

we will nevertheless vary parameters rather freely in order to most clearly illustrate various dependences. Evidently, the actual values of A and B can vary quite widely depending on the sizes of D , P , ϵ_b , $|\psi(0)|$, and M , for example.

²³The analogy here is to a vibrating string with fixed vs free ends.

²⁴This follows from an equation-of-motion analysis as detailed, e.g., by B. Bendow, Ref. 18(c).

²⁵See, e.g., R. Loudon, *J. Phys.* **26**, 667 (1965).

²⁶General theory of gap variation due to pressure and temperature in semiconductors is discussed by E. J. Johnson, in Ref. 6(b), and references therein; for specifics regarding narrow-gap materials see Ref. 11.

Nonlocal Corrections to the Band Structure of Si, Ge, and α -Sn[†]

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The electronic structure of three group-IV elements is examined using a nonlocal pseudopotential determined primarily by physical considerations. An ionic contribution to the potential is separated from the valence and covalent portion of the interaction, and is constructed in an empty-core approximation, in terms of a set of angular-momentum-dependent core radii R_l . A modified version of the Penn dielectric function is used to determine the valence charge potential. Comparison with experiment results in substantial improvement over what has previously been achieved using the local empirical model (EPM).

I. INTRODUCTION

Over the past several years the pseudopotential method has proven to be effective in describing the electronic spectra of many covalently bonded semiconductors. In the early studies the Fourier coefficients of potential were treated as disposable parameters and fitted to selected experimental data.¹ The resulting analysis for a wide range of experiment was sufficiently good that one could be reasonably certain that no major revisions of the electronic structure of the materials studied would thereafter be necessary. Continuation of the original scheme to a variety of compounds by Cohen and collaborators² showed that the technique would work with the same effectiveness as for the group-IV materials. Further work by Saravia and the author³ demonstrated that one could in addition successfully calculate deformations of the electronic structure associated with hydrostatic and uniaxial strains.

Several considerations make it worthwhile to reexamine the electronic structure of the group-IV materials. Perhaps the most compelling of these is the central role played by these substances in the Periodic Table. For example, given the electronic structure of Ge, one would hope to be able to get those of GaAs, ZnSe, CuBr, etc., as a series of well-defined ever-increasing perturbations on that of the central member of the sequence. Indeed, within a pseudopotential framework such a start has already been made by the author.⁴ Using a nearly self-consistent model, he found it possible to construct potentials for several of the III-V compounds without the use of any empirical inputs other than those provided by the group-IV elements.

Comparison was made between calculated and experimental values for 42 electronic transitions in these materials. The over-all agreement was as good as that achieved through either first-principles⁵ or purely empirical methods.⁶ It is natural, therefore, to suppose that any improvements in the pseudopotentials for the group-IV crystals will put us in a position to do more definitive work in the related AB compounds.

Examination of the current situation in Ge will suffice to indicate the present state of the art regarding band-structure theory in semiconductors. The original local version of the pseudopotential was able to specify the important energy levels to an accuracy of about 0.1 eV.¹ There were, however, a few levels that could only be located to within something slightly better than 0.5 eV. Of most concern at the time was the large optical-reflectivity peak near 4.3 eV. This appeared to be 0.4 eV too low in the theoretical spectrum.^{1,7} A subsequent paper using the pseudopotential method did not meet with any more success in improving upon this problem.² Passing on to electronic multiplet associated with the $\Gamma_{25'} \rightarrow \Gamma_{15}$ transition, we note that considerable and intensive efforts have been made recently which apparently finally resolve this elusive transition. Donovan *et al.*⁸ have made an exhaustive examination of the leading edge of their photoemission EDC's and place the center of mass of the multiplet slightly below 3.2 eV. The same authors, noting the lack of polarization dependence of their transverse electro-reflectance signal, definitively assign the 3.2-eV multiplet to this Γ excitation. Careful piezo-optic measurements also place the gap at the above

value.⁹ Our own studies¹ as well as subsequent ones² put it at 3.5 eV¹⁰—an error of somewhat over 0.3 eV.

