\vec{r} -space method for the total energy applied to silicon

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We present an \vec{r} -space method for calculating crystalline total energies based on our \vec{r} -space technique for generating Wannier functions which we now call the orthogonality chemical pseudopotential method. Applied to silicon, the method yields good results for the lattice constant and bulk modulus. This indicates that the method should be valuable when applied to problems of lower symmetry which are difficult to treat in \vec{k} space. The contributions to the total energy from ion-ion, electron-electron, and eigenvalue energies are identified separately in the traditional manner. It is emphasized that this separation is nonphysical, being dependent on the grouping of terms in the Madelung sums. The total energy is unique, of course.

I. INTRODUCTION AND SUMMARY

For many years the interest in semiconductor physics has centered on the problem of the band structure of the perfect crystal. The lattice constant is known from x-ray measurements, hence the problem of predicting the lattice constant from *a priori* total energy calculations could be bypassed. Interest has now shifted to the study of surfaces and deep defects where important atomic displacements occur which cannot be measured in a straightforward manner. One approach is to predict them theoretically by minimizing the total energy. A first and crucial step in this process is to be sure that our pseudopotentials and calculational techniques are adequate to reproduce the bulk lattice constant and bulk modulus.

A recent publication by Ihm and Cohen¹ has presented a \bar{k} -space method for calculation of the total energy and has given results for silicon. They obtain good values for the lattice constant but find a bulk modulus which is 70% too large. They use a pseudopotential which was empirically derived to fit the band structure and have treated exchange and correlation using Slater's $X\alpha$ (localdensity) method² with an $X\alpha = \frac{2}{3}$ as suggested by general arguments of Kohn and Sham.³ It is not clear at the moment whether their poor value of the bulk modulus is due to an inadequacy of the assumed potential or to some approximation made in the calculation. The calculation of the total energy involves large cancellations which are magnified by taking the second derivative to obtain the bulk modulus.

We have developed an \vec{r} -space method for the total energy based on an *a priori* method for calculating Wannier functions as described in Kane and Kane.⁴ In zeroth order the method is very simple and should be more easily generalizable to lower symmetry situations than is a \vec{k} -space method based on crystal periodicity. Since \vec{r} space is closer to the language of chemistry and intuitive-empirical arguments of a Pauling type, our approach is also valuable in that it describes the total energy in different terms than the \bar{k} -space method.

In checking the accuracy of our method we return to \vec{k} space for the evaluation of overlap and antibonding admixture corrections. These corrections could also be made entirely in \vec{r} space, but with more effort. We find the corrections to be important but still small enough to encourage the application of our \vec{r} -space method to more complex and interesting problems such as surface reconstruction and lattice relaxation around deep defects.

We have studied silicon using the same core pseudopotential employed by Ihm and Cohen.¹ Our results are similar to theirs for the total energy and lattice constant but differ considerably for the bulk modulus. We find a lattice constant 4%smaller than experiment and a bulk modulus which is 13% too small, in contrast to Ihm and Cohen's value which is 70% too large. Comparison to experiment is not a satisfactory criterion for choosing between the two calculations since the potential employed may not be correct. However, we note that in our method it is intrinsically easier to handle the repulsive core of the pseudopotential. The band-structure pseudopotential is generally thought to have too soft a core, compatible with our result, whereas Ihm and Cohen's result suggests it may be too hard. More work to clear up this discrepancy is clearly desirable.

In Sec. IIA we present the details of our \vec{r} space method for the total energy. We review our *a priori* method of calculating Wannier functions in \vec{r} space which is closely related to work first done by Koster.⁵ We call our technique the orthogonality chemical pseudopotential method (OCP) where by "chemical pseudopotential" we indicate a broad class of pseudopotentials which allow the calculation of localized orbitals in infinite or extended potentials. In such a system

4600

the ordinary potential leads to extended states. The orthogonality constraint prevents spreading of the wave function. Anderson⁶ has proposed another type of chemical pseudopotential and there are doubtless many other possibilities just as there are many types of the more familiar pseudopotentials which eliminate the deep core states in the atom. This paper is the latest in a series demonstrating the usefulness of the OCP.⁷ It is the first paper to incorporate the important ingredient of self-consistency.

In Sec. IIB we describe the fitting of the unscreened core pseudopotential to a sum of Gaussians plus the smeared Coulomb potential of a Gaussian charge density. In Sec. IIC we describe our fit of the valence charge density to a sum of spherical Gaussian charges centered on atomic and bond sites. This leads easily to a potential which is then fit to spherical Gaussians centered on lattice sites.

