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TOTAL ENERGY METHOD FOR SOLIDS AND SOLID SURFACES

J.R. Chelikowsky, S.G. Louie, D. Vanderbilt, and
C.T. Chan

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James R. Chelikowsky
Corporate Research-Science Laboratories
Exxon Research and Engineering Company
Annandale, New Jersey 08801

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and

Steven G. Louie, David Vanderbilt and C. T. Chan
Department of Physics, University of California and Lawrence
Berkeley Laboratory, Berkeley, California 94720

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ABSTRACT

We present a method for the computation of cohesive and structural properties of solids. The method is based on a local orbital description of the wavefunctions, an ab initio pseudopotential construction for the ion-core potential, and a local density treatment of exchange and correlation energies. Key elements of the method include the direct computation in real space of all the matrix elements, a non-iterative evaluation of the total energy and the transferability of the total electronic potential. The combination of these elements allows an accurate, yet less complex, treatment of a wide variety of systems. We shall illustrate the method by considering several prototypical systems: the diamond crystal, the diamond (111) surface, the silicon crystal, and the molybdenum crystal. With respect to the bulk crystalline properties, i.e., the cohesive energy, the lattice constant, the bulk modulus, etc., we obtain state of the art agreement with experiment. With respect to the diamond surface, we have considered several models for the reconstructed 2×1 surface. Of the models considered, we find only the undimerized π -bonded chain reconstruction has a total energy lower than the relaxed 1×1 surface.

I. INTRODUCTION

In the past decade, it has become possible to compute, with good accuracy, a number of ground state properties for simple solids [1-11] without resort to empirical means. This development has opened up a new area for the study of condensed matter, as one is now in a position to predict the ground state properties of systems which were formerly inaccessible to theory or experiment. For example, we can predict, with some confidence, the properties of matter in pressure regimes which are currently inaccessible to experiment [3,12,13]. Or, we can predict surface structure not amenable to currently available surface probes [14,15].

In this paper, we illustrate a new method which allows us to calculate ground state properties with the same degree of accuracy as current methods, but with less effort than the conventional techniques. We shall concentrate our efforts on several systems representing different types of cohesion. The systems are the diamond crystal and surface, crystalline silicon, and crystalline molybdenum. In each case we will calculate a number of ground state properties and compare to other calculations and experiments.

II. COMPUTATIONAL METHODS

A. Construction of the One Electron Potential

The potential in our calculation has the form:

$$V_T(\vec{r}) = V_{ion}^P(\vec{r}) + V_H[\rho] + \mu_{xc}[\rho] \quad (1)$$

where V_{ion}^P is the ionic component which, in our pseudopotential framework, may have multiple angular momentum components, l , V_H is the Hartree or coulomb potential constructed via Poisson's equation, and μ_{xc} is the exchange-correlation potential which is a function of the charge density, $\rho(\vec{r})$.

The ionic pseudopotential was formed by using the method of Hamann et al. [16] with some minor modification [17,18]. This pseudopotential is constructed to match exactly the all-electron eigenvalues for the valence electrons, and the eigenfunctions for the valence states outside some core radius, for the isolated atom. The ionic pseudopotential involves no parameters fit to bulk properties and it is known to be accurately transferrable from the atom to the solid state [16].

The Hartree part of the potential, V_H , is constructed by using the wavefunctions from a solution of the pseudoatom. This may easily be done as the atomic Hartree potentials can be superposed for the solid. For the exchange-correlation potential, we superpose the atomic charges in the

crystal structure of merit and then construct the exchange-correlation potential [17]. The formalism we use is from Hedin and Lundqvist [19]. We find our results to be weakly dependent on the atomic configuration [17]. For carbon and silicon we use an sp^3 configuration; for molybdenum we use a $d^{4.9}s^{0.9}p^{0.2}$ configuration [20].

