Gaussian representations of covalent wave functions; silicon

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We represent the pseudo wave functions of silicon using Bloch sums of s, p, and d Gaussians on atom sites. Maximal energy errors of 0.17 eV for the valence band and 0.28 eV for the two lowest conduction bands can be achieved with 18 states per atom. Localization to zeroth, first, and second neighbors is achieved with some contribution from third neighbors. The localization is similar to free atoms. d states are needed in the valence band but are much more important in the conduction band. A four-state s, p band fit is reasonable for the valence band but bad for the conduction band as found in earlier empirical work. We attribute the conduction-band errors to the need for d functions. The Appelbaum-Hamann self-consistent pseudopotential is represented in Gaussian form with three coefficients. These coefficients could lead to a more efficient tight-binding parameterization scheme than the conventional overlap intergral method.

I. INTRODUCTION AND CONCLUSIONS

The tight-binding method was one of the earliest methods applied to the study of crystal band structure.[1-3] For many years it was eclipsed by the quasi-plane-wave methods such as the augmented-plane-wave,[4] orthogonalized-plane-wave,[5] or empirical-pseudopotential methods.[6] More recently there has been a considerable revival of interest in the tight-binding picture. The renewed attention has been motivated in part by the extreme simplicity of the method and in part by the localization in r space of the basis set. The atomic picture is still the framework in which most chemical ideas about crystal properties are expressed, hence the tight-binding picture forms a natural bridge between chemical concepts and band-structure properties.[7] Another useful aspect of the localization is that it is well adapted to study problems where the crystal is perturbed by a spatially localized imperfection such as an impurity or a surface[8] or to study amorphous covalent materials.[9]

In its simplest form the tight-binding method is not as accurate as the quasi-plane-wave methods. However, it has been demonstrated that localized orbitals,[10] particularly the analytically tractable Gaussians,[11] are quite competitive with plane-wave methods even when high accuracy is required and even for those materials such as the alkali metals for which plane-wave methods seem most natural. Most of the work based on the tight-binding method excepting that of Refs. 10 and 11 has been of an empirical nature.[8,12,13] The parameters of the problem are the overlap integrals of the potential between atomic functions on different sites, adjusted to fit the energy bands determined by other methods. In contrast, we give the wave functions explicitly as Bloch sums of Gaussians and calculate their energies using a pseudopotential Hamiltonian.[14] We study silicon in detail. We use s, p, and d "Gaussians" $e^{-\alpha r^2}$, $xe^{-\alpha r^2}$, $yze^{-\alpha r^2}$ located

on atomic sites as basis functions for tight-binding sums. We have also considered s and p Gaussians on bonding and antibonding sites, $(a/8)(1,1,1)$ and $(-a/8)(1,1,1)$.

We find a value of $\alpha = 0.20$ to be nearly optimal which leads to a localization similar to that of the neutral atom. The bulk of the interaction occurs between zero, first, and second neighbors but third neighbors are not completely negligible. We find that the three d functions which hybridize with p are quite important in fitting valence- and conduction-band energies. The other two d functions also play an important role in the conduction band. Our conclusions with respect to d functions are similar to those of Chaney *et al.*[10] but more detailed.

We find that the valence bands are much easier to fit than are the conduction bands in agreement with empirical studies.[8,13] We blame the conduction-band fitting problems on the importance of d functions.

For a 10-state per atom fit using two s Gaussians and one p and d Gaussian we find a maximum valence-band error of 0.35 eV and a maximum error in the two lowest conduction bands of 0.48 eV. For an 18-state fit with two Gaussians each for s, p, and d, the maximum errors are reduced to 0.17 and 0.28 eV, respectively. For a four-state fit the maximum valence-band error is 0.93 or ±0.36 eV relative to an average valence-band shift of 0.57 eV. (We must compare to empirical fits in this way since they have no absolute reference point.)

We have also been able to achieve reasonable fits to the energy bands using Gaussians located on atom, bond, and antibond sites. The bond-site states are most important to fit the valence band and the antibond site states are needed in the conduction band as expected. For the same number of states the atom centered fits are somewhat better and are also simpler.