The above paragraph then suggests the order of magnitude of the corrections that we will be seeking in this paper. Sufficient work has been done with the local pseudopotential model to assure us that we cannot look for any further improvements by a variation of the Fourier coefficients; instead, it will be necessary to explore nonlocal effects. It should be clear that only a small departure from the early local version will be required.

An additional goal here will be the clear separation of valence and core contributions to the pseudopotential. This is necessary as we wish to make a strict distinction between environmental and intrinsic ion effects within the framework of our model. Indeed, as will become apparent, it is precisely this classification which is necessary to make possible a systematic derivation of the potential for a wide range of materials and structures.

II. CONSTRUCTION OF POTENTIAL

A. Ionic Component

Since the early studies of Kleinman and Phillips,¹¹ considerable effort has been made to formally justify the use of a pseudopotential to replace the true atomic potential in the core region. By the core region we mean that portion of space occupied by the tightly bound electrons which normally do not enter into the chemical or valency characteristics of the atomic species. For the materials considered here this is simply the region of space occupied by all the electrons inside the valence shell of the atom. This point must be reconsidered when we have weakly bound *d* states present, as is the case for the transition substances, or weakly bonded *f* orbitals, as is the case for the rare earths.

Cohen and Heine¹² showed that one could use the requirement of orthogonalization of the core and valence wave functions together with the Pauli exclusion principle to generate an operator V_R . This extra term has the characteristic of nearly canceling the true potential in the core. Ashcroft¹³ simply allowed the total pseudopotential to go to zero inside the core radius. The author has shown^{4, 14} that the empty-core approximation will work reasonably well when applied directly to the III-V compounds. In its conventional form one writes the empty core model

$$V(r) = 0, \quad r < R_c \\ = Ze/r, \quad r > R_c. \quad (1)$$

Recent considerations by Heine and Abarenkov,¹⁵ Shaw and Harrison,¹⁶ and Shaw¹⁷ have shown how one can justify the use of a similar potential from

the standpoint of the quantum-defect method. The basic idea is to examine the bare ion. One then chooses a model core potential in such a manner that a Coulomb wave function in the exterior region has a continuous logarithmic derivative at the core boundary. An additional constraint on the surrogate core potential is that it reproduces the observed ionic spectrum. In order to make the spectra come out right for states of arbitrary angular momentum it is necessary to make the core potential depend somewhat on *l* value. In this way the potential becomes momentum dependent and the local restriction is lifted.

The point of view adopted in this paper is somewhat different from that of the above authors. In order to motivate it we reexamine the central result of Cohen and Heine. Through the use of a variational argument on the kinetic energy they arrived at the following result for the core potential of the ion:

$$V_{\text{ionic, pseudo}} = V_{\text{ion}} - \sum_l V_R^l, \quad (2)$$

where

$$V_R^l = \sum_n \langle \theta_n^l | V_{\text{ion}} | \phi \rangle \theta_n^l. \quad (3)$$

In Eq. (3) θ_n^l are occupied core orbitals with principal quantum number *n*. ϕ is the smooth pseudo-wave-function which in the region exterior to the core of the bare ion is expected to be Coulombic. The form of V_R^l is such that one would indeed expect to find the potential canceled inside the region occupied by the core orbitals. One would, however, expect the range of the cancellation to depend on *l*, as the core orbital dimension will quite certainly depend on angular momentum. Bearing this in mind we then shall write an angular-dependent empty-core model for the bare ion as follows:

$$V_{\text{ionic, pseudo}}^l(r) = 0, \quad r < R_l \\ = Ze/r, \quad r > R_l \\ \text{for } l \text{ occupied in the core,} \quad (4)$$

$$V_{\text{ionic, pseudo}}^l(r) = Ze/r \\ \text{for } l \text{ unoccupied in the core,} \quad (5)$$

where *Z* is the ionic charge. The core radii should be roughly proportional to the dimension of the largest core orbital of corresponding momentum. For example, in the case of Ge we expect to have as a first approximation

$$R_{s,p,d} = C \times (\text{dimension of core orbital of } s, p, \text{ or } d \text{ symmetry}). \quad (6)$$

Following Lee and Falicov¹⁸ we may summarize Eqs. (4)–(6) in the convenient form

$$V_{\text{ionic, pseudo}} = \sum_l \pi_l^+ V_{\text{ionic, pseudo}}^l \pi_l, \quad (7)$$

where π_l is a projection operator for the *l*th com-

TABLE I. Some of the principal gaps in Si, Ge, and α -Sn with spin-orbit effects removed.