In Sec. IID we discuss the ion-ion and electronelectron interaction energies. These interaction energies are conveniently rendered finite by adding one-half the electron-smeared ion-interaction energy to each. The energies are then expressible via the ionic and electronic charge densities times a potential which is calculated from a Madelung-type sum over Gaussian charges on atom and bond sites. We group the terms in this sum into symmetric units which are electrostatically neutral and which have no Coulombic moments lower than octupole. With this grouping of terms, the sum converges rapidly to the potential. Nonetheless, the potential is not unique to within a constant which depends on the specific manner in which the symmetric units are chosen. Although the constant manifestly cancels in the total energy, it does contribute to the ion-ion energy, to the electron-electron energy, and to the band energies, which means that none of these three quantities has a unique physical meaning to within a volume dependent constant. We emphasize this point because in another work⁸ these quantities are treated separately and unsymmetrically, which we think is nonphysical. The nonuniqueness is a consequence of the long range of the Coulomb interaction. This example shows that rapid convergence (of the symmetric units) and "short range" are not synonymous.

In Sec. IIE we describe a \vec{k} -space method for evaluating corrections to our results arising from overlap of second-neighbor and more distant bonds and also the admixture of antibonding wave functions into the valence band. For convenience we approximate the \vec{k} -space sum by the value at the Baldereschi point.⁹

In Sec. III we present our results in detail. We

find that most of the charge distribution is in the bond charges (~2|e| per bond). These are static charges. The dynamic charge would roughly equal the static charge screened by the dielectric constant in agreement with Phillip's bond-charge model.¹⁰

II. F-SPACE METHOD FOR THE TOTAL ENERGY

A. Bond Wannier functions

We follow the prescription for the *a priori* generation of Wannier functions via the orthogonality chemical pseudopotential (OCP) as described in Kane and Kane.⁴

In summary, we define bonding and anti-bonding functions as sums of Gaussians on nearestneighbor atoms

$$b(\mathbf{\vec{r}}) = [\phi(\mathbf{\vec{r}}_{1}) + \phi(\mathbf{\vec{r}}_{2})] / [2(1+S)]^{1/2}$$

$$a(\mathbf{\vec{r}}) = [\phi(\mathbf{\vec{r}}_{1}) - \phi(\mathbf{\vec{r}}_{2})] / [2(1-S)]^{1/2}, \qquad (1)$$

$$\phi = \sum_{i} c_{bi} \phi_{i},$$

where $i = s\alpha$, $px\alpha$, or $dx\alpha$ according to the definitions

$$\begin{aligned}
\phi_{s\alpha} &= e^{-\alpha r^{2}}, \\
\phi_{px\alpha} &= x e^{-\alpha r^{2}}, \\
\phi_{dx\alpha} &= y z e^{-\alpha r^{2}}, \\
S &= \int \phi(\vec{\mathbf{r}}_{1}) \phi(\vec{\mathbf{r}}_{2}) d\vec{\mathbf{r}}, \\
\vec{\mathbf{r}}_{1} &= \vec{\mathbf{r}} - \vec{\mathbf{R}}_{1}, \quad \vec{\mathbf{r}}_{2} &= \vec{\mathbf{r}} - \vec{\mathbf{R}}_{2},
\end{aligned}$$
(2)

where the p (and d) functions are directed along $\vec{\tau} = \vec{R}_2 - \vec{R}_1$, and \vec{R}_i are the atom coordinates. We have used eight functions per bond, 3s and 3p ($\alpha = 0.2, 0.3, 0.4$ a.u.) and 2d ($\alpha = 0.2, 0.3$).

The coefficients c_{bi} are determined by minimizing the usual Hamiltonian energy $\langle b_1 | H | b_1 \rangle$ plus the orthogonality chemical pseudopotential term $\lambda \langle b_1 | b_2 \rangle$, where b_1 and b_2 are different bonds with a common atom and λ is a Lagrange parameter to be determined such that $\langle b_1 | b_2 \rangle = 0$.

We ignore overlaps between more distant bonds and do not incorporate antibonding functions. These approximations are discussed at length in Kane and Kane.⁴ We will correct for them later in the present context by use of the Baldereschi point.⁹

B. Ionic-core pseudopotential

We follow very closely the procedure of Ihm and Cohen¹ except that we work in \vec{r} space. We use their ion-core pseudopotential

$$\tilde{V}_{ion\,k}(k) = \frac{-16\pi e^2}{k^2} \frac{(a_3 + \cos a_2 k)}{(1+a_3)\upsilon} \exp(a_4 k^4) \,. \tag{3}$$

The total volume v is arbitrary. The ion cores are then screened by the self-consistent Hartree potential plus the Slater $X\alpha$ exchange potential with $X\alpha = \frac{2}{3}$. At large distances $(k \rightarrow 0) \tilde{V}_{ionk}(k)$ corresponds to an ionic charge, 4|e|. We fit this ionic potential energy to a sum of Gaussians plus the Coulomb potential energy of a Gaussian smeared charge, 4|e|.

$$\rho_{\rm ISC} = 4(\alpha_{\rm ion}/\pi)^{3/2} \exp(-\alpha_{\rm ion}r^2) \,. \tag{4}$$

