[12] P. Soven, Phys. Rev. 156, 809 (1967).

[13] D. W. Taylor, Phys. Rev. 156, 1017 (1967).

[14] B. Velický, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. 175, 747 (1968).

[15] P. L. Leath, Phys. Rev. 171, 725 (1968).

[16] J. S. Faulkner, Phys. Rev. B 1, 934 (1970).

[17] B. L. Gyorffy, Phys. Rev. B 1, 3290 (1970).

[18] M. Lax, Phys. Rev. 85, 621 (1952).

[19] E. de Dycker and P. Phariseau, Advan. Phys. 16, 401 (1967).

[20] Although the word "explicitly" is used to emphasize that W appears alone on the left-hand side of Eq. (34), it should be remembered that since the CPA is a self-consistent approach, a knowledge of W is also required for the evaluation of the right-hand side.

[21] M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964).

[22] The same symbol is used here for the transition operator as in Eq. (26), for obvious reasons. In order to aid the reader with the proliferating notation we briefly summarize here the loose physical meaning associated with, for example, the symbols derived from the arbitrary operator A, namely, $\hat{A}$ and $\tilde{A}$. Respectively, these denote A operating in free space, in the coherent potential created by $N-1$ scatterers, and in the coherent potential created by N scatterers.

[23] J. Korringa, Physica 13, 392 (1947).

[24] W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).

[25] A. B. Bhatia and D. E. Thornton, Phys. Rev. B 2, 3004 (1970).

[26] A. B. Bhatia and D. E. Thornton, Phys. Rev. B 4, 2326 (1971).

PHYSICAL REVIEW B VOLUME 4, NUMBER 10 15 NOVEMBER 1971

First-Principles Full-Zone $\vec{k}\cdot\vec{p}$ Extrapolations Critically Evaluated*

J. P. Van Dyke
Sandia Laboratories, Albuquerque, New Mexico 87115

(Received 28 June 1971)

The extrapolation technique that results from using calculated velocity matrix elements to couple a first-principles band calculation at Γ with a $\vec{k}\cdot\vec{p}$ expansion for mapping out energy bands over the entire zone is critically explored. Results for Bi, PbTe, and Al are discussed. The crucial finding is that the extent to which the $\vec{k}\cdot\vec{p}$ results correctly solve the eigenvalue problem is due to a fortuitous cancellation between states omitted in the truncation. Consequently, a significant augmentation of the $\vec{k}\cdot\vec{p}$ expansion set can produce little improvement. Results of orthogonalized-plane-wave calculations for PbTe are compared with existing augmented-plane-wave results, with excellent agreement in the nonrelativistic case. It is also found that relativistic band calculations by the double-expansion technique need more intermediate (nonrelativistic) basis states than were used in the PbTe work.

I. INTRODUCTION

The idea of coupling a first-principles band calculation, including velocity matrix elements at a single point in the Brillouin zone with a $\vec{k}\cdot\vec{p}$ extrapolation to map out the energy bands over the entire zone, has been explored recently by a large number of workers.[1–11] Since the $\vec{k}\cdot\vec{p}$ expansion[12] is exact until truncation, it is particularly appealing as a technique for inexpensively extrapolating not only first-principles energies, but also wave functions (and, hence, matrix elements, charge densities, etc.). Many properties now being calculated require some integral of the wave functions over the Brillouin zone. Brinkman and Goodman[1] used this technique to obtain the valence charge density in performing a self-consistent orthogonalized-plane-wave (OPW) calculation for Si. Trickey and Conklin[8] proposed a self-consistent augmented-plane-wave (APW) technique, starting from this ansatz, that simultaneously avoids iterating the APW calculation and removes the muffin-tin restriction without actually doing a non-muffin-tin APW calculation. Parada and Pratt[3–5] used the combined APW $\vec{k}\cdot\vec{p}$ technique to treat the PbTe vacancy problem in the Wannier representation. The optical constants for PbTe were calculated by Buss and Parada,[6] and a similar calculation was attempted by the present author for Bi.[9] Results[2–6] on PbTe led a number of workers to attempt other materials.[7,9–11] These latter calculations were consistently less than satisfactory. The utility of the techniques is obviously dependent on the faithfulness of the calculated wave functions. The purpose of this paper is to explore the limitations of full-zone $\vec{k}\cdot\vec{p}$.

Several workers have recognized the inadequacies for materials in which the d bands[7,11] are important. Kuebbing *et al.*[7] examined TiC and found the $\vec{k}\cdot\vec{p}$ convergence very poor (discrepancies up to 8 eV) for the relevant d levels. They then carefully reexamined PbTe and found that, while they could reproduce the original results (which had discrepancies up to 1 eV), even doubling the $\vec{k}\cdot\vec{p}$ basis did not significantly improve the energy level agreement. Williams[11] also found full-zone $\vec{k}\cdot\vec{p}$ lacking for transition metals. Williams adopted the obvious solution of doing the first-principles calculation, including matrix elements, at many points and then using local $\vec{k}\cdot\vec{p}$ extrapolation.[13] This solution has been previously employed in connection with pseudopotential ϵ_2 calculations,[14] but can be very unattractive if high symmetry is being exploited either by the technique for calculating matrix elements[7] or in the k-space integration.[4,5]

Full-zone $\vec{k}\cdot\vec{p}$ is highly convergent for a nearly-free-electron gas. Brinkman and Goodman[1] obtained good results when they compared full-zone $\vec{k}\cdot\vec{p}$ using matrix elements calculated from a pseudopotential with the direct results of the pseudopotential calculation. This reflects the fact that the $\vec{k}\cdot\vec{p}$ expansion of the pseudo-wave-function[15] is excellent. However, there are energy levels in their OPW $\vec{k}\cdot\vec{p}$ calculation for which the agreement with direct OPW calculation is an order of magnitude poorer.

