

7. Impurity states

Semiconductors: a small concentration of (suitable) impurities has a strong effect on the transport of electric current. The modification of pristine ("pure", "intrinsic") material is usually denoted as *doping*.

Point (vacancies, substitutional or interstitial) and line defects (dislocations), complexes (e.g., Frenkel's pair of vacancy-interstitial), precipitates.

Donors and acceptors, in Si mainly P, As, Sb and B, Ga, In.

The energy levels within gap are usually denoted as *shallow* (hydrogen-like) or *deep*.

Shallow states, effective mass approximation

Screened Coulomb potential of a donor:

$$\hat{V}_d(\vec{r}) = \frac{|e|}{4\pi\epsilon_0\epsilon_r r} , \quad (7.1)$$

where ϵ_r is the relative permittivity of the host crystal. Electron belonging to the donor atom obeys the Schroedinger equation

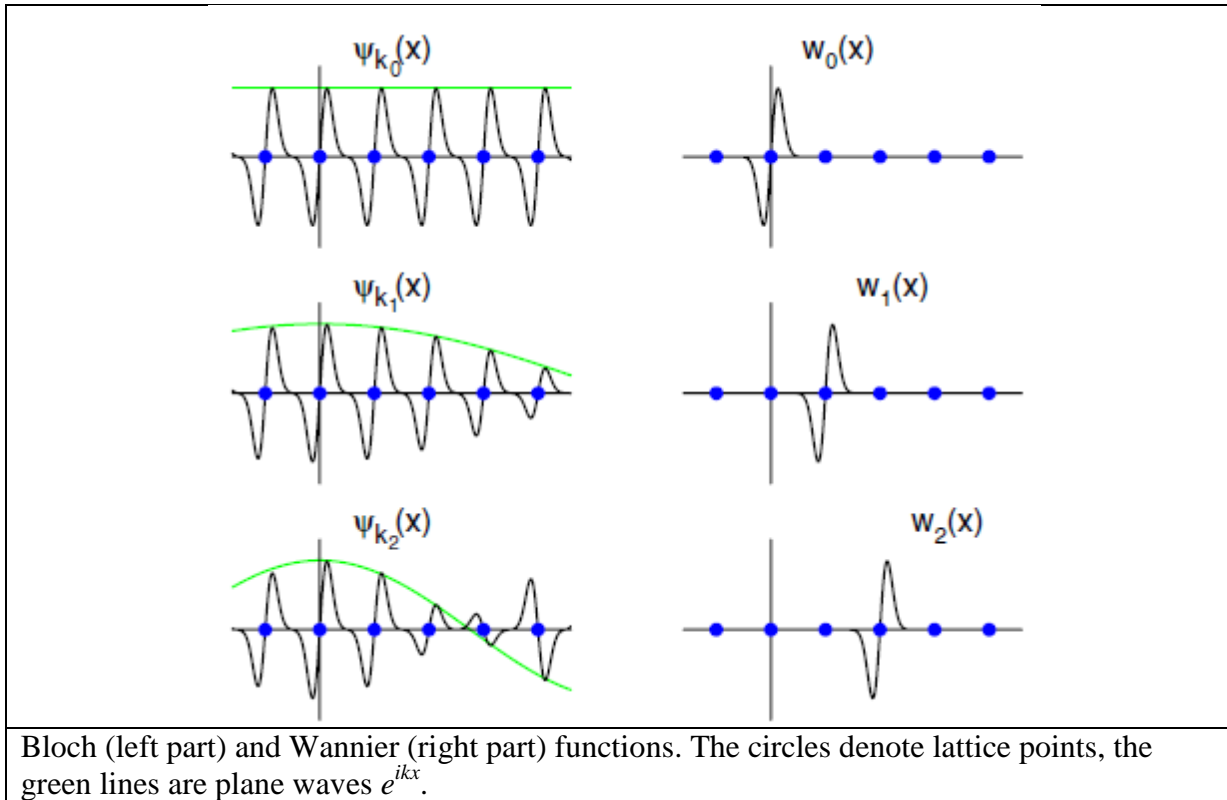
$$(\hat{H}^0 - |e|\hat{V}_d)\psi(\vec{r}) = E\psi(\vec{r}) , \quad (7.2)$$

where H^0 is the one-electron Hamiltonian of the unperturbed crystal.

