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Calculation of structurally related properties of bulk and surface Si

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The self-consistent pseudopotential method is applied to study the bulk and surface structurally related properties of Si. Equilibrium configurations are determined by minimizing the total energy of the system; the calculated bulk properties and the surface relaxation of Si are found to be in good agreement with experiment. The surface energy and the surface reconstruction of Si are briefly discussed.

I. INTRODUCTION

Structural properties of Si involving the total energy have been studied extensively using the pseudopotential method.[1-3] Among these properties are the equilibrium lattice constant, crystal energy, cohesive energy, bulk modulus, and the stable crystal structure. On the other hand, although the surface structure of Si and the structural energy gained in the surface formation have drawn considerable attention,[4-10] accurate calculations are difficult and, hence, rare. In fact, the present work represents the first self-consistent attempt to calculate the total energy of both bulk and surface Si. A momentum-space formalism derived previously[11] has been used to simplify the computational procedure. The only input is the ionic pseudopotential[12] obtained by fitting to atomic spectra. Although this pseudopotential is a local version of the more accurate nonlocal pseudopotential, the agreement between the present local calculation and experimental data is satisfactory for most properties of bulk Si.

The calculations presented here of the total energy of the unrelaxed and relaxed surface predict an inward relaxation of ~0.16 Å for the Si (111) surface, in good agreement with experiment.[4,5] There is no essential difficulty in calculating the surface energy, but we have found that a much bigger unit cell (and, hence, more computation time) is required to obtain an accurate estimate of the surface energy. Determination of the equilibrium surface reconstruction by minimizing the total energy of the system does not seem possible at present. In particular, the required matrix size is unmanageably large for the reconstructed geometries (e.g., for the Si 7×7 surface). In addition, there are many possible configurations of reconstruction to be tested (unless the calculation is restricted to comparison among a few simple configurations as was done successfully by Chadi[10]). A more difficult point is the lack of detailed knowledge of the surface energetics since surface reconstruction is known to be temperature dependent and sensitive to environment.[9] The experimental temperature dependence indicates that the reconstruction probably involves an energy gain of the order of 0.01 eV per surface atom between different configurations; calculations of this accuracy for the surface cannot be claimed at present. The question of the reliability of the pseudopotential method in studying the phase stability is also discussed in the text.

The rest of this paper is organized as follows: The calculational procedure of the self-consistent pseudopotential method is briefly described in Sec. II, and the total energy formulas derived in Ref. 11 are given. The results of the bulk and surface Si calculations are presented in Sec. III and Sec. IV, respectively.

II. CALCULATIONAL PROCEDURE

The self-consistent pseudopotential method has been described in detail elsewhere.[12] Self-consistency here means the self-consistent response of the valence electrons to a given structure of ions. In the present calculations, self-consistent iterations continue until the screening potential is stable within 10^{-4} Ry together with the same degree of stability for the total energy. For surface calculations in Sec. IV, the criterion is somewhat relaxed to ~10^{-3} Ry.

The local pseudopotential of Si used here is

$$U_{\mathrm{ps}}(G)=\frac{a_1}{G^2}(\cos a_2 G+a_3)e^{a_4 G_4}\,, \tag{1}$$

where $a_1=-1.1463$ (for the bulk with $a_c=5.43$ Å), $a_2=0.790\,65$, $a_3=-0.352\,01$, and $a_4=-0.018\,07$, respectively. Rydberg atomic units are used throughout the paper. This pseudopotential for Si has been used successfully for various solid-state calculations.[12] The total energy *per atom* is[11]

$$E_{\mathrm{total}}=\Omega_{\mathrm{at}}\Big(\sum_{i,\vec{G}}|\psi_i(\vec{k}_i+\vec{G})|^2(\vec{k}_i+\vec{G})^2+\frac{1}{2}\sum_{\vec{G}\neq 0}V_H(\vec{G})\rho(\vec{G})+\frac{3}{4}\sum_{\vec{G}}\mu_{xc}(\vec{G})\rho(\vec{G})+\sum_{\vec{G}\neq 0}S(\vec{G})U_{\mathrm{ps}}(\vec{G})\rho(\vec{G})\Big)+\alpha_1 Z+\gamma_{\mathrm{Ewald}}\,, \tag{2}$$

where Ω_{at} is the atomic volume, Z is the valency, the $\vec{G}$'s are reciprocal-lattice vectors, and $S(\vec{G})$ is the structure factor. $\psi_i(\vec{k}_i+\vec{G})$, $V_H(\vec{G})$, $\rho(\vec{G})$, $\mu_{xc}(\vec{G})$, and $U_{\text{ps}}(\vec{G})$ are Fourier transforms of the electron wave function, the Hartree potential, the total (valence) charge density, the exchange-correlation potential, and the local pseudopotential. The index i represents both the wave vector k_i and band index n and runs over occupied states of the valence electrons. α_1 and γ_{Ewald} are[11]

$$\alpha_1=\lim_{G\to 0}\left(U_{\text{ps}}(G)+\frac{8\pi Z}{\Omega_{\text{at}}G^2}\right)=\frac{1}{\Omega_{\text{at}}}\int\left(U_{\text{ps}}(r)+\frac{2Z}{r}\right)d^3r\,, \tag{3}$$

