Tight binding in diamond anc zinc-blende crystals

- Tight binding approximation for tetrahedrally coordinated orbitals
- Combination of s, p_x, p_Y and p_z orbitals: the sp^3 model
- Orbital symmetry and overlap integrals
- The sp^3s^* model
- The bandstructure of Si, Ge and GaAs

TB in a zinc-blende lattice with sp3 orbitals

Hamiltonian

$$H_c|\Psi_{\mathbf{k}}>=E(\mathbf{k})|\Psi_{\mathbf{k}}>,$$

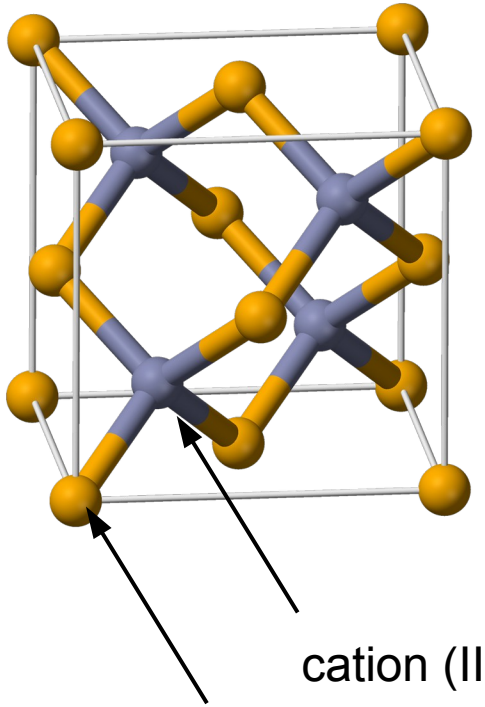
The guess wavefunction: summation of wavefunctions placed on the atomic sites

$$\Psi_{\mathbf{k}}=\sum_{\mathbf{R}}\exp\left(i\mathbf{R}\mathbf{k}\right)\left(\phi_a(\mathbf{r}-\mathbf{R})+\exp\left(i\mathbf{d}\mathbf{k}\right)\phi_c(\mathbf{r}-\mathbf{R}-\mathbf{d})\right),$$

Each wavefunction is the linear combination of different orbitals

$$\begin{aligned}\phi_a(\mathbf{r}) &= a_s\phi_a^s(\mathbf{r})+a_{p_x}\phi_a^{p_x}(\mathbf{r})+a_{p_y}\phi_a^{p_y}(\mathbf{r})+a_{p_z}\phi_a^{p_z}(\mathbf{r})\\ &= \sum_{i=s,p_x,p_y,p_z} a_i\phi_a^i(\mathbf{r}),\end{aligned}$$

$$\begin{aligned}\phi_c(\mathbf{r}-\mathbf{d}) &= c_s\phi_c^s(\mathbf{r}-\mathbf{d})+c_{p_x}\phi_c^{p_x}(\mathbf{r}-\mathbf{d})+c_{p_y}\phi_c^{p_y}(\mathbf{r}-\mathbf{d})+c_{p_z}\phi_c^{p_z}(\mathbf{r}-\mathbf{d})\\ &= \sum_{i=s,p_x,p_y,p_z} c_i\phi_c^i(r),\end{aligned}$$



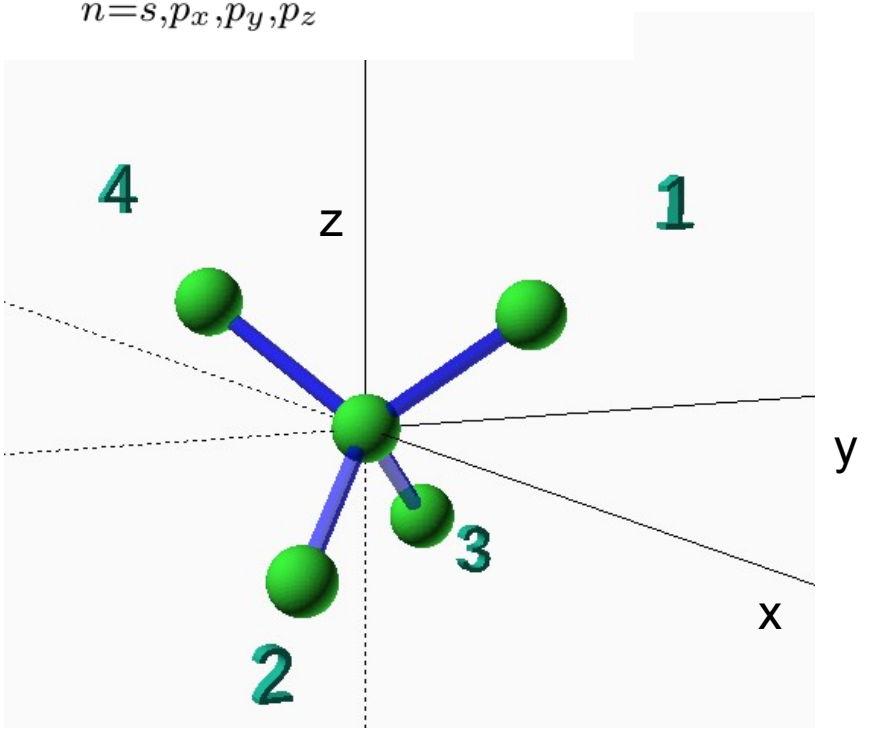
TB in a zinc-blende lattice and sp orbitals