TABLE I. Pseudopotential energies in eV relative to $\Gamma_{25'}$. Pseudopotential from Ref. 14. Valence states and two lowest conduction states. $\Sigma = K = (2\pi/a)(\frac{3}{4}, \frac{3}{4}, 0)$.

$L_3 = 3.94$	$\Gamma_{2'} = 3.92$		$\Sigma_1 = 4.55$
$L_1 = 1.83$	$\Gamma_{15} = 3.39$	$X_1 = 0.90$	$\Sigma_3 = 1.44$
$L_{3'} = -1.28$	$\Gamma_{25'} = 0.00$	$X_4 = -3.04$	$\Sigma_2 = -2.60$
$L_1 = -7.44$		$X_1 = -8.41$	$\Sigma_1 = -4.57$
$L_{2'} = -10.31$	$\Gamma_1 = -12.69$		$\Sigma_3 = -7.79$
			$\Sigma_1 = -8.84$

We cannot easily compare our results to the empirically adjusted methods. In our method the basis functions overlap strongly hence there would be too many parameters for empirical adjustment. Instead of proceeding in this manner we believe a much simpler method is to represent the potential in tight-binding form and parametrize from this point. We have used the self-consistent pseudopotential of Appelbaum and Hamann[15] and have shown that it can be represented in terms of three-atom centered Gaussians. This is a considerable simplification compared to the seven parameters of overlap parametrization schemes.[8]

In summary we believe a description based on Gaussian atom site orbitals possesses many advantages relative to plane-wave or pseudo-plane-wave descriptions for almost any application where r-space localization is important. To go beyond the pseudopotential approximation one need only add more highly localized Gaussians to represent the core functions. (Probably Slater orbitals would require fewer functions. This must be balanced against the analytic convenience of Gaussians.)

II. GAUSSIAN REPRESENTATIONS

A. Calculational method

We make a detailed study of Gaussian representations of pseudo wave functions using silicon as a prototype covalent material. We use the empirical pseudopotential of Brust.[14] For this potential a plane-wave representation provides quite accurate wave functions and energies if we use a kinetic-energy cutoff T_{max} of 99.4 eV to limit the number of basis states:

$$T_{max} = (2\pi/a)^2 \, 19.5/2 \text{ a.u.} \qquad (1)$$

This leads to 89 plane waves at the Γ point.

We calculate the valence-band and low conduction-band energy levels at the Γ, X, L, and K points using these plane-wave basis states and we use these energies as a standard of reference for the tight-binding calculations.

We construct tight-binding functions as Bloch

sums over atom centered s, p, and d "Gaussians" defined as

$$\varphi_{s\alpha} = e^{-\alpha r^2}, \qquad \varphi_{p_1\alpha} = xe^{-\alpha r^2},$$

$$\varphi_{d_1^3\alpha} = yze^{-\alpha r^2}, \qquad \varphi_{d_1^2\alpha} = (3x^2 - r^2)e^{-\alpha r^2}, \qquad (2)$$

$$\varphi_{d^1\alpha} = r^2 e^{-\alpha r^2}.$$

The $\varphi_{p_j\alpha}$, $\varphi_{d_j^3\alpha}$ functions are threefold degenerate while the $\varphi_{d^2\alpha}$ functions are doubly degenerate. In Eq. (2) we list one representative of each degenerate set. We Fourier analyze each of these Bloch sums in the plane-wave basis set just described and compute the wave functions and energies variationally. By this procedure the tight-binding states necessarily lie at higher energies than the plane-wave states which have full variational freedom. The plane-wave energies of the states investigated are given in Table I in eV. The tight-binding energies are always quoted in eV as differences from these values.

