PHYSICAL REVIEW B VOLUME 25, NUMBER 2 15 JANUARY 1982

Total-energy calculations for Si with a first-principles linear-combination-of-atomic-orbitals method

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(Received 8 July 1981; revised manuscript received 24 September 1981)

The total energy for Si with various lattice distortions has been calculated using a first-principles linear-combination-of-atomic-orbitals method. The physical properties derived from these calculations include not only the equilibrium lattice constant, cohesive energy, and bulk modulus, but also the internal strain parameter and several phonon frequencies including anharmonic terms. For all these properties there is good agreement with experiment. The frozen-core approximation was tested and found to be valid for Si in a large region about the equilibrium lattice position.

I. INTRODUCTION

Many calculations of the ground-state electronic properties of solids have firmly established the utility of modern band-structure methods when combined with the local density approximation for exchange and correlation. Indeed, with little more input than the atomic numbers of the constituent atoms, theory based on calculation of the total energy is coming within reach of determining the structural and vibrational properties of solids. Among the various schemes used for such calculations the linear-combination-of-atomic-orbitals (LCAO) method — offering a physically intuitive local basis — is enjoying a revival as a first-principles technique,[1] and in this paper we investigate the suitability of a particular LCAO approach for the evaluation of total energies in solids. Applying the method to Si we find very good agreement with experiment, not only for structural properties, but also for the internal strain parameter as well as for phonon frequencies including anharmonic terms. These latter properties involve calculations for a distorted lattice and represent one of the more challenging applications of band theory. In the course of these calculations we tested the frozen-core approximation for Si and find it valid within a considerable region around the equilibrium lattice constant. This approximation has been assumed for a similar, very successful investigation of Si,[2] using norm-conserving pseudopotentials extracted from *ab initio* atomic calculations.[3]

II. METHOD

The specific LCAO method used here has been described elsewhere,[4] and therefore we limit our discussion to aspects pertinent to total-energy calculations. The Bloch wave functions of Si are expanded in a basis set of 18 localized orbitals (1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, 4*s*, and 4*p*) centered at the atom sites. The radial parts of these orbitals are linear combinations of 18 Gaussian functions, whose exponential coefficients are distributed following a geometrical series. The orbitals have been obtained from a converged self-consistent atomic calculation, where the longest-range Gaussians were dropped in a special run to avoid overcompleteness problems in the solid. The crystal charge density and potential are also expanded in a Gaussian basis to avoid the problem of evaluating and storing four-center integrals. For Si, this basis set consisted of 18 individual Gaussians located at each atomic site, as well as some additional Gaussians centered at auxiliary sites. Without the latter, the charge density and potential would be restricted to being a sum of spherically symmetric functions centered on atomic sites — a description well suited for close packed materials but less adequate for the open diamond structure, although still an improvement over the muffin-tin approximation. The coefficients for the charge-density expansion are determined by a least-squares fit to the exact charge density obtained from the occupied wave functions. All the integrals in the fit are evaluated analytically.

The electrostatic potential and energy are evaluated using a combination of real-space and Fourier-series computations. The total charge, consisting of the valence charge plus the (fixed) core charge, fitted as described above, is partitioned into two terms. One term, the "neutral" charge, is formed by changing the coefficient of the longest-ranged Gaussian at each site so that the total spherically symmetric charge on that site (including the nuclear charge for atom sites) is zero. The "polar" charge is the difference between this and the total charge, and has nonzero coefficients only for the longest-ranged Gaussian on each site. The polar charge, which produces all the long-range Coulomb potentials, has a rapidly convergent Fourier series and the potential it produces is evaluated in a reciprocal-lattice expansion. The integrals necessary for the least-mean-squares fit to this potential (using all the Gaussians, long and short range) are easily evaluated analytically. The Coulomb potential due to the neutral charge at each site decays in a Gaussian manner, and a direct-space lattice summation for the (analytic) integrals involved in fitting this contribution to the potential converges rapidly. At each atom site, a Z/r Coulomb potential screened by a short-range Gaussian is assumed as a constant component of the potential, and appropriately subtracted in the fit. This allows much better convergence of the total potential near the nuclei. The real-space summation for the neutral charge is partitioned into atom-site-diagonal and off-diagonal terms to avoid calculating the electrostatic energy of a core interacting with itself, which could cause a loss of precision in the structurally significant parts of the total energy.