In this paper we will examine the strengths and weaknesses of full-zone $\vec{k}\cdot\vec{p}$ (first using results for Bi). Then we will demonstrate the precision of the first-principles part of the calculation by comparing OPW results for PbTe with the results of APW work.[4,5,16] Finally, we will use Al, a material selected for its expected amenability to full-zone $\vec{k}\cdot\vec{p}$ treatment, to illustrate the limitations of full-zone $\vec{k}\cdot\vec{p}$.

The question here is in no sense the validity of $\vec{k}\cdot\vec{p}$ expansions; the question is whether a conveniently truncated $\vec{k}\cdot\vec{p}$ expansion can yield satisfactorily converged results over the entire Brillouin zone. The technique being discussed here differs somewhat from the empirical interpolation technique based on extended-zone $\vec{k}\cdot\vec{p}$.[17] In the empirical approach, zone-boundary information as well as zone-center information is used in the selection of parameters. Thus, the parameters chosen can, to some extent, compensate for the effects of the truncation.

II. CALCULATIONS

In this paper, "satisfactory" refers to the accuracy of the solutions to the eigenvalue problem, starting from an assumed one-electron potential. For these purposes, we will ignore the question of potential selection. We are not seeking the comparison of experiment with theory; we are interested only in the precision of the solution to a given eigenvalue problem. Except for PbTe, the potential we will use is a spatial superposition of spherically symmetric overlapping atomic potentials. The self-consistent free atoms are calculated using a version of the Liberman, Waber, and Cromer Dirac-Slater code.[18] For Al and Bi, the value $\frac{2}{3}$ was used for the exchange coefficient α. For PbTe, the potential used is the muffin-tin potential of Conklin, Johnson, and Pratt.[19]

The OPW results reported here were all obtained using our relativistic OPW code—hence solving the Dirac equation. For Al and comparing PbTe, a fictitiously augmented speed of light has been used to simulate a nonrelativistic calculation. We discuss velocity rather than momentum matrix elements because, for the Dirac equation, velocity and momentum correspond to different operators and it is, in fact, velocity matrix elements that enter a $\vec{k}\cdot\vec{p}$ exapnsion and are used for interband optical transitions. It is reported[2,4,10] that the distinction between velocity and momentum is not important even for PbTe. We cannot easily verify this, since for the Dirac equation the velocity operator is not the gradient plus a sum of terms, as it is after a Foldy-Wouthuysen transformation. However, we wish to point out that the estimate in Ref. 4 of 0.01% for the difference between p/m and v at specific symmetry points is probably much too small for a general estimate in a material with as large a Z as Pb.[20]

A. Bi

A local $\vec{k}\cdot\vec{p}$ expansion is a very natural way to parametrize the Bi Fermi surface which occupies a tiny fraction of the Brillouin zone.[21] This has been done using matrix elements from two recent band calculations.[22-24] The calculated matrix elements differed from each other sufficiently that we calculated matrix elements by a third method (unfortunately resulting in a third set of answers). We attribute these differences to the fact that different potential models are used in all three cases. Thus, within the context of the paper, they may all

TABLE I. Velocity matrix elements in Bi.[a]

Matrix element[b]	Pseudo Golin[c]	APW Ferreira[d]	OPW Present work
$\pi^{(1)}$	0.372	$0.397+i.001$	$0.419+i.002$
$\pi_2^{(2)}$	$0.176+i.374$	$0.194+i.454$	$0.096+i.585$
$\pi_3^{(2)}$	$-0.378+i.200$	$-0.4858+i.1708$	$-0.5747+i.1202$
$\pi_{22}^{(3)}$		-0.156	-0.278
$\pi_{23}^{(3)}$	-0.206	-0.063	$+0.274$
$\pi_{32}^{(3)}$	0.204	0.377	0.326
$\pi_{33}^{(3)}$	-0.256	$+0.094$	0.266
$\pi_{22}^{(4)}$		-0.473	-0.599
$\pi_{23}^{(4)}$	-0.416	-0.501	-0.526
$\pi_{32}^{(4)}$	0.392	-0.450	-0.498
$\pi_{33}^{(4)}$	0.350	0.434	0.578
$\pi_2^{(8)}$		$-0.446+i.185$	$-0.504+i.277$
$\pi_3^{(8)}$		$-0.235-i.414$	$-0.308-i.495$

where[b]

$$\langle T_4^-(1)\,|\,\vec{\pi}\,|\,UT_4^+(1)\rangle=\pi^{(1)}\,(0,0,1)$$

$$\langle T_4^-(1)\,|\,\vec{\pi}\,|\,T_6^+(j)\rangle=\pi_j^{(2)}\,(-1,+i,0)$$

$$\langle T_6^+(j)\,|\,\vec{\pi}\,|\,T_6^-(j')\rangle=\pi_{jj'}{}^{(3)}\,(0,0,1)$$

$$\langle T_6^+(j)\,|\,\vec{\pi}\,|\,UT_6^-(j')\rangle=\pi_{jj'}{}^{(4)}\,(-1,+i,0)$$

$$\langle T_4^+(1)\,|\,\vec{\pi}\,|\,T_6^-(j)\rangle=\pi_j{}^{(8)}\,(-1,+i,0)$$

[a] Atomic units ($\hbar=1$, $e^2=2$, $m=\frac{1}{2}$).