The fit is done by a least squares method plus a Lagrange constraint to ensure that the average value of the neutral potential energy $V_{\text{neut}}(r)$ be exactly satisfied; i.e.,

$$\tilde{V}_{\text{neut}}(0) = \int d\vec{\mathbf{r}} [V_{\text{ion}\,\mathbf{k}}(\vec{\mathbf{r}}) + 4e^2/r]/\upsilon$$

$$= \frac{8\pi e^2 a_2^2}{(1+a_2)\upsilon}.$$
(5)

The integral is over all space of the arbitrary volume, v, even though $V_{ionk}(\vec{r})$ refers to a single core. The exact satisfaction of Eq. (5) is not essential. It was introduced to parallel the work of Ihm and Cohen as closely as possible. (We use \tilde{V} for the Fourier transform of V throughout.)

We have, as a least-squares equality,

$$\tilde{V}_{ion} = \tilde{V}_{ionG} + \tilde{V}_{ISC}; \qquad (6)$$

$$\begin{split} \tilde{V}_{i \text{ on } G} &= \sum_{i} c_{Ii} (\pi/\alpha_{i})^{3/2} e^{-k^{2}/4\alpha_{i}} / \mathfrak{V} , \qquad (7) \\ \tilde{V}_{ISC} &= \frac{-16\pi e^{2}}{k^{2} \mathfrak{V}} \exp\left(\frac{-k^{2}}{4\alpha_{i \text{ on }}}\right). \end{split}$$

The parameters of the potential are given in Table I.

C. Crystal charge density and potential

The crystal valence electron density is calculated using the bond wave functions of Eqs. (1) and (2)

TABLE I. Parameters of the Fourier-transformed core pseudopotential and its fit to Gaussians plus a smeared Coulomb potential. Symbols as in Eqs. (3) and (7).

$a_2 = 0.790 \ 65 \ a_0^{-1}$ $a_3 = -0.352 \ 01$ $a_4 = -0.018 \ 07 \ a_0^{-4}$	
$\alpha_i (\ln a_0^{-2})$	C_{Ii} (2 R_{∞})
0.4	2.2947
0.6	-20.3091
0.8	33.4528
1.2	-16.3800
1.6	4.9264
$\alpha_{ion} = 1.0 a_0^{-2}$	

and summing over all fcc lattice sites with 4 bonds per site.

$$\rho_{e}(\vec{\mathbf{r}}) = \sum_{\mathbf{a}, \, \mathbf{j}=1, \, 4}^{\mathbf{fcc\ latt}} \left| b_{j}(\vec{\mathbf{r}} - \vec{\mathbf{a}}) \right|^{2}.$$
(8)

The calculation is done for a mesh of points in the unit cell and the result is least-squares fitted to a sum of spherical Gaussians centered on atom and bond sites.

$$\rho_{e}(\mathbf{\hat{r}}) = \sum_{LSQ} c_{\rho i j} e^{-\alpha i |\mathbf{\hat{r}} - \mathbf{\hat{r}} - \mathbf{\hat{t}}_{j}|^{2}},$$

$$\mathbf{\hat{t}}_{1} = 0, \quad \mathbf{\hat{t}}_{2} = (a/8) (1, 1, 1).$$
(9)

We have used the values $\alpha = 0.4$, 0.8, and 1.2 a.u. for both the bond and atomic sites.

The use of a Gaussian density distribution is very convenient because the resulting Coulomb potential can be described in terms of error functions. A larger set of sites to serve as origins for spherical distributions could easily be used but lattice plus bond sites appear to give sufficient accuracy and are sufficiently simple that the "bond" and "atom" charges may suggest physical processes. (These are static, not dynamic charges. Our static bond charge is very much larger than the empirical dynamic bond charge of lattice dynamical models.¹¹)

The total electron density per atom site, $\rho_{tot} = \rho_{atom} + 2\rho_{bond}$, should equal 4 and we have enforced this constraint via a Lagrange multiplier in our least-squares fit. Of course, ρ_{atom} and ρ_{bond} are given by

$$\rho_{\text{atom}} = \sum_{i} \int d\mathbf{\dot{r}} c_{\rho i 1} e^{-\alpha_{i} r^{2}},$$

$$\rho_{\text{bond}} = \sum_{i} \int d\mathbf{\dot{r}} c_{\rho i 2} e^{-\alpha_{i} |\mathbf{\dot{r}} - \mathbf{\dot{t}}_{2}|^{2}}.$$
(10)

A valence potential energy is then constructed from the spherical density distribution of Eq. (9) plus the smeared Gaussian distribution ρ_{ISC} in Eq. (4). The potential energy is smooth because we use ρ_{ISC} rather than a point charge; hence it can easily be fitted to a sum of spherical Gaussians centered on lattice sites plus a constant. We could have used a basis of lattice and bond sites as we did for the charge but lattice sites alone give sufficient accuracy.