$$\gamma_{\text{Ewald}}=\frac{1}{2}\left(\sum_{\nu}\frac{2Z^2}{|\vec{R}_\nu|}-\frac{1}{\Omega_{\text{at}}}\int\frac{2Z^2}{r}d^3r\right), \tag{4}$$

where the $\vec{R}_\nu$'s are lattice vectors to ionic sites. An alternative form for the total energy is[11]

$$E_{\text{total}}=\sum_i\epsilon_i-\Omega_{\text{at}}\left(\frac{1}{2}\sum_{\vec{G}\neq 0}V_H(\vec{G})\rho(\vec{G})+\frac{1}{4}\sum_{\vec{G}}\mu_{xc}(\vec{G})\rho(\vec{G})\right)+\alpha_1Z+\gamma_{\text{Ewald}} \tag{5}$$

where the ϵ_i's represent the eigenvalues of the valence electron wave functions. α_1Z is calculated and shown in Table I for typical pseudopotentials of Si appearing in the literature.[13-19] For nonlocal pseudopotentials, the average of the s and p pseudopotentials is given. Note that the choice of the local part from the nonlocal pseudopotentials is not unique as discussed in Ref. 11. Not all the pseudopotentials derived from the atomic properties can be used in the momentum-space formalism. For example, α_1 for the Simons-Bloch pseudopotential[18] diverges (unless an artificial cutoff of the $1/r^2$ tail is introduced) because of the unphysically long-range character of the $1/r^2$ potential added to $-2Z/r$. The relatively large fluctuation of α_1Z (~1 Ry) among different pseudopotentials does not invalidate the

TABLE I. Typical ionic pseudopotentials of Si. α_1Z is evaluated for these pseudopotentials ($Z=4$).

Reference	Pseudopotential	α_1Z (numerical value in Ry; at $a_c=5.43$ Å)
SCLC[a]	$\frac{a_1}{q^2}[\cos(a_2q)+a_3]\exp(a_4q^4)$	1.433 17
AH[b]	$\frac{2}{\Omega_{\text{at}}}\left[-\frac{4\pi Z}{q^2}+\left(\frac{\pi}{\alpha}\right)^{3/2}\nu_1+\left(\frac{\pi}{\alpha}\right)^{3/2}\left(\frac{3}{2\alpha}-\frac{q^2}{4\alpha^2}\right)\nu_2\right]\exp(-q^2/4\alpha)$	0.990 60
FK[c]	$-\frac{e^2}{r}(Z'-Q+Qe^{-\alpha r})+\frac{Z'e^2}{r}\exp[-\sqrt{(Q/Z)}\,\alpha r]+\frac{V_c\gamma^3}{(2\pi)^{3/2}}\exp[-(\gamma^2r^2/2)]$	1.652 93
Ashcroft[d]	$U(r)=\begin{cases}0, & r<r_c\\ -\frac{2Z}{r}, & r>r_c\end{cases}$	1.392 12
TH[e]	$U(r)=\begin{cases}V_0\cos kr+C_0, & r<r_c\\ -\frac{2Z}{r}, & r>r_c\end{cases}$	?
Heine[f]	$U(r)=\begin{cases}-\sum A_lP_l, & r<r_c\\ -\frac{2Z}{r}, & r>r_c\end{cases}$	1.518 58
Simons[g]	$U(r)=\frac{-2Z}{r}+\sum_l\frac{A_lP_l}{r^2}$	∞
Zunger-Cohen[h]	(first-principles pseudopotential)	1.962

[a] Reference 12. This is used in the present calculations.
[b] Reference 13. This gives the smallest α_1Z, i.e., it is most attractive.
[c] Reference 14. $Z'-Q=4$ here.
[d] References 2 and 15. We used an *unadjusted* r_c in Ref. 2.
[e] References 3 and 16. C_0 and V_0 are not given in Ref. 3.
[f] Reference 17. The given value is the average of the s and p pseudopotentials.
[g] Reference 18. This pseudopotential cannot be used in our scheme as discussed in the text.
[h] Reference 19. The given value is the average of the s and p pseudopotentials. The unusually large α_1Z originates from the r^{-2} behavior near $r=0$ typical for any *ab initio* pseudopotentials.

pseudopotential scheme. For example, the pseudopotential used by Zunger and Cohen[19] has a very strong repulsive core, hence, a large $\alpha_1 Z$, but its major effect is a rigid shift of the band structure downward with respect to the average potential.[11] Therefore, $\sum_i \epsilon_i + \alpha_1 Z$ is insensitive to the pseudopotentials used as long as they are not pathological. γ_{Ewald} is readily available in the literature.[20] γ_{Ewald}'s for representative structures normalized to one electron per atom are listed below:

$$\gamma_{\text{Ewald}}{}^{(\text{diamond})} = -5.386\,80/a_c = -1.670\,85/r_s\,, \qquad (6)$$

$$\gamma_{\text{Ewald}}{}^{(\text{fcc})} = -4.584\,88/a_c = -1.791\,75/r_s\,, \qquad (7)$$

$$\gamma_{\text{Ewald}}{}^{(\text{bcc})} = -3.639\,24/a_c = -1.791\,86/r_s\,, \qquad (8)$$

$$\gamma_{\text{Ewald}}{}^{(\text{hcp})} = -3.241\,87/a = -1.791\,68/r_s\,, \qquad (9)$$

$$\gamma_{\text{Ewald}}{}^{(\text{white Sn})} = -5.524\,08/a = -1.773\,02/r_s\,, \qquad (10)$$

where a_c is the lattice constant of the cubic system. $c/a = \sqrt{8/3}$ and 0.554 are assumed for the hcp and white Sn structures, respectively. Values for the diamond, fcc, and bcc structures are quoted from Ref. 20 [γ(diamond) can be calculated from the relation $\gamma(\text{diamond}) = \gamma(\text{fcc}) + \gamma(\text{bcc}) - \gamma(\text{sc})$ for the same a_c], and values for the hcp, white Sn, and the slab structure (appearing in the surface calculation in Sec. IV) are calculated analytically using the method of Ref. 20.