[b] Notation is that of Golin, Ref. 23. Basis vectors are along binary, bisectrix, and trigonal axes.

[c] Reference 23.

[d] Reference 22.

be correct. These three sets of relativistic velocity matrix elements calculated for the symmetry point T in Bi are shown in Table I. In addition to the OPW matrix elements, we list those calculated from a nonlocal pseudopotential by Golin[23] and those calculated by Ferreira[22] using the APW method.[25]

As we were aware of the apparent success of Parada and co-workers[3-5] with PbTe, it was natural to attempt Bi interpolation (extrapolation) by relativistic OPW full-zone $\vec{k}\cdot\vec{p}$. For these purposes we expect Bi to be much like PbTe. The crystal structure of Bi is only slightly distorted from PbTe and the position of Bi in the Periodic Table indicates that it should be quite similar to PbTe from an atomic point of view. Since the $\vec{k}\cdot\vec{p}$ expansion may be about any point, we first attempted full-zone $\vec{k}\cdot\vec{p}$ in Bi starting from T. Preliminary results were unsatisfactory.

Results using a zone-center expansion point are shown in Fig. 1 for the two most interesting directions in Bi. Here we employ the first 30 valence states (with spin) as basis functions (the same number Parada used in PbTe). Several facts are to be noted. First, the over-all reproduction of the OPW results is inadequate in a material where the details around the Fermi surface are discussed in meV. Both of these directions in Bi correspond to the Λ axis in PbTe, where PbTe $\vec{k}\cdot\vec{p}$ is the best. Γ to X, for example, is significantly worse in Bi. A reasonable augmenting of the expansion basis set did not significantly help in agreement with the PbTe conclusion of Kuebbing *et al.*[7]

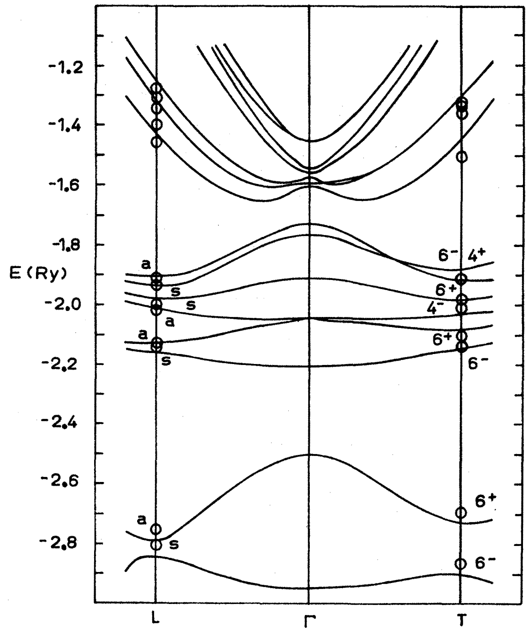

FIG. 1. Energy bands in Bi by OPW full-zone $\vec{k}\cdot\vec{p}$. Circles are relativistic OPW values. OPW states at T are labeled according to the symmetry index and states at L are labeled according to whether they are symmetric or antisymmetric.

TABLE II. Magnitude squared of $\vec{k}\cdot\vec{p}$ and OPW velocity matrix elements at T in Bi.[a]

	T_6^-	T_6^+	T_6^-	T_6^+	T_{45}^-	T_6^+	T_{45}^+
$T_6^- k\cdot p$	(0.02)	0.45	(0.02)	0.32	(0.01)	0.44	0.50
OPW	(0)	0.48	(0)	0.38	(0)	0.45	0.49
$T_6^+ k\cdot p$		(0.01)	0.50	(0.05)	0.75	(0.01)	(0.02)
OPW		(0)	0.50	(0)	0.75	(0)	(0)
$T_6^- k\cdot p$			(0.04)	0.75	(0.15)	0.51	1.20
OPW			(0)	0.80	(0)	0.60	1.32
$T_6^+ k\cdot p$				(0.00)	1.21	(0.03)	(0.20)
OPW				(0)	1.41	(0)	(0)
$T_{45}^- k\cdot p$					(0.01)	1.36	0.10
OPW					(0)	1.38	0.18
$T_6^+ k\cdot p$						(0.00)	(0.06)
OPW						(0)	(0)

[a] Atomic units ($\hbar=1$, $e^2=2$, $m=\frac{1}{2}$). Parentheses enclose those entries that should vanish by parity. Since all states have twofold degeneracy and the $\vec{k}\cdot\vec{p}$ states do not actually transform according to the indicated symmetries, we choose to use the quantity $|\langle T_n|\pi|T_n'\rangle|^2+|\langle T_n|\pi|UT_n'\rangle|^2$ (where T_n' and UT_n' are orthogonal degenerate states) for comparisons.

Second, in the figure at T and L, the lowest $\vec{k}\cdot\vec{p}$ state is below the correct OPW energy. There is no way that adding higher basis states can raise the lowest state. The point is that the core states at Γ comprise a part of the complete set of $\vec{k}\cdot\vec{p}$ states which has been truncated. Our Bi calculations, which included selected core basis states, yielded degraded results. Since the 156 core states of Bi are untractable, we will defer discussion of core states in $\vec{k}\cdot\vec{p}$ until a later section, in which we will treat Al including all five core states.