If we limit the interaction over near-neighbours the summation is limited to the four tetrahedrally coordinated atoms around a central atom

$$\Psi_{\mathbf{k}} = \phi_a(\mathbf{r}) + \sum_{\mathbf{d}} \exp(i\mathbf{dk})\, \phi_c(\mathbf{r}-\mathbf{d}),$$

$$= \sum_{n=s,p_x,p_y,p_z} a_n \phi_a^n(r) + \sum_{\mathbf{d}} \exp(i\mathbf{dk}) \sum_{n=s,p_x,p_y,p_z} c_n \phi_c^n(r-\mathbf{d})$$

$$\mathbf{d_1} = \frac{a}{4}[1,1,1]$$
$$\mathbf{d_2} = \frac{a}{4}[1,-1,-1]$$
$$\mathbf{d_3} = \frac{a}{4}[-1,1,-1]$$
$$\mathbf{d_4} = \frac{a}{4}[-1,-1,1].$$



TB in a zinc-blende lattice and sp orbitals

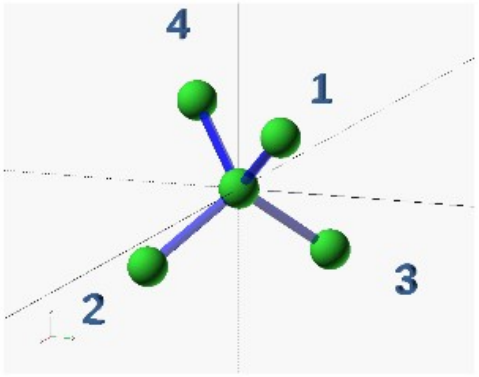
	ϕ_a^s	ϕ_c^s	$\phi_a^{p_x}$	$\phi_c^{p_x}$	$\phi_a^{p_y}$	$\phi_c^{p_y}$	$\phi_a^{p_z}$	$\phi_c^{p_z}$
ϕ_a^s	$E(s,a)$	$V(s_a,s_c)g_0$	0	$V(s_a,p_c)g_1$	0	$V(s_a,p_c)g_2$	0	$V(s_a,p_c)g_3$
ϕ_c^s	$V(s_a,s_c)g_0^*$	$E(s,c)$	$-V(s_c,p_a)g_1^*$	0	$-V(s_c,p_a)g_2^*$	0	$-V(s_c,p_a)g_3^*$	0
$\phi_a^{p_x}$	0	$-V(s_c,p_a)g_1$	$E(p,a)$	$V(z,z)g_0$	0	$V(z,y)g_3$	0	$V(z,y)g_2$
$\phi_c^{p_x}$	$V(s_a,p_c)g_1^*$	0	$V(z,z)g_0^*$	$E(p,c)$	$V(z,y)g_3^*$	0	$V(z,y)g_2^*$	0
$\phi_a^{p_y}$	0	$-V(s_c,p_a)g_2$	0	$V(z,y)g_3$	$E(p,a)$	$V(z,z)g_0$	0	$V(z,y)g_1$
$\phi_c^{p_y}$	$V(s_a,p_c)g_2^*$	0	$V(z,y)g_3^*$	0	$V(z,z)g_0^*$	$E(p,c)$	$V(z,y)g_1^*$	0
$\phi_a^{p_z}$	0	$-V(s_c,p_a)g_3$	0	$V(z,y)g_2$	0	$V(z,y)g_1$	$E(p,a)$	$V(z,z)g_0$
$\phi_c^{p_z}$	$V(s_a,p_c)g_3^*$	0	$V(z,y)g_2^*$	0	$V(z,y)g_1^*$	0	$V(z,z)g_0^*$	$E(p,c)$

Diagonal terms are obtained by the overlap of the same atomic orbital on the same atomic site

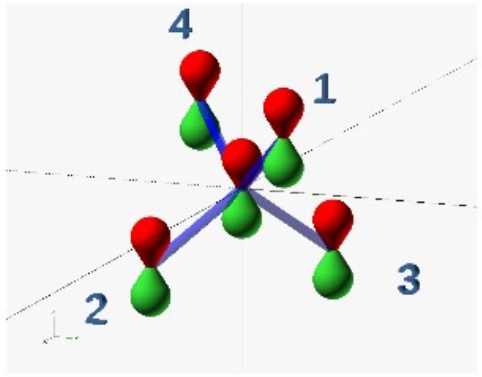
Null term are obtain by the overlap of orbitals of different parity on the same atomic site

TB in a zinc-blende lattice and sp orbitals

$V(s_a,s_c)g_0$



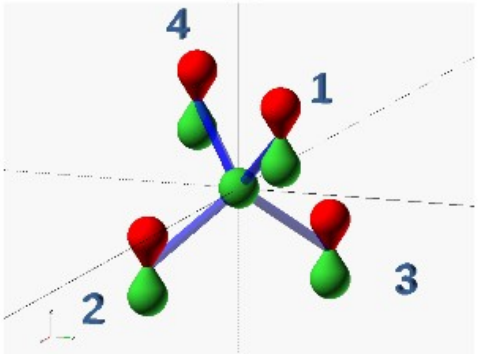
(a)