In order to expedite the evaluation of various matrix elements, we expand the potentials in gaussians which are centered on atomic sites. The most difficult part of our formalism, from a practical point of view, is fitting gaussians to a numerically derived potential. The fitting involves a multiparameter minimization. For this purpose, we use a Monte-Carlo method as outlined by Vanderbilt and Louie [21]. In Table I we compile the parameters determined for our fitted potentials. We write the total crystalline electronic potential by constructing the sum:

$$V^C(\vec{r}) = \sum_{\vec{R}, \vec{\tau}} V_T(\vec{r} - \vec{R} - \vec{\tau}) \quad (2)$$

where V^C is the crystalline potential and V_T is our total electronic potential from Eq. (1) as given in Table I. $\vec{R}$ is a lattice vector and $\vec{\tau}$ labels the basis.

Our method must be modified to determine surface or heteropolar compound charge densities. At a surface we may have charge transfer. Any charge imbalance invalidates our potential expansion in Eq. (2). Suppose charge transfer at the surface results in a site charge $Q(\vec{\tau})$ on

site $\vec{r}$ which differs from the bulk charge Q_0 . To account for the charge transfer and the concurrent change in potential, we write

$$V_{sc}(\vec{r}) = V^C(\vec{r}) + \sum_{\vec{R}, \vec{r}} c(\vec{r}) g(\vec{r} - \vec{R} - \vec{r}) \quad (3)$$

where g is a broad gaussian [22]. The coefficients of the gaussian, $c(\vec{r})$, are chosen by requiring that $Q(\vec{r})$ be self consistent with the charge density constructed by

$$\rho_{crys}(\vec{r}) = \sum_{\vec{R}, \vec{r}} \frac{Q(\vec{r})}{Q_0} \rho_a(\vec{r} - \vec{R} - \vec{r}) \quad (4)$$

with ρ_a being the reference atom charge density. First, Schrodinger's equation is solved with V^C and $Q(\vec{r})$ determined. The $Q(\vec{r})$ are used to generate ρ_{crys} and a new potential, V_{sc} , is formed by adjusting $c(\vec{r})$ to agree with the new V_H , and μ_{xc} calculated from ρ_{crys} . The new potential is used to generate new $Q(\vec{r})$ and new a V_{sc} . The loop is iterated to self consistency in $Q(\vec{r})$.

This self-consistency procedure is consistent with our desire to maintain an accurate description of the potential, yet not invoke the full machinery of a self-consistent calculation. Thus, here we have only a simple correction to the total crystalline potential. We do not have to re-compute the matrix elements involving V^C , but only those involving a single gaussian, g .

B. Solution of the Schrodinger Equation Using a Local Basis

Given the potentials in Table I, we use a basis consisting of Bloch sums of gaussians with angular dependent prefactors. Our wavefunctions have the form:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_{\ell,m,\mu,\nu} a_{\ell,m,\mu,\nu}^n(\vec{k}) \phi_{\ell,m,\mu,\nu}(\vec{k},\vec{r}),$$

$$\phi_{\ell,m,\mu,\nu}(\vec{k},\vec{r}) = \frac{1}{\Omega} \sum_{\vec{R}} \exp(i\vec{k} \cdot \vec{R}) f_{\ell,m,\nu}(\vec{r} - \vec{R} - \vec{\tau}_{\mu}),$$

(5)

where

$$f_{\ell,m,\nu}(\vec{r}) = K_{\ell,m}(\theta,\phi) \exp(-\beta_{\nu} r^2).$$

$K_{\ell,m}$ are cubic harmonics. The indices ℓ,m,μ,ν label the angular momentum component character of the orbital, ℓ , the azimuthal quantum number, m , the site within the unit cell, μ , and the decay constant of the local orbital, ν . n is the band index, $\vec{k}$ is the wave vector, and Ω is the crystal volume.

Since we have expanded the potential in gaussians, all the matrix elements consist of integrals of gaussians and polynomials. These integrals can be evaluated in closed form. The most difficult integrals in-

volve three centers with the potential containing non-local projection operators. These integrals are performed using standard quantum chemistry routines [23]. An advantage of this method is that the essential matrix elements are wave vector independent. Thus, once these elements have been determined they may be stored and retrieved as necessary for the wave vector in question.

