PHYSICAL REVIEW B VOLUME 24, NUMBER 8 15 OCTOBER 1981

Structural-energy calculations based on norm-conserving pseudopotentials and localized Gaussian orbitals

G. B. Bachelet, H. S. Greenside, G. A. Baraff, and M. Schlüter
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 14 May 1981)

The total energy, equilibrium lattice constant, and bulk modulus are calculated for diamond, silicon, and GaP. These ground-state calculations are carried out in a localized Gaussian basis (20 orbitals per atom) using a real-space formalism devised for defect crystal studies. High-precision norm-conserving pseudopotentials simulate the interaction of the valence electrons with the atomic cores. The results are typically within 1−4% of experiment, which is not good enough to determine absolute cohesive energies but should be sufficient for studies of structural deformations and elastic properties. An analysis and comparison with other calculations show that the errors arise predominantly from the use of a minimum local-orbital basis and not from pseudopotentials.

I. INTRODUCTION

The newest first-principles pseudopotentials,[1] derived and used within the local-density-functional (LDF) approximation for exchange and correlation,[2] have recently been used to calculate the ground-state total energy of periodic crystals with sufficient accuracy to predict lattice constants, compressibilities, cohesive energies, phonon frequencies, and even to account for crystal structures.[3] The calculations were carried out in a plane-wave basis using a momentum-space formalism. This representation makes optimal use of the three-dimensional periodicity of the solid. There is interest, however, in systems such as surfaces and localized defects in solids where the full periodicity is absent. Although periodicity can be artificially restored to such systems by the device of the large unit cell, i.e., a periodic array of surfaces or defects,[4] it is not evident that this is the best way of studying such systems. Indeed, recent progress has been made using the Green's-function technique[5−7] in which the advantages of periodicity are traded for the advantages of a smaller volume of crystal over which calculations have to be made.

There are computational difficulties in using the Green's function constructed from states expressed directly in a plane-wave basis. As a consequence, virtually all of the recent work has used a Green's function described either in terms of matrix elements with respect to some localized and necessarily incomplete basis,[6] in terms of a decomposition using such a basis as an intermediary construct,[5] or in terms of a direct expansion with respect to such a basis,[7] e.g.,

$$G_E(r,r')=\sum_{ab}\phi_a(r)G_{ab}(E)\phi_b(r')^* \; . \tag{1.1}$$

Such an expression is obtained directly when the Green's function is expressed in terms of the Bloch waves of the perfect crystal while the Bloch waves, in turn, are expressed in terms of these same localized orbitals as a basis:

$$G_E(r,r')=\sum_n \int_{\mathrm{BZ}} \frac{d^3k\,\psi_n(k,r)\psi_n(k,r')^*}{(2\pi)^3E+i\eta-E_n(k)} \; , \tag{1.2a}$$

$$\psi_n(k,r)=\sum_a c_a(n,k)\phi_a(r) \; , \tag{1.2b}$$

where BZ denotes Brillouin zone. Before such a Green's function can be used with any confidence in calculating the total energy of some defect, it is necessary to verify that the orbital set is sufficiently complete to calculate the total energy of the perfect crystal.

In this paper, we present calculations of the total energy, lattice constant, and compressibility of the crystalline semiconductors silicon, gallium phosphide, and diamond which verify the completeness of a local orbital set. They are carried out using Hamann-Schlüter-Chiang (HSC) pseudopotentials,[1] employing *only* localized Gaussian orbitals in the basis set. Using far fewer orbitals per unit cell than the number of plane waves reported in the momentum-space calculations[3] and using the same potential, we obtain comparable accuracy. This is not a claim that the Gaussian orbitals are inherently more efficient in the perfect crystal calculation. Indeed they are not: the real-space formalism we use (because it is better adapted to the localized orbitals) is more cumbersome for the perfect crystal than is the momentum-space formalism. The localized orbitals and real-space formalism have definite advantages when defect crystals are being studied, as we shall show elsewhere.

In the second section of this paper, we describe the real-space formalism used for these total-energy calculations. In the third section we briefly discuss some characteristic features of the HSC pseudopotentials and describe a method of fitting Gaussian functions to the numerically derived potentials. The last section contains a discussion of the calculated structural parameters.