Ten special points[21] in the irreducible Brillouin zone ($\frac{1}{48}$ of the Brillouin zone) are sampled in the bulk calculation for the diamond structure and equivalently for other structures. Stability of the summation over $\vec{k}_i$ is tested by comparing the results with 34 evenly spaced points using the Gilat-Raubenheimer scheme.[22] For surface calculations, 18 special points[23] in the irreducible zone ($\frac{1}{12}$ of the whole zone) are taken and tested against 28 evenly spaced points. Three or four iterations are sufficient to achieve the desired self-consistency of bulk Si starting with the empirical pseudopotential used in Ref. 12. In the bulk calculation, we include plane waves up to 6.4 Ry in kinetic energy in the basis set and another set of plane waves up to 12 Ry through Löwdin's second-order perturbation scheme.[24] These numbers correspond to ~80 plane waves and another ~100 plane waves in the basis set. The criterion is relaxed to 2.7 Ry and 5.5 Ry in the kinetic energy for the surface calculation.

III. BULK Si

The results for bulk Si are listed in Tables II–IV. A portion of these results has been reported elsewhere.[25] Before proceeding to the discussion of the results, it is helpful to illustrate the validity of Eq. (2) or (5) in a somewhat more "physically transparent" way. We first calculated the total energy of the Si *atom* in real space using the same pseudopotential as used in the bulk. In this case, terms such as α_1 and γ_{Ewald} do not appear (Table II). The total energy of the bulk is then calculated with a large lattice constant ($a_c = 10.6$ Å) using Eq. (5). This should yield the atomic total energy in the limit of $a_c = \infty$. $\alpha_1 Z$ and γ_{Ewald}, which are artifacts of the periodicity introduced deliberately to facilitate the momentum-space formalism, still have sizable contributions at $a_c = 10.6$ Å, but the total energy of this system converges to the total energy of the atom to within 0.04 Ry. This represents evidence of the validity of Eq. (2) or (5).

The total energies of Si for different lattice constants and α's in the $X\alpha$ scheme are listed in Table III. The value $\alpha = \frac{2}{3}$ corresponds to Kohn and Sham's[26] choice, and $\alpha = 1.0$ is Slater's[27] value.

TABLE II. The atomic energy of Si is compared to the bulk energy calculated from Eq. (2) with a very large lattice constant ($a_c = 20a_{\text{Bohr}}$). $\alpha = 0.794$ in the $X\alpha$ scheme is used here (see text). At $a_c = 20a_{\text{Bohr}}$ (=10.58 Å), the bulk total energy is quite close to that for isolated atoms (within 0.04 Ry). Values are in Ry.

Atom		Bulk ($a_c = 20a_{\text{Bohr}}$)	
Kinetic	2.366 61	Kinetic	2.141 57
$\int U_{ps}\rho\, d^3r$	−13.664 42	$\Omega_{at}\sum' S(G)U_{ps}(G)\rho(G)$	−5.547 11
		$\alpha_1 Z$	0.193 56
$\frac{1}{2}\int V_H\rho\, d^3r$	5.749 50	$\frac{\Omega_{at}}{2}\sum' V_H(G)\rho(G)$	1.943 18
		γ_{Ewald}	−4.309 45
$\frac{3}{4}\int \mu_{xc}\rho\, d^3r$	−1.866 89	$\frac{3\Omega_{at}}{4}\sum_G \mu_{xc}(G)\rho(G)$	−1.877 38
Total	−7.415 20	Total	−7.455 63

To see the dependence of the total energy on α, we make one more choice of α at an intermediate value. $\alpha = 0.794$ has been chosen in accordance with the choice of Appelbaum and Hamann (AH),[13] which brings Slater's exchange into agreement with Wigner's interpolation formula[28] for the average valence charge density of Si ($r_s = 2.005$). This value is very close to that suggested by Hedin and Lundqvist[29] for the *average* charge density of Si ($\alpha = \frac{2}{3} \times 1.18$) although their α is density dependent.

In Eq. (2) we have a numerical factor, $\frac{3}{4}$, multiplying μ_{xc}. For any terms coming from electron-electron interactions, we normally expect to have an overall factor of $\frac{1}{2}$ as in the electron-electron Coulomb energy. Since $3\alpha/4$ is the effective factor multiplying the original Slater exchange potential,

TABLE III. The total energy of Si for different lattice constants using $\alpha = \frac{2}{3}$, $\alpha = 0.794$, and $\alpha = 1.0$ as explained in the text. For $\alpha = 1.0$, both $\frac{3}{4}\mu_{xc}$ and $\frac{1}{2}\mu_{xc}$ + correlation are given.