B. Single-Gaussian description

In selecting tight-binding states our aim is to satisfy as well as possible the conflicting requirements of states which are highly localized, which consist of a small number of Gaussian components and which give accurate energies. The simplest possible description is that of a single s and p "Gaussian." We find that the optimum fit here occurs for an α of the order of 0.125. The energy errors resulting from this approximation are shown in Table II. Although the errors in the valence band are as large as 0.83 eV the fluctuation in the errors is small. If the valence states were rigidly shifted by 0.72 eV, the maximum error would be only 0.11 eV. The biggest defect of the single Gaussian representation is the localization. For the $\Gamma_{25'}$ state, for example, an energy of 0.29 eV is contributed by sixth-neighbor interactions.

TABLE II. Energy-band fits with 4 or 8 states per atom. Upper values are for a single s and p Gaussian with $\alpha = 0.125$. Lower values at Γ are for two s or p Gaussians with the α values in parentheses. Energies in eV relative to pseudopotential values in Table I.

L_3	1.25	$\Gamma_{2'}$	0.15.		Σ_1	2.25
			0.07 (0.15, 0.20)			
L_1	0.86	Γ_{15}	0.42	X_1 1.10	Σ_3	0.85
			0.21 (0.25, 0.30)			
$L_{3'}$	0.78	$\Gamma_{25'}$	0.79	X_4 0.83	Σ_2	0.80
			0.78 (0.10, 0.15)			
L_1	0.76				Σ_1	0.66
$L_{2'}$	0.64			X_1 0.73	Σ_3	0.73
		Γ_1	0.61		Σ_1	0.69
			0.16 (0.25, 0.30)			

C. Two Gaussian approximation

The addition of a second Gaussian of the same symmetry type was checked at the Γ point. Values of $\alpha = \alpha_0$, $\alpha_0 + 0.05$ were studied. The optimum fit is given in Table II together with the optimum values of α which are seen to be considerably different for the different symmetry types. The value of $\Gamma_{25'}$ is very little improved by the second Gaussian. A very dramatic improvement occurs when d_j^3 "Gaussians" are added to the basis set. This is a clear indication of the importance of d functions in the silicon valence band. Phenomenologically the d_j^3 functions have the same symmetry as the p_j functions and hence are not easily distinguished in empirical treatments.

D. Accuracy versus localization and spherical harmonic content

We have studied Bloch sums involving better localized Gaussians for the three cases $\alpha_{min} = 0.20$, 0.25, 0.30. As α increases, the average fit gets worse, or alternatively, to achieve the same accuracy one needs to use more Gaussians. We have studied the case of $\alpha_{min} = 0.20$ most extensively to see how the fit depends on the number and symmetry of the Gaussians. The results are given in Table III. All states when present have $\alpha = 0.2$. A value $\alpha = 0.3$ is also used when two states of the

TABLE III. Energy-band fits using 8-, 10-, and 18-Gaussian states per atom as indicated in braces. s, p, d^3, d^2 refer to the dominant spherical harmonic content of the wave function. Energies in eV relative to pseudo-potential energies in Table I. α is in a.u.

L_3	0.09	$\Gamma_{2'}$	0.11			Σ_1	0.28
d^2	0.09	s	0.11			d^3,p	0.46
	1.96		0.11				1.23
L_1	0.26	Γ_{15}	0.13	X_1	0.13	Σ_3	0.15
d^3	0.48	p	0.23	d^3	0.33	d^3	0.32
	0.48		0.23		0.91		0.95
$L_{3'}$	0.12	$\Gamma_{25'}$	0.07	X_4	0.14	Σ_2	0.14
p	0.19	p	0.12	p	0.28	p	0.25
	0.34		0.12		0.28		0.37
L_1	0.12					Σ_1	0.11
s,p	0.25					p	0.35
	0.25						0.47
$L_{2'}$	0.16			X_1	0.17	Σ_3	0.17
s	0.17			s	0.22	s	0.21
	0.17				0.27		0.24
		Γ_1	0.13			Σ_1	0.15
		s	0.13			s	0.18
			0.13				0.19

$\left\{\begin{array}{l} \text{18 states } 2s, \ 2p, \ 2d^3, \ 2d^2 \quad \alpha = 0.2, \ 0.3 \\ \text{10 states } 2s, \ p, \ d^3, \ d^2 \quad \ \alpha = 0.2, \ \alpha = 0.3 \ s_2 \\ \ \ 8 \text{ states } 2s, \ p, \ d^3 \quad\quad\quad \alpha = 0.2, \ \alpha = 0.3 \ s_2 \end{array}\right\}$

same symmetry are present.

