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New tight-binding parameters for covalent solids obtained using Louie peripheral states

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Excited *s* states are added to the minimal-basis tight-binding theory of covalent solids using Louie's perturbation approach. This brings the conduction bands into better accord with experiment without appreciably complicating the calculation of properties in the bond-orbital approximation. Universal interatomic matrix elements are obtained by fitting the free-electron bands, and then adjusted to accord with the bands of germanium. Bands based upon these interatomic matrix elements, and upon Hartree-Fock term values, are then compared with pseudopotential bands for Si, Ge, Sn, GaAs, InSb, ZnSe, and CdTe. A single set of metallic, covalent, and polar energies for sp^3 hybrids obtained from the new matrix elements are found to predict good values for both the dielectric and elastic properties; in contrast, two different sets were required for the two classes of properties in the earlier theory.

I. INTRODUCTION

By simplifying the description of the electronic structure of covalent and ionic solids sufficiently, it has become possible to estimate the entire range of dielectric and structural properties in terms of that electronic structure.[1] The procedure consisted of a tight-binding formulation based upon a minimal-basis set of atomic orbitals (only those occupied or partially occupied in the free atom) and nearest-neighbor interatomic interaction. For the diagonal terms in the corresponding Hamiltonian matrix it proved adequate to use atomic term values for the free atom, and formulas for the interatomic matrix elements were derived by requiring consistency between the tight-binding bands and nearly-free-electron bands.[2] The dimensionless coefficients in these formulas were then adjusted to fit a known band structure and taken as universal.

The resulting description was sufficiently simple that the bands could be calculated analytically. Alternatively, one could make unitary transformations on the minimal basis leading to sp^3 hybrids and then to bond orbitals without further approximation. Then the bond-orbital approximation of neglecting the coupling between these bond orbitals and neighboring antibonding orbitals made the estimates of total energies (as a function of atomic position) or dielectric polarizations (entering the susceptibilities and infrared couplings, for example) quite trivial. It was even possible to correct for the neglected coupling in perturbation theory (the method of extended bond orbitals[1]) to estimate the error or to correct the bond-orbital approximation.

There were nevertheless significant residual errors arising from the use of the minimal-basis set; these showed up as important errors in the form of the conduction bands. This led also to significant uncertainties in the parameters giving interatomic matrix elements since these required fitting the tight-binding bands to the conduction, as well as the valence bands. It did not seem possible to remove these errors without expanding the basis set and thus replacing the elementary analytical predictions by numerical procedures.

A recent approach given by Louie,[3] however, provides a way around this difficulty. Louie showed that additional orbitals may be added to the basis set as perturbations. He showed that these can rectify the principal errors in the tight-binding energy bands without increasing the size of the Hamiltonian matrix which must be diagonalized. They can therefore remove a major source of error in the calculation of properties and the uncertainty in the parameters, without requiring the abandoning of analytical solutions. In the present study we apply Louie's approach to the elementary tight-binding theory, redetermine the universal parameters to be used in the calculation of properties, and explore the consequences with respect to the calculation of individual properties.

II. LOUIE PERIPHERAL STATES

Specifically, Louie added the effect of atomic *d* states on the energy bands of semiconductors without expanding the *sp*-LCAO (linear combination of atomic orbitals) basis.[3] His approach depended upon the fact that these d states spanned very nearly the same Hilbert space as the s and p states. Thus while this d state might have an energy expectation value only three volts above the p states, by the time it is suitably orthogonalized the remanent is shifted more than ten volts above the p states and could be incorporated by perturbation theory.

This analysis not only provided a simple method for doing accurate band calculations, but also made clearer why minimal-basis tight-binding theory works as well as it does. The one conspicuous flaw of minimal-basis theory had been in its failure to give low-energy conduction bands near X as in the real bands. (In silicon the absolute minimum is near X.) This can, in principle, be accomplished in tight-binding theory by including matrix elements with sufficiently distant neighbors, but the more natural resolution has been the expansion of the basis. Indeed Louie[3] included a second s state in what he called a "minimal basis." A basis set of five orbitals per atom, rather than four, is not an appreciable complication when one numerically diagonalizes matrices and this was appropriate.

However, in calculation of bonding and dielectric properties it may be the difference between the analytic solution of a quadratic equation and a numerical procedure. We therefore are motivated to incorporate the second s state as a "Louie peripheral state" in perturbation theory in order to return to a true minimal-basis set. This is justified, as is the treatment of the d states in perturbation theory, by the fact that the corresponding bands in the crystal are at high energy.