Wannier functions are defined via the discrete Fourier transform of the Bloch functions (eigenfunctions of the one-electron Hamiltonian); for n -th band, this and inverse Fourier transform reads

$$\begin{aligned}
 a_n(\vec{r} - \vec{R}_j) &= \frac{1}{\sqrt{N}} \sum_{\vec{k}_l} \exp(-i\vec{k}_l \vec{R}_j) \psi_{n\vec{k}}(\vec{r}) , \\
 \psi_{n\vec{k}}(\vec{r}) &= \frac{1}{\sqrt{N}} \sum_{\vec{R}_j} \exp(i\vec{k} \vec{R}_j) a_n(\vec{r} - \vec{R}_j) .
 \end{aligned}
 \tag{7.3}$$

The sum for Wannier functions a_n extends over the quasicontinuum of the wavefunctions from the first Brillouin zone, in the inverse transform the sum extend over the lattice points of the basic Born-Kármán volume of the crystal, see the definition of Eq. (1.13); $N=N_1N_2N_3$ is the number of primitive cells in this volume.



Wannier functions are localized around the lattice points, as shown schematically in the above figure. The localization can be fairly strong (exponential in one dimension: W. Kohn, Phys. Rev. 115, 809 (1959)), see also Marzari et al., REVIEWS OF MODERN PHYSICS, VOLUME 84, OCTOBER–DECEMBER 2012.

Wannier functions $a_n(\vec{r} - \vec{R}_j)$ are eigenfunctions of the vector operator $\hat{\vec{R}}$, belonging to the eigenvalue R_j (i.e., to the j -th lattice vector):

$$\hat{\vec{R}} a_n(\vec{r} - \vec{R}_j) = \vec{R}_j a_n(\vec{r} - \vec{R}_j) . \quad (7.4)$$

Let us assume a general wavefunction in the form of the linear combination of the stationary states of one-electron Hamiltonian without impurities, i.e., the Bloch functions,

$$\psi(\vec{r}) = \sum_{n, \vec{k}_l} A_n(\vec{k}_l) \psi_{n\vec{k}}(\vec{r}) = \sum_{n, \vec{k}_l} A_n(\vec{k}_l) \frac{1}{\sqrt{N}} \sum_{\vec{R}_j} \exp(i\vec{k}_l \vec{R}_j) a_n(\vec{r} - \vec{R}_j) ; \quad (7.5)$$

the action of the operator \hat{R} leads to

$$\begin{aligned} \hat{R}\psi(\vec{r}) &= \sum_{n, \vec{k}_l} A_n(\vec{k}_l) \frac{1}{\sqrt{N}} \sum_{\vec{R}_j} \exp(i\vec{k}_l \vec{R}_j) \vec{R}_j a_n(\vec{r} - \vec{R}_j) \\ &= \sum_{n, \vec{k}_l} A_n(\vec{k}_l) \frac{1}{\sqrt{N}} \sum_{\vec{R}_j} (-i\nabla_{\vec{k}}) \exp(i\vec{k}_l \vec{R}_j) a_n(\vec{r} - \vec{R}_j) . \end{aligned} \quad (7.6)$$

We will approximate the possible values of the vector k_l by a continuous set; consequently, (in this limit of infinite crystal) the action of the gradient operator is

$$\nabla_{\vec{k}} \exp(i\vec{k}_l \vec{R}_j) = i\vec{R}_j \exp(i\vec{k}_l \vec{R}_j) \quad (7.7)$$

for any vector k_l . Additionally, Eq. (7.6) can be brought to the following form:

$$\begin{aligned} \hat{R}\psi(\vec{r}) &= \sum_{n, \vec{k}_l} (-i\nabla_{\vec{k}}) \left[A_n(\vec{k}_l) \psi_{n\vec{k}_l}(\vec{r}) \right] - \sum_{n, \vec{k}_l} \left[-i\nabla_{\vec{k}} A_n(\vec{k}_l) \right] \psi_{n\vec{k}_l}(\vec{r}) \\ &= \sum_{n, \vec{k}_l} \left[i\nabla_{\vec{k}} A_n(\vec{k}_l) \right] \psi_{n\vec{k}_l}(\vec{r}) . \end{aligned} \quad (7.8)$$

The first sum in the upper row of Eq. (7.8) vanishes; in fact, in the approximation of infinite crystal the sum over k is replaced by the volume integral over the Brillouin zone and the resulting value is the difference of the products $A\psi$ in the two equivalent points at the opposite boundaries of the BZ.