In general the valence bands are more accurate than the conduction bands as would be expected for a "tight-binding" type of representation. For the 18-state case the maximum error in the conduction band is 0.28 eV and in the valence band is 0.17 eV. Relative to an average shift of 0.12 eV the valence band is accurate to ± 0.05 eV. In going from 18 states to 10 states we keep the same symmetries present but reduce the number of degrees of freedom. The errors roughly double but the fit is still quite good.

When we go to the 8-state fit in which the d^2 states have been dropped the maximum change in the valence band is only 0.15 eV. Errors in the conduction band are now much bigger, particularly for the L_3 state. We can get some further indication of the symmetry of the states by looking at the tight-binding coefficients. It must be remembered here that Gaussian Bloch sums of different spherical harmonics may not be orthogonal. For instance, p states on first neighbors generate d states about the origin even at the Γ point. Hence our tight-binding coefficients are very rough indications of spherical harmonic content. For instance

$$\langle \psi_{\Gamma_{25'}}(p) | \psi_{\Gamma_{25'}}(d^3) \rangle_{\alpha=0.20} = -0.69 ,$$
$$\langle \psi_{\Gamma_{15}}(p) | \psi_{\Gamma_{15}}(d^3) \rangle_{\alpha=0.20} = -0.95 . \tag{3}$$

(These numbers explain why the d^3 states are much more important for fitting $\Gamma_{25'}$ than they are for Γ_{15}.) With this caveat the spherical harmonic type of the dominant Bloch sum is indicated in Table III as determined in the 10-state fit. When two harmonics are listed they have roughly equal weight. The occurrence of two p and two s states in the valence band at Σ is surprising (instead of three p and one s). It is probably due both to the admixture of antibonding s and to the lack of orthogonality between "s" and "p."

The fitting dependence is consistent with the dominant tight binding harmonic assignment. L_3 is more seriously perturbed by the omission of d^2 states than any other level. In the valence band "p" states the p harmonic dominates while in the conduction band d^3 is dominant. We believe this explains the fact that good fits to the valence band in the traditional s-p tight binding scheme give very poor conduction bands. As α decreases, the overlap between p and d^3 increases. This might explain why both valence and conduction bands are poorly fit in Table II, i.e., there is too much d^3 for the valence band and too little for the conduction band.

In Table IV we examine the quality of the fit as we increase the Gaussian localization. In general the valence bands remain quite well fit up to $\alpha_{min} = 0.30$, the worst case being the upper Σ_1 level.

TABLE IV. Energy-band fits vs localization of Gaussians, 18 and 19 states per atom. Parameters indicated in braces. Energies in eV relative to pseudopotential energies in Table I. α is in a.u..

L_3	0.09	$\Gamma_{2'}$	0.11			Σ_1	0.28
	0.13		0.21				0.60
	0.38		0.22				1.14
L_1	0.26	Γ_{15}	0.13	X_1	0.13	Σ_3	0.15
	0.47		0.15		0.40		0.41
	0.73		0.31		1.04		0.95
$L_{3'}$	0.12	$\Gamma_{25'}$	0.07	X_4	0.14	Σ_2	0.14
	0.05		0.03		0.12		0.10
	0.06		0.05		0.28		0.23
L_1	0.12			X_1	0.17	Σ_1	0.11
	0.14				0.07		0.14
	0.36				0.12		0.53
$L_{2'}$	0.16					Σ_3	0.17
	0.07						0.07
	0.08						0.12
		Γ_1	0.13			Σ_1	0.15
			0.24				0.03
			0.19				0.06

$$\left\{\begin{array}{l}\text{18 states } 2s, 2p, 2d^3, 2d^2 \quad \alpha = 0.2, 0.3 \\ \text{18 states } 2s, 2p, 2d^3, 2d^2 \quad \alpha = 0.25, 0.35 \\ \text{19 states } 3s, 2p, 2d^3, 2d^2 \quad \alpha = 0.30, 0.40 \ s,p,d \ \alpha = 0.35 \ s_3\end{array}\right\}$$