Our approach then will be to add the second s state to the tight-binding theory as a perturbation, and proceed through the calculation of bands, the fitting of parameters, and finally the calculation of properties as before. We, in fact, find that it is not necessary in this approach to introduce the d states which were the focus of Louie's work. If at some later time it proves necessary to add these states also, it will be necessary to redo the formulation and the adjustment of parameters with the additional terms included from the beginning.

It is interesting that this approach with only a single peripheral state does rectify the principle defect in the bands obtained with minimal-basis set of four orbitals per atom. It is also interesting that in Louie's calculation a large part of the lowering of the level at X_1 came from peripheral d levels which we have not included. This followed directly from his orbitals and his procedure, but it does not mean that our fit is in error. For just the reason that these excited-state orbitals span the same Hilbert space, the same effects can be attributed to different sets of orbitals or to different orders of orthogonalization. This arbitrariness might suggest that orthogonalized plane waves be used as the peripheral functions. This is exactly the approach called the orbital correction method.[4] If only wave numbers in the first Brillouin zone are used, it correctly gives an additional drop in the p bands quadratic in wave number as required, but it leads to unphysical cusps in the bands at the Brillouin zone. It becomes necessary to include additional waves and the method becomes more complicated than the simple peripheral s state. The expansion in orthogonalized plane waves (OPW) can, in principle, be made as accurate as one likes but may not be the most convenient approach.

III. FITTING THE BANDS

For a true minimal-basis set (a single s and three p states per atom) and nearest-neighbor coupling the tight-binding bands for $\vec{k}$ in a [100] direction in the diamond structure can be obtained analytically; they were given by Chadi and Cohen.[5] The doubly degenerate bands are given by

$$\Delta_5=\epsilon_p \pm \{ [\tfrac{4}{3}(V_{pp\sigma}+2V_{pp\pi})\cos\phi]^2 + [\tfrac{4}{3}(V_{pp\sigma}-V_{pp\pi})\sin\phi]^2 \}^{1/2} , \qquad (1$$

with $\phi=ka/4$. They are unaffected by adding the peripheral s state since it enters as another Bloch sum of symmetry Δ_1 which is not coupled to states of symmetry Δ_5.

We incorporated the effect of this peripheral s state s^* through its coupling with the s state and p state Bloch sums of symmetry Δ_1. The sole effect then is to replace the p-state energy in the Chadi-Cohen expression for the Δ_1 bands by

$$\epsilon_p' = \epsilon_p + \frac{16}{3}\frac{V_{s^*p\sigma}^2}{(\epsilon_p-\epsilon_{s^*})}\sin^2\phi , \tag{2}$$

and the s-state energy by an analogous expression with the sine replaced by a cosine. In Eq. (2), ϵ_{s^*} is the energy of the peripheral s state and $V_{s^*p\sigma}$ is the $m=0$ matrix element between it and a nearest-neighbor p state. In the equation for ϵ_s', ϵ_p is replaced by ϵ_s and $V_{s^*p\sigma}$ by $\sqrt{3}V_{s^*s\sigma}$. We correct the Chadi-Cohen expression for a misprint and write it as

$$\Delta_1=[\epsilon_s'+\epsilon_p'\pm(4V_{ss\sigma}+\tfrac{4}{3}V_{pp\sigma}+\tfrac{8}{3}V_{pp\pi})\cos\phi]/2$$
$$\mp\{\tfrac{1}{4}[\epsilon_p'-\epsilon_s'\pm(\tfrac{4}{3}V_{pp\sigma}+\tfrac{8}{3}V_{pp\pi}-4V_{ss\sigma})\cos\phi]^2+\tfrac{16}{3}V_{sp\sigma}^2\sin^2\phi\}^{1/2}\,. \tag{3}$$

The meaning of the $\mp$ notation is that four combinations of signs arise; they are $+++$, $+-+$, $-+-$, and $---$.