		Δ_1	L_1	(E_0) $\Gamma_{25'} \rightarrow \Gamma_{25'}$	(E_1) $\Lambda_3 \rightarrow \Lambda_1$	$L_{3'} \rightarrow L_1$	(E_2) $\Sigma_2 \rightarrow \Sigma_3$	$X_4 \rightarrow X_1$	(E_0') $\Gamma_{25'} \rightarrow \Gamma_{15}$	(E_1') $L_{3'} \rightarrow L_3$
Si	local empirical model ^a	1.1	1.9	3.8	3.1	3.1	4.4	4.0	3.4	5.4
	present study	1.0	2.0	3.6	3.3	3.3	4.3	4.2	3.4	5.2
	experiment	1.1 ^b	(2.1?) ^c	(4.0?) ^d	3.4 ^e	...	4.4 ^f	...	3.4 ^e	5.5 ^g
Ge	local empirical model ^a	1.0	0.6	0.6	2.0	1.8	3.8	3.6	3.6	5.4
	present study	0.8	0.8	0.9	2.5	2.4	4.3	4.5	3.1	5.8
	experiment	1.0 ^a	0.8 ^b	1.0 ^e	2.3 ^e	...	4.3 ^f	...	3.2 ^{h,i}	5.8 ^g
α -Sn	local empirical model ^l	1.1	0.6	-0.1	$\sim 1.5^k$	1.4	$\sim 3.1^k$	3.1	3.0	4.4
	present study	0.9	0.3	-0.2	1.6 ^k	1.5	3.4 ^k	3.5	2.5	4.6
	experiment	...	0.3 ^l	-0.2 ^l	1.6 ^e	...	3.5 ^{f,j}	...	2.4 ^e	4.4 ^e

^aReference 1.

^bF. Herman, R. L. Kortum, and C. D. Kuglin, in *Quantum Theory of Atoms Molecules and Solids*, edited by P. O. Löwdin (Academic, New York, 1966).

^cThis is based on an extended extrapolation of Ge, GeSi alloy data and has not been directly observed; see F. Bassani and D. Brust, *Phys. Rev.* **131**, 1524 (1963).

^dThis is—like Ref. c—an alloy extrapolation and could easily be in error by the amount of the difference between experiment and theory; see J. S. Kline, F. H. Pollak, and M. Cardona, *Helv. Phys. Acta* **172**, 816 (1968).

^eM. Cardona, *Solid State Physics*, Suppl. 11, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969).

^fWe identify this transition with the energy of the large optical peak. For a discussion and experimental literature see Ref. a.

^gR. R. Zucca and Y. R. Shen, *Phys. Rev. B* **1**, 2669 (1970).

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^jM. L. Cohen and T. K. Bergstresser, *Phys. Rev.* **141**, 789 (1966).

^kThese values are based on $\epsilon_2(\omega)$ calculations performed by the author (unpublished). The local (EPM) study was done by repeating the calculations of Cohen and Bergstresser, and may not be final.