The quality of fit in the conduction band decreases monotonically as the localization increases in keeping with the more delocalized states to be expected at higher energy. To achieve a good fit for larger α_{min} has required a larger number of states. The 10-state fit which is good for $\alpha_{min} = 0.20$ in Table III, is very bad at $\alpha_{min} = 0.25$ (not tabulated). Thus we find that to reduce the number of interacting atom sites we have to increase the number of interacting states per site. The optimum situation occurs around $\alpha_{min} = 0.20$ or 0.25.

E. Energy overlap versus shell number

We have computed the energy overlap as a function of neighbor distance for bonding Bloch sums of single s or p Gaussians at the Γ point. We write

$$\psi_\Gamma = \sum_{\vec{R}} \varphi_\gamma (\vec{r} - \vec{R}) \ , \tag{4}$$

$$E_\Gamma = \langle \psi_\Gamma | H | \psi_\Gamma \rangle / \langle \psi_\Gamma | \psi_\Gamma \rangle \ , \tag{5}$$

where $\Gamma = \Gamma_1$, $\Gamma_{25'}$; $\gamma = s\alpha$, $p\alpha$

$$E_\Gamma = \sum_{\vec{R}} \mathcal{E}_\Gamma (\vec{R}) \ ,$$

$$\mathcal{E}_\Gamma (\vec{R}) = \frac{N \langle \varphi_\gamma (\vec{r}) | H | \varphi_\gamma (\vec{r} - \vec{R}) \rangle}{\langle \psi_\Gamma | \psi_\Gamma \rangle} \ ,$$

$$\mathcal{E}_\Gamma (n) = \sum_{\text{star } \vec{R}} \mathcal{E}_\Gamma (\vec{R}) \ , \tag{6}$$

where N is the number of atoms. The quantity $\mathcal{E}_\Gamma (n)$ is tabulated in eV as a function of neighbor shell number n in Table V. The total of all shells is given in the lower line and it is clear that the single Gaussian wave function is very inaccurate for large α. Nevertheless the results should be reasonably good in indicating the rate of convergence with shell number. In general the p state converges more slowly since the polynomial factor pushes the Gaussian falloff to larger r values. The falloff is more rapid for large α as expected. Contributions beyond second neighbors are small for $\alpha = 0.3$. For the "best compromise value" $\alpha = 0.2$ the contribution from third neighbors is not negligible but should be small enough to be handled by some form of perturbative technique.

It is interesting to compare the localization we find for our Gaussian representations with that obtaining in the free atom. Using Clementi's Hartree-Fock wave functions[16] for neutral silicon in the ^1S state we calculate the shell charge maximum $r^2 |\psi(r)|^2$ for the $3p$ state to occur at $r = 2.18$ a_0. For a p Gaussian the shell charge maximum occurs at the same value for $\alpha = 0.21$ a.u. The

TABLE V. Energy contributions in eV to overlap energies $\mathcal{E}_\Gamma(n)$ vs shell number for Γ_1 ($s+$) and $\Gamma_{25'}$ ($p+$) for several values of α. Bottom line is sum over all shells. See Eq. (6). α is in a.u..