A. The free-electron bands

It is useful as a first step to match these expressions to the free-electron bands, following Froyen and Harrison.[2] These bands are given for the [100] direction in Fig. 1, along with sets of bands for silicon to be discussed. The tight-binding bands, Eqs. (1) and (3), give four eigenvalues at Γ ($\phi=0$) and four at X ($\phi=\pi/2$). They depend upon eight parameters, ϵ_s, ϵ_p, $V_{ss\sigma}$, $V_{sp\sigma}$, $V_{pp\sigma}$, $V_{pp\pi}$, and the combinations $V_{s^*p\sigma}^2/(\epsilon_p-\epsilon_{s^*})$ and $V_{s^*s\sigma}^2/(\epsilon_s-\epsilon_{s^*})$. In fact this last combination is not uniquely determined in the fit so we take it to vanish and are left with seven parameters. Thus we can fit all but the highest band at X, which is not well described by the tight-binding fit in any case.

Mattheiss[6] has noted that all three of the upper-band energies at Γ, that is, Γ_{15}, Γ_{25}', Γ_2' (and a higher Γ_1), originate from the eightfold degenerate free-electron bands at $(9\pi^2/8)\hbar^2/(md^2)$; Froyen and Harrison[2] were in error in associating the Γ_{15} level with the free-electron bands at $(3\pi^2/2)\hbar^2/(md^2)$. We correct that error here. In addition, of course, we have a nonzero $V_{s^*p\sigma}^2/(\epsilon_p-\epsilon_{s^*})$. That fit then leads to

$$V_{ll'm}=\eta_{ll'm}\hbar^2/(md^2)\,, \tag{4}$$

$$V_{s^*p\sigma}^2/(\epsilon_p-\epsilon_{s^*})=\lambda_{sp\sigma}\hbar^2/(md^2)\,, \tag{5}$$

and

$$\epsilon_p-\epsilon_s=\frac{9\pi^2}{16}\hbar^2/(md^2)$$
$$=5.55\hbar^2/(md^2)\,, \tag{6}$$

with

$$\eta_{ss\sigma}=-9\pi^2/64\,,$$
$$\eta_{sp\sigma}=3^{3/2}\pi^2/64\,,$$
$$\eta_{pp\sigma}=3\pi^2/16\,, \tag{7}$$
$$\eta_{pp\pi}=-3\pi^2/32\,,$$
$$\lambda_{sp\sigma}=-27\pi^2/256.$$

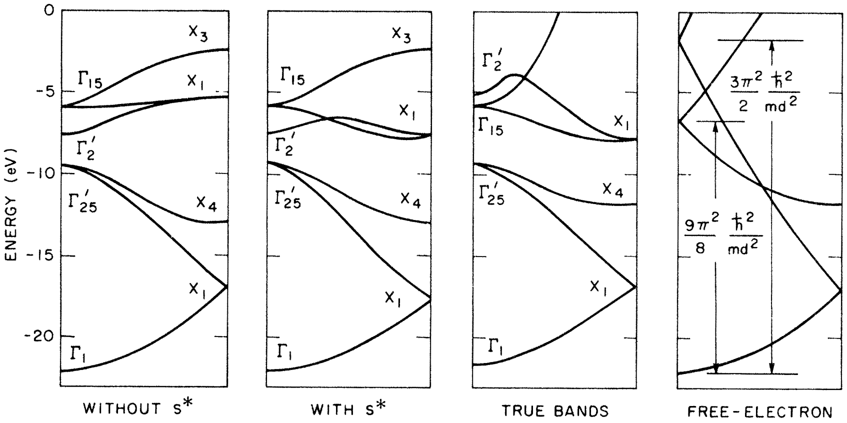

FIG. 1. In the first panel are the bands for silicon, obtained with the parameters proposed here but without the inclusion of the peripheral state s^*. The second panel shows how the peripheral state lowers the conduction band at X as in the true silicon bands, obtained from Ref. 8 and shown in the third panel. In the final panel are the free-electron bands. The parameters for the first and second panel were Hartree-Fock term values and η coefficients fit to germanium; a small shift in parameters could interchange the Γ_2' and Γ_{15} levels without disrupting the rest of the agreement. The zero of energy in the third and fourth panels was selected for easy comparison.

B. Use of atomic term values

Of course, use of these parameters gives vanishing band gaps and bands which scale directly from one element to the other. To obtain meaningful bands we use atomic term values for $\epsilon_p - \epsilon_s$, rather than Eq. (6). These are rather constant for the series C, Si, Ge, and Sn, rather than varying as d^{-2} as suggested by Eq. (6), and this gives rise to the principal trends in the bands through this series. We choose also to use Hartree-Fock term values[7] rather than the Herman-Skillman values which were used earlier. These are listed, for convenience, in Table I.