II. REAL-SPACE FORMALISM FOR THE TOTAL ENERGY

The total-energy functional in local-density pseudopotential theory,

$$E_{\text{tot}}=T+V+\Phi+V_I+\int E^{\text{xc}}(r)dr\ , \tag{2.1a}$$

$$T=\sum_i \int \psi_i(r)^*(-\tfrac{1}{2}\nabla^2)\psi_i(r)dr\ , \tag{2.1b}$$

$$V=\sum_i \int \int \psi_i(r)^* \sum_A U_A^{\text{ps}}(r,r')\psi_i(r')dr\,dr'\ , \tag{2.1c}$$

$$\Phi=\tfrac{1}{2}\int\int \frac{dr\,dr'}{|r-r'|}\rho(r)\rho(r')\ , \tag{2.1d}$$

$$V_I=\tfrac{1}{2}\sum_A \sum_{B\neq A} \frac{Q_A Q_B}{|R_A-R_B|}\ , \tag{2.1e}$$

$$E^{\text{xc}}(r)=\rho(r)\epsilon_{\text{xc}}[\rho(r)]\ , \tag{2.1f}$$

$$\rho(r)\equiv \sum_i \psi_i(r)^*\psi_i(r)\ , \tag{2.1g}$$

is made stationary if the wave functions satisfy the Schrödinger-type equation

$$[\tfrac{1}{2}\nabla^2+\phi(r)+U^{\text{ps}}(r)+\mu_{\text{xc}}(r)-\epsilon_i]\psi_i(r)=0\ , \tag{2.2}$$

where

$$\phi(r)\equiv \int \frac{dr'}{|r-r'|}\rho(r')\ , \tag{2.3a}$$

$$V^{\text{ps}}(r)\psi_i(r)\equiv \sum_A \int U_A^{\text{ps}}(r,r')\psi_i(r')dr'\ , \tag{2.3b}$$

and

$$\mu_{\text{xc}}(r)=\frac{d}{d\rho}\rho\epsilon_{\text{xc}}(\rho)\ . \tag{2.3c}$$

As a result, it can also be written as

$$E_{\text{tot}}=\sum_i \epsilon_i+V_I-\Phi+\int \rho(r)(\epsilon_{\text{xc}}-\mu_{\text{xc}})dr\ . \tag{2.4}$$

The HSC form of the bare-ion pseudopotential[1] can be regarded as being made up of three components: a short-range nonlocal l-dependent component, a short-range local (i.e., l-independent) component, and a long-range Coulomb component

$$U_A^{\text{ps}}(r,r')=\sum_l U_A^l(|r-R_A|)\hat{P}_l(r-R_A) +U_A(|r-R_A|)+\phi_A(|r-R_A|)\ . \tag{2.5}$$

$\hat{P}_l$ is the projection operator for angular momentum l with respect to the center at R_A. Both short-range components are fitted to Gaussian functions. The Coulomb part ϕ_A arises from a smeared Gaussian distribution of charge with center at R_A, Gaussian decay constant α_A, and total charge Q_A:

$$g_A(r)=-Q_A(\alpha_A/\pi)^{3/2}e^{-\alpha_A r^2}\ , \tag{2.6}$$

$$\phi_A(r)=\int \frac{d^3r'}{|r-r'|}g_A(r') \tag{2.7a}$$

$$=-(Q_A/r)\text{erf}(r\alpha_A^{1/2})\ , \tag{2.7b}$$

where

$$\text{erf}(x)\equiv\frac{2}{\sqrt{\pi}}\int_0^x e^{-u^2}du\ .$$

It is convenient to define an "ionic charge distribution" $\rho_I(r)$ by means of

$$\rho_I(r)\equiv\sum_A g_A(|r-R_A|)\ . \tag{2.8}$$

We can then write the Coulomb terms in Eq. (2.4) as

$$V_I-\Phi=\tfrac{1}{2}\left[\int V_T(r)[\rho_I(r)-\rho(r)]dr + \sum_A \sum_{B\neq A} J_{AB}-\sum_A C_A\right]\ , \tag{2.9}$$

where

$$V_T(r)\equiv\int \frac{dr'}{|r-r'|}[\rho_I(r')+\rho(r')] \tag{2.10a}$$

is the Hartree potential generated by an overall *neutral* distribution of charges and where

$$J_{AB} \equiv \frac{Q_A Q_B}{R_{AB}} \operatorname{erfc}(R_{AB}\gamma_{AB}^{1/2}) , \tag{2.10b}$$