			$\alpha = \frac{2}{3}$		
a_c	5.658 Å	5.43 Å	5.21 Å	5.0 Å	4.8 Å
Kinetic	2.614 11	2.775 66	2.944 10	3.122 24	3.300 28
$\Omega_{\mathrm{at}} \sum' S(G) U_{\mathrm{ps}}(G) \rho(G)$	−1.972 20	−1.861 82	−1.748 78	−1.631 49	−1.498 33
$\alpha_1 Z$	1.266 83	1.433 17	1.622 52	1.835 64	2.074 81
$\frac{1}{2}\Omega_{\mathrm{at}} \sum' V_H(G) \rho(G)$	0.516 75	0.465 45	0.413 19	0.360 00	0.305 31
γ_{Ewald}	−8.061 03	−8.399 49	−8.754 17	−9.121 84	−9.501 92
$\frac{3}{4}\Omega_{\mathrm{at}} \sum \mu_{xc}(G) \rho(G)$	−1.938 44	−1.999 08	−2.061 78	−2.126 09	−2.191 27
Correlation [a]	−0.368 64	−0.373 74	−0.378 87	−0.383 97	−0.389 03
Total	−7.942 63	−7.959 86	−7.963 79	−7.945 52	−7.900 15
			$\alpha = 0.794$		
Kinetic	2.651 54	2.811 53	2.977 40	3.152 08	3.325 63
$\Omega_{\mathrm{at}} \sum' S(G) U_{\mathrm{ps}}(G) \rho(G)$	−2.029 02	−1.915 55	−1.798 59	−1.676 48	−1.537 43
$\alpha_1 Z$	1.266 83	1.433 17	1.622 52	1.835 64	2.074 81
$\frac{1}{2}\Omega_{\mathrm{at}} \sum' V_H(G) \rho(G)$	0.547 61	0.493 46	0.438 12	0.381 60	0.323 37
γ_{Ewald}	−8.061 03	−8.399 49	−8.754 17	−9.121 84	−9.501 92
$\frac{3}{4}\Omega_{\mathrm{at}} \sum \mu_{xc}(G) \rho(G)$	−2.322 39	−2.393 58	−2.466 98	−2.542 15	−2.618 17
Total	−7.946 46	−7.970 46	−7.981 69	−7.971 09	−7.933 72
			$\alpha = 1.0$		
Kinetic	2.718 56	2.876 30	3.037 47	3.205 86	3.371 30
$\Omega_{\mathrm{at}} \sum' S(G) U_{\mathrm{ps}}(G) \rho(G)$	−2.124 92	−2.007 47	−1.883 79	−1.753 47	−1.604 19
$\alpha_1 Z$	1.266 83	1.433 17	1.622 52	1.835 64	2.074 81
$\frac{1}{2}\Omega_{\mathrm{at}} \sum' V_H(G) \rho(G)$	0.601 89	0.543 46	0.482 63	0.420 22	0.355 60
γ_{Ewald}	−8.061 03	−8.399 49	−8.754 17	−9.121 84	−9.501 92
$\frac{3}{4}\Omega_{\mathrm{at}} \sum \mu_{xc}(G) \rho(G)$	−2.955 51	−3.043 22	−3.132 76	−3.224 16	−3.316 25
(Total) [b]	(−8.554 18)	(−8.597 25)	(8.628 10)	(−8.637 75)	(−8.620 64)
$\frac{1}{2}\Omega_{\mathrm{at}} \sum \mu_x(G) \rho(G)$	−1.970 34	−2.028 81	−2.088 51	−2.149 44	−2.210 83
Correlation	−0.368 64	−0.373 74	−0.378 87	−0.383 97	−0.389 03
Total [c]	−7.937 65	−7.956 58	−7.962 72	−7.947 00	−7.904 25

[a] Reference 30. Nozières-Pines correlation = $Z(-0.115 + 0.031 \ln r_s)$.

[b] Using $\alpha = 1.0$ we overestimate the exchange correlation.

[c] This row is obtained by replacing $\frac{3}{4}\Omega_{\mathrm{at}} \sum \mu_{xc}\rho$ by $\frac{1}{2}\Omega_{\mathrm{at}} \sum \mu_x \rho$ + correlation.

TABLE IV. The total energy of Si ($\alpha = \frac{2}{3}$) for different phases of their respective equilibrium lattice constants. The exchange coefficient C_x (see text) is also given.

Structure	Diamond	bcc	fcc	hcp	White Sn
	$a_c = 5.21$ Å	$a_c = 2.77$ Å	$a_c = 3.49$ Å	$a = 2.47$ Å	$a = 4.64$ Å
	($r_s = 1.924$)	($r_s = 1.625$)	($r_s = 1.625$)	($r_s = 1.625$)	($r_s = 1.772$)
Kinetic	2.944 10	3.411 39	3.424 12	3.167 23	2.773 70
$\Omega_{at} \sum' S(G) U_{ps}(G) \rho(G)$	−1.748 78	−0.264 87	−0.294 37	−0.041 64	−0.276 09
$\alpha_1 Z$	1.622 52	2.693 68	2.693 68	2.693 68	2.074 81
$\frac{1}{2} \Omega_{at} \sum' V_H(G) \rho(G)$	0.413 19	0.014 75	0.023 41	0.003 99	0.033 18
γ_{Ewald}	−8.754 17	−11.116 44	−11.115 76	−11.115 29	−10.082 91
$\frac{3}{4} \Omega_{at} \sum \mu_{xc}(G) \rho(G)$	−2.061 78	−2.267 00	−2.271 64	−2.258 33	−2.089 68
Correlation	−0.378 87	−0.399 82	−0.399 82	−0.399 82	−0.389 03
Total	−7.963 79	−7.928 30	−7.940 39	−7.950 18	−7.956 02
C_x factor	0.991 61	0.920 97	0.922 85	0.917 45	0.925 73