In spite of the deficiencies in energy eigenvalues in Bi at the symmetry point T, the $\vec{k}\cdot\vec{p}$ technique yields quite good interband velocity matrix elements. The magnitude of the matrix elements squared calculated by $\vec{k}\cdot\vec{p}$ and those calculated directly are shown in Table II.

B. PbTe

The PbTe work[2-6] which stimulated the current wave of activity has been critically examined and the essence of it subsequently reproduced by others.[7,9,26] Since our examination of the PbTe first-principles $\vec{k}\cdot\vec{p}$ work has been carried out in an OPW framework and all previous work has been APW, the comparisons can be quite illuminating. In Table III, the velocity matrix elements at Γ calculated by the APW method[4,16,27] and those calculated by the OPW method are shown. The agreement is striking. The methods and basis functions are distinct enough so that the agreement of these two calculations represents a strong check on the precision of this as-

TABLE III. PbTe velocity matrix elements.[a]

Matrix elements[b]	APW[c]	OPW	Pseudo[d]	OPW contributions[e]				
				PW-PW	PW-s	PW-p	PW-d	Core-core
$M_{1;15}^{1;1}$	0.969	0.991	0.972	1.367	−0.774	−0.189	0	0.587
$M_{1;15}^{1;2}$	0.250	0.242	0.225	0.325	−0.290	−0.043	0	0.250
$M_{1;15}^{2;1}$	−0.155	−0.151	−0.168	−0.218	0.083	0.031	0	−0.047
$M_{1;15}^{2;2}$	1.180	1.168	1.140	1.513	−0.680	−0.212	0	0.547
$M_{1;15}^{3;1}$	0.437	0.433	0.530	0.676	−0.489	−0.103	0	0.349
$M_{1;15}^{3;2}$	−0.225	−0.223	−0.319	−0.417	0.488	0.071	0	−0.365
$M_{12;15}^{1;1}$	0.534[f]	0.534	0.542	0.645	0	−0.105	−0.103	0.097
$M_{12;15}^{1;2}$	−1.456[f]	−1.460	−1.316	−1.602	0	0.280	0.293	−0.432
$M_{25;2}$	0.949	0.962	1.032	1.091	0	0	−0.128	−0.001
$M_{25;15}^{1;1}$	1.068[f]	1.069	0.984	1.138	0	−0.192	−0.150	0.273
$M_{25;15}^{1;2}$	0.460[f]	0.453	0.362	0.429	0	−0.077	−0.077	0.177
$M_{25;15}^{d;1}$	0.066	0.087						
$M_{25;15}^{d;2}$	0.631	0.613						
$M_{12;15}^{d;1}$	0.533	0.497						
$M_{12;15}^{d;2}$	0.376	0.415						
$M_{25;2}^{d}$	0.395	0.337						

[a] In atomic units ($\hbar=1$, $e^2=2$, $m=\frac{1}{2}$).

[b] Notation is that of Refs. 4–6; subscripts denote symmetries; superscripts index states of given symmetry; superscript d refers to Pb 5d core band.

[c] References 4–6 except Ref. 16 for M^d values.

[d] Calculated using pseudo-wave-function (see text).

[e] PW-f contributions are less than 0.0005.

[f] As interpreted, Ref. 27.

pect of the calculation.

A separate question of interest is the comparison between matrix elements based on pseudo-wave-functions and those based on the full wave function. To show how much the non-plane-wave terms contribute, we list in Table III the decomposition of the OPW matrix elements into the plane-wave–plane-wave contribution, the plane-wave–core contribution (divided according to the angular momentum of the core term), and the core-core contribution. (Most of these elements also allow plane-wave–f-core contributions. These were included in the calculation but contribute less than 0.0005 in a.u. The core-core contributions were calculated by individual l and l' terms and the f contributions to Γ_{15} are also negligible.)

The OPW calculation may be formulated as a nonlocal pseudopotential calculation.[15] The expansion of the pseudo-wave-function in plane waves is then identical, aside from normalization, to the expansion of the wave function in OPW's. The numbers in the column labeled Pseudo are the results for matrix elements calculated from only the pseudo-wave-function (i.e., the plane-wave–plane-wave term with pseudo-wave-function normalization). We see that while the orthogonalization terms make large contributions to the OPW matrix elements, for this one case, Γ in PbTe, these contributions nearly cancel out and the pseudopotential matrix elements look very much like OPW matrix elements (For a detailed treatment of this topic as it bears on ϵ_2 in Si and Ge, where the details of the band structure are well understood, see Ref. 28.)

The PbTe discussion up to this point has dealt with the nonrelativistic aspect of the calculation, although Parada and co-workers' final results were relativistic. Following Conklin *et al.*,[19] Parada expanded the relativistic corrections using the nonrelativistic APW wave functions as a basis set. In the course of our OPW treatment we carried out a direct relativistic solution from the potential of Conklin *et al.*[19] In Table IV we show our relativistic and nonrelativistic OPW eigenvalues, as well as the double-expansion relativistic results of Conklin *et al.* The agreement of the nonrelativistic calculations is quite satisfactory; aside from the $\Gamma_2{}'$ and the Γ_{12} levels, the difference is 4 mRy or less. However, relativistically we find differences up to 70 mRy. In view of the extent of nonrelativistic agreement, we interpret this larger discrepancy as a probable inadequacy of the basis set used to expand the relativistic corrections. We conclude

TABLE IV. Energy levels in PbTe (Ry).