$$C_A \equiv Q_A^2 (2\alpha_A/\pi)^{1/2} . \tag{2.10c}$$

In deriving (2.9) and (2.10), the following integrals are used:

$$\int \frac{g_A(r-R_A|)g_B(|r'-R_B|)}{|r-r'|} dr\, dr' = \frac{Q_A Q_B}{R_{AB}} \operatorname{erf}(R_{AB}\gamma_{AB}^{1/2}) , \tag{2.11a}$$

where

$$\gamma_{AB} = \alpha_B \alpha_B/(\alpha_A + \alpha_B) \tag{2.11b}$$

$$\operatorname{erfc}(x) = 1 - \operatorname{erf} = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2} du . \tag{2.11c}$$

The term $-C_A$ arises because in the Coulomb interaction of $\rho_I(r)$ with itself, core A interacts not only with all other cores B but also with itself. This self-interaction does not occur in Eq. (2.1e) and must be subtracted out. The term J_{AB} arises because cores A and B, being smeared distributions, do not repel each other as strongly as the point charges in Eq. (2.1e) do. J_{AB} is the difference between the repulsion of the point charges and the smeared charges. It vanishes very rapidly with separation R_{AB}.

The potential $V_T(r)$, defined by Eq. (2.10a) is also part of the interaction $\phi(r) + U^{\text{ps}}(r)$ which appears in the Schrödinger equation (2.2). In an infinite crystal, the definition Eq. (2.10a) is incomplete because there is no unambiguous way to assign a reference level for $V_T(r)$. This is not a real problem since one is free to regard the crystal as being a large but finite molecule with surfaces. The reference level for the potential $V_T(r)$, which appears both in Eq. (2.2) and [via Eq. (2.9)] in Eq. (2.4), is in that case zero as $r \rightarrow \infty$. Note that a constant potential, V_0, can be added to $V_T(r)$ without affecting E_{tot} for a neutral crystal. Such a potential shift in the Schrödinger equation (2.2) shifts every eigenvalue ϵ_i by V_0. This produces a shift of amount $V_0 N$, where N is the number of occupied states, in the first term in Eq. (2.4). There is a compensating shift in the term $V_I - \Phi$ arising from the fact that, in using Eq. (2.9), we have

$$\tfrac{1}{2} \int V_0[\rho_I(r) - \rho(r)] dr = -V_0 N .$$

The point is that any reference value can be used for $V_T(r)$. One has to be certain only that the eigenvalues ϵ_i and the Coulomb term $V_I - \Phi$ are both evaluated using the same definition of $V_T(r)$. We go to the limit of an infinite crystal and, for convenience only, set the additive constant V_0 (whose value is not really known) by the condition

$$\langle V_T(r) \rangle_{\text{cell}} = 0 . \tag{2.12}$$

Finally, we rewrite Eq. (2.4) to be the energy per unit cell. All spatial integrals are restricted to a single unit cell and all single sums over A are confined to the atoms within a single unit cell. All double sums over A and B have B running over the whole crystal and A confined to a single unit cell. Since the potential $V_T(r)$ in Eq. (2.10a) arises from a neutral unit cell, the integral in Eq. (2.9) over the whole crystal converges rapidly. If the electronic charge distribution $\rho(r)$ is fitted to Gaussian orbitals,[8,9] this integral is analytic and consists of terms of the form given in Eq. (2.11a). Similarly all integrals of Hamiltonian or total-energy matrix elements, with the exception of those involving ϵ_{xc} or μ_{xc} can be evaluated analytically involving one-, two-, or three-center integrals with Gaussians and error functions. Among those, the three-center Hamiltonian matrix elements connecting two Gaussians orbitals with a nonlocal l-dependent Gaussian pseudopotential are most involved. Their evaluation, though analytic, is sufficiently involved that it shall be described elsewhere.[10] The exchange correlation integrals in Eqs. (2.2) and (2.4) involve nonlinear functionals ($\epsilon_{\text{xc}} - \mu_{\text{xc}}$) as, e.g., $\rho^{1/3}$ in the simple Slater form. They are most conveniently numerically evaluated by summing over fine space grids covering the unit cell.[8,9]

