



SEMI-EMPIRICAL APW CALCULATION OF THE BAND STRUCTURE OF SILICON*

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Abstract

We propose a modification to the usual augmented-plane-wave muffin-tin approximation approach which fits exactly the measured value of the band gap of Si. The method involves one adjustable parameter which is introduced by a uniform shift of the *s*-like logarithmic derivatives. The results are in good agreement with those of the empirical pseudopotential method not only for the gap but also for an energy range of approximately 3eV from the top of the valence band.

There have been numerous calculations of the band structure of silicon with varying degrees of success. The general consensus is that empirical pseudopotentials (especially energy-dependent nonlocal pseudopotentials¹) give the most accurate representation of both the measured optical gaps and the cyclotron masses for Si. State of the art first principles calculations², underestimate the band gap by 50%. This fact has been demonstrated by Hamann² who used the linearized augmented plane wave (APW) method and also by Hamann and Zunger³ using a pseudopotential approach. Both of these calculations were performed self-consistently and assumed no shape approximation for the potential.

On the other hand the standard APW method within the muffin-tin approximation (APW-MT) gives no gap at all, even if one iterates to self-consistency⁴.

Motivated by potential applications (e.g. cluster calculations of hydrogenated amorphous silicon) of a muffin-tin-like representation for the energy bands of Si, we have constructed a modified APW-MT approach involving one adjustable parameter which reproduces the measured band gap exactly, and also describes well the general band structure near the valence and conduction band edges. Although the results far away from the band gap are not in very good agreement with the empirical pseudopotential results, we obtain a qualitatively adequate representation of the overall band structure with this method using only the measured band gap as input.

In the present approach we have constructed a Si MT potential in the standard manner using overlapping spherical charge densities obtained from the relativistic atomic structure program of Liberman, et al.⁵ with full Slater exchange ($\alpha = 1$). A Si valence electron configuration of $3s^1 3p^3$ was used. Using this MT potential logarithmic derivatives, L_l , were constructed and APW eigenvalues and wavefunctions were determined using our symmetrized APW programs. The one adjustment that was made was to shift uniformly the *s*-like logarithmic derivatives, L_s , with respect to L_l ($l \neq s$) until the calculated band gap matched the experimental value. This is illustrated in Fig. 1. In the KKR language this adjustment of the logarithmic derivatives would correspond to a similar shift of the *s*-like phase shifts.

Our energy bands, shown in Fig. 2, are in quantitative agreement with the pseudopotential results¹ in the region around the gap. As can be seen from Table I, we have very good agreement in the energy range bracketed by the symmetry points X_4 and Γ_2' . For the low energy part of the valence band

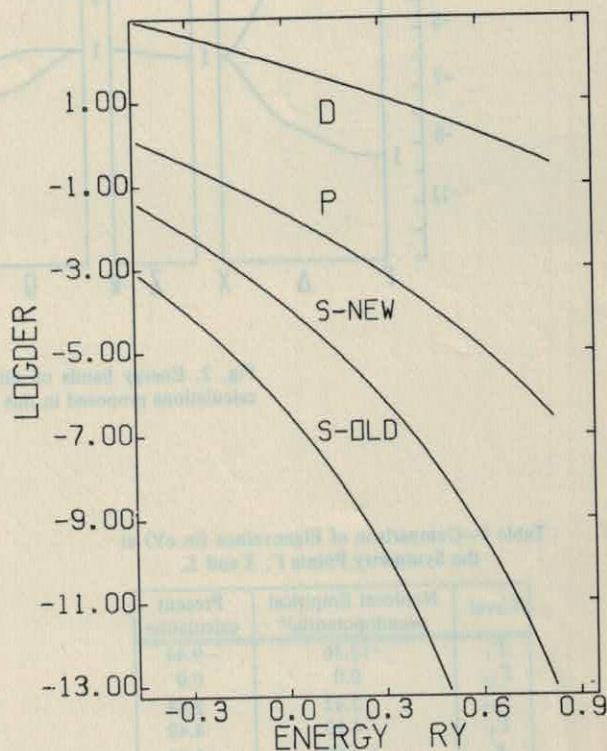


Fig. 1. Logarithmic derivatives as a function of energy. The energy scale is with respect to the muffin-tin zero. S-OLD are the unshifted *s*-like logarithmic derivatives, and S-NEW the shifted ones which are used in the present calculation.