The exchange-correlation potential V_{xc} is also expanded in Gaussians and is determined by a fit to the $V_{xc}(r_i)$ evaluated on a real-space mesh. The mesh consists of logarithmically spaced radial points along rays which give an approximately uniform sampling of the unit sphere. Only symmetry-inequivalent rays are needed. Cells are drawn enclosing each site of the charge-potential basis using a Wigner-type construction, with the bisecting plane between each pair of sites placed at a position determined by the ratio of appropriate radii assigned to the sites. Weighting factors calculated for each mesh point are approximately proportional to the volume nearest that point. (A Wigner-cell construction and exact volume calculation for each of several thousand mesh points would be prohibitive). Both the exchange-correlation potential and the exchange-correlation energy density are least-squares fitted. The self-overlap matrix needed in this fit is evaluated on the mesh using these weights for consistency, despite the fact that it can be evaluated analytically (and is for the charge and electrostatic potential fits). The fitted exchange-correlation energy density is then integrated analytically to obtain this contribution to the total energy. (Actually, the difference between the exchange-correlation energy density due to the total charge and to the core charge alone is fit and integrated for greater precision.)

Although these procedures result in an efficient general potential band-structure program, they can introduce annoying problems associated with monitoring the quality of the fitting. We have found that the total energy is more sensitive than the band structure to these problems. Total-energy calculations for small molecules closely paralleling the present calculations were carried out by Sambe and Felton with considerable success for bonding geometries and energies.[5] The convergence of the charge fit proved to be a significant problem in this work also. A recent proposal for modifying the weighting of the fit to minimize the error in the electrostatic energy rather than the charge density itself has yielded substantial improvements for molecular problems.[6] Difficulties in converging lattice sums of the required Coulomb integrals have so far kept us from applying this technique to solids, however.

The convergence of the total energy was tested by increasing the number and radial extent of the Gaussians. For the majority of the calculations the forzen-core approximation was used. The resulting band energies and the charge denstiy are in excellent agreement with general potential linearized augmented plane-wave (LAPW) results using the same local-density approximation.[7] Therefore, no attempt was made to extend the number of valence functions in the LCAO basis set.

When calculating differences in total energy for a series of lattice structures, care must be exercised in avoiding systematic errors associated with changes in the structural parameters, while errors like those associated with the inexact form of the exchange-correlation potential are expected to cancel. For example, when evaluating total energy as a function of volume, we found it necessary to scale the radial extent of the Gaussians (in both basis sets) with the lattice parameter to avoid a $\sim 1\%$ systematic error in the equilibrium lattice constant. (By coincidence, the first calculations with unscaled Gaussians gave the exact experimental equilibrium lattice constant, but the value was found to depend on the radial extent of the Gaussians until the scaling procedure was adopted.) Another systematic error was reduced by keeping the number and angular distribtution of the real-space exchange-correlation sampling points fixed. For example, when a phonon distortion would shift the nearest-neighbor charge maximum off the [111] direction, the sampling mesh was also shifted. Such manipulations are easily carried out, and we believe reduce the systematic errors sufficiently to make the method viable and not unduly cumbersome.

For the potential and charge basis set, auxiliary Gaussian functions were placed on the interstitial sites (forming a second diamond-type lattice) and on the bond-charge sites. Each of these auxiliary sites contained three geometrically distributed Gaussian functions. Including more sites or more functions on these sites quickly leads to overcompleteness.

It has not proved practical to test the suitability of this basis set by evaluating the rms error of the charge fit. Instead we follow the procedure used previously[4] of comparing the value of the unconstrained fit charge to the actual charge in the unit cell. Plots of the fitted charge density and smooth variation of the fit coefficients provide additional checks for fit quality. For the frozen-core approximation the fitted valence charge was accurate to 5×10^{-5} of the actual eight valence electrons per cell, and for the all-electron calculation the accuracy was better than 5×10^{-6} of the total charge (28 electrons per cell). The unconstrained fit was only used to provide this figure of merit, and a constrained fit was then made to ensure charge neutrality for evaluation of the potential.