^lFor a comprehensive discussion of the band structure near the valence band maximum in α -Sn see R. J. Wagner, Ph. D. thesis (Northwestern University) (unpublished), and C. F. Lavine, Ph. D. thesis (Northwestern University) (unpublished).

ponent of angular momentum. Using the expansion in spherical harmonics appropriate for plane waves results in

$$\begin{aligned} \langle k' | V_{\text{ionic, pseudo}} | k \rangle \\ = \sum_{l=0}^{\infty} \frac{4\pi}{\Omega_0} (2l+1) P_l(\theta_{kk'}) \\ \times \int_0^{R_l} V_{\text{ionic, pseudo}}(r) j_l(kr) j_l(k'r) r^2 dr. \quad (8) \end{aligned}$$

Here j_l are spherical Bessel functions, $\theta_{kk'}$ is the angle between k and k' , and Ω_0 is the volume of a unit cell. Provided we are far from a resonance, it is possible to make an expansion of the integral in Eq. (8). In order to get good convergence it is necessary to expand out to terms including combinations of k and k' to the sixth power. Such an expansion greatly facilitates the speed of computation compared to what is required if the integrals are explicitly evaluated.

The core size is approximately determined according to Slater's rules. We can then write

$$R_l(n) = \frac{C(n)}{Z_{\text{eff}}(n, l)}, \quad Z_{\text{eff}}(n, l) = Z_N - Z_{\text{scr}}(n, l), \quad (9)$$

where Z_N is the nuclear charge and $Z_{\text{scr}}(n, l)$ is a screening parameter determined by Slater's rules. The coefficient $C(n)$ which appears in the above equation is evaluated approximately by requiring that the potential in the local limit reproduce the well-known form factors for Si, Ge, and α -Sn.

In order to make the fine corrections discussed in Sec. I it is necessary to lift the equality between R_s and R_p as implied by Slater's rules (although $R_s \approx R_p$). The final results for the range parameters are shown in Table I together with $C_l(n)$ now taken as momentum dependent. We note that $R_p < R_s$ for all the cases studied. One can deduce the same result in fitting the ionic spectra by the quantum-defect method.¹⁷

Before going on, we might note that in Shaw's discussion particular emphasis was placed on making the model potential continuous at the cell boundary. This it was shown will minimize the kinetic energy most effectively. With respect to the momentum representation of the potential such a choice will make the tail oscillations damp out most rapidly. This is not an important consideration for the present discussion as we will only be interested in the relatively small k components of

the potential. Differences between the Shaw model and the empty-core model will be quite small as far as the band structure is concerned. It should also be pointed out that Shaw found a weak energy dependence in the model potential. Again, we are working over a sufficiently small energy range to neglect this effect.

B. Valence Component

The total atomic pseudopotential may be written as the sum of two terms:

$$V_{\text{atomic, pseudo}} = V_{\text{ionic, pseudo}} + V_{\text{screening}}, \quad (10)$$

with the ionic portion determined as fully discussed in Sec. II A. Utilizing the RPA approximation we shall write the screening potential induced by the ionic component:

$$V_{\text{screening}} = V_{\text{ionic, pseudo}} \left(\frac{1}{\epsilon(q)} - 1 \right). \quad (11)$$

To properly account for the presence of a sizable gap in the electronic spectra of the crystals under consideration we start with Penn's dielectric function.¹⁹

To be explicit we shall use the symbol $\epsilon_p(q, E_e)$ to represent Penn's function. The quantity E_e which appears is not to be taken as the energy gap of the semiconductor in the conventional sense of the minimum spacing between the valence and conduction bands. As proved by Heine and Jones²⁰ it represents the average gap across the large (Jones's) zone face. As Heine and Jones demonstrated, the spherical model of the electronic dispersion relations taken by Penn is a satisfactory approximation for the purpose of computing the wave-number dependence of the dielectric function. On the other hand, the simple two-plane wave expansion for bonding and antibonding states used by Penn substantially overestimates the interband coupling strength.²¹ In order to account for this in a satisfactory way we make the following replacement:

$$\epsilon'_p(q, E_e) = 1 + B[\epsilon_p(q, E_e) - 1]. \quad (12)$$

The appropriate choice is $B = 0.65$.²¹

In addition we must correct the Penn model so as to include exchange. This is done according to the substitution^{22, 23}

$$\epsilon^*(q, E_e) = 1 + [\epsilon'_p(q, E_e) - 1][1 - f_H(q)], \quad (13)$$

with

$$f_H(q) = \frac{1}{2} \left(1 + \frac{K_s^2}{q^2} + \frac{K_f^2}{q^2} \right)^{-1}, \quad (14)$$

and we choose

$$K_s = (2/\pi)K_f. \quad (15)$$

Here K_f is the Fermi momentum of a free electron gas with a density equal to the system under study.