	Nonrelativistic			Relativistic	
	APW[a]	OPW		APW[b]	OPW
$^2\Gamma_1$	0.906	0.908	$^2\Gamma_6^+$	0.769	0.720
Γ_{12}	0.868	0.863	$^2\Gamma_8^+$	0.841	0.839
Γ_2	0.715	0.723	Γ_7^-	0.715	0.724
$\Gamma_{25'}$	0.674	0.672	$^1\Gamma_8^+$	0.656	0.661
			Γ_7^+	0.656	0.653
$^2\Gamma_{15}$	0.609	0.613	$^2\Gamma_8^-$	0.539	0.538
			$^2\Gamma_6^-$	0.411	0.365
$^1\Gamma_{15}$	0.179	0.180	$^1\Gamma_8^-$	0.142	0.142
			$^1\Gamma_6^-$	0.067	0.052
$^1\Gamma_1$	0.103	0.105	$^1\Gamma_6^+$	−0.201	−0.272
$^3\Gamma_1$	−0.538	−0.537	$^3\Gamma_6^+$	−0.672	−0.695
$^d\Gamma_{12}$	−1.043	−1.038[c]	$J=\frac{5}{2}$		−1.185
$^d\Gamma_{25'}$	−1.043		$J=\frac{3}{2}$		−1.396

[a] Reference 19 or Refs. 4 and 5.

[b] References 4 and 5.

[c] This is a core state in the OPW calculation.

that a double-expansion relativistic calculation required more nonrelativistic APW states than were employed by Conklin or Parada.

The $\vec{k}\cdot\vec{p}$ PbTe calculation is less than a total success. At X and K there are energy discrepancies up to 1.0 eV for levels in the range of interest. For much current semiconductor work, this is an order of magnitude above the resolution being sought. A more subtle quantity to measure is the quality of the wave functions. The easiest measure of this is the zone-boundary parity selection rules.

The question of zone-boundary parity in $\vec{k}\cdot\vec{p}$ can be a point of considerable confusion. The untruncated $\vec{k}\cdot\vec{p}$ expansion contains complete information even at zone boundary. However, the individual matrix elements of the Hamiltonian between $\vec{k}\cdot\vec{p}$ basis functions do not preserve the indeterminacy in $\vec{k}$ required by lattice periodicity. Thus, since a reciprocal-lattice vector is required to carry a zone-boundary k value into itself under inversion, zone-boundary inversion symmetry is only approximate after truncation. To the extent that the wave functions are well converged, they must still possess definite parity at X or L. Zone-boundary parity is well camouflaged in the $\vec{k}\cdot\vec{p}$ representation. The parity projection operator can be used to write a wave function that has manifestly definite parity. However, this wave function is not really amenable to use. It is generally unnormalized[29] since the approximate wave function has a contribution of the opposite parity. The normalization of the resulting wave function requires matrix elements of the inversion operator between $\vec{k}\cdot\vec{p}$ basis functions $e^{i\vec{k}\cdot\vec{r}}\times u_n(\vec{0},\vec{r})$. These depend on $\vec{k}$, are not diagonal in the band index n, and require a volume integration to calculate.

If one wanted a better wave function at X or L, the parity projection operator could be used to obtain one. If one is doing a zonal integration, a wave-function improvement scheme for selected points on the zone surface is probably not worthwhile. For these purposes, zone-boundary wave functions are examined primarily to evaluate the over-all quality of the wave function throughout the zone. Thus, the relative parity of states is a convenient measure of the quality of zone-boundary wave functions. Table V shows the magnitudes of the $\vec{k}\cdot\vec{p}$ zone-boundary velocity matrix elements squared between various states at L for $\vec{k}\cdot\vec{p}$ PbTe. Those matrix elements which should vanish (being between states of the same parity) are enclosed in parentheses. We see that the calculated band-edge states are thoroughly mixed.

C. Al

Having recognized the nonconvergence of our Bi full-zone $\vec{k}\cdot\vec{p}$ expansion and verified the precision of our calculation through the PbTe work, we undertook to examine the subject of full-zone $\vec{k}\cdot\vec{p}$ using Al, a material in which (a) there should be little trouble with OPW convergence, (b) the calculation could be done without spin, avoiding doubling of the basis set, (c) all core states could be included, (d) the d bands should be unimportant so that we can distinguish our findings from those of Keubbing *et al.*,[7] and (e) because its free-electron nature is expected to be well suited for full-zone $\vec{k}\cdot\vec{p}$ treatment.

Our results for full-zone $\vec{k}\cdot\vec{p}$ Al are displayed in Figs. 2 and 3 in the form of a convergency study. The OPW $\vec{k}\cdot\vec{p}$ zone-boundary energies are shown as a function of the number of valence basis states used both with and without core states in the $\vec{k}\cdot\vec{p}$

TABLE V. Magnitude squared of $\vec{k}\cdot\vec{p}$ velocity matrix elements at L in PbTe.[a]

	L_6^-	L_6^+	L_6^+	L_{45}^+	L_6^+	L_6^-	L_6^-	L_{45}^-
L_6^-	(0.01)	0.45	0.43	0.43	0.11	(0.10)	(0.08)	(0.01)
L_6^+		(0.01)	(0.01)	(0.01)	(0.27)	0.17	0.22	0.26
L_6^+			(0.04)	(0.02)	(0.64)	0.07	0.36	1.20
L_{45}^+				(0.03)	(0.76)	0.81	0.56	0.10
L_6^+					(0.14)	0.46	0.01	0.29
L_6^-						(0.00)	(0.75)	(0.40)
L_6^-							(0.00)	(0.59)
L_{45}^-								(0.01)