our results show an overall shift upward which reduces the total width of the valence band in poor agreement with the pseudopotential method results. However, we obtain the correct ordering of levels for the whole electronic spectrum.

We have also calculated the density of electronic states and its angular momentum components using the tetrahedral interpolation scheme⁶. This is shown in Fig. 3 where one notes

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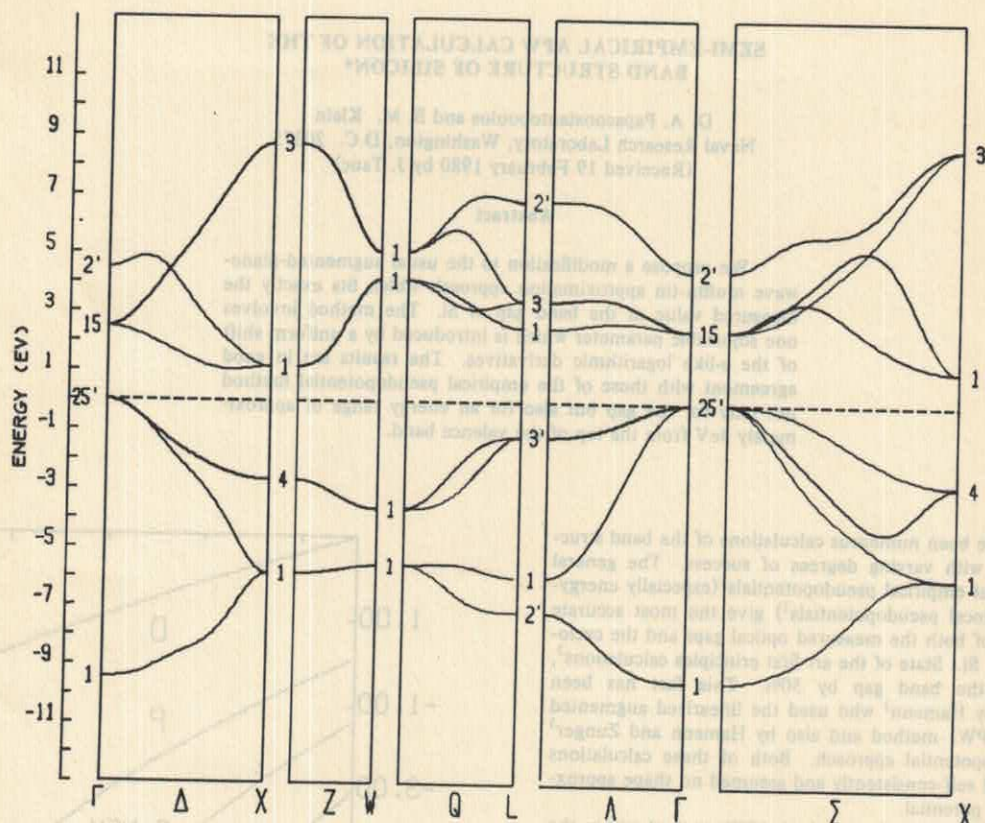


Fig. 2. Energy bands of silicon from the modified APW calculations proposed in this paper.

Table I—Comparison of Eigenvalues (in eV) at the Symmetry Points Γ , X and L.