C. Adjusted coefficients

In addition it is necessary to make empirical adjustments of the coefficients given in Eq. (7), though the theoretical forms, Eqs. (4) and (5), are retained. We do this by fitting the known energy bands. The use of Hartree-Fock term values eliminates one adjustable parameter for the fitting of a known set of bands, but by again allowing a nonzero $V^2_{s^*s\sigma}/(\epsilon_s - \epsilon_{s^*})$ we may again fit the same seven band energies for the homopolar semiconductors. Use of atomic term values allows the calculation of band energies also for the polar semiconductors using the same coefficients and the generalization of Eqs. (2) and (3) to the polar case, given by Chadi and Cohen[5] for the points Γ and X. We have used this procedure to fit the parameters of Eq. (7) to the band energies for Si, Ge, Sn, GaAs, InSb, ZnSe, and CdTe as given by Chelikowsky and Cohen.[8] For the polar semiconductors the X_1 band energies split into an X_1 and an X_3 and we fit to the X_1. We shall describe qualitatively the results of this fit, which led us to suggest a universal set of parameter, and will then compare the band energies obtained with these parameters with Chelikowsky and Cohen's values for the seven materials.

The values of $\eta_{pp\sigma}$ and $\eta_{pp\pi}$ as deduced from the different materials were quite independent of material, with standard deviations of 6% and 9%, respectively, the largest deviations being for silicon. This suggests that these matrix elements, which dominate the dielectric properties of semiconductors, are well given by the formula, Eq. (4). We take the values for Ge, near the average, as universal. The parameter $\eta_{ss\sigma}$ was found also to be quite independent of material, except for ZnSe and

TABLE I. Hartree-Fock term values after Fischer (1972) in eV. The magnitude of ϵ_s values are given first for each element and of ϵ_p values next. ϵ_p values in the first two columns were obtained by extrapolation.

1	2	3	4	5	6	7	8	9	10	11
							He	Li		
							24.97	5.34		
	Be	B	C	N	O	F	Ne	Na		
	8.41	13.46	19.37	26.22	34.02	42.78	52.51	4.95		
	5.79	8.43	11.07	13.84	16.72	19.86	23.13			
	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc
	6.88	10.70	14.79	19.22	24.01	29.19	34.75	4.01	5.32	5.72
	3.84	5.71	7.58	9.54	11.60	13.78	16.08			
Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y
7.72	7.96	11.55	15.15	18.91	22.86	27.00	31.37	3.75	4.85	5.34
2.37	4.02	5.67	7.33	8.98	10.68	12.43	14.26			
Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	La
7.06	7.21	10.14	13.04	16.02	19.12	22.34	25.69	3.36	4.29	4.35
2.61	3.99	5.37	6.76	8.14	9.54	10.97	12.44			
Au	Hg	Tl	Pb	Bi	Po	At	Rn			
6.98	7.10	9.82	12.48	15.19	17.96	20.82	23.78			
2.67	3.95	5.23	6.53	7.79	9.05	10.33	11.64			

CdTe, where the band energies were quite insensitive to its value; again we take the Ge value as universal. $\eta_{sp\sigma}$ was found to be independent of polarity in each isoelectronic sequence but was found to increase significantly from Si to Ge to Sn, as if $V_{sp\sigma}$, rather than $\eta_{sp\sigma}$, were independent of d. Similarly, $\lambda_{sp\sigma}$ increased from Si to Ge to Sn and also increased with polarity. We nevertheless retain the free-electron formula Eq. (4) and germanium values and will see that this gives a reasonable description of the bands and properties. It seems likely that the origin of this different behavior is not intrinsic to these matrix elements but is due to the omission of other peripheral states or more distant-neighbor matrix elements. Finally, $\lambda_{ss\sigma}$ was found to vary in sign from material to material but never to be large, so we took it to vanish as for the free-electron fit. The resulting universal parameters are given in Table II, along with the free-electron values obtained from Eq. (7).

It is interesting that the required adjustments from the free-electron values are not large, except for $\lambda_{sp\sigma}$. It is also interesting that the differences from the earlier fit are not so large but are large enough to make a significant difference in the predictions for a number of properties, as we shall see.