Neighbor shell number	$\Gamma_1 = S+$				$\Gamma_{25'} = p+$			
	$\alpha = 0.125$	0.20	0.25	0.30	0.125	0.20	0.25	0.30
0	0.70	2.77	5.02	7.68	13.50	9.15	10.52	13.05
1	-0.79	-2.49	-3.09	-3.18	0.34	1.85	1.23	0.42
2	-1.00	-0.79	-0.43	-0.19	-3.42	1.17	0.94	0.56
3	-0.35	-0.14	-0.05	-0.01	1.11	-0.42	-0.18	-0.06
4	-0.04	0.00	0.00	0.00	0.27	0.03	0.00	0.00
5	-0.04	0.00	0.00	0.00	-0.69	-0.02	0.00	0.00
6	-0.01	0.00	0.00	0.00	0.29	0.00	0.00	0.00
$\Sigma(n)$	-1.55	-0.66	1.45	4.29	11.42	11.76	12.52	13.97

TABLE VI. Four state per atom fit based on linear combination of 8 states in Table III optimized at the states starred. $p(s)$ state optimized for upper (lower) star. Energies in eV relative to pseudopotential energies in Table I.

L_3	2.84	$\Gamma_{2'}$	0.38			Σ_1	6.58
	3.39		0.14				4.74
L_1	1.37	Γ_{15}	0.28	X_1	1.90	Σ_3	2.13
	1.89		0.75		3.96		3.71
$L_{3'}$	0.60	$\Gamma_{25'}$	0.13*	X_4	0.67	Σ_2	1.00
	0.49		0.93		0.34		0.38*
L_1	0.48					Σ_1	1.51
	0.28						0.60
$L_{2'}$	0.21			X_1	0.39	Σ_3	0.33
	0.28				0.30		0.32
		Γ_1	0.13*			Σ_1	0.33
			0.20				0.27*

Gaussian functions drop off more rapidly at larger distances than the atomic functions.

F. Composite s, p band description

We have investigated another way of reducing the number of degrees of freedom in the wave function which leads to an effective 4-state approximation analogous to the conventional "atomic" description in terms of s and p functions. In principal, the method is to allow the s and p states to be described by arbitrarily many Gaussians but to keep their coefficients fixed.

In Table VI we give the results of such a "4-state" approximation based on the 8-state fit described in Table III. The s and p states are constructed from optimum linear combinations of Gaussians appropriate to the states starred; the s state from the lower-energy state and the p state from the upper. In interpreting the results we refer to the dominant spherical harmonic designated in Table III. The s states are reasonably well represented in both sets of numbers. The p-state fit at the Γ point fits rather poorly at Σ and vice versa. The Σ point fit is better in the valence band at the X and L points than is the Γ fit. The d-type conduction-band fits are very bad in both cases. This agrees with the d designation which implies that the relative weights of p and d^3 states are reversed between the valence and conduction bands. Since the ratio is kept fixed at the value optimal for the valence band we expect poor conduction band results. The 4-band single Gaussian fit in Table II is much better for the conduction band than the states in Table VI. The drawback here is that the states are not well localized.

G. Bond and antibond site description

We have also tested the possibility of representing the pseudo wave functions with Gaussians located on sites other than atomic sites in the unit cell. The most obvious site to add is the bond site. We have also added s Gaussians at the antibond site and p Gaussians parallel to the bond at the bond sites. The results are shown in Table VII. The 8-state model with s and p Gaussians on atom sites and s Gaussians on bond sites fits the valence bands very well and the conduction bands rather poorly. The addition of Gaussians on antibond sites ($\vec{r}_{antibond} = - \vec{r}_{bondsite}$) and $p_{\parallel}$ Gaussians on bond sites has relatively little effect on the valence bands but improves the conduction bands considerably. The antibond states are more important than the $p_{\parallel}$ bond states. The fit to the valence bands is comparable to what is achieved with atom centered Gaussians but the conduction band fit is not as good. Another disadvantage of the bond site model is that the overlap between different Bloch sums is much greater. For example, the dot products analogous to Eq. (3) are

$$\langle \psi_{\Gamma_{25'}}(\text{atom}) | \psi_{\Gamma_{25'}}(\text{bond})\rangle = 0.982 ,$$
$$\langle \psi_{\Gamma_{15}}(\text{atom}) | \psi_{\Gamma_{15}}(\text{bond})\rangle = 0.992 . \tag{7}$$

The large overlap is not a serious defect computationally although it clearly increases round-off error problems. It is more of a difficulty conceptually in forming a picture of what the new degree

TABLE VII. Energy-band fits with s and p Gaussians on atom sites, s and $p_{\parallel}$ Gaussians on bond sites $\vec{b}$ = $(a/8)(1,1,1)$, s Gaussians on antibond sites $\vec{a}\vec{b} = -\vec{b}$. See braces. Energies in eV relative to pseudopotential energies in Table I. α is in a.u..

