Nevertheless, the novelty of the pseudofunction method has caused its predictions to be called into question when they have disagreed with the predictions of more established methods, most notably for a K monolayer on the Si(001)2×1 surface.[7] In this case, the pseudofunction method predicts that the adsorbed K is metallic, with a K—Si bond length of 3.3 Å, in apparent agreement with subsequent data featuring a bond length of 3.14 ± 0.1 Å.[8]

FIG. 2. Computed band structure (in eV) of bulk Si. Solid line, pseudofunction method; dashed line, norm-conserving pseudopotential method (Ref. 10). The symmetry points are $\Gamma = (0,0,0)$, $X = (2\pi/a_L)(1,0,0)$, $U = (2\pi/a_L)(\frac{1}{4},\frac{1}{4},1)$, $K = (2\pi/a_L)(0,\frac{3}{4},\frac{3}{4})$, and $L = (2\pi/a_L)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, where a_L is the lattice constant.
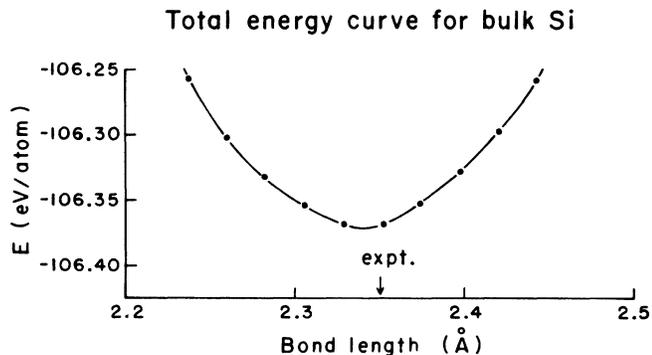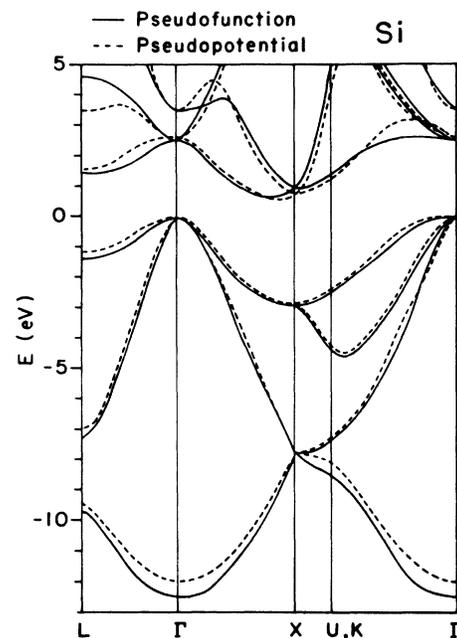

FIG. 1. Computed total energy of bulk Si (in eV per atom) vs Si—Si bond length (in Å). The solid circles are the points computed. The experimental bond length is indicated by the arrow labeled "expt."

BRIEF REPORTS

TABLE I. Energies (in eV) of symmetry points in the Si band structure.

Level	LAPW (Ref. 4)	EMTO (Ref. 15)	Pseudopotential (Ref. 6)	Present	Expt.
Γ_1	−12.02	−11.87	−11.93	−12.52	−12.5±0.6
$\Gamma_{25'}$	0	0	0	0	0
$\Gamma_{15,c}$	2.49	2.44	2.57	2.46	3.4
$\Gamma_{2',c}$	3.18	3.38		3.55	4.2
X_1	−7.84	−7.88		−7.86	
X_4	−2.82	−2.92		−2.98	−2.9, −3.3±0.2
$X_{1,c}$	0.55	0.57		0.90	1.3
$X_{4,c}$	10.32	10.18		9.99	
$L_{2'}$	−9.64	−9.69		−9.77	−9.3±0.4
L_1	−7.06	−6.98		−7.23	−6.7±0.2
$L_{3,c'}$	−1.16	−1.27	−1.21	−1.38	−1.2±0.2, −1.5
$L_{1,c}$	1.40	1.47	1.51	1.42	2.1, 2.4±0.15
$L_{3,c}$	3.37	3.25	3.07	4.61	4.15±0.1

However, the more established version of local-density theory, based on the norm-conserving pseudopotential approach,[9] finds a significantly different bond length of 2.59 Å. This raises the question of whether agreement between the pseudofunction theory and experiment is fortuitously good (in which case the pseudofunction method must be judged as unable to predict bond lengths reliably) or whether the method is indeed as good as other commonly employed implementations of local-density theory.

II. CALCULATIONS AND RESULTS

In order to address this question, we have computed the equilibrium bond length, bulk modulus, pressure derivative of the bulk modulus, and electronic structure of bulk Si using the pseudofunction method. The computed total ground-state energy, as a function of Si—Si bond length, is displayed in Fig. 1, and predicts an equilibrium bond length (at zero temperature) of 2.34 Å. The observed bond length is 2.3508 Å,[10,11] which is virtually the same as both the bond length we find theoretically, and the value of 2.36 Å found by Yin and Cohen using the norm-conserving pseudopotential method.[10] Clearly the pseudofunction method does a rather good job of predicting the bulk Si bond length.

The bulk modulus $B_0 = -dp/(dV/V_0)$ and its derivative with respect to pressure, dB_0/dp, are 0.99 Mbar (Refs. 10 and 12) and 4.2 (Refs. 10 and 12) experimentally. B_0 and dB_0/dp can be determined from our calculated total energy by least-squares fitting the volume dependence of the total energy to Murnaghan's equation of state,[10,13,14] which (to within an arbitrary additive constant) is

$$E = \{B_0/[(dB_0/dp)(dB_0/dp - 1)]\}$$

$$\times [V(V_0/V)^{dB_0/dp} + V(dB_0/dp - 1)] .$$

The resulting least-squares-fitting parameters are B_0 = 1.03 Mbar and dB_0/dp=3.44, in general agreement

with both the data and Yin and Cohen's results obtained using the norm-conserving pseudopotential method: a bulk modulus of 0.98 Mbar and dB_0/dp=3.2.[10]

A by-product of our total-energy calculations is the band structure of Si (Fig. 2) which is in quite good agreement both with that predicted by other total-energy calculations[4,15,16] and with data.[16−19] (See Table I.) Of course, we find a fundamental band gap of 0.62 eV, similar to the fundamental gaps of other local-density theories, about half the experimental value. This is a well-known shortcoming of local-density theory, which can be corrected[16]—but not easily.

There should be and are slight differences among the predictions of the various local-density schemes even when executed to perfect convergence, because of the different exchange-correlation potentials used. We employed the parametrization of Hedin and Lundquist,[20] following the extended muffin-tin orbital (EMTO) work of Kasowski.[15] Hybertsen and Louie[16] take the Ceperly-Alder exchange potential,[21] while Hamann's LAPW calculations were based on Wigner's interpolation formula.[22] Thus, to within the limits imposed by the different basis sets and treatments of exchange-correlation, all of the local-density methods, including the pseudofunction scheme, give essentially the same predictions for Si.

III. SUMMARY

In summary, the pseudofunction method produces a good bond length, an accurate bulk modulus, a pressure derivative of the bulk modulus in agreement with the data, and a reliable band structure for Si—and hence should be viewed as an established implementation of local-density theory for covalent semiconductors.

ACKNOWLEDGMENT

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