Elementary prediction of linear combination
of atomic orbitals matrix elements

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For solids in the diamond structure there is a close resemblance between the true bands, the nearest-neighbor linear combination of atomic orbitals (LCAO) bands, and the free-electron bands. Making use of the similarity of the last two we have derived universal LCAO parameters for the interatomic matrix elements between s- and p-like states. They are all of the form $\eta(\hbar^2/md^2)$, and for the diamond structure they are in good agreement with Harrison's earlier empirical results. For more closely packed structures the η coefficients deviate from Harrison's values.

INTRODUCTION

The description of the electronic structure of solids in terms of linear combination of atomic orbitals (LCAO) theory has proven extremely useful.[1] The main problem in carrying out this approach is the determination of the parameters (matrix elements) that enter, and for an accurate description of the bands they are usually adjusted by matching the LCAO bands to the bands obtained by other methods.

Harrison[2] has found that an approximate fit can be obtained using universal parameters. The s- and p-state energies, s_0 and p_0, are taken equal to the Herman-Skillman atomic-term values.[3] (The notation follows Koster and Slater.[4]) The interatomic matrix elements are taken to be

$$(ll'm) = \eta_{ll'm}\frac{\hbar^2}{md^2} , \qquad (1)$$

where

$$\eta_{ss\sigma} = -1.40 , \quad \eta_{pp\sigma} = 3.24 , \qquad (2)$$

$$\eta_{sp\sigma} = 1.84 , \quad \eta_{pp\pi} = -0.81 .$$

d is the nearest-neighbor distance, and only the nearest-neighbor matrix elements are included. So far this has been an empirical finding. It is the result of considering the numbers obtained from detailed LCAO fits to the bands by Chadi and Cohen.[5] We will, however, now show that the same result can be derived theoretically by matching the LCAO bands to free-electron bands.

I. DIAMOND STRUCTURE

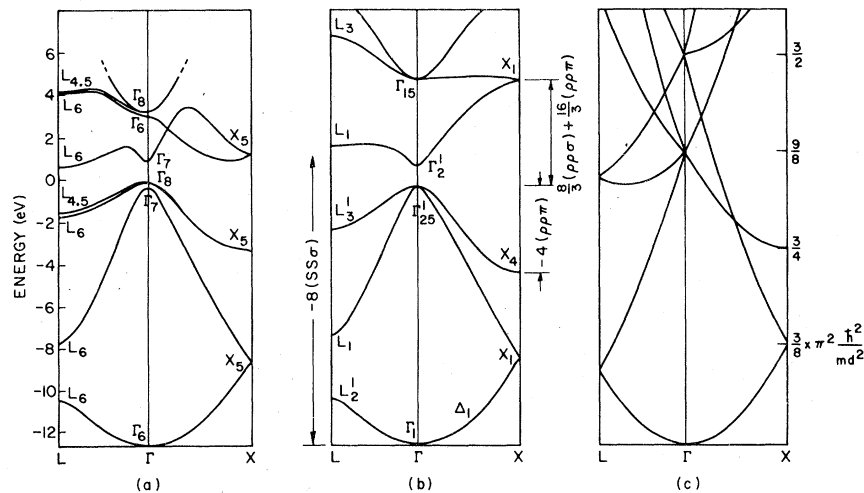Figure 1 shows the energy bands of germanium together with LCAO bands based on s and p states with

FIG. 1. Energy bands for germanium. Part (a) shows the bands as determined by Chelikowsky and Cohen (Ref. 6) using an empirical-nonlocal-pseudopotential scheme. Part (b) shows an LCAO fit by Chadi and Cohen (Ref. 5) using only nearest-neighbor matrix elements. Part (c) shows the free-electron bands.

TABLE I. LCAO and free-electron expressions for band energies.

Point	LCAO bands	Free electrons
Γ_1	$s_0 + 4(ss\,\sigma)$	0 (arbitrary)
Γ_2'	$s_0 - 4(ss\,\sigma)$	$\frac{9}{8}\pi^2\frac{\hbar^2}{md^2}$
Γ_{25}'	$p_0 - \frac{4}{3}(pp\,\sigma) - \frac{8}{3}(pp\,\pi)$	$\frac{9}{8}\pi^2\frac{\hbar^2}{md^2}$
Γ_{15}	$p_0 + \frac{4}{3}(pp\,\sigma) + \frac{8}{3}(pp\,\pi)$	$\frac{3}{2}\pi^2\frac{\hbar^2}{md^2}$
X_1	$\frac{s_0 + p_0}{2} - \left[\left(\frac{p_0 - s_0}{2}\right)^2 + \frac{16}{3}(sp\,\sigma)^2\right]^{1/2}$	$\frac{3}{8}\pi^2\frac{\hbar^2}{md^2}$
X_4	$p_0 - \frac{4}{3}(pp\,\sigma) + \frac{4}{3}(pp\,\pi)$	$\frac{3}{4}\pi^2\frac{\hbar^2}{md^2}$

nearest-neighbor coupling. Also shown are the free-electron bands. The LCAO bands provide a good description of the true valence bands, and they both resemble the free-electron bands. This suggests the possibility of obtaining the LCAO parameters by fitting the LCAO bands to the free-electron bands directly. There are different ways of doing this, so we choose to equate the bands where they resemble each other the most, i.e., at the points of highest symmetry Γ and X. We need six points to determine

the six parameters (see Table I). The LCAO energy levels are taken from Chadi and Cohen.[5]