L_3	3.78	$\Gamma_{2'}$	0.55			Σ_1	3.54
	1.75		0.05				0.74
L_1	1.27	Γ_{15}	1.02	X_1	3.66	Σ_3	3.68
	0.23		0.23		0.59		0.65
$L_{3'}$	0.28	$\Gamma_{25'}$	0.07	X_4	0.25	Σ_2	0.33
	0.26		0.07		0.21		0.28
L_1	0.37					Σ_1	0.59
	0.17						0.27
$L_{2'}$	0.19			X_1	0.29	Σ_3	0.28
	0.07				0.19		0.19
		Γ_1	0.15			Σ_1	0.19
			0.10				0.14

$$\alpha = 0.20$$

{ 8 states s, p Gaussians on atom site, s Gaussian on bond site

{ 16 states s, p atom site, s bond and antibond site, $p_{\parallel}$ on bond site

of freedom looks like spatially and in interpreting the meaning of tight-binding coefficients of strongly overlapping functions.

If we had picked other cell sites we could have generated a greater number of symmetries which would undoubtedly give better fits. The ultimate in localized functions would presumably be achieved by locating sharply peaked Gaussians on many sites in the unit cell. Thus we could achieve minimal overlap between unit cells at the expense of many degrees of freedom in each cell. Our experience to date suggests that atom centered Gaussians yield the simplest and most accurate description.

H. Gaussian pseudopotential represention

In our calculations we have used a plane-wave representation. It would undoubtedly be simpler to work directly in the Gaussian-atom-site representation. In this connection it would be desirable to have the crystal potential in a Gaussian description rather than in the tranditional plane-wave form. Appelbaum and Hamann have given a self-consistent pseudopotential[15] in which they represent the atomic cores in Gaussian form

$$V_{\text{core}}(r) = \sum_{\vec{R}} (v_1^c + v_2^c |\vec{r} - \vec{R}|^2) e^{-\alpha_c |\vec{r} - \vec{R}|^2} \,. \qquad (8)$$

They gave the self-consistent potential including the electronic response in plane-wave form, however.

We find that by varying the coefficients v_1 and v_2 and adding a second Gaussian to represent the more spread out electronic charge we can fit Appelbaum and Hamann's potential to an accuracy better than 2%. We write the total potential

TABLE VIII. Appelbaum and Hamann pseudopotential (Ref. 15) in Gaussian form. Coefficients in atomic units v_1^c, v_2^c, α^c from Ref. 15. See Eqs. (8) and (9).

v_1^c	v_2^c	α^c	
3.042	-1.372	0.6102	
v_1	v_2	v_3	α_3
2.454	-1.585	-0.934	0.30

$$V_{\text{tot}}(\vec{r}) = \sum_{\vec{R}} (v_1 + v_2 |\vec{r} - \vec{R}|^2) e^{-\alpha_c |\vec{r} - \vec{R}|^2}$$
$$+ v_3 e^{-\alpha_3 |\vec{r} - \vec{R}|^2} \,. \qquad (9)$$

The coefficients are given in Table VIII.

It may be argued as to whether we have a 3- or 4-parameter fit since we are free to vary α_3. We believe α_3 represents the scale of the electronic interactions and hence will not change under small perturbations of the atomic environment. It should be possible to describe these changes in terms of variations in the three coefficients v_1, v_2, and v_3. We suggest that empirical fitting procedures based on these three parameters may be more useful than the customary methods of parameterizing the overlap integrals which involve a much larger number of parameters. (For cases where the electronic screening length varies appreciably α_3 should also be treated as a parameter.)

ACKNOWLEDGMENTS

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