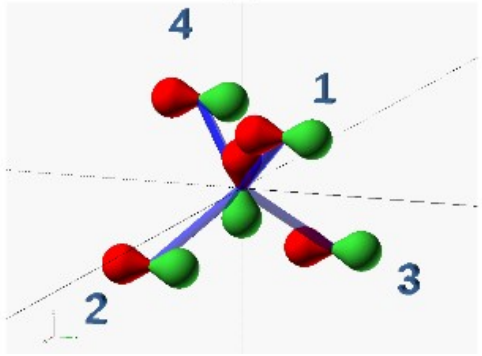


(b)

$V(z,z)g_0$

$V(sa,pc)g_3$





$V(z,y)g_1$

$$g_0(\mathbf{k}) = \frac{1}{4}\left(+\exp\left(i\mathbf{k}\,\mathbf{d_1}\right) + \exp\left(i\mathbf{k}\,\mathbf{d_2}\right) + \exp\left(i\mathbf{k}\,\mathbf{d_3}\right) + \exp\left(i\mathbf{k}\,\mathbf{d_4}\right)\right)$$

$$g_1(\mathbf{k}) = \frac{1}{4}\left(+\exp\left(i\mathbf{k}\,\mathbf{d_1}\right) + \exp\left(i\mathbf{k}\,\mathbf{d_2}\right) - \exp\left(i\mathbf{k}\,\mathbf{d_3}\right) - \exp\left(i\mathbf{k}\,\mathbf{d_4}\right)\right)$$

$$g_2(\mathbf{k}) = \frac{1}{4}\left(+\exp\left(i\mathbf{k}\,\mathbf{d_1}\right) - \exp\left(i\mathbf{k}\,\mathbf{d_2}\right) + \exp\left(i\mathbf{k}\,\mathbf{d_3}\right) - \exp\left(i\mathbf{k}\,\mathbf{d_4}\right)\right)$$

$$g_3(\mathbf{k}) = \frac{1}{4}\left(+\exp\left(i\mathbf{k}\,\mathbf{d_1}\right) - \exp\left(i\mathbf{k}\,\mathbf{d_2}\right) - \exp\left(i\mathbf{k}\,\mathbf{d_3}\right) + \exp\left(i\mathbf{k}\,\mathbf{d_4}\right)\right),$$

TB in a zinc-blende lattice and sp orbitals

Table 3

Interaction parameters (in eV) appropriate for C, Si, and Ge when second-nearest-neighbor interactions are ignored. The parameter E_s is arbitrary

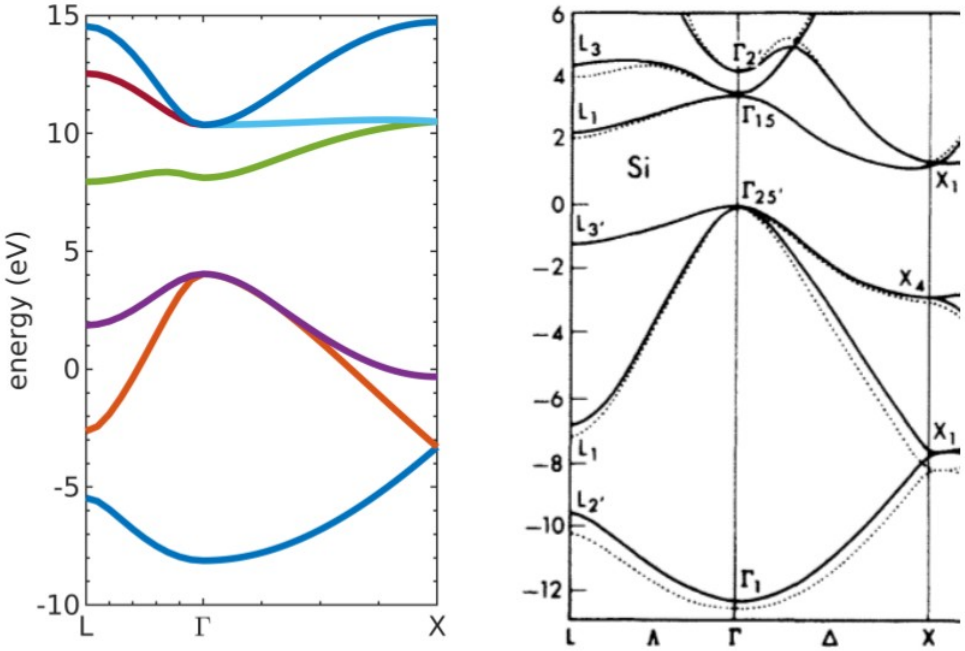
	E_s	$(E_p - E_s)$	V_{ss}	V_{sp}	V_{xx}	V_{xy}
C	—	7.40	−15.2	10.25	3.0	8.3
Si	—	7.20	−8.13	5.88	3.17	7.51
Ge	—	8.41	−6.78	5.31	2.62	6.82

Table 5

Interaction parameters (in eV) for GaAs and ZnSe. The four intra-atomic parameters E_{s_0}, E_{s_1}, E_{p_0}, and E_{p_1} give information only on the relative energy differences between the tight-binding s- and p-functions. The subscripts 0 and 1 refer to As (or Se) and Ga (or Zn), respectively