We then have

$$V_{\rm NC}(\vec{r}) = \sum_{\rm R, i}^{\rm atom \, sites} c_{\nu i} e^{-\alpha_{i} |\vec{r} - \vec{R}|^{2}} + c_{\nu 0} , \qquad (11)$$

where NC refers to neutral Coulomb. In computing $V_{\rm NC}(\vec{\mathbf{r}})$ from $\rho_{\rm val} - \rho_{\rm ISC}$, i.e.,

$$V_{\rm NC}(\vec{\mathbf{r}}) = e^2 \int d\vec{\mathbf{r}}' [\rho_{\rm val}(\vec{\mathbf{r}}') - \rho_{\rm ISC}(\vec{\mathbf{r}}')] / \left| \vec{\mathbf{r}} - \vec{\mathbf{r}}' \right|$$
(11a)

it is desirable for convergence to sum over symmetric units. We have chosen $\rho_{\rm sym}$ as defined by

$$\rho_{\text{sym}}(\vec{\mathbf{r}} - \vec{\mathbf{R}}) \equiv -\rho_{\text{ISC}}(\vec{\mathbf{r}} - \vec{\mathbf{R}}) + \rho_{\text{atom}}(\vec{\mathbf{r}} - \vec{\mathbf{R}}) + \frac{1}{2} \sum_{j=1}^{4} \rho_{\text{bond}}(\vec{\mathbf{r}} - \vec{\mathbf{R}} - \vec{\tau}_j/2), \qquad (12)$$

with $\frac{1}{2}$ the bond charge on each of the four bond sites per atom. \overline{R} is the atom coordinate. These symmetric units are electrostatically neutral and have no moments lower than octupole. It is important to emphasize that this choice is not unique. Other equally reasonable and convergent choices could be made which would result in different values for c_{vo} . Furthermore, the nonuniqueness is volume dependent. We obtain a unique result for the total energy, of course, but only by using the same definition of symmetric units for the ion-ion, ion-electron, and electron-electron interactions. The care that must be exercised here is the unavoidable consequence of the conditional convergence of the Coulomb interaction. Even though the sum over symmetric units converges very rapidly the potential is not short range in the sense of being unique. We further hasten convergence by summing over shells of atoms having tetrahedral symmetry.

The Slater exchange potential energy is derived from the valence electron density according to^2

$$V_{\text{SLX}}(\vec{\mathbf{r}}) = -X_{\alpha}^{\frac{3}{2}} (3/\pi)^{1/3} e^2 \rho_e(\vec{\mathbf{r}})^{1/3} .$$
(13)

The Slater potential is then fit to Gaussians as in Eq. (11) for the valence potential. The total potential energy is obtained as a Gaussian expansion by combining Slater, valence, and ion-core potentials,

$$V_{tot}(\vec{r}) = \sum_{\vec{R}_{\tau}, t}^{\text{atom sites}} c_{T t} e^{-\alpha t |\vec{r} - \vec{R}|^2} + c_{T 0}, \qquad (14)$$

$$c_{Ti} = c_{vi} + c_{SLXi} + c_{Ii} . (15)$$

The valence and Slater potentials are fit with six Gaussians plus a constant, $\alpha_i = 0.2$, 0.4, 0.6, 0.8, 1.2, and 1.6 in atomic units, α_0^{-2} . The core potential is fit with $\alpha_i = 0.4$, 0.6, 0.8, 1.2, and 1.6 and no constant.

These Gaussians are reasonably short range so that the wave function in Eqs. (1) and (2) can be computed accurately by summing only those potentials whose atom sites are third neighbor or closer to one of the two atoms of the bond.

D. Ion-ion and electron-electron interactions

The total energy per atom, E_{tot} , may be written

 $E_{tot} = E_{II} + E_{eeC} + E_{eeX} + T_e + E_{e ISC} + E_{e IG} , \quad (16)$ where E_{II} is the ion-ion energy, E_{eeC} is the electron-electron Coulomb energy, E_{eeX} is the electron-electron exchange and correlation energy, and T_e is the electronic kinetic energy. We divide the electronic interaction energy with the core pseudopotential into two pieces, E_{eISC} , the interaction with the smeared Coulomb ionic charge, and E_{eIG} , the interaction with the Gaussian part. This subdivision is contained in Eq. (7).