The charge fit was performed by solving a system of coupled linear equations. The eigenvalues of its homogeneous part had to be monitored carefully to avoid linear dependences between the various prefactors of the charge-density Gaussian functions. Eigenvalues very close to zero were indicative of overcompleteness. They could be caused by inappropriate sets of auxiliary sites and/or Gaussian functions as well as by too large cutoffs in the evaluation of the overlap integrals. The near-zero solutions led to large and oscillatory prefactors of the longest-ranging Gaussians and consequently to large numerical noise in the total-energy results. When we choose (usually at the atomic sites) the full width at half maximum (FWHM) of the longest-ranging Gaussian ~ 10 a.u., then an overlap cutoff of $\sim 10^{-10}$ had to be taken to suppress this part of the numerical noise problem. In addition, it was necessary to choose rather contracted Gaussians at the auxiliary sites (FWHM $\approx 2-4$ a.u.) to avoid that the smallest eigenvalues of the homogeneous part dropped below $\sim 10^{-5}$. A further decrease in the overlap cutoff to $\sim 10^{-12}$ allowed even smaller eignevalues of $\sim 10^{-6}$ (and thus longer-ranging Gaussians), yet the total-energy results varied only insignificantly. However, the large increase in computer time was of significance.

The local exchange-correlation potential was evaluated using the Wigner interpolation formula.[7,8] For Brillouin-zone integrations six special points were chosen for the undistorted lattice.[9,10] For the transverse-optic phonon at Γ, TO(Γ), and the internal strain the same set of $\vec{k}$ vectors along with members of their stars which become inequivalent under the distortion were used. For the TA(X) phonon the $\vec{k}$ vectors corresponding to $q=4$ in the Monkhorst and Pack notation[10] were used. All calculations were carried to self-consistency with the total energy stable to seven significant digits.

The computations have been performed on the IMB 370/3033 of the Kernforschungszentrum Karlsruhe using a FORTRAN program package of ~ 8000 lines. The computational time per given distortion was between 1 and 4 min.

III. RESULTS

We first present the total energy versus lattice constant calculations, from which the equilibrium properties are derived, and we also comment on the validity of the frozen-core approximation. We then give the results for the frequencies of the TO(Γ) and TA(X) phonons, and finally describe the evaluation of the internal strain parameter which involves calculations for the lattice strained along the [111] direction.

Using the frozen-core approximation, the total valence energy was evaluated for eight values of the lattice constant and fit with a 4th-order polynomial. The lattice constant varied from 8.6 a.u. ($V/V_0\approx0.59$) to 10.8 a.u. ($V/V_0\approx1.16$), and the rms error was 6×10^{-5} Ry/atom, with a maximum error of 8.6×10^{-5} Ry/atom. The fitted curve is shown in Fig. 1. The derived values for the equili-

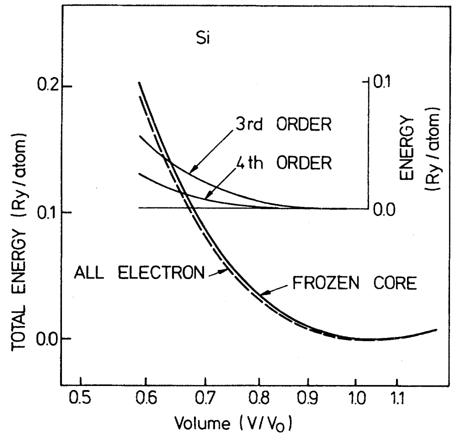

FIG. 1. The fourth-order polynomial fits to the total energy versus volume for the frozen core and all-electron calculations. The energies have been shifted by $-8.003\,17$ Ry and $-576.076\,34$ Ry, respectively. The third- and fourth-order contributions to the all-electron result are also shown. $V_0=270.0$ a.u.^{3}, the experimental volume.

brium lattice constant, the bulk modulus, its pressure derivative, and the cohesive energy are listed in Table I along with the corresponding experimental values. The cohesive energy was obtained by subtracting the total valence energy of the corresponding atomic calculation (which included the extended Gaussian functions) and making corrections for spin polarization and the zero-point motion. The pressure derivative of the bulk modulus depends on the third-order derivative of the potential and is more sensitive to the fit than the other quantities. Additional calculations in which the radial extent of the Gaussian functions were varied resulted in changes of 0.1% for the lattice constant, 1.1% for the bulk modulus, and as much as 10% for dB/dP, with little or no change in the cohesive energy.