C. Total Energy Expressions

Once the single particle Schrodinger's equation has been solved, the formalism of Hohenberg, Kohn and Sham [24] may be used to evaluate the total energy of the system. The total energy in this formalism is usually cast in the form:

$$E_{\text{total}} = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \int V_H(\vec{r}) \rho(\vec{r}) d^3r - \int \mu_{xc}(\rho) \rho(\vec{r}) d^3r$$

(6)

$$+ \int \epsilon_{xc}[\rho] \rho(\vec{r}) d^3r + E_{\text{ion-ion}}$$

where the sum is over all occupied states, ϵ_i are the one electron eigenvalues, ρ is the self consistent charge density, ϵ_{xc} is the exchange-correlation energy density and μ_{xc} is the exchange-correlation potential. $E_{\text{ion-ion}}$ is the electrostatic interaction energy among the bare ions.

We have not chosen to use this expression directly, as it requires a fully self-consistent charge density. Rather, we consider a situation where we have used an initial charge density, ρ_{in} , e.g., from the superposition of atomic charge densities, and solved the single particle Schrodinger equation to obtain a new charge density, $\tilde{\rho}$. One can show [17] that the total energy can be written as

$$E_{total} = \sum_{i=1}^N \epsilon_i - \int V_H[\rho_{in}] \tilde{\rho}(\vec{r}) d^3r + 1/2 \int V_H[\tilde{\rho}] \tilde{\rho}(\vec{r}) d^3r$$

$$- \int \mu_{xc}[\rho_{in}] \tilde{\rho}(\vec{r}) d^3r + \int \epsilon_{xc}[\tilde{\rho}] \tilde{\rho}(\vec{r}) d^3r \quad (7)$$

$$+ E_{ion-ion}$$

which is accurate to second order in $\Delta\rho = \rho - \tilde{\rho}$. In Eq. (7) ρ_{in} (and hence V^C) is explicitly removed from the energy expression. The sole function of ρ_{in} is to provide a way of obtaining a good approximation to $\tilde{\rho}$. Often, we may obtain accurate ground state properties by using the superposition of atomic charge for ρ_{in} and only solve Schrodinger's equation once to obtain $\tilde{\rho}$. In this fashion, we eliminate any self-consistent cycling in obtaining an accurate solution for the total energy. Moreover, we find that under most circumstances, e.g., a volume change of the crystal structure, we can transfer our potentials in Table I without any alteration to obtain accurate total energies. Thus, given the potential for a reference crystal volume, we

need not do any further computations for V_T to obtain the ground state properties of the solid in question.

To evaluate the total energy terms in Eq. (7), we use the formalism of Ihm et al. [11]. This formalism expresses the energy in momentum space and involves the Fourier transform of the potential and charge density. We write the energy per atom in the form:

$$\begin{aligned}
 E_{\text{total}} = & \frac{1}{N} \sum_{n, \vec{k}} \epsilon_{n, \vec{k}} - \Omega_a \sum_{\vec{G} \neq \vec{0}} [v_H^{\text{in}}(\vec{G}) + v_{xc}^{\text{in}}(\vec{G})] \tilde{\rho}(\vec{G}) \\
 & + \frac{1}{2} \Omega_a \sum_{\vec{G} \neq \vec{0}} \tilde{V}_H(\vec{G}) \tilde{\rho}(\vec{G}) + \Omega_a \sum_{\vec{G}} \tilde{\epsilon}_{xc}[\vec{G}] \tilde{\rho}(\vec{G}) \\
 & + \gamma_{\text{Ewald}} + \alpha_1 Z
 \end{aligned}
 \tag{8}$$

where

$$\begin{aligned}
 \gamma_{\text{Ewald}} = & \frac{1}{2} \sum_{\vec{R} \neq \vec{0}} \frac{Z^2}{|\vec{R}|} - \lim_{\vec{G} \rightarrow \vec{0}} \frac{4\pi Z^2}{\Omega_a |\vec{G}|^2}, \\
 \alpha_1 Z = & \frac{Z}{\Omega_a} \int \left(v_{\text{ion}} + \frac{Z}{r} \right) d^3 r.
 \end{aligned}$$

Here, Ω_a is the atomic volume in the crystal, and the sum is over all occupied bands. $\tilde{\rho}(\vec{G})$ is the Fourier transform of $\rho(\vec{r})$, etc.