Level	Nonlocal Empirical pseudopotential ^a	Present calculation
Γ_1	-12.36	-9.44
$\Gamma_{25'}$	0.0	0.0
Γ_{15}	3.42	2.48
Γ_2'	4.10	4.49
X_1	-7.69	-5.88
X_4	-2.86	-2.69
X_1	1.17	1.14
L_2'	-9.55	-7.14
L_1	-6.96	-5.98
L_3'	-1.23	-1.17
L_1	2.23	2.50
L_3	4.34	3.41

^aRef. 1

that we obtain the exact value of the band gap, but an overall width of the valence band which is almost 3eV smaller than

that given by Chelikowsky and Cohen¹. An inspection of the *l*-components of the density of states reveals strong *s*-character for the low energy part and strong *p*-character at the top of the valence band and in the conduction band. The conduction band has also a significant *d* contribution which could be attributed to *p*-like contributions from a neighboring site.

In conclusion we have presented a semi-empirical APW calculation of the band structure of Si which is of comparable accuracy to the empirical pseudopotential method in the vicinity of the band gap. Our results have encouraged us to explore the possibility of constructing an *l*-dependent potential from first principles which could give the correct band structure of silicon within the muffin-tin APW or KKR methods.

We are currently using the phase shifts found from our logarithmic derivatives to perform cluster calculations for amorphous and hydrogenated amorphous silicon.

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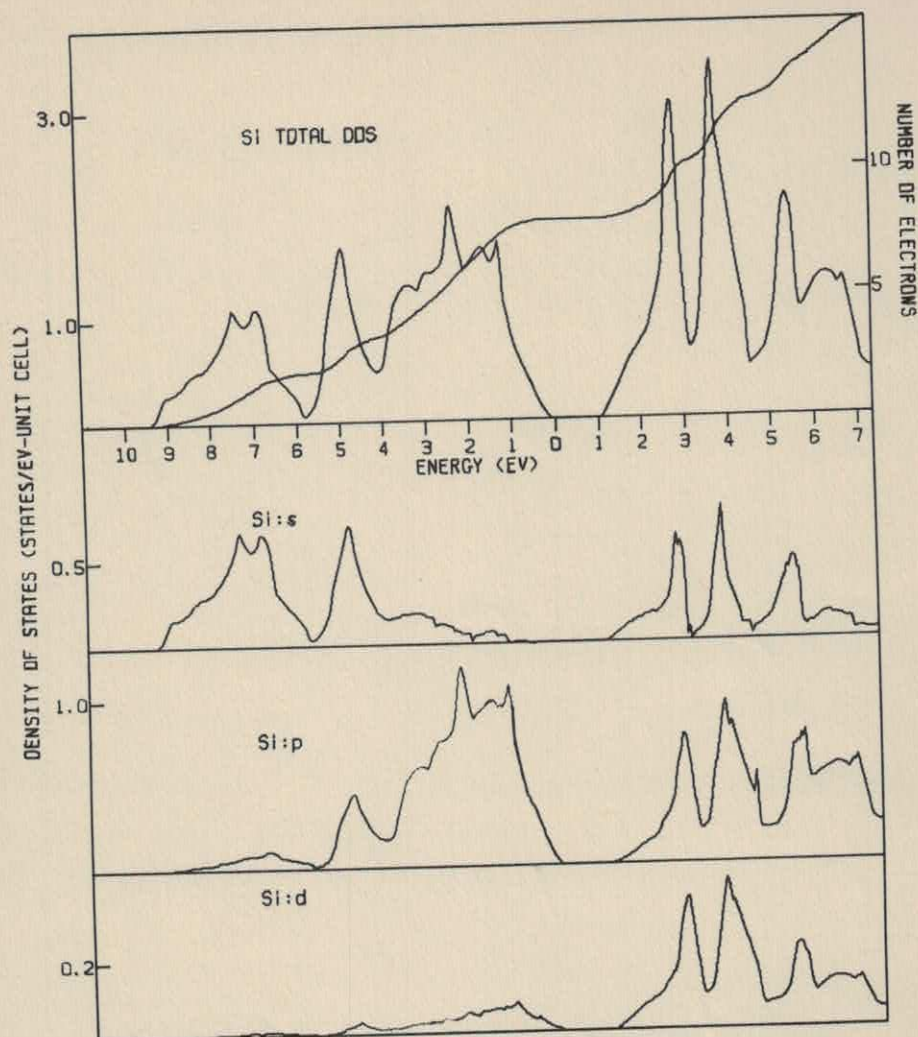


Fig. 3. Total and decomposed densities of states for Si. Note that the decomposed DOS are given within the muffin-tin sphere volume.