Solving for the parameters we obtain

$$(ss\,\sigma) = -\frac{9}{64}\pi^2\frac{\hbar^2}{md^2} = -1.39\frac{\hbar^2}{md^2}, \qquad (3)$$

$$(sp\,\sigma) = \frac{3\sqrt{15}}{64}\pi^2\frac{\hbar^2}{md^2} = 1.79\frac{\hbar^2}{md^2}, \qquad (4)$$

$$(pp\,\sigma) = \frac{21}{64}\pi^2\frac{\hbar^2}{md^2} = 3.24\frac{\hbar^2}{md^2}, \qquad (5)$$

$$(pp\,\pi) = -\frac{3}{32}\pi^2\frac{\hbar^2}{md^2} = -0.93\frac{\hbar^2}{md^2}, \qquad (6)$$

$$p_0 - s_0 = \frac{3}{4}\pi^2\frac{\hbar^2}{md^2} = 7.40\frac{\hbar^2}{md^2}. \qquad (7)$$

The parameters from Eqs. (3)–(6) are in excellent agreement with Harrison's earlier empirical results. We have obtained the correct functional dependence as well as the numerical coefficients.

In order to obtain the correct band gaps, however, we have to disregard the expression, Eq. (7), for $p_0 - s_0$ and return to the atomic-term values. Only the parameter $(sp\,\sigma)$ depends explicitly on this difference, and it is useful to determine $(sp\,\sigma)$ in a different way. We will set the effective mass at the bottom of the s band (Δ_1) equal to the free-electron mass.

The energy along Δ_1 is given by[4]

$$E(\Delta_1) - E(\Gamma_1) = \frac{1}{2}\left\{p_0 - s_0 - 8(ss\,\sigma) + 4[(ss\,\sigma) + \frac{1}{3}(pp\,\sigma) + \frac{2}{3}(pp\,\pi)]\cos\frac{kd}{\sqrt{3}}\right.$$

$$\left. - \left[\left[p_0 - s_0 - 4[(ss\,\sigma) - \frac{1}{3}(pp\,\sigma) - \frac{2}{3}(pp\,\pi)]\cos\frac{kd}{\sqrt{3}}\right]^2 + \frac{64}{3}(sp\,\sigma)^2\sin^2\frac{kd}{\sqrt{3}}\right]^{1/2}\right\}. \qquad (8)$$

Expand this for small k

$$E(\Delta_1) - E(\Gamma_1) \approx \frac{1}{2}\left[-\frac{4}{3}(ss\,\sigma) - \frac{32}{9}\frac{(sp\,\sigma)^2}{p_0 - s_0 - 4[(ss\,\sigma) - \frac{1}{3}(pp\,\sigma) - \frac{2}{3}(pp\,\pi)]}\right]k^2d^2. \qquad (9)$$

Equate this to $\hbar^2k^2/2m$ and substitute for $(ss\,\sigma)$, $(pp\,\sigma)$, and $(pp\,\pi)$. Solving for $(sp\,\sigma)$ we find

$$(sp\,\sigma) = \frac{3\pi^2}{16}\left[\left(\frac{3}{2} - \frac{8}{\pi^2}\right)\left(\frac{3}{4} + \frac{p_0 - s_0}{\pi^2\hbar^2/md^2}\right)\right]^{1/2}\frac{\hbar^2}{md^2}. \qquad (10)$$

When we substitute Eq. (7) for $p_0 - s_0$, we get

$$(sp\,\sigma) = \frac{9\pi^2}{32}\left[1 - \frac{16}{3\pi^2}\right]^{1/2}\frac{\hbar^2}{md^2} = 1.88\frac{\hbar^2}{md^2}, \qquad (11)$$