D. The resulting bands

Using the proposed parameters we have calculated the band energies for the seven semiconductors, compared with the values from Chelikowsky and Cohen in Table III. We have included values at L, also. The symmetry designations are given for the diamond and for the zinc-blende structures. The Chelikowsky and Cohen values have been placed on the same scale by taking the zero of energy such that the energy $(\Gamma_{15}+\Gamma'_{25})/2$ comes at the Hartree-Fock energy ϵ_p and the corresponding generalization for the polar semiconductors. Except for the adjustment of the five parameters of Table II to germanium, the two calculations are independent and similar agreement can be expected for the elementary band calculation for any other tetrahedral semiconductor. The agreement is better for the valence bands than for the conduction bands but, in contrast to the earlier fit, even the conduction-band levels are rather well given. The agreement is sufficiently good to suggest a considerable improvement in predicted properties such as the dielectric constant.

TABLE II. Parameters obtained from the free-electron fit (Sec. III A), the values obtained earlier from the Chadi-Cohen fit,[a] and the universal values proposed here.

	Free electron	Earlier fit	Proposal
$\eta_{ss\sigma}$	-1.39	-1.40	-1.32
$\eta_{sp\sigma}$	0.80	1.84	1.42
$\eta_{pp\sigma}$	1.85	3.24	2.22
$\eta_{pp\pi}$	-0.93	-0.81	-0.63
$\lambda_{sp\sigma}$	-1.04	0	-0.40

[a] Reference 5.

The agreement is the worst for silicon, but even for that case the description of the bands is not bad, as indicated in Fig. 1. The improper ordering of the degenerate (Γ_{15}) and nondegenerate (Γ'_2) conduction band levels at Γ could be corrected by a small adjustment of $\epsilon_p-\epsilon_s$ and that would be appropriate for a study directed specifically at silicon.

IV. THE CRYSTAL PROPERTIES

We have seen that the effect of the peripheral s states on the bands is very large, and for sensitive properties such as the optical spectrum or the conductivity of n-type material the effects will also be large. Many other properties, such as the dielectric or elastic constants, depend upon integrals over the bands and should be considered separately.

A. The role of the peripheral state

The shift in the energy of a p state oriented in the [100] direction may be generalized from Eq. (2) to arbitrary wave number

$$\epsilon'_p(\vec{k})=\epsilon_p+V^2_{s^*p\sigma}\left|\sum_{d_j}e^{i\vec{k}\cdot\vec{d}_j}(d_{jx}/d_j)\right|^2\Big/(\epsilon_p-\epsilon_{s^*}) , \tag{8}$$

where the sum is over nearest-neighbor vectors $\vec{d}_j$. By expanding the sum over phase factors one may see that in the average over the Brillouin zone (or a primitive cell in wave-number space) only the diagonal terms survive and

$$\langle\epsilon'_p\rangle=\epsilon_p+\tfrac{4}{3}V^2_{s^*p\sigma}/(\epsilon_p-\epsilon_{s^*}) . \tag{9}$$

Our use of perturbation theory in this form is equivalent to assuming that $\epsilon_{s^*}-\epsilon_p$ is so large that

TABLE III. Band values predicted from Eqs. (1) and (3) with Hartree-Fock term values, and the proposed parameters of Table I. Values from Chelikowsky and Cohen[a] are in parentheses. All are in eV.