[a] Atomic units ($\hbar=1$, $e^2=2$, $m=\frac{1}{2}$). Parentheses enclose those entries that should vanish by parity. Based on relativistic PbTe of Refs. 4–6 (see Ref. 27). This uses $M^{2;2}_{1;15}$ equal to 1.180, the first-principles value; the adjusted value of Refs. 4–6 was also tried and while the values were different, they were neither systematically better nor worse. Since all states have twofold degeneracy and the $\vec{k}\cdot\vec{p}$ states do not actually transform according to the indicated symmetries, we choose to use the quantity $|\langle T_n|\pi|T_n'\rangle|^2+|\langle T_n|\pi|UT_n'\rangle|^2$ (where T_n' and UT_n' are orthogonal degenerate states) for comparisons.

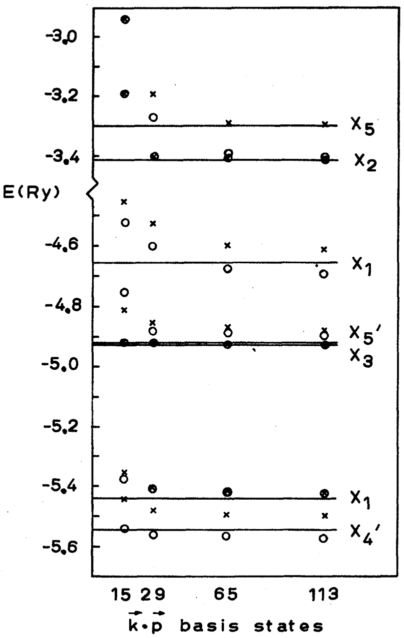

FIG. 2. Convergence study of OPW full-zone $\vec{k}\cdot\vec{p}$ at X in Al. The crosses and circles are $\vec{k}\cdot\vec{p}$ values including and excluding core basis states, respectively. The OPW values are shown as solid lines. The count of basis states always excludes the five core states.

basis set. Several things are apparent.

First, in no case is the over-all agreement between OPW and $\vec{k}\cdot\vec{p}$ values particularly good. Almost without exception, including core basis states makes things worse. We will find the difficulties inexorably related to core states or corelike behavior. We see that the lowest state of a given symmetry converges very rapidly with or without core; in particular, note the X_2 and X_3 states. As we noted earlier, for a truncated $\vec{k}\cdot\vec{p}$ expansion, the zone-boundary inversion symmetry is only approximate, thus the symmetry at X is only Δ axis symmetry, and at L is Λ axis symmetry. The X_2 and X_3 have Δ_2 and Δ_2' characters which are absent in the Al core states. There are several levels which are well converged only when core basis states are included. These are levels for which there is no state of identical symmetry in the core (for example, L_3 near -4.5 Ry, L_3 near -3.4 Ry, and X_5 near -3.3 Ry).

Without core states, we find that the two Λ_3 states (L_3 and L_3' near -4.5 Ry) are thoroughly mixed. Λ_3 is a degenerate representation; one indication of the mixing is the fact that the velocity matrix elements between partners within degenerate pairs are very large (> 1.0 in a.u.). Including core basis states and using a small number of valence basis states, the d-like L_3 is essentially converged, but the p-like L_3' is significantly too high. Under these conditions, the intrarepresentation matrix element drops several orders of magnitude. As the number of basis states is increased and the L_3' approaches a convergence crossing of the L_3 level, mixing is again observed. The extent of s- and p-band nonconvergence in the core calculation is such that using 113 $\vec{k}\cdot\vec{p}$ basis states still does not bring the L_3' to its correct position below the L_3 state.

One of the apparent inconsistencies in the Al $\vec{k}\cdot\vec{p}$ calculation is the good convergence of the L_2' state near -4.2 Ry. An examination of the OPW calculation reveals that this state has very little core p character and, hence, the wave function and pseudowave-function are quite similar. Finally, we note that at the symmetry point W, the lowest W_1 state is unconverged by more than 2.0 eV for 15 basis states (with core excluded). W_1 is the fourth valence state and should be very near the Fermi energy.

III. DISCUSSION AND CONCLUSIONS

We have found that for a small expansion set the addition of core basis states not only fails to improve the eigenvalue agreement but actually makes it worse. Yet, contributions from the core basis states are clearly necessary, at least for some states. The role of core states can be understood, in part, by realizing that $\vec{k}\cdot\vec{p}$ without core states is dependent on the approximate orthogonality of the

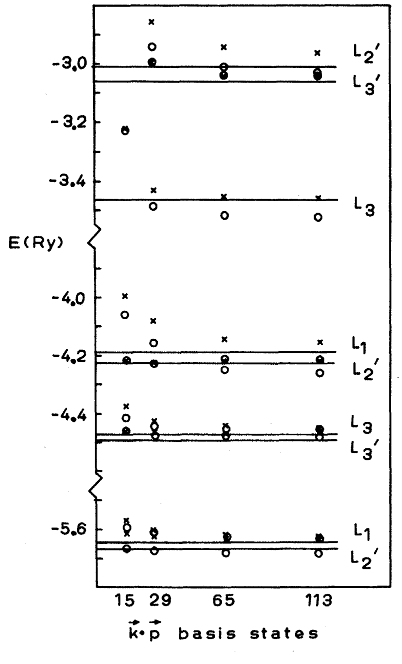

FIG. 3. Convergence study of OPW full-zone $\vec{k}\cdot\vec{p}$ at L in Al. The crosses and circles are $\vec{k}\cdot\vec{p}$ values including and excluding core basis states, respectively. The OPW values are shown as solid lines. The count of basis states always excludes the five core states.