	E_{s_0}	E_{s_1}	E_{p_0}	E_{p_1}	V_{ss}	V_{s_0p}	V_{s_1p}	V_{xx}	V_{xy}
GaAs	−6.01	−4.79	0.19	4.59	−7.00	7.28	3.70	0.93	4.72
ZnSe	−8.92	−0.28	0.12	7.42	−6.14	5.47	4.73	0.96	4.38

TB in a zinc-blende lattice and sp orbitals



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Tight-Binding Calculations of the Valence Bands of Diamond and Zincblende Crystals

By

D. J. CHADI and M. L. COHEN

Using the tight-binding method, the valence band structures and densities of states for C, Si, Ge, GaAs, and ZnSe are calculated. Very good agreement is obtained with other calculations when all nearest- and one second-nearest-neighbor interactions are included. The effects of the various interactions on the density of states are discussed.

Sp3s* tight binding

A SEMI-EMPIRICAL TIGHT-BINDING THEORY OF THE ELECTRONIC STRUCTURE OF SEMICONDUCTORS†

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Table (A)

	$\|sa\rangle$	$\|sc\rangle$	$\|p_x a\rangle$	$\|p_y a\rangle$	$\|p_z a\rangle$	$\|p_x c\rangle$	$\|p_y c\rangle$	$\|p_z c\rangle$	$\|s^* a\rangle$	$\|s^* c\rangle$
$\|sa\rangle$	$E(s,a)$	$V(s,s)g_0$	0	0	0	$V(sa,pc)g_1$	$V(sa,pc)g_2$	$V(sa,pc)g_3$	0	0
$\|sc\rangle$	$V(s,s)g_0^*$	$E(s,c)$	$-V(pa,sc)g_1^*$	$-V(pa,sc)g_2^*$	$-V(pa,sc)g_3^*$	0	0	0	0	0
$\|p_x a\rangle$	0	$-V(pa,sc)g_1$	$E(p,a)$	0	0	$V(x,x)g_0$	$V(x,y)g_3$	$V(x,y)g_2$	0	$-V(pa,s^*c)g_1$
$\|p_y a\rangle$	0	$-V(pa,sc)g_2$	0	$E(p,a)$	0	$V(x,y)g_3$	$V(x,x)g_0$	$V(x,y)g_1$	0	$-V(pa,s^*c)g_2$
$\|p_z a\rangle$	0	$-V(pa,sc)g_3$	0	0	$E(p,a)$	$V(x,y)g_2$	$V(x,y)g_1$	$V(x,x)g_0$	0	$-V(pa,s^*c)g_3$
$\|p_x c\rangle$	$V(sa,pc)g_1^*$	0	$V(x,x)g_0^*$	$V(x,y)g_3^*$	$V(x,y)g_2^*$	$E(p,c)$	0	0	$V(s^*a,pc)g_1^*$	0
$\|p_y c\rangle$	$V(sa,pc)g_2^*$	0	$V(x,y)g_3^*$	$V(x,x)g_0^*$	$V(x,y)g_1^*$	0	$E(p,c)$	0	$V(s^*a,pc)g_2^*$	0
$\|p_z c\rangle$	$V(sa,pc)g_3^*$	0	$V(x,y)g_2^*$	$V(x,y)g_1^*$	$V(x,x)g_0^*$	0	0	$E(p,c)$	$V(s^*a,pc)g_3^*$	0
$\|s^* a\rangle$	0	0	0	0	0	$V(s^*a,pc)g_1$	$V(s^*a,pc)g_2$	$V(s^*a,pc)g_3$	$E(s^*,a)$	$V(s^*,s^*)g_0$
$\|s^* c\rangle$	0	0	$-V(pa,s^*c)g_1^*$	$-V(pa,s^*c)g_2^*$	$-V(pa,s^*c)g_3^*$	0	0	0	$V(s^*,s^*)g_0^*$	$E(s^*,c)$

Sp3s* tight binding

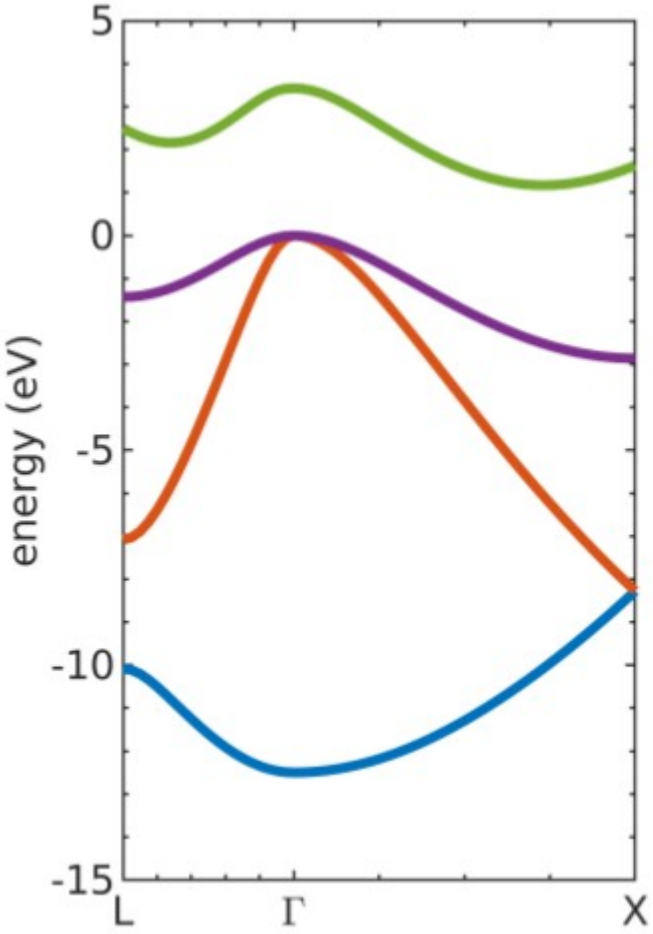
Table I. Empirical matrix elements of the sp^3s^* Hamiltonian in eV. Although only three digits are significant, we reproduce the actual numbers used to generate the figures in order to eliminate any problem with round-off errors