We can find from Eq. (8) the total energy as a function of volume. With such information, we may use a standard equation of state curve fit to the energy versus volume points to determine the cohesive energy, the lattice constant, the bulk modulus and the derivative of the bulk modulus with pressure. The equation of state curve we use is from Murnaghan [25] and has the form:

$$E(V) = E(V_0) + \frac{B_0 V}{B_0' (B_0' - 1)} \left\{ B_0' \left(1 - \frac{V_0}{V}\right) + \left(\frac{V_0}{V}\right)^{B_0'} - 1 \right\} \quad (9)$$

where $E(V_0)$ is the equilibrium energy, V_0 is the equilibrium volume, B_0 is the bulk modulus and B_0' is the derivative of the bulk modulus. We can find other structural parameters by similar means, e.g., we can do a frozen phonon calculation to obtain the vibrational spectrum.

III. RESULTS

A. Diamond Crystal

Using the potential for carbon [26] in Table I, we solved Schrodinger's equation for the wavefunctions and eigenvalues and evaluated the total energy. The gaussian decay constants, B_v , were determined by optimizing

the total energy at a reference volume. We used three decays with a set of s- and p-gaussians for each. Thus, our basis consisted of 12 orbitals per atom. Our decay constants are presented in Table II. These decays provide an accurate description of the carbon charge density for the volumes of interest, i.e., within ~20% of the known volume.

With the basis fixed, we calculated the energy per atom of carbon in the diamond lattice as a function of the crystal volume. In this process, we transferred the total electronic potential to the volume of interest with no alteration. Also, we did not iterate, but took the output charge as $\tilde{\rho}$. We found no biasing by the initial construction of the exchange-correlation potential at the known lattice constant of diamond. We tested our procedure by constructing the potential at several initial volumes and checking the resulting equation of state. We found no significant changes in the equation of state, e.g., the lattice constant change was less than 0.01Å by using potentials constructed at $\pm 5\%$ ^{of} $\wedge$ the known lattice constant of diamond.

The equation of state curve fit to our computed energy versus volume points is presented in Figure 1. The ground state properties determined from the equation of state are presented in Table III and compared to experiment and to other calculations. Compared to experiment, our numbers are quite good. The largest error is the cohesive energy. Since the cohesive energy involves both atomic and solid state computations, it is hardly surprising that a large error in the cohesive energy could exist if small errors exist in either the atom or solid state energies. Properties which depend only on the solid state are in very good agreement with experiment. The lattice constant is accurate to within 0.01Å. The bulk modulus, given the uncertainty in the experimental values, is in essen-

tially exact agreement. The derivative of the bulk modulus with pressure has not been accurately measured, but the estimate for this quantity is consistent with predictions based on a knowledge of other diamond structure semiconductors. With respect to other calculations, our numbers are in essential agreement with the work of Yin and Cohen [27], but not with the cohesive energy of Bachelet et al. [5]. It is not clear why their number is so different from that of ours and Yin and Cohen; they have suggested that their basis is inadequate [5]. In conjunction with the ground state properties, we should mention that we have completed a frozen phonon calculation for diamond for the zone center phonons. Our calculated value is 40.1 THz as compared to the experimental value of 40.0 THz (see Ref. 17).

In Figure 2, we present the band structure for diamond at the calculated equilibrium lattice constant. Our band structure is in quite good agreement with those calculated previously [5,10]. Our valence band width of 21.0 eV is in accordance with the experimental value of -21 ± 1 eV [29]. The band gap is slightly smaller than experiment: the calculated value is 5.05 eV; the experimental value is 5.5 eV [29]. This discrepancy can be attributed to the local density formalism which, in principle, yields only ground state properties.

In Figure 3, we present the valence charge density for diamond at the equilibrium lattice constant. The density corresponds to $\tilde{\rho}$ in our total energy expression, Eq. (7). Thus, the agreement we obtain with other calculations for this density is reassuring. Specifically, Holzwarth et al. [18], and Yin and Cohen [27] have presented pseudocharge density calculations for diamond. Overall, the agreement between the densities is quite good. Our calculated density maxima along the bonding directions are a few percent less than the Yin and Cohen result, but the topology is nearly identical.