III. GAUSSIAN FITTING OF NORM-CONSERVING PSEUDOPOTENTIALS

The recently proposed HSC pseudopotentials are derived from self-consistent first-principles atom calculations. The pseudopotentials are constructed to reproduce the chosen atomic reference state exactly, i.e., all valence eigenvalues are identical and all valence wave functions agree identically outside the core region. The pseudo-wave-functions are nodeless and normalized and are used to self-consistently screen the pseudoatom. Through the relation

$$-2\pi \left[(r\psi)^2 \frac{d}{dE} (\ln\psi)' \right]_{r=R_c} = 4\pi \int_0^{R_c} r^2 \psi^2 dr , \tag{3.1}$$

the exact norm conservation guarantees that first-energy derivatives of the logarithmic derivatives $(\ln\psi)'$ are identical for pseudo- and full-core wave functions. This implies that for radii $r>R_c$, the phase shifts $\Phi(E)$ for pseudo- and full-core atoms agree in their value and their slope at eigenenergies. For energies deviating from these atomic eigenenergies, the error in phase shift is small because the slopes agree at the eigenenergies. This phase-shift relationship, a consequence of norm conservation, guarantees optimum transferability of the pseudopotentials to different chemical environments. Various calculations[3,11] employing the HSC potentials confirm this essential property.

The procedure, outlined in Ref. 1 to produce these potentials, is purely numerical and yields l-dependent bare-ion pseudopotentials in terms of numerical values on a chosen grid of atomic radii. Typical curves for the elements C, P, Si and Ga are shown in Fig. 1. This figure illustrates the short-range nature of the nonlocality of l dependence and simple $-Z/r$ behavior at large distance. The potentials can thus be regarded as being made up of three components, a long-range Coulomb component, a short-range l-independent component, and a short-range l-dependent correction, as suggested in Eq. (2.5). The Coulomb part is chosen to arise from a smeared Gaussian distribution of charge, yielding the form given in Eq. (2.7b). It smoothly approaches $(1/\pi)4\sqrt{\sigma_0}$ as $r\rightarrow 0$. The Gaussian decay constant α_0 can either be chosen to minimize the remaining short-range pseudopotential components or be determined otherwise, e.g., by considering the size of the underlying atomic cores.

In practice we choose one particular l component, e.g., $l_0=0$, as the local potential and consider all other $(V_l-V_{l_0})$ components as nonlocal corrections. The differences between the smeared Gaussian Coulomb potential and the chosen local component and the nonlocal corrections are fitted by nonlinear least-squares procedures to a series of Gaussian functions (five in the present case). The pseudopotentials thus have the form

$$V_l(r)=V_{l_0}(r)+\Delta V_l(r)\,, \tag{3.2}$$

with

$$V_{l_0}(r)=-\frac{Z}{r}\mathrm{erf}(\sqrt{\alpha_0 r}\,)+\sum_{i=1}^{5}c_i(l_0)e^{-\alpha_i(l_0)r^2} \tag{3.3}$$

and

$$\Delta V_l(r)=V_l(r)-V_{l_0}(r)=\sum_{i=1}^{5}c_i(l)e^{-\alpha_i(l)r^2}\,. \tag{3.4}$$