Then Eq. (11) becomes

$$V_{\text{screening}} = V_{\text{ionic, pseudo}} \left(\frac{1}{\epsilon^*(q, E_e)} - 1 \right). \quad (16)$$

We now have a complete prescription for calculating the atomic contribution to the crystal pseudopotential. First we find the ionic portion according to the procedures delineated in Sec. II A. Then using Eqs. (10) and (11) together with the dielectric function discussed just above we arrive at the necessary result.

The argument is not yet complete at this point. It is well known that one can expect a fairly substantial amount of charge to be localized in covalent bonds for the diamond crystals due to interference effects outside the RPA approximation. For the present study Phillips's²⁴ expression is adequate:

$$Q_b = 2e/\epsilon(0). \quad (17)$$

Using Poisson's equation this is immediately converted to a term in the crystal pseudopotential:

$$V_b(3) = \frac{4e}{\Omega_0 q^2} Q_b(3)[1 - f_H(3)]. \quad (18)$$

We need only consider the term $V_b(3)$. This is true since first of all q^2 appears in the denominator of Eq. (18). Furthermore the charge is not localized at a point, and we can expect $Q_b(11)$ to be about 20% of $Q_b(3)$.²⁰

We then construct the entire pseudopotential by inserting the structure factors appropriate to the diamond structure.²⁵ The entire procedure for setting up and solving the secular equations discussed in Ref. 25 is then invoked.

Before going on to Sec. III, we should point out that the energy gap which appears in the dielectric function is determined in an approximately self-consistent way. We take

$$E_e \approx E(\Sigma_2^V \rightarrow \Sigma_3^C), \quad (19)$$

with the Σ gap evaluated at a point $\frac{2}{3}$ of the distance from the zone center to the zone boundary (Brillouin zone).²⁶ Thus given the ionic potential we can make a guess for E_e and determine ϵ^* and thus the crystal pseudopotential. Then the energy bands are calculated and E_e redetermined. If it is not in satisfactory agreement with E_e as guessed, a new cycle is performed. A little experience with the group-IV materials makes it possible to guess a sufficiently good value of E_e at the outset to obviate the need for a second cycle. We should also point out that very small adjustments in $V(8)$ and $V(11)$ are required; however, these make corrections in the band structure of only ~ 0.1 eV.

III. RESULTS AND CONCLUSIONS

In Table II we give the theoretical results for the

TABLE II. Effective charge, scaling constant, and empty-core radius (in atomic units). Here n refers to the principal quantum of the last filled shell of the atom ($n=2$, Si) and l is the orbital angular momentum.

	$Z_{\text{eff}}(n, l)$	$C_l(n)$	$R_l(n)$
$n=2, l=0$	9.85	9.53	0.968
$n=2, l=1$	9.85	8.01	0.813
$n=3, l=0$	20.75	20.44	0.985
$n=3, l=1$	20.75	18.78	0.905
$n=3, l=2$	10.85	17.64	1.626
$n=4, l=0$	22.25	24.39	1.096
$n=4, l=1$	22.25	23.63	1.062
$n=4, l=2$	10.85	19.53	1.800

important band gaps of Si, Ge, and α -Sn, along with experiment. A comparison is also made with the

results of the empirical local model. The very substantial improvement we have made is immediately evident. It is particularly gratifying that the transition energy of the large reflectivity peak now comes out so well.

It would appear then that future efforts should be aimed at improving on the theoretical foundations of the present model. Of particular interest would be an improved analysis of the corrections to the RPA. We might also hope to get some improvement in the exchange and correlation approximation, as well as a better representation of the screening than is given by Eq. (11).

The reader might note that spin splitting has been left out of the present calculation. This is easily included using the formulation of Saravia and the author,⁷ and will be done in the near future.

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