B. Silicon Crystal

To establish the accuracy of our method for other diamond structure materials, we computed the ground state properties of silicon by a simple rescaling of the diamond basis. The silicon ionic potential was constructed in a similar manner to the carbon potential [30]. In particular, no d potential components were used and no d-symmetry gaussians were used. The calculated equation of state curve is presented in Figure 4 and the calculated charge density at the equilibrium lattice constant is presented in Figure 5.

Considering that the basis has not been optimized, the ground state properties we calculate are in remarkably good agreement with experiment. The computed cohesive energy is 3.9 eV, compared to an experimental value of 4.6 eV. We under estimate the cohesive energy owing to our approximate basis. However, the structural properties are quite good. The lattice constant agrees within 0.01Å of the experimental value. Our calculated lattice constant is 5.44Å versus the known lattice constant of 5.43Å. The bulk modulus we obtained is 1.03 Mbar versus an experimental value of 0.98 Mbar [31]. In order to test the sensitivity of our calculation to d-symmetry gaussians in the basis, we repeated our silicon calculation with d-components both in the basis and potential. The decay constants for the s-, p- and d- gaussians are given in Table II. The cohesive energy improved dramatically, from 3.9eV to 4.9eV; however, the lattice constant and the bulk modulus were not greatly altered. The calculated values were 5.35Å and 1.15 Mbar for the lattice constant and bulk modulus respectively.

The charge density we obtain for silicon is in good agreement with the previous calculations [5,12]. In particular, the maximum of the

bond charge is nearly equal to the previous work and the topology is nearly identical. The topology is of particular interest, as the exclusion of d-symmetry components in both the potential and wavefunctions has not resulted in a differing bond shape. We should note that while the inclusion of d-symmetry does not appear to be necessary for an accurate description of the bond charge and the ground state properties of silicon, it is necessary to include d-components in the wavefunctions to obtain an accurate conduction band spectrum [32].

C. Molybdenum Crystal

Transition metal crystals appear to be a more difficult case to study as contrasted to the diamond crystal. Given the open nature of the crystal and the covalent nature of diamond, it might appear that a close packed metal would be a better candidate for our method. This is not true, as the delicate s-d interactions in transition metals require a more careful treatment. We found that we could not unambiguously superpose the atomic densities for an initial screening potential and obtain structural properties with accuracy comparable to the diamond or silicon results. However, we found that we could extract an accurate screening potential by using the solid state charge density obtained from a potential constructed with the atomic superposed densities. The potential we used is presented in Table I; the basis functions in Table II [33].

From the equation of state curve shown in Figure 6, we have calculated the ground state properties shown in Table IV. We compare to a fully self-consistent pseudopotential calculation of Ho et al. [7]; they

used a mixed basis opposed to our local orbital basis. We obtain a very good value for the cohesive energy and bulk modulus. Our calculated lattice constant is slightly less than the calculated value of Ho et al.; however, the error is probably within the differences expected from using different approximations to the exchange-correlation energies.

D. The Diamond (111) Surface

The diamond cleavage plane, the (111) surface, was examined by considering a slab geometry ten atomic layers thick. The (111) surface was exposed on both sides. The wavefunction basis was identical to the diamond bulk basis; the potential was made self-consistent as described in Section II.

The results of our total energy calculations for the surface are summarized in Table V. In addition to the 1×1 unreconstructed surface, four topologically distinct 2×1 models have been considered for the reconstructed surface. These models include the Haneman buckling model [34], the Pandey π -bonded chain model [14], the Chadi π -bonded molecule model [35], and the Seiwatz single chain model [36]. Spectroscopic data and total energy calculations tend to favor the Pandey model. Our discussion will center on this model.

The Pandey model shown in Figure 7 was optimized for the diamond surface both by direct total energy calculations and by valence force field calculations. First, the energy for the Pandey model was minimized by adjusting bond lengths of the outer two layers. A surprising feature of the resulting geometry was the 8% expansion of the subsurface interlayer bond. The surface chain bond was contracted by 4%. It is interesting to

note that the surface double layer in some sense resembles a "graphitic" overlayer. This can be seen in Figure 8. Namely, the bond lengths are roughly the average of the diamond and graphitic bond lengths and the "puckering" of the surface six-fold rings of bulk diamond has been reduced bringing the surface double layer to resemble a single layer of graphite. Contrary to some speculations [14], we find that dimerization of the chain does not lower the surface energy. However, we could lower the energy of this model further by considering valence force fields. We used a Keating force constant model [37]. We froze the surface double layer and bonds between the surface and sublayer; the inner layers were moved to relieve the surface strain fields. The final geometry has an energy lowered by an additional 0.21 eV per surface atom. This energy gain upon relaxation is larger for diamond than the case of silicon [15]. We attribute this difference in diamond to an increase in bond angle stiffness. This results in the 8% expansion of the diamond subsurface interlayer bond which we ascribe to bond weakening resulting from the bond angle distortion.