For a crystal, E_{II} and E_{eeC} tend to infinity with crystal volume. We can eliminate the infinity by adding half the smeared Coulomb interaction $\frac{1}{2}E_{e\,ISC}$ to both pieces.

$$E'_{II} = E_{II} + \frac{1}{2} E_{e \, ISC} , \qquad (17)$$
$$E'_{eeC} = E_{eeC} + \frac{1}{2} E_{e \, ISC} .$$

We use the Slater $X\alpha$ potential of Eq. (13) for E_{eex} and minimize E_{tot} variationally, leading to the usual one electron Schrödinger equation. The one-electron eigenvalue energy E_{eig} (summed over all occupied valence states) is then given by

$$E_{eig} = T_e + E_{eISC} + E_{eIG} + 2E_{eeC} + \frac{4}{3}E_{eeX} ,$$

$$E_{eeX} = \frac{3}{4} \int d\vec{\mathbf{r}} \rho_e(\vec{\mathbf{r}}) V_{SLX}(\vec{\mathbf{r}}) .$$
(18)

The total energy may be written

$$E_{tot} = E_{eig} - E'_{eeC} + E'_{II} - \frac{1}{3}E_{eeX} .$$
 (19)

In our Wannier function representation all Wannier functions (Pauling bonds) have the same energy $E_{\rm bond}$. Hence

$$E_{\rm eig} = 4E_{\rm bond} \,. \tag{20}$$

Bloch sums of Wannier functions spread the individual eigenvalues over a band, but the trace remains equal to $4E_{bond}$. The energies in Eq. (19) are conveniently represented in terms of potentials.

In order to demonstrate the cancellation of terms we carefully define our symbols as follows: V(r) is the potential energy of an electron, and $\rho_e(\vec{\mathbf{r}})$, $\rho_I(\vec{\mathbf{r}})$ are the electron and positive ion densities, respectively (both positive and equal to the absolute value of the charge density divided by |e|). Then the various energies may be written

$$E_{eeC}^{\prime} = \frac{1}{2} \int d\vec{\mathbf{r}} \rho_e(\vec{\mathbf{r}}) V_{\rm NC}(\vec{\mathbf{r}}) , \qquad (21)$$

$$E'_{II} = -\frac{1}{2} \int d\mathbf{\tilde{r}} \rho_{\rm ISC}(\mathbf{\tilde{r}}) V_{\rm NC}(\mathbf{\tilde{r}}) + \frac{1}{2} \int d\mathbf{\tilde{r}} [\rho_{\rm ISC}(\mathbf{\tilde{r}}) V_{\rm ISC}(\mathbf{\tilde{r}}) - \rho_{I}(\mathbf{\tilde{r}}) V'_{I}(\mathbf{\tilde{r}})], \quad (22)$$

$$E_{eig} = T_e + \int d\vec{\mathbf{r}} \rho_e(\vec{\mathbf{r}}) [V_{\rm NC}(\vec{\mathbf{r}}) + V_{\rm IG}(\vec{\mathbf{r}}) + V_{\rm SLX}(\vec{\mathbf{r}})], \qquad (23)$$

The prime on $V_f(\vec{r})$ in Eq. (22) means that the ion self-interaction is to be excluded. Since $\alpha_{ion} = 1.0 \ a_0^{-2}$ in Eq. (4) the interaction between two nearest-neighbor ions is accurately point-like so that the two bracketed terms in Eq. (22) cancel except for the self-interaction of the smeared Coulomb charge. This is easily evaluated using Eq. (4) as

$$\frac{1}{2} \int d\mathbf{\vec{r}} [\rho_{\rm ISC}(\mathbf{\vec{r}}) V_{\rm ISC}(\mathbf{\vec{r}}) - \rho_I(\mathbf{\vec{r}}) V_I'(\mathbf{\vec{r}})] = -8(2\alpha_{\rm Ior}/\pi)^{1/2} e^2.$$
(25)

As remarked earlier, the symmetric Coulomb potential $V_{\rm NC}(\vec{\mathbf{r}})$ is not unique within an additive constant. The constant (which will generally be volume dependent) depends on how the symmetric units are chosen. The choice we have made in Eq. (12) is mathematically convenient but not very physical, leading as it does to large charge overlap between neighboring cells. Since $\int d\vec{\mathbf{r}} \rho_{\rm ISC}(\vec{\mathbf{r}}) = \int d\vec{\mathbf{r}} \rho_e(\vec{\mathbf{r}}) = 4$, it is easily seen that the constant cancels between the three terms $E_{\rm eig} - E'_{eeC} + E'_{II}$ contained in Eq. (19) for the total energy. Neither the energy nor its volume dependence has any physical significance for any of the individual terms.

The above cancellation of terms in the total energy also means that contributions from distant clusters affect the total energy much less than they affect the potential. This is consistent with the well-known fact that chemical properties are effectively very short range.

E. Orthogonality and antibonding corrections using the Baldereschi point

Up to this point we have computed the crystalline total energy entirely by using the \vec{r} -space representation. For a perfect crystal this is not necessarily easier or more accurate than \vec{k} -space methods although our procedure so far has been very simple and leads to a description of the total energy in terms which are closely related to the chemical description. The methods given should also be easily generalized to systems lacking translational symmetry, and this was the motivation of the present work.