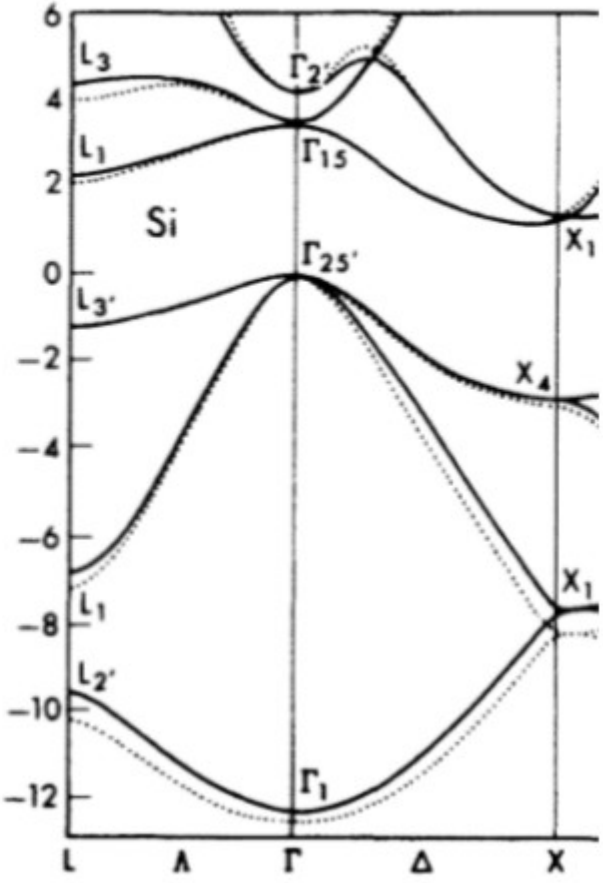
Compound	E(s,a)	E(p,a)	E(s,c)	E(p,c)	E(s*,a)	E(s*,c)
C	-4.5450	3.8400	-4.5450	3.8400	11.3700	11.3700
Si	-4.2000	1.7150	-4.2000	1.7150	6.6850	6.6850
Ge	-5.8800	1.6100	-5.8800	1.6100	6.3900	6.3900
Sn	-5.6700	1.3300	-5.6700	1.3300	5.9000	5.9000
SiC	-8.4537	2.1234	-4.8463	4.3466	9.6534	9.3166
AlP	-7.8466	1.3169	-1.2534	4.2831	8.7069	7.4231
AlAs	-7.5273	0.9833	-1.1627	3.5867	7.4833	6.7267
AlSb	-6.1714	0.9807	-2.0716	3.0163	6.7607	6.1543
GaP	-8.1124	1.1250	-2.1976	4.1150	8.5150	7.1850
GaAs	-8.3431	1.0414	-2.6569	3.6686	8.5014	6.7586
~~GaSb~~	~~-7.3207~~	~~0.8554~~	~~-3.8993~~	~~2.9146~~	~~6.6354~~	~~5.9846~~
InP	-8.5274	0.8735	-1.4826	4.0465	8.2635	7.0665
InAs	-9.5381	0.9099	-2.7219	3.7201	7.4099	6.7401
InSb	-8.0157	0.6738	-3.4643	2.9162	6.4530	5.9362
ZnSe	-11.8383	1.5072	0.0183	5.9928	7.5872	8.9928
ZnTe	-9.8150	1.4834	-0.9350	5.2666	7.0834	8.2666
GaSb	-7.1256	0.6718	-3.7042	2.7312	6.6354	5.9846