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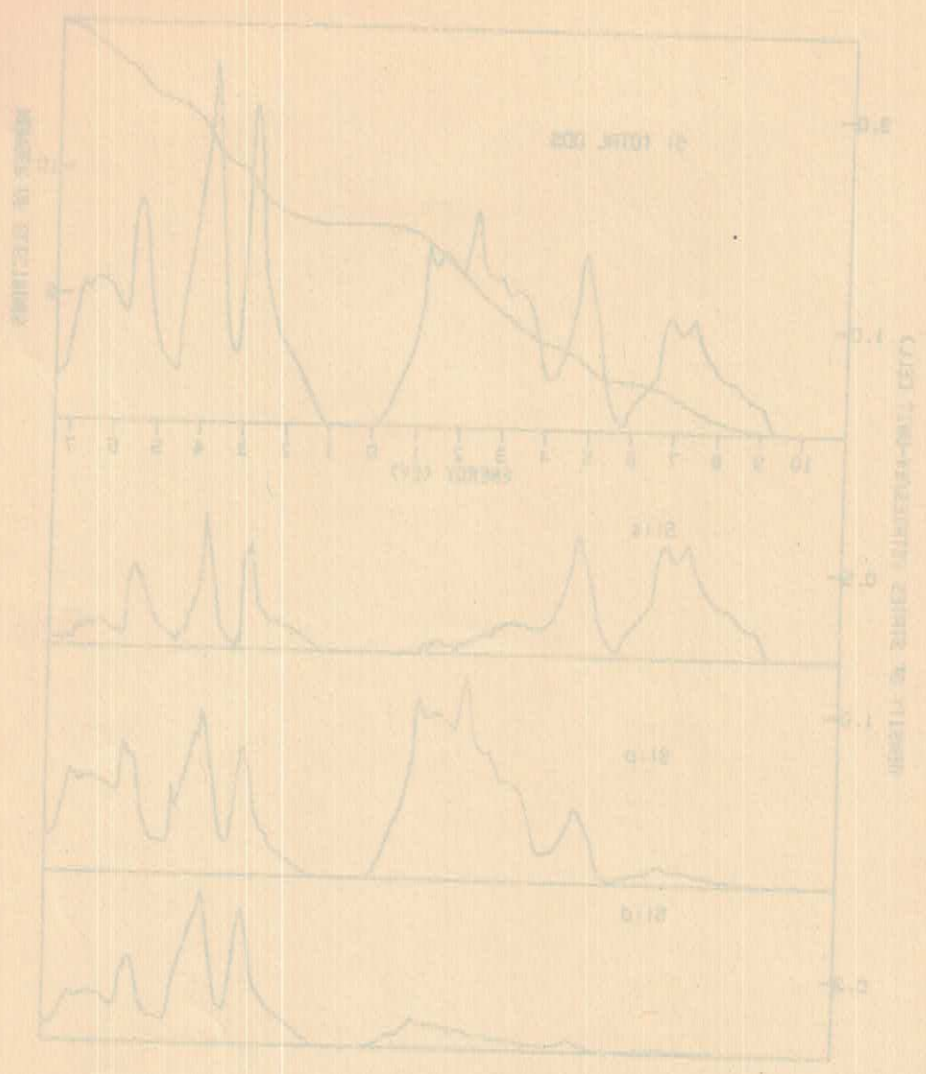


Fig. 1. Total and unoccupied density of states for 21. Note that the unoccupied DOS are given with the double the scale values.

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