the self-consistent $X\alpha$ method is consistent with Slater's exchange energy if and only if $\alpha = \frac{2}{3}$. In this case, μ_{xc} represents pure exchange. If α is larger than $\frac{2}{3}$, we effectively include some correlation contributions in an approximate way. No attempt was made to include a separate correlation potential (e.g., Hedin-Lundqvist potentials in Ref. 29) in the Schrödinger equation. Rather, an *ad hoc* correlation term was added to Eq. (2) when $\frac{2}{3}$ was chosen for α. The correlation energy of the free electron gas given by Nozières and Pines[30] was used for the average charge density of Si giving good results as shown below. We can see in Table III that the total energy for $\alpha = \frac{2}{3}$, including the correlation correction, turns out to be very close to that for $\alpha = 0.794$. With $\alpha = 1.0$ we have obviously overestimated (in magnitude) the exchange-correlation energy. Therefore, the change of the numerical factor of $\frac{3}{4}$ to $\frac{1}{2}$ is made here as is usually done for non-self-consistent calculations. The result is in remarkable agreement with that for $\alpha = \frac{2}{3}$. This implies that the choice of α in the total energy calculation can be balanced by a corresponding change in the numerical factor multiplying μ_{xc}. For instance, the total energy for $\alpha = 0.794$ agrees with that for $\alpha = \frac{2}{3}$ if the numerical coefficient of $\frac{1}{2} \times 1/0.794$ is assumed. On the other hand, if we consistently have the multiplying factor of $\frac{3}{4}$, then the total energy is linear in α up to 10^{-3} Ry,

$$E_{\text{total}}(\alpha) = E_{\text{total}}(\tfrac{2}{3}) + A(\alpha - \tfrac{2}{3}), \tag{11}$$

where A is a constant. $E_{\text{total}}(0.79)$ coincides with $E_{\text{total}}(\frac{2}{3})$ plus the Nozières-Pines correlations.

The equilibrium lattice constant a_c, the total (crystal) energy E_{total}, and the bulk modulus B are obtained by a weighted least-square fitting to data points with a parabola. Using $\alpha = \frac{2}{3}$, we get $a_c = 5.32$ Å, $E_{\text{total}} = -7.96$ Ry, and $B = 1.8 \times 10^{12}$ dyn/cm^2. The zero-point vibrational energy (~0.06 eV) is neglected. Results for $\alpha = 0.794$ or $\alpha = 1.0$ do not differ significantly. Experimentally, $a_c = 5.43$ Å, $E_{\text{total}} = -7.919$ Ry, and $B = 0.99 \times 10^{12}$ dyn/cm^2.[31,32] Previously reported values in Ref. 25 differ slightly from the present results. Equation (2) was used in Ref. 21 while Eq. (5) is used at present. The difference arises because folded-down elements of the wave functions are not reexpanded in our approximate treatment of the second-order terms. However, both equations give similar values for a_c and B; i.e., the difference between them is an almost rigid shift of the total energy. We tested the validity of our scheme by doing separate calculations without the second-order perturbation approximation (solving ~180 ×180 matrices for bulk Si). The result agrees very well with Eq. (5) using 80 plane waves plus an extra 100 planes through the second-order perturbation scheme. The difference is only 0.005 Ry, and more importantly, the difference is almost a constant, resulting in no change in a_c and B.

In Tables II-IV, the total energy is first obtained from Eq. (5); the ion-valence-electron interaction energy $\Omega_{at} \sum S(G) U_{ps}(G) \rho(G)$ is evaluated independently, and the kinetic energy is deduced by subtracting out all other contributions from the sum of eigenvalues. This decomposition is done to see the trends of various components. Some individual components like the kinetic energy and the ion-electron interaction energy may not be as accurate as the total energy. (The kinetic energy is that of the pseudovalence electrons; it is not directly observable anyway.)

The calculated bulk modulus seems to be very sensitive to the pseudopotential used. It is overestimated by about 80% here while Morita *et al.*[2] have obtained a value which is an underestimate by 20–30% using Ashcroft's pseudopotential with the equilibrium lattice constant *adjusted* to experiment. Ohkoshi *et al.*[3] get $B=1.39\times10^{12}$ dyn/cm^2 while Wendel *et al.*[33] obtain $B=0.70\times10^{12}$ dyn/cm^2 using the AH pseudopotential. We believe that more refined nonlocal pseudopotentials which reproduce the atomic wave functions and eigenvalues more accurately would account for the discrepancy.