We have made the approximation of neglecting the overlaps of our bonding functions on second and further neighbors. We also have not allowed for admixture of antibonding functions into the valence band Wannier functions. Both these corrections tend to spread out the Wannier functions and hence make \tilde{r} -space methods more cumbersome. These corrections can be treated in $\mathbf{\tilde{r}}$ space also. An initial attempt to do so is given in Kane and Kane.⁴ However, we believe a $\mathbf{\tilde{k}}$ -space method is easier to handle and since our point is that these corrections are small, we justify the use of a "hybrid method" to prove the point.

We form \bar{k} -space functions from the bonding and antibonding functions of Eq. (1) with the help of Bloch sums.

$$\begin{split} \psi_{\vec{k}b_{n}}(\vec{r}) &= \sum_{\vec{a}} e^{i\vec{k}\cdot(\vec{a}+\vec{r}_{n}/2)} b_{n}(\vec{r}) ,\\ \psi_{\vec{k}a_{n}}(\vec{r}) &= i \sum_{\vec{a}} e^{i\vec{k}\cdot(\vec{a}+\vec{r}_{n}/2)} a_{n}(\vec{r}) ,\\ \vec{\tau}_{1,2,3,4} &= \frac{1}{4} a((1,1,1), (1,-1,-1), (-1,1,1)) . \end{split}$$
(26)

The bonding (antibonding) functions $b_n(a_n)$ have their bonds oriented along $\vec{\tau}_n$. The choice of phase gives real matrix elements. We then have an 8×8 matrix which we diagonalize exactly including the nonorthogonality from the overlap. We "integrate" over \vec{k} space with the use of the Baldereschi point,⁹ $\vec{k}_B = (2\pi/a)$ (0.6223, 0.2953, 0).

The functions b_n , a_n were determined from the Schrödinger equation including a term coming from the variational derivative of the orthogonality constraint $\lambda \langle b_1 | b_2 \rangle$. The charge density determining the potential was iterated to self-consistency. Call this potential and charge density V_r and ρ_r and the total energy, $E_{\text{tot}\,r}$.

Using the Bloch sums of Eq. (26) at the Baldereschi point as basis functions without changing b_n or a_n , we diagonalize the ordinary Schrödinger equation with the potential V_{τ} , including overlap exactly. The lowest four eigenfunctions then lead to a new charge density and potential ρ_k and V_k .

We calculate the total energy, E_{totk} , from the formulas of Eqs. (19)-(25) using ρ_k and V_k . Since the Baldereschi-point method is approximate, we calculate the corrections in the form of differences between the three quantities $E_{\text{tot}\,k}^{\text{UB}}$, $E_{\text{tot}\,k}^{\text{NB}}$, and $E_{\text{tot}\,k}^{\text{NAB}}$, where U and N denote unnormalized and normalized, respectively. $E_{tot\,k}^{NAB}$ corresponds exactly to what we have just described, treating overlap rigorously and using bonding (B) and antibonding (AB) functions. $E_{tot k}^{NB}$ is similar but only bonding functions are used. In $E_{tot k}^{UB}$ only bonding functions are used and the overlap matrix between the b_{n} on different sites is taken as the identity matrix. Thus $E_{\text{tot} k}^{UB}$ corresponds most closely to E_{totr} but is not identical since the Baldereschipoint method is only approximate. The correction for orthogonality is then defined as

$$\Delta E_{\text{tot}\ k}^{\text{orth}\ } = E_{\text{tot}\ k}^{\text{NB}\ } - E_{\text{tot}\ k}^{\text{UB}\ }, \qquad (27)$$

4604

TABLE II. Total energy per atom in eV vs lattice constant in a.u. The columns give the band energy, ion-ion energy, electron-electron Coulomb energy, electron-electron exchange and correlation energy, and the total energy. The symbols are those of Eq. (19). All quantities from the \vec{r} -space calculations.

A (a.u.)	E_{eig}	E_{II}^{\prime}	E'eec	E _{eeX}	E _{tot} r
9.070	5.802	-121.069	-3.578	-29.444	-101.874
10.263	-0.444	-115.894	-5.472	-27.294	-101.768
10.8595	-2.752	-113.334	-6.204	-26.361	-101.095
11.456	-4.557	-111.024	-6.896	-25.587	-100.156

and the antibonding correction is

$$\Delta E_{\text{tot } k}^{\text{ABND}} = E_{\text{tot } k}^{\text{NAB}} - E_{\text{tot } k}^{\text{NB}}.$$
(28)

III. RESULTS

A. Total energy, bulk modulus, and lattice constant

We have evaluated the total energy per atom as described in Sec. II for four lattice constants, A = 9.070, 10.263, 10.8595, 11.456 a_0 . The results are given in Tables II and III for both the \vec{r} -space method, E_{totr} , and the \vec{k} -space method, E_{totk} , using the Baldereschi point, \vec{k}_B .⁹ As discussed in Sec. II, the individual components E_{elg} , E'_{II} , and E'_{eeC} do not have any physical meaning separately but depend on the choice made for symmetric units in the Coulomb sums.