	Si	Ge	Sn	GaAs	InSb	ZnSe	CdTe
Γ_1, Γ_1^v	−22.08	−21.91	−18.17	−22.88	−18.96	−25.43	−22.00
	(−21.66)	(−21.52)	(−19.20)	(−22.15)	(−20.06)	(−23.22)	(−20.46)
Γ_2', Γ_1^c	−7.50	−8.39	−7.91	−7.58	−7.20	−5.39	−5.33
	(−5.20)	(−7.96)	(−8.28)	(−8.09)	(−8.10)	(−8.21)	(−7.80)
$\Gamma_{25}', \Gamma_{15}^v$	−9.35	−8.97	−8.00	−9.64	−8.61	−11.06	−9.80
	(−9.30)	(−8.96)	(−8.13)	(−9.72)	(−8.62)	(−11.12)	(−9.69)
$\Gamma_{15}, \Gamma_{15}^c$	−5.81	−5.69	−5.52	−5.01	−4.90	−3.64	−3.73
	(−5.78)	(−5.71)	(−5.39)	(−4.94)	(−4.90)	(−3.58)	(−3.86)
X_1^v, X_1^v	−17.66	−17.52	−14.76	−15.79	−13.34	−15.66	−13.27
	(−16.99)	(−17.51)	(−15.74)	(−16.48)	(−14.78)	(−15.93)	(14.44)
X_3^v				−20.36	−17.06	−23.87	−19.85
				(−19.43)	(−17.55)	(−21.69)	(−18.51)
X_1^c, X_1^c	−7.67	−7.71	−7.13	−7.46	−7.01	−5.70	−5.56
	(−8.13)	(−7.70)	(−6.96)	(−7.69)	(−6.64)	(−6.43)	(−5.91)
X_3^c				−6.95	−6.40	−5.73	−5.34
				(−7.34)	(−6.52)	(−5.80)	(−5.44)
X_4^v, X_5^v	−12.82	−12.19	−10.45	−12.42	−10.67	−13.21	−11.36
	(−12.16)	(−12.15)	(−10.61)	(−12.56)	(−10.73)	(−13.07)	(−11.24)
X_3^c, X_5^c	−2.34	−2.47	−3.07	−2.23	−2.84	−1.49	−2.17
L_1^v	−19.52	−19.46	−16.30	−21.07	−17.60	−24.26	−20.14
	(−18.85)	(−19.25)	(−17.30)	(−20.20)	(−18.30)	(−22.05)	(−19.03)
L_2^v	−16.85	−16.33	−13.73	−15.87	−13.35	−15.97	−13.47
	(−16.26)	(−16.47)	(−14.46)	(−16.43)	(−14.27)	(−16.05)	(−14.12)
L_3^v	−11.08	−10.58	−9.23	−10.95	−8.57	−11.99	−10.47
	(−10.53)	(−10.39)	(−9.30)	(−10.91)	(−9.47)	(−11.82)	(−10.22)
L_1^c	−8.46	−8.87	−8.14	−8.12	−7.51	−6.02	−5.75
	(−7.07)	(−8.10)	(−7.72)	(−7.78)	(−7.32)	(−7.01)	(−6.57)
L_3^c	−4.35	−4.41	−4.56	−4.15	−4.32	−3.36	−3.61
	(−4.96)	(−4.65)	(−4.24)	(−4.10)	(−3.90)	(−3.26)	(−3.10)

[a] Reference 8.

we may neglect the variation of the energy of the bands in comparison to it; our band calculation using Eq. (2) also implicitly makes this assumption. In that band calculation the peripheral state had two effects; one was the shift in the average energy $\langle \epsilon_p' \rangle$, and the other was a coupling between second-neighboring p states through the intervening peripheral state. [This coupling is the origin of the k dependence, or ϕ dependence, of Eq. (2).] This latter effect was quite large because the coupled p states were degenerate or nearly so. Thus it contributes to the splitting between the valence and conduction bands and an average of the energy $E(\vec{k})$ over the valence bands is not equal to an average over the bands obtained with ϵ_p' replaced by $\langle \epsilon_p' \rangle$, even to lowest order in $V_{s^*p\sigma}$. We are not able to solve the eight-by-eight matrix to obtain $E(\vec{k})$ analytically for arbitrary $\vec{k}$ in any case, but must resort to numerical methods or approximate methods such as the bond-orbital approximation in order to obtain analytical results. We may ask how the peripheral states affect this procedure.

Once we have transformed to bonding and antibonding orbitals in terms of the minimal-basis set we may note that these are coupled to the peripheral states. This again has the effect of shifting the average energy $\langle \epsilon_p' \rangle$ and coupling the neighboring bond orbitals with each other and with the antibonding orbitals. However, we neglect the coupling between bonding and antibonding orbitals, the bond-orbital approximation, and the coupling between neighboring bond orbitals does not affect the total energy nor the sum of the expectation value of any one-electron operator over the valence bands. Thus within the bond-orbital approximation the effect of the peripheral orbitals can be incorporated by simply modifying the term values (ϵ_p becomes $\langle \epsilon_p' \rangle$) which enter the theory.

Note in particular that shifts in the individual atomic term values ϵ_p' may be calculated individually in perturbation theory. In the perfect crystal, with each p state coupled to four neighboring peripheral s states by $V_{s^*p\sigma}/\sqrt{3}$, we obtain directly Eq. (9). This shift is small, less than a volt for silicon.

Thus there are just two effects on the calculation of properties in the bond-orbital approximation due to the addition of peripheral s states: the modified parameters shown in Table I and the corrected p-states energies ϵ_p' calculated atom by atom. We see first how this affects the metallic, covalent, and polar energies.