The crystal energy is defined by

$$\text{crystal energy (per atom)} = -\text{cohesive energy} - \sum_{i\,(\text{valence electrons})} (i\text{th ionization potential})\,. \qquad (12)$$

For Si, the sum of the four ionization potentials is 103.12 eV,[32] and the experimental cohesive energy is 4.63 eV,[31] hence, the crystal energy is −7.919 Ry. Though our calculated crystal energy −7.96 Ry is in good agreement with experiment, there is a more stringent test to check the reliability of the pseudopotential method. The calculated atomic energy using the pseudopotential should agree with the sum of the four ionization potentials of the atom. Additional complications, however, are involved in the atomic energy calculation because spin polarization[34] must be considered for an atom with an unfilled outer shell. We have shown in Table II that the calculated atomic energy without spin polarization is −100.88 eV using $\alpha=0.794$. Comparing the E_{total} for $\alpha=0.794$, we get ~7.7 eV for the cohesive energy without spin polarization. (We have chosen $\alpha=0.794$ rather than $\alpha=\frac{2}{3}$ because the Nozières-Pines correlation is not applicable for an isolated atom.) We do not know the energy gain due to the spin polarization for Si. For diamond, the calculated cohesive energy is reduced by 4.1 eV by including spin polarization in the all-electron calculation.[35] A smaller reduction is expected for Si. A reduction of the total energy of the Si atom by 3 eV would bring the calculated cohesive energy in agreement with experiment.

In a non-self-consistent calculation, Wendel *et al.*[33] obtained $a_c=4.7$ Å using the AH pseudopotential with $\alpha=0.855$. Using the present self-consistent scheme, the AH pseudopotential ($\alpha=0.794$) yields $a_c=4.95$ Å; $a_c=4.9$ Å would be obtained with $\alpha=0.855$. The AH pseudopotential is, indeed, too attractive as pointed out in Ref. 33. We can see immediately from Table I that the AH potential gives an unusually small $\alpha_1 Z$.

In Fig. 1, each term contributing to the total energy is plotted as a function of the lattice constant. Note that the kinetic energy here corresponds to the smoothed pseudo-wave functions. Therefore, the behavior of the kinetic energy is far from the free electron value $2.21Z/r_s^2$. As has been shown in Ref. 11, the usual virial theorem ($E_{\text{kin.}}=-\frac{1}{2}E_{\text{pot.}}$ at equilibrium) does not hold. $\alpha_1 Z$, γ_{Ewald}, the Hartree energy, and the ion-electron interaction energy are considered together because they are not independent. The exchange energy is larger in magnitude than the free electron value of $0.916Z/r_s$ as expected for covalent materials. The correlation energy, while contributing significantly to the crystal energy, plays a minor role in determining the equilibrium lattice constant. Without the correlation term, a_c and B change only by order of 1%. This in part justifies our approxi-

TABLE V. The average energy *per atom* of the Si (111) surface (unrelaxed and relaxed) simulated by 12 layers of Si and five equivalent vacuum layers. Therefore, the total energy in this table is the total energy of the unit supercell divided by 12. α is $\frac{2}{3}$ and correlation energies are assumed the same.

	Unrelaxed	Relaxed (0.165 Å)	Relaxed (0.33 Å)
Kinetic	2.688 69	2.710 43	2.725 15
$\Omega_{\text{at}}\sum' S(G)U_{\text{ps}}(G)\rho(G)$	−40.677 85	−42.060 42	−43.524 61
$\alpha_1 Z$	1.011 65	1.011 65	1.011 65
$\frac{1}{2}\Omega_{\text{at}}\sum' V_H(G)\rho(G)$	19.597 31	20.236 48	20.957 56
γ_{Ewald}	11.827 74	12.555 58	13.291 90
$\frac{3}{4}\Omega_{\text{at}}\sum \mu_{xc}(G)\rho(G)$	−1.937 53	−1.945 22	−1.951 35
Correlation	−0.373 74	−0.373 74	−0.373 74
Total	−7.863 73	−7.865 24	−7.863 54

mation to the correlation contribution.

In considering the structural stability of bulk Si, the total energy and the equilibrium lattice constant are calculated for the bcc, fcc, hcp, and white Sn structures. We find that the equilibrium r_s's for bcc, fcc, and hcp structures are almost the same ($r_s \simeq 1.63$), and the r_s for the white tin structure (~1.8) is midway between the diamond structure and the others. The calculated nearest-neighbor distance is ~2.4 Å for the white Sn and bcc structures and ~2.5 Å for the fcc and hcp structures compared with ~2.3 Å for the diamond structure. These four structures (white Sn, bcc, fcc, and hcp) are all found to be metallic from the calculated band structures. The total energies near the respective equilibrium lattice constants are presented in Table IV. The diamond structure does give a lower energy than any metallic structures. Morita *et al.* obtained similar results[2] while the hcp structure was the most stable one in Weaire's calculation.[1] The pseudopotential form factors for the smallest G for three structures [$V(111)$ for fcc, $V(110)$ for bcc, and $V(001)$ for hcp] are non-negative, which is another feature characteristic of metals.[36] $V(001)$ for the hcp structure is zero in effect when we multiply by the structure factor, and the next smallest component [$V(100)$] is positive. The smallest nonzero form factor for white Sn structure [$V(200)$] is very slightly negative.

It is generally believed that the diamond structure is stable relative to the others because of the exchange energy gained in forming covalent bonds. The exchange energies listed in Table IV cannot be compared to each other directly since the respective lattice constants are different. The exchange energy for each structure has been calculated with the same r_s ($=2.005$), and the diamond structure has been found to have the largest exchange energy in magnitude. To examine the behavior of the exchange term in more detail, the exchange energy may be expressed as $-C_x Z/r_s$ where C_x is 0.916 for a free-electron model. C_x is a measure of the covalent character of the homopolar material. C_x for the structures studied here are presented in the same table. C_x is only slightly greater than 0.916 for metallic structures. We note that core orthogonalization may bring about additional contribution to C_x. C_x is closely related to the maximum charge density at the center of the covalent bond.