Figure 9 shows the calculated surface band structure for the fully relaxed Pandey chain model. Experimental angle resolved photoemission data [38] for this surface are shown for comparison. While the dispersion for the computed surface band is in good agreement with the photoemission data, the placement of the band is too high by a uniform shift of ~ 1 eV. Such a shift has also been observed for the surface bands of other tetravalent semiconductors such as Si and Ge.

IV. CONCLUSIONS

We have presented a method for computing the total energies of solids and their surfaces. The method combines ab initio pseudopotentials with local orbitals, i.e., gaussians. Key elements of our study include the evaluation of all matrix element integrals in real space, a non-iterative evaluation of the total energy and the transferability of the total electronic potential.

We presented results using our method for several prototypical solids: silicon and carbon in the diamond structure and molybdenum in the body centered cubic structure. We obtained state of the art agreement between the calculated ground state properties and the experimentally known properties. Our results also agree with other theoretical calculations.

In addition to bulk properties, we examined the diamond (111) surface by considering a number of proposed surface structures. Of the models that we examined, the undimerized π -bonded chain reconstruction had the lowest surface energy and a surface band structure in the best agreement with photoemission data.

In summary, our total energy method possesses several advantages. It involves no adjustable parameters and is widely applicable.

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TABLE CAPTIONS

Table I. Gaussian expansion for the total electronic potential for carbon, silicon and molybdenum in their elemental structures.

$$V_T(\vec{r}) = \sum_i a_i \exp(-b_i r^2)$$

with V_T in units of Ry. Different l -components of V_T are expressed as $\Delta V_l = \rho_l^+ (V_l - V_{l0}) \rho_l$ where l_0 is the reference potential and ρ_l are projection operators.

Table II. Gaussian decay exponents for carbon, molybdenum and silicon. The silicon exponents have not been optimized with respect to the total energy, but are rescaled from the diamond results.

Table III. Ground state properties of diamond from a fit to a Murnaghan equation of state. Other contemporary self-consistent field calculations are listed for comparisons.

Table IV. Ground state properties of molybdenum from a fit to a Murnaghan equation of state. For comparison results from the mixed basis calculation of Ho et al. (Ref. 7) are presented.

Table V. Calculated total energies of C (111) 1 x 1 and 2 x 1 surface reconstruction models. The zero of energy is taken as the ideal 1 x 1 surface. For a detailed description of the various surface models, see the text.

TABLE I.

CARBON POTENTIAL

V_p		$V_s - V_p$	
a_i	b_i	a_i	b_i
6.87567	5.84465	5.13522	8.03319
-44.15766	2.38596	-47.91462	4.33680
29.19330	1.66223	137.95831	3.13267
-10.29119	0.97335	-66.25571	2.56421
- 1.09153	0.23137		

SILICON POTENTIAL

V_p		$V_s - V_p$	
a_i	b_i	a_i	b_i
- 6.75837	11.5660	- 55.26999	9.82923
28.35010	7.81203	279.56170	7.64865
-47.64348	5.15760	- 717.88513	5.68122
40.71898	2.98831	1330.59146	4.04612
- 9.34731	1.69707	-1674.56038	2.89905
0.55803	0.82190	1904.63042	1.93939
- 1.70228	0.42193	-1754.54105	1.47837
- 1.95882	0.18506	823.18952	1.17525
		- 140.21713	0.87099
		6.99902	0.54920