B. Bond-orbital parameters

The first step in the formation of bond orbitals is the construction of sp^3 hybrids, of energy $(\epsilon_s + 3\epsilon_p)/4$, oriented in the direction of each nearest-neighbor atom. The addition of the peripheral s state shifts the energy ϵ_p to $\langle \epsilon_p' \rangle$ as in Eq. (9). This has the effect of lowering every hybrid energy by $\lambda_{sp\sigma}\hbar^2/md^2$. Note that in a polar semiconductor the same shift applies to hybrids on both atoms so that the polar energy, obtained from the difference between the two hybrid energies is not modified,

$$V_3 = (\epsilon_h^c - \epsilon_h^a)/2 \tag{10}$$

and the ϵ_h values are obtained from the atomic term values of Table II directly.

The metallic energy V_1, which is the matrix element between two hybrids on the same atom, is affected. It becomes

$$\begin{aligned} V_1 &= (\epsilon_s - \langle \epsilon_p' \rangle)/4 \\ &= (\epsilon_s - \epsilon_p)/4 - \lambda_{sp\sigma}\hbar^2/(3md^2) \; . \end{aligned} \tag{11}$$

We have changed the sign convention from Ref. 1 so that V_1 is negative and its magnitude is decreased by the presence of the peripheral state, but only 10% or so.

The covalent energy, which is the matrix element between two hybrids into the same bond, is modified by the use of new interatomic matrix elements,

$$\begin{aligned} V_2 &= (V_{ss\sigma} - 2\sqrt{3}V_{sp\sigma} - 3V_{pp\sigma})/4 \\ &= -3.22\hbar^2/md^2 \; . \end{aligned} \tag{12}$$

Again we have changed the sign convention so that V_2 is negative.

These are the hybrid polar, metallic, and covalent energies modified by the addition of peripheral states. In Ref. 1 the corresponding energies were used directly in the study of elasticity in the covalent solids. However, in the calculation of dielectric properties it was recognized that the dielectric constant was dominated by p states and a different set of polar and covalent energies, based upon p-state parameters, was introduced. In the present study we shall use only the single set, Eqs. (10)–(12). We then have the option of correcting the results by using extended bond orbitals, as mentioned in the introduction.

C. The dielectric susceptibility

The dielectric susceptibility is easily derived in terms of the polarizability of individual bonds and is given by[1]

$$\chi = \frac{Ne^2\gamma^2 d^2}{12V_2}\left[\frac{V_2^2}{V_2^2 + V_3^2}\right]^{3/2} . \tag{13}$$

N is the electron density and γ^2 is a scale factor which is unity in the direct derivation. A convenient way of presenting the results is to deduce the value of γ^2 required to bring the theory into agreement with experiment; it is then the ratio of the experimental to the simplest theoretical value.

For the series C, Si, Ge, and Sn we obtain γ^2 equal to 1.91, 2.93, 3.85, and 5.14, respectively. These are somewhat larger than the values obtained earlier (1.28, 1.96, 2.56, and 3.39, respectively), but not greatly so. Ren and Harrison indicated that the increase of the error factor with atomic number arises from the decrease in the energy of the s-like conduction band in comparison to the p-like conduction band, an effect left out of the two-level formula, Eq. (13). Even when they used the full LCAO bands (but of course without peripheral states) and oscillator strengths, they found the predicted susceptibility too small by a factor of order 2. The only additional approximation required to obtain Eq. (13) is the bond-orbital approximation.

We conclude that Eq. (13) may be a good first estimate of the susceptibility; and that one might systematically add corrections to the bond-orbital approximation. The first is from the coupling $V_1/2$ of the bond orbitals to the nearest-neighbor antibonding orbitals. This gives correction factors which increase with atomic number but only increase to 1.25 for tin. There are also considerably larger corrections due to coupling with neighboring antibonding orbitals arising from interatomic matrix elements and arising from intervening peripheral states. These have not been explored in detail. However, we note that though the coupling $V_{s^*p\sigma}$ transfer charge to sites neighboring upon the bond orbital, our assumption that $V_{s^*p\sigma}$ is very small in comparison to $\epsilon_{s^*}-\epsilon_p$ implies that this charge transfer is negligible compared to other terms even if $V_{s^*p\sigma}^2/(\epsilon_{s^*}-\epsilon_p)$ is comparable to V_1 and V_2. Thus the leading effects of the peripheral states enter as modifications of the parameters in the minimal-basis theory, not as additional interband contributions, as suggested in Sec. IV A.