The wavefunction of Eq. (7.5) can also be expressed as the following linear combination of Wannier functions,

$$\psi(\vec{r}) = \sum_{n, \vec{R}_j} C_n(\vec{R}_j) a_n(\vec{r} - \vec{R}_j) ; \quad (7.9)$$

the coefficients C_n are usually denoted as envelope functions. Rearranging Eq. (7.5), we obtain

$$\psi(\vec{r}) = \sum_{n, \vec{R}_j} \left[\frac{1}{\sqrt{N}} \sum_{\vec{k}_l} A_n(\vec{k}_l) \exp(i\vec{k}_l \vec{R}_j) \right] a_n(\vec{r} - \vec{R}_j) ; \quad (7.10)$$

the envelope functions C_n are therefore Fourier transforms of the coefficients A_n . In analogy with (7.7), we will further approximate the changes of wavefunctions at the distances much larger than those of the nearest-neighbors,

$$\nabla_{\vec{R}} \exp(i\vec{k}_l \vec{R}_j) = i\vec{k}_l \exp(i\vec{k}_l \vec{R}_j) . \quad (7.11)$$

In searching for the electronic structure of the crystal including defects (solving the wave equation (7.2)), we make use the electronic structure of the unperturbed crystal. Let us select the n -th band, with the Bloch eigenfunctions and eigenenergies $E_n^0(\vec{k})$:

$$\hat{H}^0 \psi_{n, \vec{k}}(\vec{r}) = E_n^0(\vec{k}) \psi_{n, \vec{k}}(\vec{r}) . \quad (7.12)$$

Using Eq. (7.11), the operator acting on the envelopes of the Wannier functions belonging to the n -th band can be expressed as

$$\hat{H}_w^0 = E_n^0(-i\nabla_{\vec{R}}) . \quad (7.13)$$

The next step consists in adding the perturbation due to the impurity atom; a simple description is based on the assumption of smooth changes of the potential (7.1) at the distances comparable with the lattice constant. In this case, we substitute the position dependence of \hat{V}_d in Eq. (7.2) by the dependence on the vector R and the equation for the envelope functions and the eigenenergies E becomes

$$\left[E_n^0(-i\nabla_{\vec{R}}) + V_d(\vec{R}) \right] C_n(\vec{R}) = EC_n(\vec{R}) . \quad (7.14)$$

In order to use the last equation, we have to specify the functional dependence $E_n^0(\vec{k})$ of the dispersion of n -th band, do replacing its argument by the gradient operator. Here, we choose the simple parabolic dependence of the isotropic non-degenerate band (which is typical of the conduction band minima in the center of the Brillouin zone, e.g., in GaAs):

$$E_n^0(\vec{k}) = E_c(0) + \frac{\hbar^2 |\vec{k}|^2}{2m^*} . \quad (7.15)$$

Equation (7.14) for the envelopes of Wannier functions reads

$$\left[-\frac{\hbar^2}{2m^*} \Delta_{\vec{R}} + V_d(\vec{R}) \right] C(\vec{R}) = [E - E_c(0)] C(\vec{R}) . \quad (7.16)$$

It has the form of Schroedinger equation for a particle of the mass m^* , moving in the potential V_d , and its energy starting at the conduction band minimum. The corresponding wavefunction is the product of the envelope and Wannier functions according to Eq. (7.9). This approach is usually called *effective mass approximation*.