We have elected to add an adjustable constant to the "neutral Coulomb" potential in Eq. (24) so that it satisfies the condition

$$\int d\mathbf{\hat{r}} V_{\rm NC}(\mathbf{\hat{r}}) = 0 \tag{29}$$

for each lattice constant. We still cannot attribute much significance to the individual terms but they show a relatively simple lattice constant dependence. The decomposition also depends on our choice of smearing parameter $\alpha_{ion} = 1$ a.u. The Slater exchange energy, E_{eex} , is meaningful, of course, and is slowly varying with lattice constant as expected from the slow $\rho^{1/3}$ dependence of the exchange potential. The variation of the total energy is small compared to that of the individual terms. The large effective cancellation is what makes all total energy calculations difficult. The large absolute value of the total energy results from the fact that it contains the binding energy of the four valence electrons in the pseudoatom. According to our choice of constant in Eq. (29), the absolute total energy comes mainly from the ion-ion term E'_{II} for which a major contribution is the volume-independent ion self-energy correction of Eq. (25).

The total energy from a \bar{k} -space calculation is given in Table III. We approximate the sum over

 \mathbf{k} space by the value at the Baldereschi point, $\mathbf{k}_B = (2\pi/a) (0.6223, 0.2953, 0)$. In column 2, $E_{\text{tot}\,\mathbf{k}}^{\text{UB}}$ is the Baldereschi-point total energy, including bonding functions only and setting the overlap matrix equal to unity. In the \mathbf{k} -space calculation we always use the same bond functions $b_n(\mathbf{r})$, $a_n(\mathbf{r})$ [see Eq. (1)] as determined in \mathbf{r} space, but we recompute the charge density and the potentials in Eqs. (21)-(24) from the \mathbf{k} -space eigenfunctions at \mathbf{k}_B .

If we had summed over \vec{k} space instead of using \vec{k}_B , $E_{tot\,k}^{UB}$ would equal $E_{tot\,r}$ since the \vec{k} -space and \vec{r} -space bonding wave functions are connected by a unitary transformation when nonorthogonality is neglected. The differences reveal the inaccuracy involved in using the Baldereschi point. The error is about 0.5 eV, relatively independent of lattice constant.

In column 3, we give the orthogonality correction determined as the difference of the \bar{k} -space energies using bonding Bloch sums only when the bond overlap is properly accounted for and when it is ignored [see Eq. (27)]. We believe that this difference is not too much affected by the error involved in using \bar{k}_B . It shows the expected variation with lattice constant, namely that the overlap correction is much more important at small lattice constants.

TABLE III. Corrections to the total energy per atom in eV vs lattice constant in a.u. as estimated from a k-space calculation at the Baldereschi point. Column 2 is Baldereschi-point total energy minus r-space total energy. Columns 3 and 4 are orthogonality corrections and antibonding correction energies as defined in Eqs. (27) and (28). Column 5 is the final total energy corrected for orthogonality and antibonding function admixture.

A (a.u.)	$E_{\text{tot k}}^{\text{UB}} - E_{\text{tot r}}$	$\Delta E_{\rm tot}^{\rm orth}$	$\Delta E_{ m tot}^{ m ABND}$	E _{tot}
9.070 10.263 10.8595	0.331 0.533 0.536	1.976 0.578 0.357	-0.329 -0.579 -0.646	-100.227 -101.769 -101.384
11.456	0.494 $E_{\text{tot}} = E_{\text{tot}t} + $	0.216 - $\Delta E_{\text{tot}}^{\text{orth}} +$	-0.733 $\Delta E_{\text{tot}}^{\text{ABND}}$	-100.673

In column 4, we give the antibonding correction defined as the difference between the energies at \vec{k}_B with overlap correctly treated, with and without the addition of antibonding Bloch sums [see Eq. (28)]. The antibonding correction decreases at small lattice constants. It shows somewhat less variation with lattice constant than the orthogonality correction and has the opposite sign. At the equilibrium lattice constant the two terms cancel almost exactly.

Column 5 gives our final value for the total energy which equals the \vec{r} -space value plus the orthogonality and antibonding corrections. The corrections are quite significant as will be seen in the calculation of the lattice constant and the bulk modulus. We believe that most of the error from the Baldereschi point has been removed in forming the differences.