in good agreement with our previous result. We will use this last method to determine $(sp\,\sigma)$ for the other structures. In Fig. 2 we show the energy bands for C, Si, Ge, and Sn obtained using atomic-term values for s_0 and p_0 and our values for the remaining parameters.
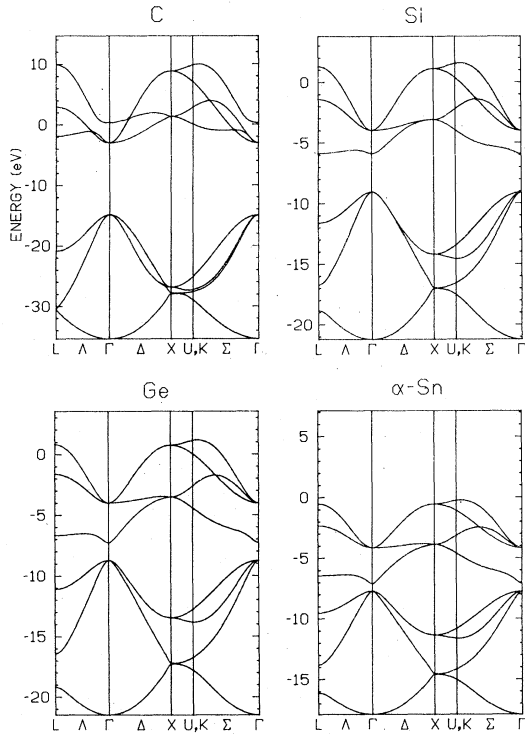
FIG. 2. LCAO bands for C, Si, Ge, and Sn using universal parameters and atomic-term values. Energies are in electron volts.

II. OTHER STRUCTURES

We can fit LCAO bands to free-electron bands for other structures just as we have for the diamond structure. The calculation is straightforward and we only give the results. For both the simple cubic and the fcc structure we match the bands at Γ and X and set the mass at the bottom of the s band equal to the free-electron mass. For the bcc structure we use the symmetry points Γ, H, and N. This gives

$$
\text{sc}\begin{cases}
\eta_{ss\sigma}=-\dfrac{1}{8}\pi^2=-1.23 \ , \quad \eta_{pp\sigma}=\dfrac{3\pi^2}{8}=3.70 \ , \\[2ex]
\eta_{sp\sigma}=\dfrac{1}{2}\pi(\dfrac{1}{4}\pi^2-1)^{1/2}=1.90 \ , \\[2ex]
\eta_{pp\pi}=-\dfrac{1}{8}\pi^2=-1.23 \ , \\[2ex]
p_0-s_0=\pi^2\,\dfrac{\hbar^2}{md^2}=9.87\,\dfrac{\hbar^2}{md^2} \ ,
\end{cases} \tag{12}
$$

$$
\text{fcc}\begin{cases}
\eta_{ss\sigma}=-\dfrac{1}{16}\pi^2=-0.62 \ , \quad \eta_{pp\sigma}=\dfrac{1}{4}\pi^2=2.47 \ , \\[2ex]
\eta_{sp\sigma}=\dfrac{1}{2}\pi[\dfrac{3}{2}(\dfrac{1}{4}\pi^2-1)]^{1/2}=2.33 \ , \\[2ex]
\eta_{pp\pi}=0 \ , \\[2ex]
p_0-s_0=\dfrac{5\pi^2}{4}\,\dfrac{\hbar^2}{md^2}=12.34\,\dfrac{\hbar^2}{md^2} \ ,
\end{cases} \tag{13}
$$

$$
\text{bcc}\begin{cases}
\eta_{ss\sigma}=-\dfrac{3\pi^2}{32}=-0.93, \quad \eta_{pp\sigma}=\dfrac{15\pi^2}{32}=4.63 \ , \\[2ex]
\eta_{sp\sigma}=\dfrac{3\pi}{8}\left[\dfrac{3}{2}\left(\dfrac{\pi^2}{4}-1\right)\right]^{1/2}=1.75 \ , \\[2ex]
\eta_{pp\pi}=-\dfrac{3\pi^2}{32}=-0.93 \ , \\[2ex]
p_0-s_0=\dfrac{3\pi^2}{2}\,\dfrac{\hbar^2}{md^2}=14.80\,\dfrac{\hbar^2}{md^2} \ .
\end{cases} \tag{14}
$$

We note that even though the functional dependence on d^{-2} is the same, the coefficients depend on the structure. Harrison's coefficients agree best with those obtained from the diamond structure. This is not surprising since his were obtained from solids in this structure. The deviation increases with the number of nearest neighbors. More distant-neighbor matrix elements and additional atomic states must be included to reproduce the free-electron-like bands of the closed-packed structures. Of course the larger set of matrix elements can be chosen to reproduce the correct free-electron-like bands but the η coefficients will differ from those obtained with a nearest-neighbor fit.

It is also clear that the d^{-2} dependence for nearest-neighbor matrix elements breaks down at large separations. Since the atomic wave functions fall off exponentially, the matrix elements must have the same behavior in this limit. However, the d^{-2} dependence is valid near the equilibrium separation and can be used to calculate properties such as the volume dependence of gaps and susceptibilities.[1]

[1]W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, to be published).

[2]W. A. Harrison, in *Festkörperprobleme*, edited by J. Treusch (Vieweg, Braunschweig, 1977), Vol. XVII, p. 135.

[3]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, 1963).

[4]J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

[5]D. J. Chadi and M. L. Cohen, Phys. Status Solidi B 68, 405 (1975).

[6]J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 14, 556 (1976).