Our results are in good agreement with experiment and compare favorably with other recent calculations.[11–15] However, the pseudopotential calculation of Yin and Cohen[2] agrees even better with the experiment, although the same Wigner local approximation for exchange and correlation was used. This suggests that our somewhat larger discrepancy with experiment does not so much indicate basic limitations of the local-density approximation, but may be caused by a less than optimum choice of auxiliary sites and Gaussian basis sets. These parameters are not yet conveniently optimized within our LCAO method.

Since for Si the frozen-core approximation is easily avoided when using the tight-binding method, we repeated the calculations treating the 1*s*, 2*s*, and 2*p* orbitals as valence states and keeping everything else the same. The total energy was again fit with a fourth-order polynomial (rms error $=2\times10^{-5}$ Ry/atom). The fit is shown in Fig. 1 and the derived properties listed in Table I. Over a volume change of $\sim\pm15\%$ the total-energy curves are essentially the same and it is only for volume compressions beyond $\sim20\%$ that the all-electron energies are relatively lower. Thus, for Si the frozen-core approximation is valid over a wide volume range and the use of pseudopotentials for studying the pressure-induced structural phase transition (diamond to β tin) seems well justified.[2] The small errors we find are consistent with a recent general theory of the frozen-core approximation by von Barth and Gelatt.[16]

Within the Born-Oppenheimer approximation, dynamic lattice distortions (phonons) are treated as static and a calculation of the total energy as a function of the normal-mode amplitude yields essentially classical potential wells or force constants from which the frequencies are obtained. These calculations are feasible for high-symmetry phonons for which group theory suffices to determine the polarization, and for which the resulting

TABLE I. Calculated and experimental properties for the ground state of Si.

	a Lattice constant (a.u.)	B Bulk modulus (Mbar)	dB/dP Pressure derivative	Cohesive energy (eV/atom)
Frozen core	10.40	0.89	3.22	4.92
All electron	10.37	0.87	4.11	4.84
Expt.	10.26[a]	0.99[a]	4.24[b]	4.66[a]

[a] Reference 22.
[b] Reference 23.

new periodicity contains a tractable number of atoms per unit cell. We performed such calculations for the TO(Γ) phonon of Si, which is dominated by bond stretching along the [111] direction, and for the TA(X) phonon which has no bond stretching in first order. The results are given in Table II. Also listed is a third-order term k_{xyz} which is allowed for the TO(Γ) phonon. This term can be derived from experimental third-order elastic constants using Keating's model.[17] We note that the TO(Γ) frequency was rather insensitive to changes in our basis-set parameters, such as adjustments in the range of the Gaussians. Even a calculation using only atomic potential sites gave very similar values for the TO(Γ) frequency.

We show in Fig. 2 the valence-charge density in the [110] plane for the TO(Γ) phonon with a displacement of ∼0.14 Å. The difference in bond charge is evident as is the characteristic bond-charge shape. The elongation of the bond charge along the bond axis is experimentally observed[18] and is obtained with accurate pseudopotential[7,14] as well as other first-principle techniques.

The value of the TA(X) frequency was sensitive to how accurately the charge density was modeled along the bonds. With the usual set of auxiliary sites the centers of the bond charges were essentially constrained to the midway positions between the atoms, and the calculated frequency was poor. However, when we added further auxiliary sites to permit distortions of the bond-charge density the frequency moved closer to experiment. Indeed, we found that the center of the bond charge moved somewhat away from the midway position, similar to what has been proposed in the adiabatic bond-charge model.[19] This motion of bond charges in zone boundary TA phonons has also been verified in previous work.[11,20]

A further structural property of the diamond lattice is the internal strain parameter ζ. As the diamond structure is a nonsymmorphic space group, an external stress may induce an internal strain between the two sublattices, in addition to the homogeneous deformation of the unit cell. This is the case for a uniaxial compression in the [111] direction. Here the [111] bonds become inequivalent to the other bonds along the $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$ directions. As a consequence, the position of the second atom in the primitive unit cell need not shift with the homogeneous deformation, but may relax along the [111] direction.