Equation (7.16) with centrosymmetric potential of Eq. (7.1) is equivalent to the quantum description of the electron in isolated hydrogen atom. The differences consist in using the effective mass of the electron, and the Coulombic attraction to the positively charged impurity is reduced due to the screening by the electrons of the host crystal. The latter is introduced by the permittivity in the denominator of Eq. (7.1). Stationary states are both discrete (bound) and continuum (delocalized); the latter lie above the bottom of the conduction band of the host crystal. The analogy with the hydrogen atom allows us to find the energies E_n of the bound states as

$$E_n - E_c(0) = -\frac{m^*}{m_0} \frac{1}{\varepsilon_r^2} \frac{e^4 m_0}{2\hbar^2 (4\pi\varepsilon_0)^2} \frac{1}{n^2} = -\frac{R}{n^2}, \quad n = 1, 2, \dots, \quad (7.17)$$

where n is the principal quantum number, e is the elementary charge, and m_0 is the mass of free electron; R denotes the Rydberg constant of the donor electron. For $m^* = \varepsilon_r = 1$ (isolated hydrogen atom), the value of R is 13.6 eV, for $m^* \approx 0.1$ and $\varepsilon_r \approx 10$, this value is reduced to about 14 meV.

Bohr radius of the donor state is

$$a^* = \frac{\varepsilon_r m_0}{m^*} \frac{4\pi\varepsilon_0 \hbar^2}{e^2 m_0}, \quad (7.18)$$

and the envelope function of the lowest state (1s) is approximated by the exponential,

$$C_{1s}(R) = \frac{1}{\sqrt{\pi(a^*)^3}} e^{-\frac{R}{a^*}}. \quad (7.19)$$

Bohr radius (7.18) is much larger than that of the hydrogen atom (0.0529 nm), due to the large values of permittivity and small effective masses. The envelopes of Wannier functions (i.e., the coefficients C) are non-negligible for a large number of the lattice points. On the contrary, the coefficients A from Eq. (7.5) multiplying the Bloch functions are non-negligible for a small number of the (discrete) values of the wave vector. This can be explained by the Fourier transform relating the two systems of coefficients, see (7.9) and (7.10). In order to estimate the exponential behavior of the envelope C , we can utilize the cosine Fourier transform

$$A(k) = \int_0^{\infty} e^{-\frac{R}{a^*}} \cos(kR) dR = \frac{a^*}{1 + (a^*k)^2} = \frac{1/a^*}{k^2 + (1/a^*)^2} . \quad (7.20)$$

At $k = 1/a^*$, the value of A is a half of its maximum (at $k = 0$); this function is "narrower" for "wider" envelope C . Equation (7.20) represents a special case of the more general uncertainty principle for a function f and its Fourier transform F :

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\omega t} f(t) dt , \quad f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} F(\omega) d\omega ; \quad (7.21)$$

for two real numbers, T and W , defined as

$$T^2 = \frac{1}{E} \int_{-\infty}^{\infty} t^2 |f(t)|^2 dt , \quad W^2 = \frac{1}{E} \int_{-\infty}^{\infty} \omega^2 |F(\omega)|^2 d\omega , \quad (7.22)$$

where

$$E = \int_{-\infty}^{\infty} |f(t)|^2 dt = \int_{-\infty}^{\infty} |F(\omega)|^2 d\omega , \quad (7.23)$$

the following inequality holds:

$$TW \geq \frac{1}{2} . \quad (7.24)$$

This result means that both functions, f and F , cannot be simultaneously "small", and, at the same time, "narrowing" one of them leads to "widening" of the other. This is important also in our case of the donor states: with increasing quantum number n , the binding energy drops as

$1/n^2$, the wavefunction lies in the volume proportional to n^2 . Higher excited states are therefore described better by our model than the ground state.

Donor states for anisotropic conduction bands of several host crystals are of considerable practical importance (e.g., Si, Ge, and GaP). Due to the crystal symmetry, the minima of conduction bands are degenerated and the position dependence of the interaction in the neighborhood of the donor atom leads to the so called "valley-orbit coupling". The above approximation requires modifications.