Compound	V(s,s)	V(x,x)	V(x,y)	V(sa,pc)	V(sc,pa)	V(s*a,pc)	V(pa,s*c)	V(sa,pc)	V(sc,pa)	V(s*a,pc)	V(pa,s*c)
C	-22.7250	3.8400	11.6700	15.2206	15.2206	8.2109	8.2109				
Si	-8.3000	1.7150	4.5750	5.7292	5.7292	5.3749	5.3749				
Ge	-6.7800	1.6100	4.9000	~~5.4649~~	~~5.4648~~	~~5.2191~~	~~5.2191~~	4.9617	4.9617	4.5434	4.5434
Sn	-5.6700	1.3300	4.0800	~~4.3286~~	~~4.3286~~	~~3.9665~~	~~3.9665~~	4.2288	4.2288	3.9665	3.9665
SiC	-12.4197	3.0380	5.9216	9.4900	9.2007	8.7138	4.4051				
AlP	-7.4535	2.3749	4.8378	5.2451	5.2775	5.2508	4.6388				
AlAs	-6.6642	1.8780	4.2919	5.1106	5.4965	4.5216	4.9950				
AlSb	-5.6448	1.7199	3.6648	4.9121	4.2137	4.3662	3.0739				
GaP	-7.4709	2.1516	5.1369	4.2771	6.3190	4.6541	5.0950				
GaAs	-6.4513	1.9546	5.0779	~~4.4800~~	~~5.7039~~	~~4.8432~~	~~4.8077~~	4.2485	5.2671	4.7515	4.2547
~~GaSb~~	~~-6.1567~~	~~1.5789~~	~~4.1285~~	~~4.9601~~	~~4.6675~~	~~4.9895~~	~~4.2180~~				
InP	-5.3614	1.8801	4.2324	2.2265	5.5825	3.4623	4.4814				
InAs	-5.6052	1.8398	4.4693	3.0354	5.4389	3.3744	3.9097				
InSb	-5.5193	1.4018	3.8761	3.7880	4.5900	3.5666	3.4048				
ZnSe	-6.2163	3.0054	5.9942	3.4980	6.3191	2.5891	3.9533				
ZnTe	-6.5765	2.7951	5.4670	5.9827	5.8199	1.3196	0.0000				
GaSb	-5.9854	1.3546	4.4436	5.1693	4.4708	5.1609	4.1199				