This relaxation depends on the relative magnitude of the different forces in the crystal. It is described by the internal strain parameter ζ, which equals zero for zero internal strain (the [111] bond is fully compressed) and equals one for a relaxation such that all four bonds have the same length. In lattice-dynamic models, ζ is given as a quotient of force constants and $(1-\zeta)$ reflects roughly the ratio of the bond bending to the bond stretching forces.

Applying a strain of ∼4.7% along the [111] direction, we have calculated the total energy as a function of the [111] bond length. The results are shown in Fig. 3. The minimum occurs at $\zeta=0.61$, which is in much better agreement to the experimental value of 0.62 ± 0.04 (Ref. 21) than the $\zeta=0.5$ obtained by the adiabatic bond-charge model (ABCM).[19] The latter value is off by ∼20% in spite of the fact that the ABCM agrees with the values of all experimental phonon frequencies within a 2% average deviation. This big discrepancy has been attributed to the assumption of constant bond charges in the ABCM. Indeed, this seems to be the case, as is evident from the top of Fig. 3. There, the difference in charge between the [111] bond site and one of the inequivalent bond sites is shown as a function of ζ. The bond charges are equal for $\zeta\approx0.5$, the same value as obtained by the ABCM.[19]

Finally, from the total curve of Fig. 3 we may also derive the shift of the TO(Γ) phonon frequen-

TABLE II. Comparison of theory and experiment for various properties of Si involving lattice distortion.

	TA(X)-phonon frequency	TO(Γ)-phonon frequency	k_{xyz}	Internal strain parameter ζ	shift of TO(Γ) frequency	
Calc.	4.9 THz	15.0 THz	-34.8 eV/Å^3	0.61	0.42	THz
Expt.	4.5 THz[a]	15.4 THz[a]	-35.1[b] eV/Å^3	0.62 ± 0.04[c]	0.53 ± 0.05[d]	THz

[a] Reference 24.
[b] Reference 25.
[c] Reference 21.
[d] Reference 26.

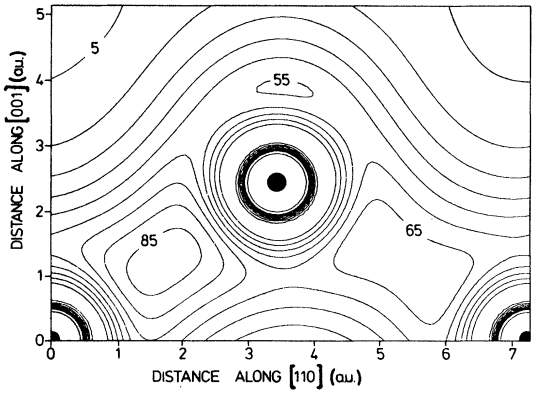

FIG. 2. The charge density in the (110) plane for the lattice distortion corresponding to the TO(Γ) phonon with a displacement of −0.137 Å along the [111] direction (in units of a.u.$\times 10^3$).

cy for the strained lattice. This number is also in reasonably good agreement with experiment (see Table II).

IV. CONCLUSION

In this paper we have shown that the LCAO method can be a viable technique for calculating the total energies of solids from first principles. For Si, the theoretical numbers deviate from experimental values by (i) ~1% for structural properties like the lattice constant, (ii) ~10% for vibrational properties like the bulk modulus of phonon force constants, and (iii) up to 30% for third-order anharmonicities. In addition, our results confirm that the frozen-core approximation is well justified in total-energy calculations for Si.