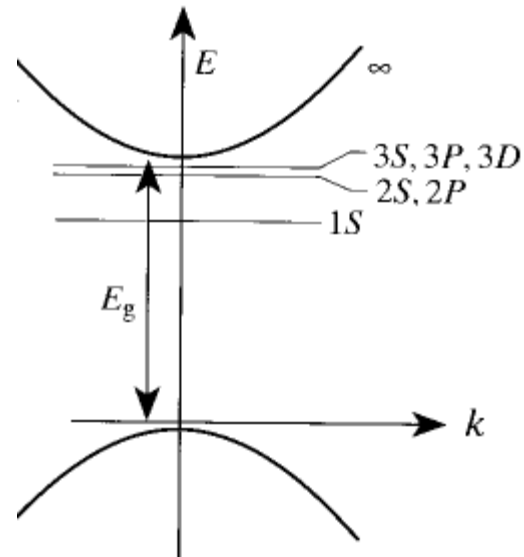
Let us mention silicon, having six equivalent minima of the conduction band, located close to the edge of the Brillouin zone X (in the [100] direction, labeled usually Δ). The first step consists in the modification of Eq. (7.16) for the envelopes; for any of the minima $j = 1, \dots, 6$ we have the equation

$$\left[-\frac{\hbar^2}{2m^*} \left(\frac{2\Delta_t}{m_t} + \frac{\Delta_l}{m_l} \right) + V_d(\vec{R}) \right] \Phi_j(\vec{R}) = [E - E_c(\vec{k}_0)] \Phi_j(\vec{R}), \quad (7.25)$$

where m_t and m_l are transverse and longitudinal effective masses, respectively ($0.19m_0$ and $0.92m_0$ for Si). Approximate solutions can be found variationally, using a suitable test function reflecting the lowering of symmetry (spherical to cylindrical). A popular approach is due to Kohn and Luttinger (1955), using the trial function with two parameters,

$$\Phi_x(\vec{R}) = e^{\sqrt{-a(y^2+z^2)-bx^2}}, \quad (7.25)$$

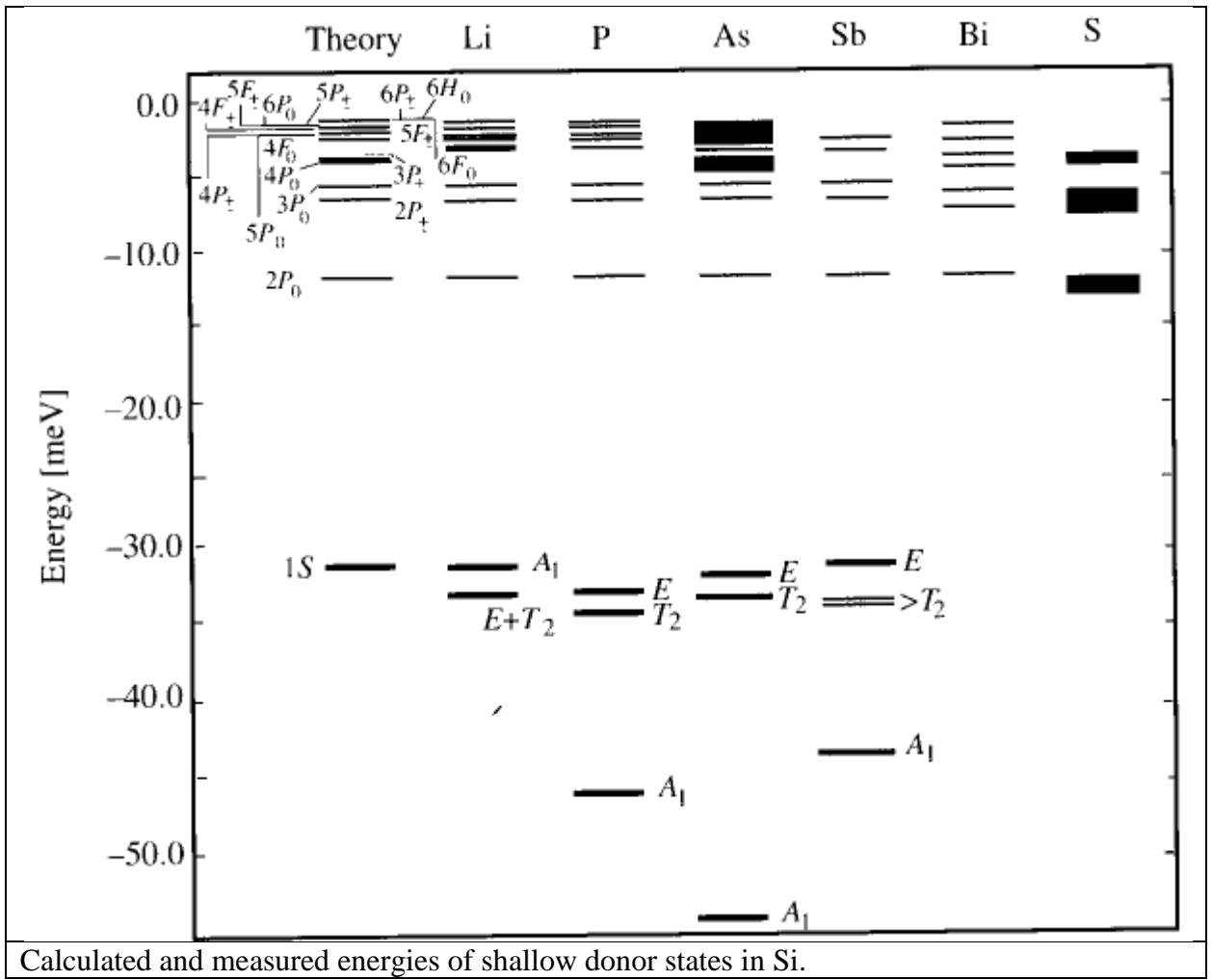
where the x direction lies along the longitudinal axis of the corresponding band minimum.