In Fig. 2, the charge density plots are shown for the diamond and white Sn structures. (See Ref. 21 for figures of other structures.) They are plotted on the same scale for comparison. The strong covalent bonds for the diamond structure are obvious, and the maximum charge density is 25 compared with 12 in the white Sn structure. There are eight electrons per unit cell in each

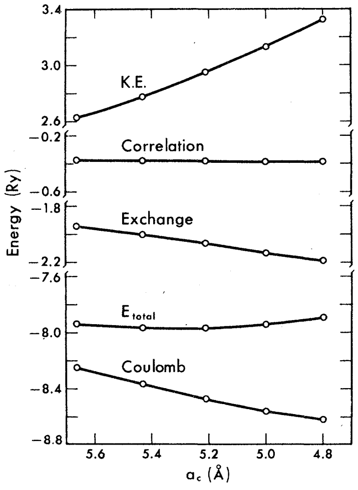
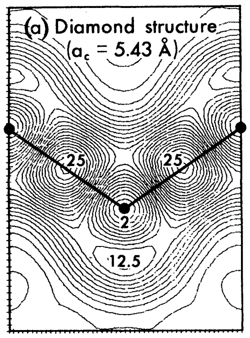


FIG. 1. Behavior of various components of the crystal energy of Si [entering Eq. (2)] as a function of the lattice constant. $\alpha_1 Z$, γ_{Ewald}, the Hartree energy, and the ion-electron interaction energy are considered together and denoted by "Coulomb" in the figure. This plot is for the diamond structure with $\alpha = \frac{2}{3}$. Note how small the variation of E_{total} is compared with each component.



(b) White Sn (a = 4.64 Å)

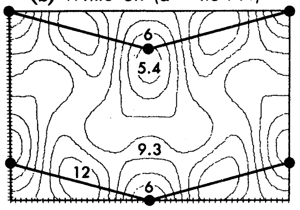


FIG. 2. The total valence charge density contours of bulk Si for (a) the diamond structure at $a_c = 5.43$ Å, and (b) the white Sn structure at $a = 4.64$ Å. Plots are in (110) plane for the diamond and in (010) plane for the white Sn structure. Heavy dots represent atomic sites, and solid lines connect nearest neighbors. Normalization corresponds to eight electrons per unit cell. Successive contours are separated by 1. The figures are plotted on the same scale for comparison.

case. The maximum charge density was 10 for all three other structures.[25] The behavior of the white tin structure is intermediate between the diamond and more metallic structures. Although the white tin structure has four nearest neighbors, the ratio of the next-nearest-neighbor distance to the nearest-neighbor distance is only 1.07 (with $c/a=0.554$). Therefore, the coordination number is almost six, falling between the diamond and the bcc structure. The same trends for the charge density, exchange energy, minimum total energy, and the normalized equilibrium lattice constant (r_s) were observed above. Indeed, the diamond structure has been found to undergo a phase transition to the white tin structure under high pressure.[1,37] The same calculations for the graphite or wurtzite structure would be desirable to study the phase stability. However, the structural energy gain relative to these structures is expected to be very small—probably of the order of 10^{-2} eV/atom. Approximations involved in the pseudopotential method and the exchange-correlation energy are of this order.

We have assumed above that the core is independent of the structure; i.e., we have used the same pseudopotential regardless of the structure. Janak[38] has carried out self-consistent KKR calculations for different phases (fcc and bcc) of Be and Na and concluded that the change in the energy of core states can be comparable to or larger than the stabilization energy between phases. We do not have data for the core state energy shift for Si. The theoretical prediction of the more stable phase between the diamond and the metallic structures is still expected to be reliable because the calculated stabilization energy for Si (~0.1 eV) is much larger than the value obtained by Janak for Na (~0.005 eV) or for Be (~0.01 eV). Approximations for the correlation energy may also be crucial in the latter cases.

IV. Si (111) SURFACE

In this section, we present results of the total energy for unrelaxed and relaxed Si(111) surfaces. The periodicity of the system which is essential in the present formalism is retained in the form of repeated slabs. The unit "supercell" has 12 Si atoms plus vacuum layers equivalent to 2.5 Si layers in thickness on each side. As each unit cell has two "surface" atoms, the surface energy per surface atom is obtained by comparing the average energy per atom in this system and in the bulk and multiplying the difference by 6. The energy gain in the surface relaxation is obtained in the same manner by comparing the average energy in the unrelaxed and the relaxed geometry. Plane waves up to 2.7 Ry are included in the expansion of the wave functions, and those up to 5.5 Ry are included through a second-order perturbation scheme. These correspond to ~180 plane waves and another ~320 plane waves in the basis set, respectively. $\alpha=\frac{2}{3}$ is chosen, and the correlation energy for each geometry is assumed the same. The ionic pseudopotential is cut at $q=3.1$ a.u. to limit computational time. To determine the lattice constant to be used in the surface calculations, calculations for the bulk were done with these input parameters. The calculated total energies are -7.91020 Ry, -7.92492 Ry, and -7.91996 Ry for $a_c=5.658$ Å, 5.43 Å, and 5.21 Å, respectively. These numbers give 5.37 Å for the equilibrium lattice constant and 1.49×10^{12} dyn/cm^2 for the bulk modulus. Correlation energy is included as before. However, as mentioned above, there is no variation of the correlation energy in the surface calculations because the *average* charge density of each supercell is the same irrespective of the relaxation. Therefore, it is reasonable to recalculate equilibrium properties without including the correlation contribution. 5.43 Å and 1.4×10^{12} dyn/cm^2 are obtained for a_c and B, respectively. Total energies for the unrelaxed and relaxed surface are then calculated with $a_c=5.43$ Å. In determining the equilibrium relaxation distance, three data points around the energy minimum are used to fit with a parabola. Other points outside this region give a much higher total energy as expected.

