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Ground-state properties of crysta11ine silicon in a density-
functional pseudopotential approach

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A first-principles nonlocal pseudopotential approach is shown for the first time to predict accu-
rately the ground-state bulk properties of a semiconductor. The calculated equilibrium lattice
constant, total valence energy, and bulk modulus of Si are within 0.2%, 0.5%, and 5%, respec-tively, of the observed values.

I. INTRODUCTION

While many of the ground-state electronic proper-ties of simple and transition-metal elemental solids
are quantitatively well understood within the local-
density formalism (DF), both in its all-electron (AE)' and valence-only'3 (pseudopotential) versions, similar nonempirical studies of the opened structure,
covalently bonded solids are scarce. '

For semicon-

ductors in particular, no self-consistent nonempirical calculation of the ground-state properties exists. For Si, empirical (local) pseudopotentials fitted to the spectra of either solids6~' or bare ions6~b~ and used successfully to predict the one-electron band struc-
ture of semiconductor surfaces, '

chemisorption, and
defects8 have so far yielded small equilbrium bond lengths for the bulk solid

'

and for the Si2

molecule. " Furthermore, these pseudopotentials
have produced systematic errors in the topology of
the ground-state charge density" (i.e.,

the elipsoidal
density contours in the bulk solid are perpendicular, rather then parallel to the bond axis) as well as signi-
ficant deviations (70%) between the calculated' and
measured bulk modulus. Empirical tight-binding methods can be parametrized to successfully predict geometries at semiconductor surfaces' but fail in predicting structural information even for the sim-plest bulk solids. In this paper I show for the first time that a self-consistent approach using a first-principles density-functional (nonlocal) pseudopoten-tial' predicts remarkably well the equilibrium lattice
constant a„, total valence energy E„„bulk modulus
B, and the ground-state charge density of bulk Si (i.e., with errors of 0.2%, 0.5%, and 5% for a,~, E„„ and 8, respectively). The origin of the discrepancies previously obtained with the empirical pseudopoten-tials hence does not lie in the pseudopotential formal-ism" or in the local-density formalism (used to screen these potentials), but rather in the approach adopted to construct the pseudopotentials.
In contrast with previous model pseudopotentials,
the present pseudopotential is derived from a well-defined electronic-interaction model (the density-

functional formalism) rather then from an empirical
adjustment. The implications of this are: (i) one can
clearly assess the effects of a chosen representation of exchange and correlation screening potential on the
ground-state properties and (ii) a contact is made
with the all-electron (i.e., treating core plus valence
wave functions on the same footing) theories which
are based on the same electronic interaction model: at the limit where the underlying pseudopotential frozen-core approximation is exact, the pseudopoten-
tial results should become identical with the AE

results. In contrast with the AE approach however, the present method has the advantage of projecting out from the total energy the large (98%) and struc-turally insensitive part associated with the nearly inert
core electrons. Hence, while the cohesive energy of
crystalline Si, Ge, and Sn as a fraction of the total AF.' energy per atom is as small as 5.5 &10~, 6.2 x10 ', and 1.7 x 10 ', respectively, the same cohesive ener-gy expressed as a fraction of the total pseudopotential
energy per atom is 4 x10, 3.4 &10 ', and 3.2 x10 ',
respectively. This increase by two to three orders of
magnitudes in the relative energies, coupled with the high precision demonstrated here in calculating the
pseudopotential total energy makes it hopeful that
the present approach may come close to predicting
quantitatively structural energies of complex systems
as well as revealing systematic trends in physical and chemical ground-state properties of classes of solids.

II. METHODOLOGY AND RESULTS

The first-principles pseudopotentials are derived from a density-functional (DF) formulation of a pseudoatom interacting with an external potential Vt(r).

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A variational procedure which includes a
number of Lagrange-multiplier constraints designed
to produce a relation between the spectral properties
and charge density of the pseudoatom and the real
atom is used to solve for the nonlocal pseudopoten-

tial VI(r) "This potential.differs from the empirical potentials V, p(r) used extensively in the literature

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(e.g., Ref. 7 and references therein) in that (cf. Fig.
1) VI(r)

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have a charge accumulation function
R

Q "(/I) -J) lx„&l'dr,
which equals the

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underlying density-functional pseudopotential ap-
proach, the only approximation made in our present
method is the truncation of basis sets and reciprocal
vectors sums to finite values. This, in turn, is a con-
trolled approximation.
The components of the self-consistent potential
[Eq. (2)1 in Si at the equilibrium lattice constant are depicted in Fig. 2. The exchange potential is seen to effectively screen the Coulomb repulsion whereas the
correlation potential is almost an order of magnitude
weaker. The Coulomb and exchange screening are strongly structured and nonuniform, while the corre-lation screening is nearly uniform. We find that the characteristic bond-elongated form of the screening is lost when the high-momentum components of the pseudopotential are ignored [viz. in using V,,(r) l.
Instead, one obtains an ellipsoidal screening which has its long axis perpendicular to the Si—Si bond. This leads to forces that tend to push the atoms too close together.
The self-consistent pseudocharge density p(r) is compared with the experimentally synthesized valence density in Fig. 3. The details as well as the
magnitude of the charge are well reproduced. Table
II shows the experimental x-ray structure factors of Si (corrected for the Debye-Wailer factor and
anomalous dispersion ') and the results calculated by
numerically Fourier transforming the density ob-

FIG. 2. Components of

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TABLE II ~ Experimental (Ref. 21) and calculated x-ray structure factors for Si in units of electrons

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core pseudopotential with

a "degree of softness"
which will shift just enough charge

0 into the core
region to produce

a desired balance between the op-
posing contributions to the total energy, at the ob-served lattice parameter. This could conceivably be achieved through the device of controlling the core orbital overmixture in the formulation of Eq. (1) (i.e.

~ adjusting Ct„C2„C2~), or in other pro-cedure' by