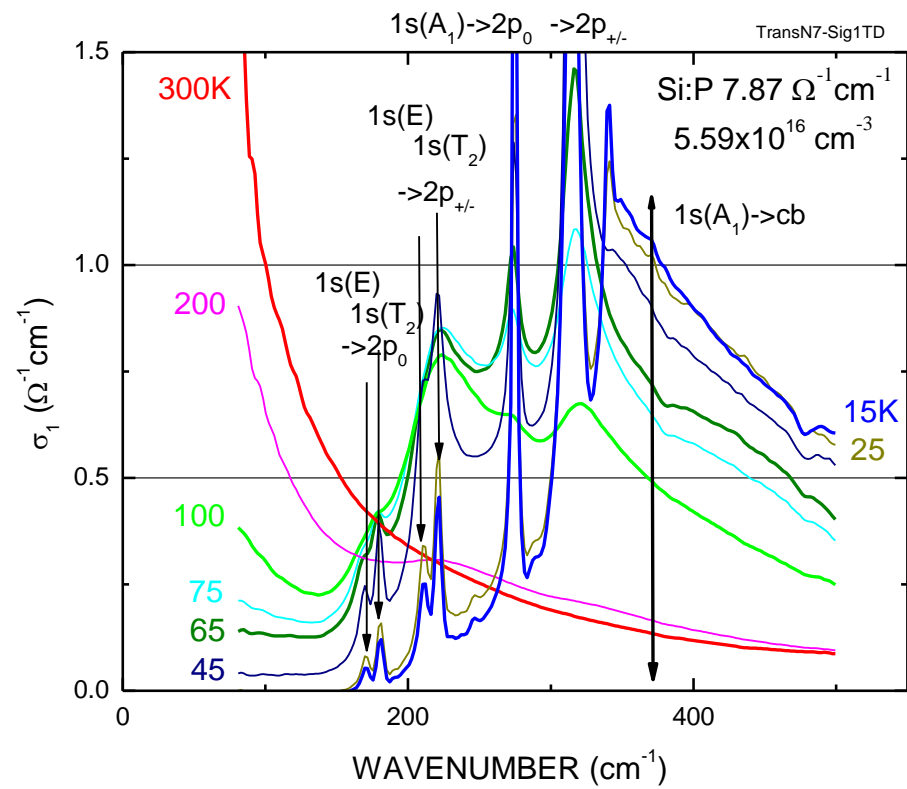
Schematics of the band structure of a direct semiconductor, donor states of $n=1,2$ a 3.