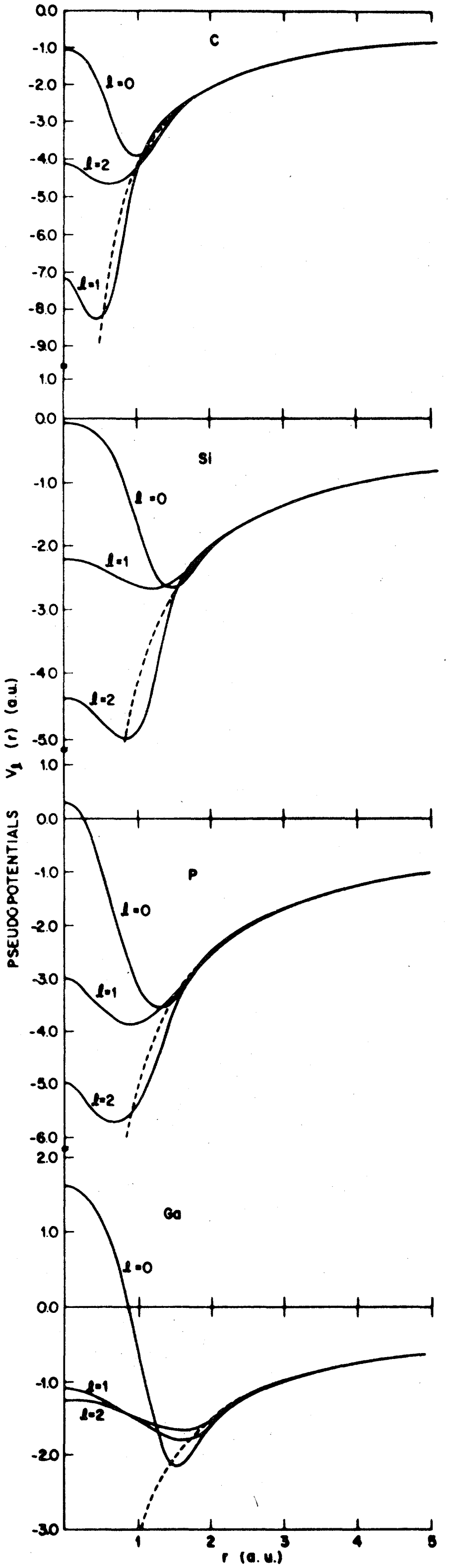

FIG. 1. Norm-conserving pseudopotentials for C, Si, Ga, and P. The potentials are derived according to the procedure outlined in Ref. 1.

TABLE I. Fitting parameters (in a.u.) for l-dependent pseudopotentials of C and Si. The errors introduced by the fitting as reflected in eigenvalues and total energies are indicated.

	$V_{l=0}$(local)		$\Delta V_{l=1}$		$\Delta V_{l=2}$	
	α_i	c_i	α_i	c_i	α_i	c_i
C	0.96803	0.28938	0.50441	−0.11834	1.69200	−0.26274
$\alpha_0=2.5$	2.04000	−6.75715	2.04000	13.10770	2.04000	−0.39033
	3.78000	40.61345	3.78000	−98.25630	5.17200	−75.68483
	5.52000	−42.28521	5.52000	130.42209	5.62288	83.56471
	7.26000	14.33595	7.26000	−51.73041	7.26000	−10.34838
$\Delta\epsilon$ (a.u.)	2×10^{-4}		-3×10^{-4}		-1×10^{-4}	
$\Delta\epsilon_{\text{tot}}/E_{\text{tot}}$	5×10^{-4}					
Si	0.92600	23.37690	0.92600	−21.71600	0.78800	−35.05500
$\alpha_0=2.5$	1.10000	−57.12710	1.10000	51.92800	0.94100	81.09700
	1.77000	157.07900	1.77000	−127.10800	1.56200	−175.20800
	2.23900	−168.91500	2.23900	136.71400	2.20400	198.86100
	2.81700	52.656200	2.81700	−41.92800	2.93600	−74.28700
$\Delta\epsilon$ (a.u.)	-4×10^{-3}		-1×10^{-4}		-1×10^{-4}	
$\Delta E_{\text{tot}}/E_{\text{tot}}$	6×10^{-4}					

The quality of the fits is monitored by reassembling the Gaussian expanded pseudopotentials, using it to solve Schrödinger's equation for the atom self-consistently and comparing eigenvalues, eigenfunctions, and atomic total energies to the original values. Calculated fitting parameters and associated errors are given in Table I for the elements C and Si and in Table II for Ga and P. Note that the local component is chosen to be the s potential for C and Si and the p potential for P and Ga. This choice is not necessary. Since angular momenta $l>2$ are described by the local component, it may be advantageous to use the higher l (the p or d potentials rather than the s potential) as

TABLE II. Fitting parameters (in a.u.) for l-dependent pseudopotentials of Ga and P.