Sp3s* tight binding

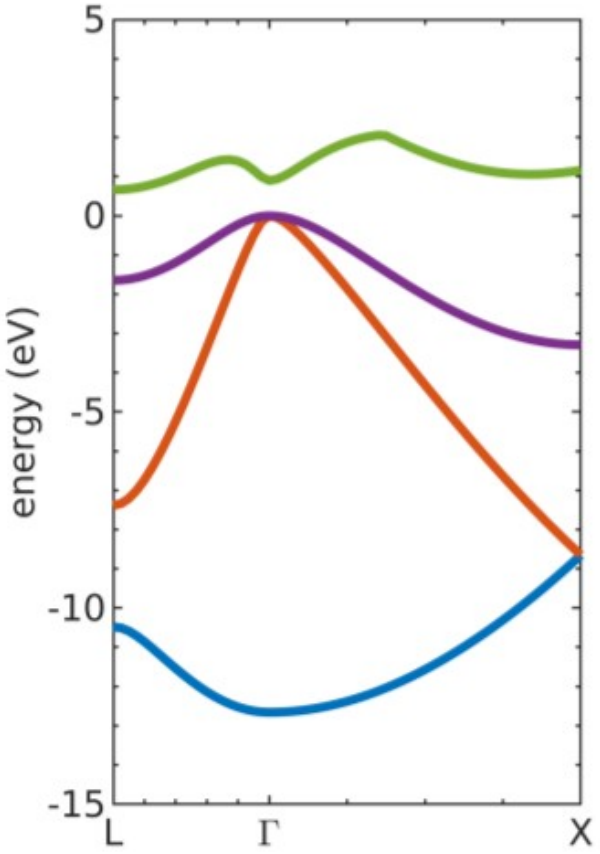
Silicon

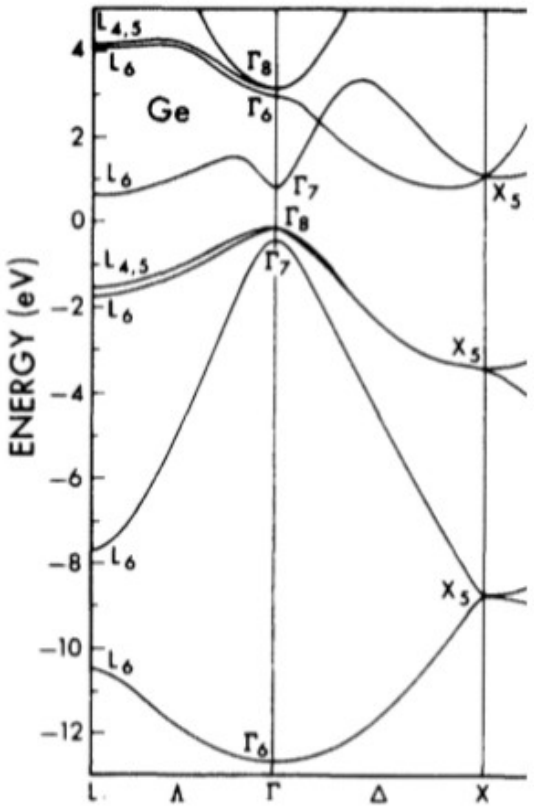




Sp3s* tight binding

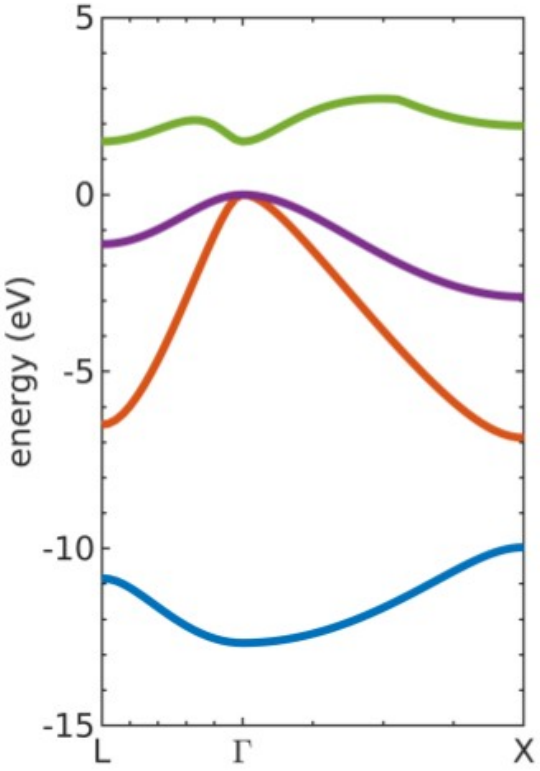
Germanium

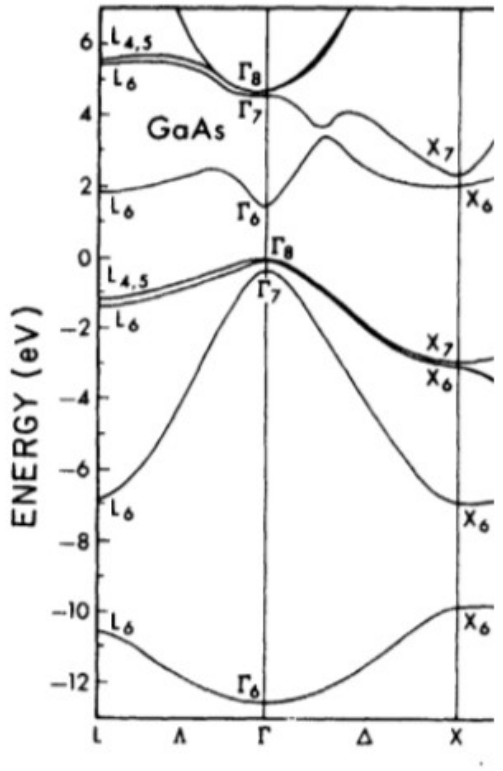




Sp3s* tight binding

Gallium Arsenide





Eigenvectors at k=0

k=0 Γ point

$g_0 \neq 0$ $g_1 = g_2 = g_3 = 0$

	ϕ_a^s	ϕ_c^s	$\phi_a^{p_x}$	$\phi_c^{p_x}$	$\phi_a^{p_y}$	$\phi_c^{p_y}$	$\phi_a^{p_z}$	$\phi_c^{p_z}$
ϕ_a^s	$E(s,a)$	$V(s_a,s_c)g_0$	0	0	0	0	0	0
ϕ_c^s	$V(s_a,s_c)g_0^*$	$E(s,c)$	0	0	0	0	0	0
$\phi_a^{p_x}$	0	0	$E(p,a)$	$V(z,z)g_0$	0	0	0	0
$\phi_c^{p_x}$	0	0	$V(z,z)g_0^*$	$E(p,c)$	0	0	0	0
$\phi_a^{p_y}$	0	0	0	0	$E(p,a)$	$V(z,z)g_0$	0	0
$\phi_c^{p_y}$	0	0	0	0	$V(z,z)g_0^*$	$E(p,c)$	0	0
$\phi_a^{p_z}$	0	0	0	0	0	0	$E(p,a)$	$V(z,z)g_0$
$\phi_c^{p_z}$	0	0	0	0	0	0	$V(z,z)g_0^*$	$E(p,c)$

Table 1: 8×8 secular matrix for the sp^3 tight-binding problem at $\mathbf{k} = 0$, Γ point.

2 (bonding and antibonding) s-type bands

6 (bonding and antibonding) p-type bands

Eigenvectors along k=[001]