GaAs	5.72	$\text{Si}_{\text{Ga}}(5.84); \text{Ge}_{\text{Ga}}(5.88)$ $\text{S}_{\text{As}}(5.87); \text{Se}_{\text{As}}(5.79)$
InP	7.14	7.14
InSb	0.6	$\text{Te}_{\text{Sb}}(0.6)$
CdTe	11.6	$\text{In}_{\text{Cd}}(14); \text{Al}_{\text{Cd}}(14)$
ZnSe	25.7	$\text{Al}_{\text{Zn}}(26.3); \text{Ga}_{\text{Zn}}(27.9)$ $\text{F}_{\text{Se}}(29.3); \text{Cl}_{\text{Se}}(26.9)$

Binding energy (the ground state, $n=1$) of shallow donors in zincblende semiconductors, in meV. The values in the middle column are results from Eq. (6.17), those in the right column are measured data for the most common dopants.



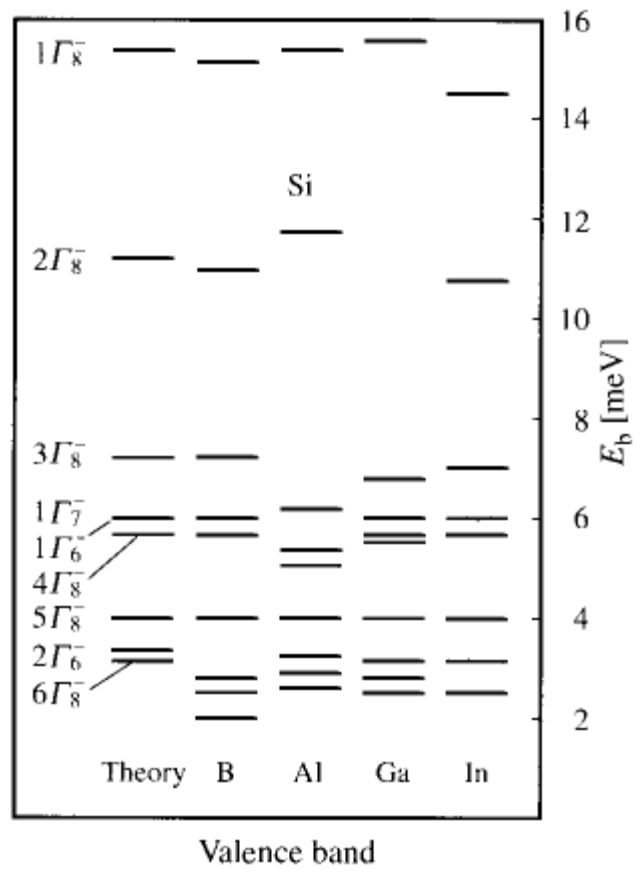
Calculated and measured energies of shallow donor states in Si.



Real part of conductivity resulting from transmission spectra of Si:P (5.59E16 cm⁻³) at different temperatures.

	Experiment	$1S_{3/2}$	$2S_{3/2}$	$2P_{1/2}$	$2P_{3/2}$	$2P_{5/2}$
Si	45, 68.9	31.6	8.6	4.2	11.2	7.6
Ge	10.8	9.8	2.9	0.6	4.2	2.5
GaP	57-64	47.5	13.7	4.2	19.1	11.7
GaAs	31	25.6	7.6	1.6	11.1	6.5
GaSb	13-15	12.5	3.8	0.65	5.6	3.2
InP	31, 56.3	35.2	10.5	2	15.5	8.9
InAs	10-20	16.6	5.1	0.4	7.9	4.4
InSb	≈10	8.6	2.7	0.2	4.2	2.3
ZnS		175.6	52	11.7	75.1	44.1
ZnSe	114	110.1	33	6.1	48.6	28
ZnTe	≈30	77.7	23	5.1	33.4	19.6
CdTe	≈30	87.4	26.5	3.7	39.9	22.6

Energy of the lowest bound acceptor state (in meV), compared with the calculation using spherical symmetry.



Calculated and measured shallow acceptor levels in Si.