	$V_{l=1}$(local)		$\Delta V_{l=0}$		$\Delta V_{l=2}$	
	α_i	c_i	α_i	c_i	α_i	c_i
Ga	0.97446	26.833334	0.47325	3.519321	0.42634	1.084243
$\alpha_0=2.5$	1.25004	−105.984920	0.70410	−33.546745	0.767742	4.698937
	1.80562	244.569894	0.93495	86.145629	1.10849	11.617661
	2.36119	−257.147758	1.16581	−81.372113	1.44957	−13.730063
	2.91677	94.603675	1.39666	29.460517	1.79064	5.607739
$\Delta\epsilon$ (a.u.)	1×10^{-4}		4×10^{-4}		-5×10^{-5}	
$\Delta E_{\text{tot}}/E_{\text{tot}}$	8×10^{-4}					
P	1.79630	−32.273329	1.03826	−1.201421	1.03827	130.003518
$\alpha_{0=2.5}$	2.27162	91.074584	1.86886	14.560759	1.14732	−217.828930
	3.28122	−120.711236	2.69947	−15.526091	1.65724	186.707831
	4.29083	98.242420	3.53008	10.077443	2.16718	−147.714424
5.30044	−33.069725	4.36068	−1.978122		2.67708	47.183376
$\Delta\epsilon$ (a.u.)	2×10^{-4}		1×10^{-4}		5×10^{-5}	
$\Delta E_{\text{tot}}/E_{\text{tot}}$	8×10^{-4}					

TABLE III. Gaussian decay lengths (in a.u.) employed in the minimum basis set for valence states. The values approximately minimize the total crystal energy.

	C	Si	Ga	P
α_1	0.35	0.2	0.2	0.3
α_2	1.40	0.5	0.6	0.8

local component. An exception of course is carbon which has no p-like core electrons. The nonlinear fitting parameters in Tables I and II are by no means unique and similar quality fits can be obtained with different sets of parameters.

IV. CHARGE DENSITIES, BAND STRUCTURES, AND TOTAL ENERGIES

As outlined in Sec. I, it is of considerable interest to represent electronic valence wave functions by a minimal local basis. Based on the experience gained in recent Green's function defect calculations,[7] we expand the crystal wave function as superposition of atom-centered Gaussian orbitals with *two* decay lengths each:

$$\psi = \sum_{R} \psi_\alpha(r - R_\alpha) , \qquad (4.1)$$

with

$$\psi_\alpha(r) = \sum_{j=1,2} \sum_{l=1,10} K_l(\hat{r}) e^{-\alpha_j r^2} .$$

These two decay lengths should approximately correspond to (i) the short-range decay of ψ in the core region to account for features in the pseudopotential, and (ii) the longer-range formation of bonding charges. For example, we found for Si that $\alpha_1 \approx 0.6$ a.u. corresponding to an effective core radius of $r_c \approx 1.3$ a.u. and that $\alpha_2 \approx 0.2$ a.u. corresponding to one-half of a bond length $d/2 \approx 2.2$ a.u. While the structural quantities to be discussed below depend only weakly on $\alpha_{1,2}$, we nevertheless optimize their values by minimizing the total energy per unit cell. The employed values of α are given in Table III. For each decay length a total of 10 angular functions $K_l(\hat{r})$ are considered, viz., s, p, d, and the s-like "trace" of d states, r^2. This amounts to 20 orbitals per atom or to a 40×40 secular system for diamond and zinc-blende crystals. This is considerably smaller than the ~ 170 plane waves used by Yin and Cohen.[3]

