

Electronic States in Semiconductors

A. Free Electrons

Most transport descriptions in semiconductors treat electrons as quasi-free particles within the effective mass approximation. For free particles, the electron wave function is the solution to the time-independent Schrödinger equation:

$$\left(\frac{\hbar^2}{2m}\nabla^2 + E\right)\!\varphi(\mathbf{r}) = 0$$

The solutions form the basis of plane waves: $\varphi_{\mathbf{k}}(\mathbf{r}) = C_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$

with:

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V

The velocity, \mathbf{v} , of a particle represented by a wave packet centered around the crystal momentum, k, is obtained from the *dispersion relation* between **k** and the energy *E* as

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} \cdots \mathbf{v} = \left\langle \left| \frac{\hbar}{i} \nabla \right| \right\rangle = \frac{1}{\hbar} \nabla_{\mathbf{k}} E_{\mathbf{k}} = \frac{\hbar \mathbf{k}}{m}$$

If we consider that the system is bounded within a volume, V, and apply periodic boundary conditions

$$\varphi_{\mathbf{k}}(x, y, z) = \varphi_{\mathbf{k}}(x + L, y + L, z + L); \quad V = L^{3}$$

$$k_{x} = \frac{2\pi}{L}n_{x}, k_{y} = \frac{2\pi}{L}n_{y}, k_{z} = \frac{2\pi}{L}n_{z}; n_{x,y,z} = 0, \pm 1, \pm 2, \dots$$
Thus, **k**, takes on discrete values, with a volume per cell in **k**-space of
$$V_{K} = \frac{8\pi^{3}}{V}$$

Electronic States in nanoHUB.org Semiconductors ... online simulations and more Normalization of the wavefunction $\int d\mathbf{r} \varphi_{\mathbf{k}}^{*}(\mathbf{r}) \varphi_{\mathbf{k}'}(\mathbf{r}) = \delta_{\mathbf{k},\mathbf{k}'}$ in the volume V requires: $\therefore \varphi_{\mathbf{k}}(\mathbf{r}) = V^{1/2} e^{i\mathbf{k}\cdot\mathbf{r}}$ The countability of the states within the system volume, and the dispersion relation between k and E leads to the *density* of electronic states per unit volume $D(E)dE = \frac{2m^{3/2}E^{1/2}}{\sqrt{2}\pi^2\hbar^3}dE = \frac{(2)V}{8\pi^3}d\mathbf{k}$ where the factor of (2) is due to the 2-fold spin degeneracy of each allowed state in k-space. Since the density of *k* states is quite large in macrosopic systems, summations over k may be replaced by the coarse grain integral

Bloch Functions

B. Bloch Functions and Reciprocal Space

Translational symmetry in a crystal implies that

 $V_1(\mathbf{r}) = V_1(\mathbf{r} + \mathbf{a}); \quad \mathbf{a} = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$

where *I*, *m*, *n* are integers, and **a** is the primitive translation vector of the real space lattice.

The eigenstates of the time independent Schrödinger equation are given by *Bloch Functions*

$$\varphi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}); \quad u_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r}+\mathbf{a})$$

$$n = band \ index \quad u_{n,\mathbf{k}}(\mathbf{r}) = cell \ periodic \ part$$

The periodic part of the Bloch function may be expanded in a Fourier series in 3D defined in *reciprocal space*

Boch Functions ... Boch Functions ... Reciprocal Space For a 1D periodic function: f(x) = f(x+l); l = naWe may expand it in a Fourier series $f(x) = \sum_{n} A_{n}e^{i2\pi nx/a} = \sum_{g} A_{g}e^{igx}$ $g = \frac{2\pi n}{a}$ The Fourier components are defined on a discrete set of periodically arranged points (analogy: frequencies) in a reciprocal space to coordinate space. **3D Generalization** $u_{n,k}(\mathbf{r}) = \sum_{G} f_{G}^{n}(\mathbf{k})e^{i\mathbf{G}\cdot\mathbf{r}};$ $\mathbf{G} = h\mathbf{b}_{1} + k\mathbf{b}_{2} + l\mathbf{b}_{3}$ $\mathbf{G} \perp \mathbf{a}$ where *hkl* are integers. \mathbf{G} =Reciprocal lattice vector





