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TITLE: THE ROLE OF D-STATES IN SEMICONDUCTORS

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THE ROLE OF D-STATES IN SEMICONDUCTORS

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The shift in the valence-band maxima due to pd-coupling is calculated in tight-binding theory using universal coupling matrix elements and Hartree-Fock term values . The resulting shifts are smaller than those predicted by Wei and Zunger in the Local Density Approximation, largerly because d-states lie much lower, relative to the valence-band maximum, from Hartree-Fock theory. Comparison with experimental energy differences indicates Hartree-Fock is more appropriate. This suggests that our much simpler theory may be preferable for estimating the valence-band shift and the many other related properties affected by d-states.

Wei and Zunger[1,2] have emphasized the possible importance of d-states in semiconductors. They note in particular that the symmetry of the d-bands even at $\boldsymbol{k} = \boldsymbol{0}$ allows coupling with the p-bands at that point. This coupling shifts the valence-band maximum, upward since the d-states in all cases lie lower, reducing the gap, and modifying band line-ups at heterojunctions. The coupling also affects the average energy of the bands, modifying the cohesive energy and the equilibrium lattice spacing, all effects considered by Wei and Zunger. It is also possible to estimate these effects independently using elementary tight-binding theory, and that is the subject of the present analysis. A more complete description will appear in Ref. 3.

We have given earlier[4] the form of the coupling between p- and d-states

$$V_{pd\sigma} = -\frac{3\sqrt{15}}{2\pi}\frac{\hbar^2\sqrt{r_p r_d^3}}{md^4}\ , \quad V_{pd\pi} = \frac{3\sqrt{5}}{2\pi}\frac{\hbar^2\sqrt{r_p r_d^3}}{md^4} \qquad (1)$$

with d the internuclear distance and with r_p and r_d parameters characteristic of the element upon which the corresponding atomic state resides. Thes p-state radii were

Table 17-1. r_p values, in Å, for atoms of nonmetallic elements, to be used to obtain matrix elements as in Eq. (1).. (After Harrison and Straub[4].) ε_p values in eV from Mann[5] are also listed.

	r_p	$-\varepsilon_p$		r_p	$-\varepsilon_p$		r_p	$-\varepsilon_p$
C	6.59	11.07	N	5.29	13.84	O	4.41	16.77
Si	13.7	7.59	P	11.4	9.54	S	10.1	11.60
Ge	14.4	7.33	As	13.2	8.98	Se	12.1	10.68
Sn	18.0	6.76	Sb	16.8	8.14	Te	15.9	9.54
Pb	19.8	6.53	Bi	18.9	7.79	Po	17.9	9.0

given in Ref. 4 for the nonmetals and we reproduce those values in Table 1, along with the Hartree-Fock p-state energies.

d-state radii r_d are available for transition metals, but not for the elements entering semiconductors, so we obtained them using the Atomic-Surface Method[5] and the atomic wavefunctions from Mann[6]. In particular, we combine the two equations for band width , Eqs. (7) and (12) from Ref. 4 (with a 6.83 in the latter, derived from the top and bottom of bcc d-bands rather than 5.53 obtained from second moments) to obtain an expression for r_d in terms of the angular average of the d-electron density $\rho_\ell = <\psi_d^*(r)\psi_d(r)>$,

$$r_d^3 \approx \frac{-4\pi r_0^7 \frac{\partial \rho_\ell}{\partial r}\Big|_{r=r_0}}{6.83\int_{0\ \mathrm{to}\ r0} 4\pi r^2 \rho_\ell \, dr} \qquad (2)$$

with r_0 the atomic sphere radius. The integral in the denominator is the normalization integral (clarifying the meaning of ρ_ℓ,) near one, and estimated by extrapolating the tails of the wavefunction.

We chose r_0 as the radius of an atomic-sphere with volume equal to $a^3/16$, obtained by dividing the volume of the semiconductor into a cell for each atom, and an equal number of cells of the same volume for the interstitial positions. The resulting values, along with the d-state energy from Mann[6], are given in Table 2.