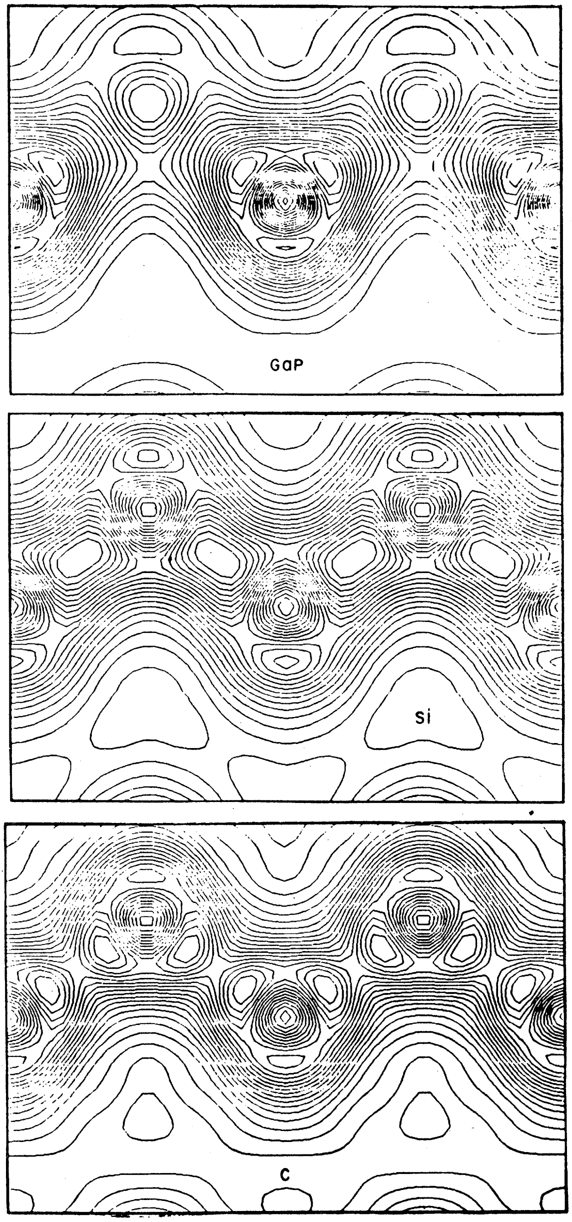

FIG. 2. Charge-density contours of diamond, silicon, and GaP. The bond-charge maxima are 0.30, 0.08, and 0.11 a.u., respectively, and the contours are subdividing these maximum values into 20 steps.

To obtain the total energy $E = E(a)$ as a function of an assumed lattice parameter a, self-consistent band-structure calculations are carried out at each step. The Hartree-exchange screening potential is evaluated in Fourier space in analogy to plane-wave or mixed-basis calculations.[3,4] In analogy to Yin and Cohen's calculations[3] on Si we use 10 special $\vec{k}$ points in the irreducible wedge of the Brillouin zone for $\vec{k}$-space sampling. Figure 2

TABLE IV. Band-structure eigenvalues calculated from HSC pseudopotentials using plane waves or local orbitals as bases. For silicon, comparison is also made to a pseudopotential LAPW calculation. LAPW full-core results are shown for diamond and silicon. All calculations are self-consistent using Wigner exchange and correlation. (LO denotes local orbital).

	Diamond			Silicon					GaP
	Pseudopotential		full-core	Pseudopotential			full-core		Pseudopotential
	PW's	40 LO's	LAPW	170 PW's	40 LO's	LAPW	LAPW		40 LO's
Γ_1	−21.45	−21.68	−21.36	−11.95	−11.72	−12.01	−12.02	Γ_1	−13.10
$\Gamma_{25'}$	0	0	0	0	0	0	0	Γ_{15}	0
$\Gamma_{15'}$	5.40	5.59	5.66	2.54	2.64	2.53	2.49	Γ_1	1.40
$\Gamma_{2'}$	13.38	13.21	13.34	3.39	3.51	3.13	3.18	Γ_{1S}	4.07
X_1	−12.65	−12.90	−12.61	−7.80	−7.66	−7.84	−7.84	X_1	−10.60
X_4	−6.22	−6.43	−5.82	−2.92	−2.74	−2.81	−2.82	X_3	−6.80
X_1	4.63	4.65	4.78	0.62	0.83	0.59	0.55	X_5	−2.58
X_4	16.73	16.87	17.30	9.99	10.32	10.32	10.32	X_1	1.43
$L_{2'}$	−15.57	−15.79	−15.53	−9.57	−9.43	−9.65	−9.64	L_1	−11.35
L_1	−13.35	−13.73	−13.27	−7.01	−6.85	−7.04	−7.06	L_2	−6.65
$L_{3'}$	−2.81	−2.86	−2.44	−1.23	−1.13	−1.15	−1.16	L_3	−1.06
L_1	8.92	8.90	8.90	1.52	1.64	1.40	1.40	L_1	1.91
L_3	8.31	8.47	8.56	3.37	3.42	3.41	3.37	L_3	4.78

shows valence charge density contour plots for diamond, Si, and GaP. The charge maxima in the bonding region are 0.30, 0.11, and 0.08 a.u. for diamond, GaP, and Si, respectively. For silicon the charge contours can be compared quantitatively to calculations employing a converged plane-wave set[12] and to full-core linearized augmented, plane-wave[13] (LAPW) calculations. Deviations of ~1% appear between the two calculations (40 Gaussians versus 170 plane waves) employing the HCS pseudopotential, while errors of ~3% outside the core region occur with respect to the full-core results. Qualitatively, the charge contours exhibit the characteristic two-peak structure in the bonding charge for diamond and exhibit the elongated form for silicon.