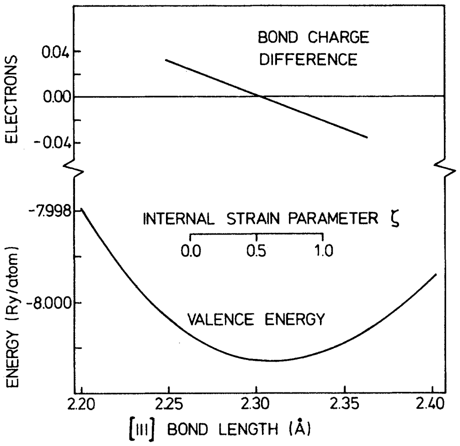

FIG. 3. The lower curve is the total valence energy per atom for the [111] strained crystal as a function of the [111] bond length. The minimum occurs at $l=2.309$ Å corresponding to an internal strain parameter value of $\zeta=0.61$. A value of $\zeta=0.0$ corresponds to maximum compression of the [111] bond, while $\zeta=1.0$ corresponds to equal bond lengths. Also shown is the difference in bond-site charge $Q[111]-Q[\bar{1}1\bar{1}]$.

Note added in proof. New measurements suggest a revised experimental value of the internal strain parameter of $\zeta\approx 0.7$ (M. Cardona, private communication).

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[1] E. A. Lafon and C. C. Lin, Phys. Rev. 152, 579 (1966); D. W. Bullett, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, p. 129, and references therein.

[2] M. T. Yin and M. L. Cohen, Phys. Rev. Lett. 45, 1004 (1980).

[3] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 194 (1979).

[4] J. A. Appelbaum and D. R. Hamann, in *Transition Metals,* edited by M. J. G. Lee, J. M. Perz, and E. Fawcett (Institute of Physics, Bristol, 1980), p. 111; P. J. Feibelmann, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. B 20, 1433 (1979).

[5] H. Sambe and R. H. Felton, J. Chem. Phys. 62, 1122 (1975).

[6] B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, J. Chem. Phys. 71, 3396 (1979); 71, 4993 (1979).

[7] D. R. Hamann, Phys. Rev. Lett. 42, 662 (1979).

[8] E. Wigner, Phys. Rev. 46, 1002 (1934).

[9] D. J. Chadi and M. L. Cohen, Phys. Rev. B 8, 5747 (1973).

[10] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).

[11] H. Wendel and R. M. Martin, Phys. Rev. Lett. 40, 950 (1978); Phys. Rev. B 19, 5251 (1979).

[12] J. Ihm and M. L. Cohen, Solid State Commun. 29, 711 (1979).

[13] E. O. Kane, Phys. Rev. B 21, 4600 (1980).

[14] A. Zunger, Phys. Rev. B 21, 4785 (1980).

[15] D. Glötzel, B. Segall, and O. K. Andersen, Solid State Commun. 36, 403 (1980).

[16] U. von Barth and C. D. Gelatt, Phys. Rev. B 21, 2222 (1980).

[17] P. N. Keating, Phys. Rev. 149, 674 (1966).

[18] Y. W. Yang and P. Coppens, Solid State Commun. 15, 1555 (1974).

[19] W. Weber, Phys. Rev. B 15, 4789 (1977).

[20] K. Maschke and A. Baldereschi, *Physics of Semiconductors 1978,* edited by B. L. H. Wilson (The Institute of Physics, Bristol, 1979), p. 673.

[21] A. Segmüller and H. R. Neyer, Phys. Kondens. Mater. 4, 63 (1965).

[22] K. A. Gschneidner, Solid State Phys. 16, 275 (1964).

[23] H. J. McSkimin and P. Andreatch, J. Appl. Phys. 35, 2161, (1964).

[24] G. Dolling, *Inelastic Scattering of Neutrons in Solids and Liquids* (IAEA, Vienna, 1963), Vol. II, p. 37; G. Nilson and G. Nelin, Phys. Rev. B 6, 3777 (1972).

[25] The value of k_{xyz} was determined using the macroscopic strain energy density equation and the third order elastic constants given in Ref. 17. The value differs somewhat from the one listed in Ref. 11.

[26] Estimated for a [111] uniaxial strain of 4.7% from measurements by E. Anastassakis, A. Pinczuk, E. Burstein, F. H. Pollak, and M. Cardona, Solid State Commun. 8, 133 (1970).