desired state to the core expansion states. If, on the other hand, we include the core states, then we are also attempting to describe the core states in the $\vec{k}\cdot\vec{p}$. Core states are not readily described by the $\vec{k}\cdot\vec{p}$ expansion. It is similar to attempting to expand the core states in plane waves. The worsened results we exhibit using core basis states are, thus, the tradeoff in our variational equation as we try to describe these core states as well as the states of actual interest.

It is not that the core contributes such a significant fraction of the wave function, but that the valence states get improperly mixed without core basis states. For example, in Al the L_3 states near -3.4 Ry have a core basis state contribution of only 0.8% (for 65 basis states) and the X_5 near -3.3 Ry has a core contribution of only 1.3%; yet the energies are significantly affected. (The L_3 and L_3' near -4.5 have only 0.14% and 0.27%, respectively, and the X_5' near -4.9 has only 0.5%.)

Brinkman and Goodman[1] point out one approach to the core problem, to orthogonalize the $\vec{k}\cdot\vec{p}$ functions to the core states. Matrix elements of the operator $P_c^k = e^{-i\vec{k}\cdot\vec{r}} P_c e^{i\vec{k}\cdot\vec{r}}$ must be included in the resulting secular equation. These matrix elements are $\vec{k}$ dependent and sufficiently difficult to calculate that we have not undertaken this refinement.

The energy bands and the pseudo-wave-functions of Bi, PbTe, and Al may be those of a nearly-free-electron gas, but the wave functions are not. The wave function of the lowest Γ_1 in Al, for example, rather than resembling the lowest state of a free-electron gas, has $3s$ character near the Al core. It has wiggles. L_1 or X_1 is, likewise, a $3s$ state (no p character). In the nearly-free-electron approximation, the $\vec{k}\cdot\vec{p}$ L_1 state is made up of one-half the lowest Γ_1 and one-half the appropriate linear combination of Γ_{25}', Γ_{15}, Γ_2', and Γ_1. This yields a good pseudo-wave-function, but a wave function so composed will not have the correct wiggles.

We have found that in some cases, Bi at T, for example, full-zone $\vec{k}\cdot\vec{p}$ can yield very good wave functions (matrix elements) at zone boundary when the states of interest are sufficiently separated from other states of the same symmetry. In Parada's calculation of PbTe,[3-5] the band edges L_6^- and L_6^+ are both states of Λ_6 symmetry and are less than 0.03 Ry apart. These states exhibit thoroughly mixed parity, which means that the $\vec{k}\cdot\vec{p}$ representation is describing each of these states as a nearly equal linear combination of the two true band-edge states. Considering the nonrelativistic calculation, the L_1 and L_2' are both Λ_1 states, but are 0.07 Ry apart.[19] These states have much smaller contributions of mixed parity. It is not clear whether all of the problems with the relativistic band-edge states are due to the closeness of those states or whether some of it may be due to faulty information in the $\vec{k}\cdot\vec{p}$ matrix due to the relativistic expansion difficulties discussed in Sec. II B.

For the eigenvalues, we find an early apparent convergence that depends on the omission of states both above and below the states of interest. We then find that the effect of adding additional basis states may be fairly large, but does not necessarily improve the faithfulness of the eigenvalue reproduction. It is very tempting to speculate that the poorer apparent convergence found using 15 spinless basis states in Al compared to PbTe might be due to Al having less core states to omit.

The degree to which the energy reproduction is satisfactory is a question that must be examined for each material. This can be easily determined if a few zone-boundary points are calculated by both $\vec{k}\cdot\vec{p}$ and the first-principles technique. The quality of the wave function is more difficult to evaluate.

Let us now review specific previous calculations in the light of these findings. Brinkman and Goodman's Si calculation[1] is probably not subject to any criticism in this context. Since they are calculating a charge density, they need only the occupied valence states, and the energy convergence is quite good for the valence band. Moreover, due to the symmetry and location of band edges in Si, there are few, if any, nearby conduction band states to be improperly mixed in. Thus, in the diamond structure, full-zone $\vec{k}\cdot\vec{p}$ may be adequate to calculate a valence charge density. To extend their Si work to include an ϵ_2 calculation, however, would not seem appropriate due to the poorer energy convergence seen in their conduction band states.

The Buss and Parada ϵ_2 calculation[6] is probably not significantly limited by our observations. Their eigenvalue limitations are obvious in their Σ axis E vs $\vec{k}$ figure. Since the three valence bands and three conduction bands at L have opposite parity, the mixed nature of the band-edge states involve allowed transitions, thus the mixing affects the amplitude but not the selection rules. The present author's[9] ϵ_2 calculation for Bi is obviously of limited value due to the poor eigenvalue results discussed in Sec. IIA. The details of Parada and Pratt's[3-5] vacancy calculation may be quite affected by our conclusions. A number of the calculated vacancy levels are at energies very near the L gap, and the use of an inadequate wave function at L would be expected to have severe consequences on the details on these results.