In Table IV we have used the total energies to calculate the bulk modulus B and the equilibrium lattice constant A_0 . These numbers are derived from a quadratic fit to the energy at the three larger lattice constants. The anharmonic energy, E_{anharm}^{tot} , is the difference of the energy at 9.070 and the quadratic extrapolation. The differences between the values derived from E_{totr} and E_{tot} are sizable but not overwhelming. This is encouraging for the use of the \vec{r} -space method in lower-symmetry situations where the corrections would be less easily made. The "anharmonic energy" is very different in the two approximations. Accordingly, we believe it is desirable to do all $\mathbf{\tilde{r}}$ -space calculations using the OCP method for the largest possible lattice constants and then extrapolate to the true lattice constant. The limitation is set by the physical anharmonicities of the crystal. Comparison of our results to experiment is quite satisfactory. The lattice constant is about 4% too small and the bulk modulus 13% too small.

In column 5 we give Ihm and Cohen's¹ results for comparison. In order to compare more accurately we add the Nozières-Pines correction¹² energy, $E_{\rm NP}$ (in Ry), to our results as they have done.

$$E_{\rm NP} = 4(-0.115 + 0.031 \ln r_s). \tag{30}$$

This term makes a large difference in the total energy, a 2% reduction in the lattice constant and a 1% reduction in the bulk modulus. At the present stage of theory, we would prefer to ignore this term as being within the uncertainties involved in the proper choice of $X\alpha$.

In comparison with Ihm and Cohen¹ we get reasonable results for the total energy and lattice constant but a very large difference in the bulk modulus. The greater disagreement for the bulk modulus is not surprising because it requires forming a second difference of numbers which are not completely accurate. Our bulk modulus agrees more closely with experiment, but this cannot be taken as proof of its correctness. Correction of this discrepancy would be highly desirable but for the moment it must await a more rigorous recalculation by one or both methods.

B. Bond charge

We have made use of spherical Gaussian charge distributions on lattice and bond sites primarily as a calculational tool. The Gaussians used were $\alpha = 0.4$, 0.8, and 1.2. With these values there is substantial overlap between the bond and the atomic distributions. Indeed at most lattice constants the atomic charge is negative even though the sum of the two distributions is everywhere positive. Nevertheless, it is interesting to study the integrated bond charge ρ_B , and its dependence on lattice constant and on the computational approximations. Of course, the total charge per atom must be 4 so that $\rho_{atom} + 2\rho_B = 4$.

The values of the bond charges are given in Table V. Most of the charges are greater than 2 so that the atomic charge is negative. The values are very large compared to the empirical bond charges of lattice dynamics.¹¹ This is hardly

TABLE IV. Bulk modulus B, in 10^{12} dyne/cm², equilibrium lattice constant in a.u., minimum total energy and anharmonic energy in eV per atom. The anharmonic energy is the total energy at A = 9.070 a.u. minus the value quadratically extrapolated from the three larger lattice constants. Comparison is made between the \hat{r} -space total energy, the energy with \hat{k} space corrections, the added correction of Nozières-Pines as treated by Ihm and Cohen, the experimental values, and the values of Ihm and Cohen. (Experimental values taken from Ihm and Cohen.)

	E _{tot r}	E _{tot}	$E_{\rm tot} + E_{\rm NP}$	Expt.	E _{MLC}
В	0.70	0.86	0.85	0.99	1.69
A_0	9.052	9.857	9.672	10.263	10.110
E_{\min}^{tot} E_{nharm}^{tot}	-102.316 0.301	-101.845 1.601	-107.011		-107.61

TABLE V. Bond charge ρ_B , in units of |e| vs lattice constant in a.u. for various approximations: ρ_{Br} from \bar{r} -space bond functions; ρ_{Br}^{UB} from the \bar{k} -space Baldereschi point neglecting overlap; ρ_{BR}^{NB} as before but including overlap; ρ_{BR}^{NAB} as before but including overlap and antibonding function admixture.

A (a.u.)	ρ _{Br}	ρ^{UB}_{Bk}	ρ_{Bk}^{NB}	$\rho_{\boldsymbol{B}k}^{\mathrm{NAB}}$
9.070	3.436	4.391	3.876	3.716
10.263	2.302	2.822	2.757	2.648
10.8595	2.022	2.363	2.346	2.277
11.456	1.789	2.004	2.004	1.973

surprising. The static charges must contain four units which can be either on the bonds or the atom. Owing to the repulsive pseudopotential, the charge prefers the bond site. Under a lattice distortion, on the other hand, any shift of the charge produces large fields which are quickly screened out by the large dielectric constant;

hence the effective dynamic charge is roughly $\rho_{\rm B}/\epsilon$. Our values of $\rho_{\rm B} \sim 2$ are thus in accord with the bond-charge model first proposed by Phillips.¹⁰ The static bond charge increases monotonically as the lattice constant is reduced. The error in the bond charge using the Baldereschi point is fairly large and increasing at small lattice constants. The corrections to the bond charge due to normalization and antibonding admixture are small except for A = 9.070. Not too much physics can be derived from the static bond charge, but the general accuracy of the bond charge for describing the charge distribution suggests that a phonon calculation along these lines might lead to interesting comparisons with Weber's empirical lattice dynamical bond-charge model.¹³

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