MOLYBDENUM POTENTIAL

V_d		$V_p - V_d$		$V_s - V_d$	
a_i	b_i	a_i	b_i	a_i	b_i
19.41300	10.25335	-16.26108	10.37931	50.12046	17.4425880
-87.62204	6.40040	94.40901	5.97890	- 74.94685	15.1108109
62.23564	4.24137	-84.92522	3.88325	93.36481	6.8906538
83.27261	3.48004	-88.86232	3.51318	-167.98480	3.7573234
-95.13981	2.08322	123.88650	2.10733	131.47496	2.1849376
33.76223	1.08240	-56.07765	1.15412	- 63.37209	1.1851181
-23.98254	0.73335	14.28558	0.77476	99.97188	0.6203312
- 1.91471	0.15568	22.93603	0.70732	- 58.69885	0.5499567

TABLE II

ELEMENT	DECAYS			
	β_1	β_2	β_3	β_4
CARBON	0.250	0.935	3.500	
SILICON	0.140	0.374	1.000	
MOLYBDENUM	0.200	0.564	1.593	4.500

TABLE III

GROUND STATE	EXPERIMENT (Ref. 30)	PRESENT THEORY	OTHER THEORIES (Ref. 5) (Ref. 26)	
COHESIVE ENERGY (in eV)	7.37	7.34	3.61	8.10
LATTICE CONSTANT (in Å)	3.567	3.560	3.69	3.60
BULK MODULUS (in Mbar)	4.42	4.37	4.56	4.33
PRESSURE DERIVATIVE OF THE BULK MODULUS	4	3.54	--	--

TABLE IV

GROUND STATE	EXPERIMENT (Ref. 30)	PRESENT THEORY	OTHER THEORY (Ref. 7)
COHESIVE ENERGY (in eV)	6.82	7.16	6.64
LATTICE CONSTANT (in Å)	3.15	3.09	3.14
BULK MODULUS (in Mbar)	2.7	2.86	2.82

TABLE V

SURFACE MODEL	SURFACE ENERGY (eV/surface atom)
Ideal 1 x 1	0.00
Relaxed 1 x 1	-0.37
Buckled ($\Delta Z = \pm 0.26\text{\AA}$)	0.35
Chadi π -bonded molecule	0.28
Seiwatz single chain	1.30
Ideal Pandey π -bonded chain	-0.05
Relaxed Pandey π -bonded chain	-0.47
-- with 2% dimerization	-0.46
-- with 4% dimerization	-0.43
-- with 6% dimerization	-0.38
Fully relaxed Pandey chain	-0.68

FIGURE CAPTIONS

- FIGURE 1. Equation of state for carbon in the diamond structure. The continuous curve is the Murnaghan equation of state; the points are the calculated energies at the indicated volume. The zero point motion energy is not included in this curve.
- FIGURE 2. Band structure for carbon in the diamond structure. The top of the valence band is taken as the zero of energy.
- FIGURE 3. Crystalline valence charge density for diamond. This density corresponds to $\tilde{\rho}$ in Eq. (7). The charge density is in units of $e/(a.u.)^3$; the contour spacing is $0.05 e/(a.u.)$.
- FIGURE 4. Equation of state for silicon in the diamond structure. The continuous curve is the Murnaghan equation of state; the points are the calculated energies at the indicated volume. The zero point motion energy is not included in this curve.
- FIGURE 5. Crystalline valence charge density for silicon. This density corresponds to $\tilde{\rho}$ in Eq. (7). The charge density is in units of $e/(a.u.)^3$; the contour spacing is $0.01 e/(a.u.)$.

FIGURE 6. Equation of state for molybdenum in the body centered cubic structure. The continuous curve is the Murnaghan equation of state; the points are the calculated energies at the indicated volume. The zero point motion energy is not included in this curve.

FIGURE 7. Model for the Pandey π -chain model. The exposed surface is the (111) surface. The π -bonding occurs along the (110) plane.

FIGURE 8. Illustration of the bond length changes (with respect to bulk) which occur upon relaxation of (a) 1×1 and (b) 2×1 Pandey chain models.

FIGURE 9. Calculated surface bands (solid lines) and resonances (dashed lines) for fully relaxed Pandey chain model. The bulk projected band structure (shaded) and the experimental angle resolved photoemission data [38] (black dots) are shown for comparison.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

(a)

(b)

Fig. 8

Fig. 9

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