K along [001] Δ

$g_0 \neq 0$ $g_3 \neq 0$ $g_1 = g_2 = 0$

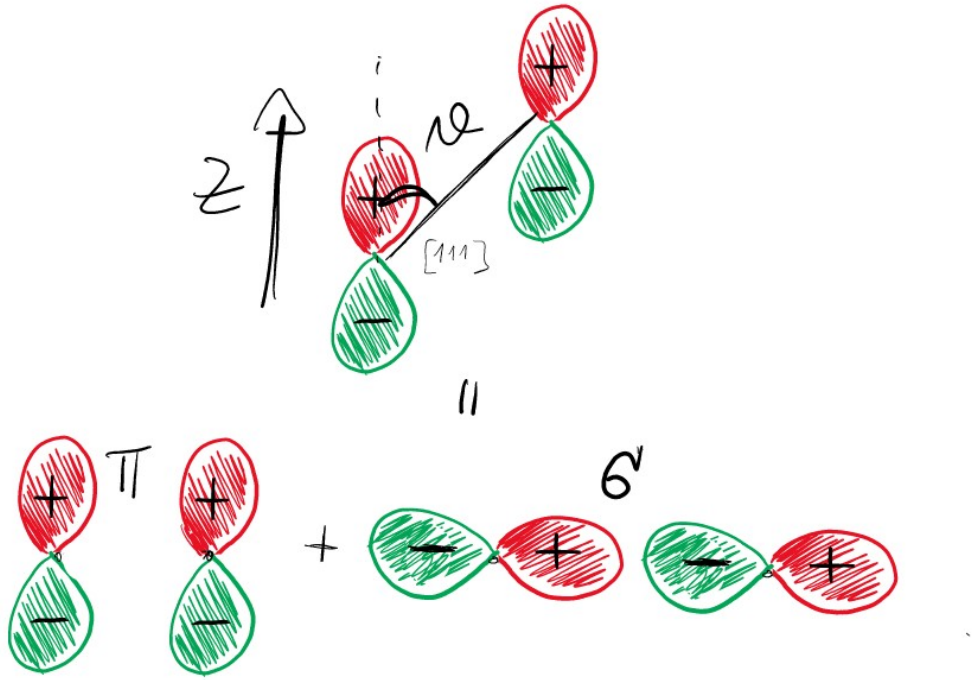
	ϕ_a^s	ϕ_c^s	$\phi_a^{p_z}$	$\phi_c^{p_z}$	$\phi_a^{p_x}$	$\phi_c^{p_x}$	$\phi_a^{p_y}$	$\phi_c^{p_y}$
ϕ_a^s	$E(s,a)$	$V(s_a,s_c)g_0$	0	$V(s_a,p_c)g_3$	0	0	0	0
ϕ_c^s	$V(s_a,s_c)g_0^*$	$E(s,c)$	$-V(s_c,p_a)g_3^*$	0	0	0	0	0
$\phi_a^{p_z}$	0	$-V(s_c,p_a)g_3$	$E(p,a)$	$V(z,z)g_0$	0	0	0	0
$\phi_c^{p_z}$	$V(s_a,p_c)g_3^*$	0	$V(z,z)g_0^*$	$E(p,c)$	0	0	0	0
$\phi_a^{p_x}$	0	0	0	0	$E(p,a)$	$V(z,z)g_0$	0	$V(z,y)g_3$
$\phi_c^{p_x}$	0	0	0	0	$V(z,z)g_0^*$	$E(p,c)$	$V(z,y)g_3^*$	
$\phi_a^{p_y}$	0	0	0	0	0	$V(z,y)g_3$	$E(p,a)$	$V(z,z)g_0$
$\phi_c^{p_y}$	0	0	0	0	$V(z,y)g_3^*$	0	$V(z,z)g_0^*$	$E(p,c)$

Table 1: 8×8 secular matrix for the sp^3 tight-binding problem along the $\mathbf{k} = [001]$ direction, Δ.

4 (bonding and antibonding) $s+p_z$ bands

4 (bonding and antibonding) p_x and p_y bands

Valence band



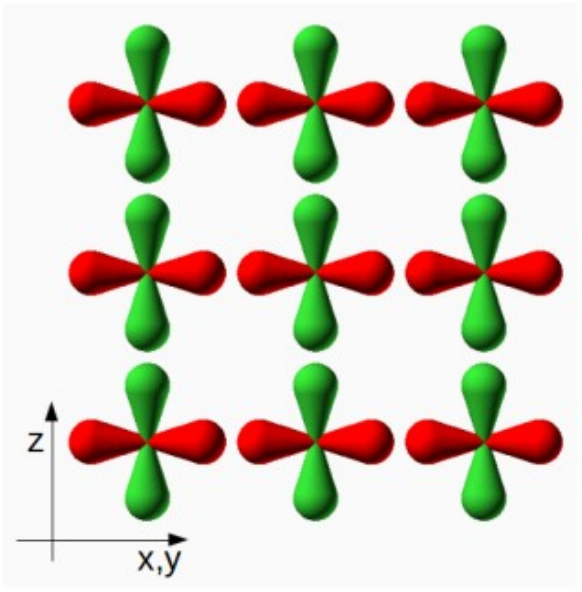
$$V_{zz} = V_{pd\sigma} \cos^2\theta + V_{pp\pi} \sin^2\theta$$

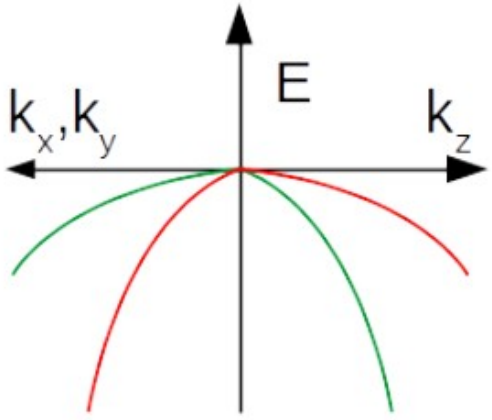
Heavy and light holes

In the TB description of semiconductor bandstructure the top of the valence band (VB) originates from p-type states. Some relevant features of the VB can be understood considering a simple cubic latice of p_x, p_y, p_z orbitals.

$$m_{LH} \propto \frac{1}{V_{pp\sigma}}$$

$$m_{HH} \propto \frac{1}{V_{pp\pi}}$$





In this picture we obtain two degenerate 'heavy hole' (HH) band and one “light hole“ (LH) band.