Table 2. The d-state radii in Å from Eq. (2) and the Hartree-Fock d-state term values in eV, all based on the calculations of Mann[6].

	r_d	$-\varepsilon_d$		r_d	$-\varepsilon_d$		r_d	$-\varepsilon_d$
Cu	0.638	13.35	Ag	0.813	14.62	Au	0.914	14.17
Zn	0.518	21.28	Cd	0.693	20.77	Hg	0.811	19.42
Ga	0.409	32.46	In	0.574	28.91	Tl	0.705	26.34
Ge	0.316	44.62	Sn	0.469	37.36	Pb	0.607	33.31

Wei and Zunger[1] used local-density theory, which yields d-state term values, and argued against the use of Hartree-Fock term values which have greater magnitude. We may test the two approaches by estimating the difference between the d-state term value and the valence-band maximum using Hartree-Fock term values (Table 1 for p-states and Table 2 for d-states) and the tight-binding expression[7] for the valence-band maximum relative to the ε_p (obtainable also from our Eq. (3) with $E_{pd} = 0$). The shifts from the coupling are less than a volt. For the LDA calculation we take the difference $\varepsilon_p - \varepsilon_d$ from Wei and Zunger[1], using the same energy for the valence-band maximum relative to the p-state energy which we used for the Hartree-Fock case. We then compare directly with the experimental difference (from photo-emission) in energy tabulated by Wei and Zunger[1]. The comparison given in Table 3 (five representative systems from their table of 15) would suggest that the Hartree-Fock values are much more appropriate and we proceed with them.

Table 3. The d-state binding energy in eV, relative to the valence-band maximum, from semirelativistic local-density (LDA) calculations by Wei and Zunger [1], from Hartree-Fock (H-F) calculations, and from experiment.[a]

Compound	LDA	H-F	Experiment [a]
GaAs	13.09	22.82	18.86
InSb	13.19	20.31	17.80
ZnSe	3.37	10.24	9.20
CdTe	5.50	10.97	10.49
HgTe	3.64	9.63	8.58

[a] Compiled by Wei and Zunger[2]

States at the valence-band maximum, are dominated by p-states, with a coupling ($k = 0$)of each p_x-state to the p_x-states on its four neighboring sites of[7] $E_{pp} = -1.28\hbar^2/md^2$. That p_x-state is also coupled to neighboring d-states. Adding them for $k = 0$, only the d-state of yz-symmetry survives, with a coupling obtained from the Slater-Koster Tables of $E_{pd} = 4V_{pd\sigma}/3 - 8V_{pd\pi}/3\sqrt{3}$. We include this coupling only for the d-state on the metallic atom (Ga) and the p-state on the nonmetallic atom (As), which are by far the dominant terms, by virtue of the smaller energy difference between these states, and by virtue of the r_d values. Thus the band energies are found by diagonalizing a three-by three Hamiltonian matrix with a secular equation

$$(\varepsilon_{p+} - \varepsilon)(\varepsilon_{p-} - \varepsilon)(\varepsilon_d - \varepsilon) - E_{pp}^2(\varepsilon_d - \varepsilon) - E_{pd}^2(\varepsilon_{p+} - \varepsilon) = 0 . \quad (3)$$

We evaluate this with, and without, E_{pd} giving the differences listed in Table 4.

Table 4 The shift upward of the valence-band maximum (eV) due to the coupling with d-states on the metallic atom. They were obtained from solution of Eq. (3), but are close to values obtained in simple perturbation theory.

GaP	0.033	InP	0.058	CdS	0.210	HgS	0.300
GaAs	0.026	GnAs	0.053	CdSe	0.167	HgSe	0.230
GaSb	0.018	InSb	0.035	CdTe	0.116	HgTe	0.264

These shifts are much smaller than those suggested by Wei and Zunger (1998), principally because the ε_d which we used is considerably deeper, a choice which we supported by the comparison in Table 3. Nevertheless, it is a real contribution to the energy of the valence-band maximum and influences the values of band off-sets in heterojunctions

There is a much smaller additional shift in these band off-sets arising from the pd-coupling coupling *across* a hetrojunction which can produce a net interface dipole. Such a shift is included in the full calculation by Wei and Zunger^2 and can be estimated from the parameters given here. Since there are contributions from the entire band, an E_{pd} based on second moments would be more appropriate than the $k = 0$ value used here. It is a subtle effect, and appears to be very small.

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