Results for these three geometries are given in Table V. The calculated relaxation distance is 0.16 Å in agreement with the measured values[4,5] of 0.12 Å and 0.16 Å for the impurity stabilized relaxed Si(111) surface. The calculated energy gain in relaxation is 0.13 eV per surface atom. No experimental data for the relaxation energy are known to the authors. The calculated surface phonon energy is 0.038 eV assuming that the reduced mass for the vertical vibration is just the mass of the Si atom. Because the bulk modulus has been overestimated by ~40%, the phonon frequency may have been overestimated by ~20%. Our results can be compared with the cluster model calculations by Redondo *et al.*,[7] which give 0.08 Å for the relaxation and 0.036 eV for the surface phonon energy. Experiments using low-energy electron spectroscopy have reported[39] a surface phonon frequency of 0.055 eV; however, identification of the peak with a surface phonon has been questioned,[7] and it is not yet clear whether this peak corresponds to the vertical vibration calculated here. Bullett[8] estimated the relaxation energy to be about 0.1 eV, but his calculated relaxation length (0.43 Å) seems unusually large. AH have assumed an inward relaxation by 0.33 Å in their calculations.[13]

The covalent bond between the surface atom and the subsurface atom is contracted as the surface atom is relaxed inward. The maximum charge density at the center of the covalent bond is found to increase until the relaxation becomes ~0.4 Å; it then starts to saturate as the relaxation increases. This exchange energy gain in relaxation is balanced by other contributions to the total energy, and the minimum total energy occurs at 0.16 Å relaxation. The relaxation of 0.16 Å corresponds to a bond length of 2.30 Å which is the average of the bulk bond of 2.35 Å and the molecular (Si_2) bond of 2.25 Å. Including correlation effects in the calculation does not give rise to first-order changes in the relaxation distance. Although proper treatment of these correlation effects would make the bond shorter, the same correlation effects contribute to a shorter equilibrium lattice constant as well, resulting in minor changes in the relaxation.

Subtracting E_{total} for the bulk in Table III from E_{total} for the surface in Table V and multiplying by 6, we can, in principle, get the surface energy per atom. However, this procedure can be misleading because the convergence of the total energy for the surface is much poorer than that of the bulk. The plane waves were truncated at 2.7 Ry compared with 6.4 Ry for the bulk. The estimated error in the surface energy is of the order of an eV. Even if we truncate the plane waves at 2.7 Ry for both the bulk and surface, the result does not improve significantly because, even though the bulk total energy has converged fairly well in this case, the abruptness of the surface charge density results in slow convergence. To have the same degree of convergence here as for the bulk, we would need at least ~650 plane waves in the basis set.

A more meaningful comparison between experiment and theory is presented below. One-half of the tetrahedral bonding energy (equivalently, $\frac{1}{4}$ of the cohesive energy 4.63 eV) minus the calculated relaxation energy (0.13 eV) is 1.03 eV, in good agreement with the experimental surface energy (0.99 eV).[6] The sign of the discrepancy (−0.04 eV) is also correct because some relaxation of *electrons* has occurred for the *unrelaxed* surface to reduce the total energy. In contrast to the case of the surface energy, the error in the relaxation energy is narrowed down to ~0.05 eV since we are actually calculating the change in the energy brought about by the relaxation. The degree of convergence in the calculation is the same, and the surface-surface interaction is essentially the same whether the surface is relaxed or unrelaxed as long as the distance between neighboring slabs remains fixed. Therefore, the two most important sources of error in our calculation are absent here.

Since a real surface undergoes reconstruction,[9] it is desirable to get the stable reconstructed geometry by minimizing the total energy. As pointed out in Sec. I, however, it is possible that other factors such as temperature, surface preparation, impurities, or defects play an important role in the surface reconstruction. It is questionable because of this whether our ground-state energy formalism is able to give results consistent with experiment. Moreover, the order of accuracy required in the calculation of reconstruction energy is beyond computational techniques now available to us.

Note added in proof. T. S. Kuan and S. L. Sass [Acta Metall. 24, 1053 (1976); Phil. Mag. 36, 1473 (1977)] have proposed a model in which the scattering intensities observed in the diffuse ω phase of Zr-Nb alloys are attributed to an extended linear defect. Since the scattering observed in the present experiments is similar to the diffuse ω phase, the same explanation would work here. However, the mechanism leading to an extended defect which locally resembles the ω-phase structure such as they propose is not clear. R. Pynn [J. Phys. F 8, 1 (1978)] has advanced an alternative description of the diffuse ω phase in terms of a one-dimensional model analogous to that used for charge density waves. This latter model, however, seems unlikely to be appropriate for the present case, given the low concentration of defects involved.

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