In Table IV we compare calculated band-structure energies at some selected high-symmetry $\vec{k}$ points. As can be seen, the local orbital and plane-wave pseudopotential results deviate from each other by less than 0.25 eV for diamond and silicon. This confirms the adequacy of our Gaussian basis set. No plane-wave results are currently available for GaP using HSC pseudopotentials. We

TABLE V. Comparison of calculated and measured structural properties of diamond, silicon, and GaP.

	$E_{\min}$ (Ry)	a_0 (Å)	B (10^{12} erg/cm^2)
Diamond			
Local orbitals	−11.107(3%)	3.69(3%)	4.56(4%)
Plane waves (Ref. 12)	−11.366	3.60	4.41
Experiment (Ref. 14)	−11.384	3.57	4.42
Si			
Local orbitals	−7.734(2%)	5.52(2%)	1.02(3%)
Plane waves (Ref. 3)	− 7.909(−0.1%)	5.46(1%)	0.97(−2%)
Experiment (Ref. 14)	−7.919	5.43	0.99
GaP			
Local orbitals	−8.790(1%)	5.16(−5%)	0.92(4%)
Experiment (Ref. 14)	−8.836	5.45	0.89

also have compared the C and Si results with the full-core LAPW calculation of Hamann.[13] The deviations are typically within ~ 0.3 eV, except for some high-energy bands where errors of up to 0.6 eV can occur. The deviations from the full-core LAPW results arise from the combination of the pseudopotential approximation on one hand, and the different numerical techniques used to solve Schrödinger's equation on the other hand. These two effects have been studied separately for silicon,[11] for which LAPW results are given using identical HCS pseudopotentials. A comparison of the values in Table IV clearly shows that the difference in numerical treatment introduces the larger error (~ 0.2 eV) while the pseudopotential approximation is only responsible for errors of ~ 0.05 eV.

The total energies are calculated for several $(3-5)$ lattice constants ranging from 0.95 to 1.1 a_0. The minimal total energy, the equilibrium lattice constant, and the bulk modulus are determined from quadratic fits to the calculated total-energy values. The results are given in Table V and compared to Yin and Cohen's[3,12] plane-wave results and experimental values. The experimental values for the minimum total crystal energy are calculated from the sum of atomic valence ionization energies,[14] the cohesive energy,[15] and the zero-point vibration energy.[15] The agreement between our calculated values and experiment is generally good $(1-4\,\%)$, but not as good as the converged plane-wave results of Yin and Cohen.[3,12] In particular, our energy parabolas are shifted upwards, almost rigidly, by about $2-4$ eV as a consequence of the limited variational freedom available with 20 Gaussians per atom. While this shift, which amounts to only $2-3\,\%$ of the total energy, does not allow us to determine cohesive energies, it does not affect adversely the computation of lattice constant and bulk modulus. This is the key result of our study and demonstrates that norm-conserving pseudopotentials (e.g., of the HSC type) combined with a reasonably sized Gaussian basis can successfully be used to self-consistently calculate structural properties. This result is a prerequisite for attempting structural total-energy studies of reconstructions at surfaces or around defects.

ACKNOWLEDGMENT

We have benefited from helpful discussions with D. R. Hamann.

---

[1] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).

[2] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, *ibid.* 140, A1133 (1965).

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

[4] S. G. Louie, M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1654 (1976).

[5] F. Bassani, G. Iadonisi, and B. Preziosi, Phys. Rev. 186, 735 (1969); M. Jaros and J. Brand, *ibid.* 14, 4494 (1976).

[6] J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. B 21, 3545 (1980).

[7] G. A. Baraff and M. Schlüter, Phys. Rev. B 19, 4965 (1979); G. A. Baraff, E. O. Kane, and M. Schlüter, *ibid.* 21, 5662 (1980).

[8] P. J. Feibelman, D. R. Hamann, and J. A. Appelbaum, Phys. Rev. B 20, 1433 (1979).

[9] V. Mednick and L. Kleinmann, Phys. Rev. B 22, 5768 (1980).

[10] G. A. Baraff (unpublished).

[11] D. R. Hamann and M. Schlüter (unpublished).

[12] M. Yin and M. L. Cohen (unpublished).

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

[14] *Handbook of Chemistry and Physics,* 58th ed., edited by R. C. Weast (CRC, Cleveland, 1978); C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D.C., 1949); Circular No. 467, Vol. I.

[15] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973); C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971).