In summary, we conclude that the apparent success in describing some materials by full-zone $\vec{k}\cdot\vec{p}$ must be, to quite an extent, fortuitous. Furthermore, those results are not readily improved by a more complete basis set and one should use full-zone $\vec{k}\cdot\vec{p}$ over the Brillouin zone with a great deal of caution.

ACKNOWLEDGMENTS

The author is indebted to A. C. Switendick for many helpful discussions during the course of this work. Enlightening discussions with K. Schwarz, S. B. Trickey, J. B. Conklin, and D. D. Buss are also acknowledged.

---

*Work supported by the U. S. AEC.

[1] W. Brinkman and B. Goodman, Phys. Rev. 149, 597 (1966).

[2] G. W. Pratt, Jr. and N. J. Parada, Intern. J. Quantum Chem. 1S, 589 (1967).

[3] N. J. Parada and G. W. Pratt, Jr., Phys. Rev. Letters 22, 180 (1969).

[4] N. J. Parada, thesis (MIT, 1968) (unpublished).

[5] N. J. Parada, Phys. Rev. B 3, 2042 (1971).

[6] D. D. Buss and N. J. Parada, Phys. Rev. B 1, 2692 (1970).

[7] T. J. Kuebbing, K. Schwarz, S. B. Trickey, and J. B. Conklin, Jr., Phys. Rev. Letters 26, 1251 (1971); see also T. J. Kuebbing, thesis (University of Florida, 1971) (unpublished).

[8] S. B. Trickey and J. B. Conklin, Jr., Phys. Letters 32A, 481 (1970).

[9] J. P. Van Dyke, Bull. Am. Phys. Soc. 16, 405 (1971).

[10] S. Rabii (private communication).

[11] A. Williams (private communication).

[12] For a review of the $\vec{k}\cdot\vec{p}$ method, see E. O. Kane in *Semiconductors and Semimetals* (Academic, New York, 1966), Vol. 1, Chap. 3.

[13] A. Williams, Bull. Am. Phys. Soc. 16, 414 (1971).

[14] L. R. Saravia and D. Brust, Phys. Rev. 171, 916 (1968).

[15] A pseudo-wave-function φ is defined as a smooth function such that the true wave function ψ is given by $\psi = (1-P_c)\varphi$, where P_c is the core-state projection operator. See J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959); or W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966), p. 11.

[16] T. J. Kuebbing, K. Schwarz, S. B. Trickey, and J. B. Conklin, Jr. (private communication).

[17] See, for example, F. H. Pollak, M. Cardona, C. W. Higginbotham, F. Herman, and J. P. Van Dyke, Phys. Rev. B 2, 352 (1970), and references therein.

[18] D. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. 137, A27 (1965).

[19] J. B. Conklin, Jr., L. E. Johnson, and G. W. Pratt, Jr., Phys. Rev. 137, A1282 (1965).

[20] In zinc, at the symmetry point K, where symmetry allows us to make a separation of the spin and spinless part, we find the spin part to be about 1.0%.

[21] This has been done empirically many times. A recent reference containing many early references is M. Maltz and M. S. Dresselhaus, Phys. Rev. B 2, 2877 (1970).

[22] L. G. Ferreira, J. Phys. Chem. Solids 28, 1891 (1967); 29, 357 (1968).

[23] S. Golin, Phys. Rev. 166, 643 (1968).

[24] R. T. Bate, N. G. Einspruch, and P. J. May, Jr., Phys. Rev. 186, 599 (1969).

[25] The APW calculation employed a muffin-tin potential obtained by the Mattheiss prescription and an exchange coefficient α of 1. The experimental energy differences lie about halfway between Ferreira's first-principles calculation and the relativistic OPW calculation which used $\alpha = \frac{2}{3}$. This suggested that the difference might lie in the exchange coefficient α. However, relativistic OPW energies using $\alpha = 1$ were further from experiment and from Ferreira's result than the original $\alpha = \frac{2}{3}$. This means that the difference is in the details of the potential model used. (This work will be described in more detail in a subsequent publication.) All three calculations were also carried out at the symmetry point L where the wave functions and, hence, matrix elements are very sensitive to details of the potential model which we verified by slightly perturbing our potential model.

[26] It should be pointed out that although Ref. 5 seems to contain everything necessary to reproduce the $\vec{k}\cdot\vec{p}$ part of the PbTe APW $\vec{k}\cdot\vec{p}$ calculation (except the lattice constant 12.1927 a.u.) there is something missing. The listed M's must be transformed by a mixing matrix that describes the expansion of relativistic states in terms of the nonrelativistic states. This matrix is found on p. 62 of Ref. 4 (see also Ref. 27).

[27] The matrix elements $M_{12;15}$ and $M_{25;15}$ differ by factors $\frac{1}{2}\sqrt{6}$ and $\frac{1}{2}\sqrt{3}$, respectively, from those listed in Refs. 4–6. The numbers listed in Table III reproduce the $\vec{k}\cdot\vec{p}$ results of Refs. 4–6 when combined with the mixing matrix (Table 3.8 of Ref. 4) and the symmetry information of Refs. 4 or 6.

[28] J. P. Van Dyke (unpublished).

[29] The eigenfunctions of the parity operator in Eq. (3.5) of Ref. 4 are also unnormalized. The equation written assumes that the wave functions of k_L and $-k_L$ are orthogonal; in fact, they should approach unit overlap.