We may also consider the prediction of Eq. (13) concerning polar semiconductors. It essentially says that χ should vary as $\alpha_c^3=[V_2^2/(V_2^2+V_3^2)]^{3/2}$ in an isoelectronic series such as Ge, GaAs, ZnSe, CuBr, where α_c is called the hybrid covalency; the other factors in Eq. (13) do not vary appreciably. This is well confirmed for the germanium isoelectronic series. Evaluating Eq. (13) for this series, and dividing by the germanium value (all with the same γ^2) gives ratios 1, 0.69, 0.32, and 0.16 in comparison to the experimental ratios 1, 0.66, 0.33, and 0.23. The CuBr discrepancy presumably comes from the presence of d states on the copper, an effect which could also be estimated.

This success is quite important since such agreement was not obtained with the hybrid covalency based upon the earlier parameters. Success was obtained only with covalencies based upon p state parameters so that different covalent and polar energies were required for different sets of properties. The use of a single set here is a considerable simplification. The similarity of the covalencies obtained here for hybrids and the values obtained earlier with p states indicates that these will be suitable for other dielectric properties such as the transverse charge and piezoelectric charge.

D. Elastic properties

It is also possible to calculate the energy change of the lattice under distortion in the bond-orbital approximation.[1] The simplest calculation is for a pure shear, $e_1=-e_2$. This distortion misaligns the two hybrids forming a bond (in such a way that the hybrids cannot be realigned if they are to be kept orthogonal). The angle of misalignment θ is given by $\theta^2=2e_1^2/3$. The change in energy of each bond orbital is then readily calculated as

$$\delta\epsilon_b=-\lambda V_2\alpha_c\theta^2\ , \tag{14}$$

with

$$\lambda=\frac{-\sqrt{3}V_{sp\sigma}-3V_{pp\sigma}+3V_{pp\pi}}{V_{ss\sigma}-2\sqrt{3}V_{sp\sigma}-3V_{pp\sigma}}$$

$$=0.85\ . \tag{15}$$

(The value differs from the 0.88 given in Ref. 1 because of the change in matrix elements. A typographical error in one of the matrix element subscripts has also been corrected.)

The elastic constant $c_{11}-c_{12}$ associated with this shear can readily be calculated and is proportional to the shift given in Eq. (14). An analysis of a one-dimensional analog to the tetrahedral structure, a treatment of corrections to the bond-orbital approximation using extended bond orbitals by Sokel,[9] and a treatment of the polar limit in terms of chemical grips,[1] all indicate that though Eq. (14) is appropriate to homopolar semiconductors, the covalency α_c should be replaced by α_c^3 for polar semiconductors.[10] This is a correction to the bond-orbital approximation. Then the elastic constant becomes

$$c_{11}-c_{12}=\sqrt{3}\lambda\alpha_c^3V_2/d^3\ . \tag{16}$$

For the homopolar semiconductors this is a universal constant divided by d^5 and for diamond, silicon, germanium, and tin gives 67.1, 8.1, 6.7, and 3.4 ergs/cm^3, to be compared with the experimental 95.1, 10.2, 8.0, and 4.5 ergs/cm^3. As noted earlier, the d^{-5} dependence is well confirmed by experiment, but our predictions are systematically over 20% too small. This discrepancy is larger than that obtained with the earlier parameters, but would seem to be within the anticipated uncertainties.

The variation as α_c^3 among an isoelectronic series is the same as predicted for the susceptibility. The ratio of the elastic constant to that for germanium is predicted to be 0.69 and 0.32 for GaAs and ZnSe, to be compared with the experimental 0.81 and 0.42.

V. SUMMARY

The addition of peripheral states to the minimal-basis set using Louie's approach very considerably improves the accuracy of the conduction bands, and therefore allows a more unambiguous determination of parameters for the theory. This improvement does not seriously complicate the elementary computation of bonding and dielectric properties. The form of the simple theory remains the same with modified parameters and it again predicts the principal trends from material to material. The absolute accuracy of the predictions using the new parameters appears to be slightly decreased, but there is a very considerable simplification in that a single set of parameters based upon hybrids determines both the bonding and the dielectric properties. This appears only to be true in the approximate theory; Yin and Cohen[11] find that the pseudopotentials which describe the bonding properties do not give good excited states (conduction bands). This distinction is lost in our cruder theory. There is also a significant advance in use of hybrid parameters for the dielectric properties in allowing one to systematically improve the results by corrections to the bond-orbital approximation as Sokel[9] was able to do for elastic constants.

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