- The periodic set of allowed points corresponding to the Fourier (reciprocal) space associated with the real (space) lattice form a periodic lattice
- The *Wigner-Seitz* unit cell corresponding to the reciprocal lattice is the First Brillouin Zone
- Γ is zone center, L is on zone face in (111) direction, X is on face in (100) direction



First Brillouin Zone

First Brillouin Zone for Zinc-Blende and Diamond real space lattices

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- Popular, straightforward technique for calculating the bandstructure in semiconductors is the *empirical pseudopotential method* (EPM).^{1,2} This technique is used, e.g., in DAMOCLES to calculate the band structure used in Monte Carlo simulation.
- Stationary Bloch state solutions calculated by expanding in reciprocal space, and adjusting the (finite set of) Fourier coefficients to fit experimental energy gaps and optical spectrum.

¹ M.L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 780-796 (1966).

² D. K. Ferry, Semiconductors (1991), pp. 137-141.

EPM Continued ...

Consider the origin at the halfway point between the cation(1) and the anion(2). Let r_b be the basis vector of FCC Bravais lattice corresponding to the zincblende (diamond) structure. (1) is located at $-r_b/2$ while (2) is at $r_b/2$.

 $\mathbf{r}_b = a_o \left(\frac{1}{4} \frac{1}{4} \frac{1}{4} \right)$

The Hamiltonian is of the form: $H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$

where $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}_1)$, $\mathbf{R}_1 = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$

with \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 primitive vectors of the FCC lattice (each lattice site represents the midpoint of the 2-atom basis

EXAMPLE 1 Define simulations and more $Expand: V(\mathbf{r}) = \sum_{\mathbf{G}} V(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}; \quad \mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ The Fourier coefficient is: $V(\mathbf{G}) = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} V(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}$ with the volume of the primitive unit cell: $\Omega = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$ Split potential into cation and anion $= \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} \left\{ V_1 \left(\mathbf{r} + \frac{\mathbf{r}_b}{2}\right) + V_2 \left(\mathbf{r} - \frac{\mathbf{r}_b}{2}\right) \right\} e^{-i\mathbf{G}\cdot\mathbf{r}}$ where V_1 and V_2 represent the atomic-like potentials centered at $\pm \mathbf{r}_b/2$ (pseudopotentials which are smooth compared to the actual rapidly varying core potential)





EXAMPLE 1
Definition and more
$$= \sum_{G} \left(\cos\left(\frac{G \cdot \mathbf{r}_{b}}{2}\right) [V_{1}(G) + V_{2}(G)] + i \sin\left(\frac{G \cdot \mathbf{r}_{b}}{2}\right) [V_{1}(G) - V_{2}(G)] e^{iG \cdot \mathbf{r}_{b}} - \sum_{G} \left(\cos\left(\frac{G \cdot \mathbf{r}_{b}}{2}\right) V_{s}(G) + i \sin\left(\frac{G \cdot \mathbf{r}_{b}}{2}\right) V_{a}(G) e^{iG \cdot \mathbf{r}_{b}} - \sum_{G} V_{a}(G) e^{iG \cdot \mathbf{r}_{b}} -$$





nanoHU online simulations ar	B.org nd more		Reciprocal Vectors						
In terms of the unit Cartesian vectors, nearest neighbor sites in reciprocal space correspond to									
G group (units 2π/a _o)	# permutations	Total number of elements	$ \mathbf{G} ^2 (2\pi/a_o)^2$ units						
(0,0,0)	1	1	0						
(1,1,1)	8	9	3						
(2,0,0)	6	15	4						
(2,2,0)	12	27	8						
(3,1,1)	24	51	11						
(2,2,2)	8	59	12						
(4,0,0)	6	65	16						
(3,3,1)	24	89	19						
The pseudopotential form factors are typically given up to $G^2=11$									
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Form Factors

The pseudopotential form factors for a number of materials have been derived for various semiconductors. Those given by Cohen and Bergstresser are shown below:

TABLE II. Pseudopotential form factors, in rydbergs, derived from the experimental energy band splittings.								
	V_{3}^{S}	V_8 ^S	$V_{11}s$	V_{2}^{A}	V_4^A	V_{11}^A		
Si Ge Sn GaP GaAs AlSb InP GaSb InAs InSb ZnS ZnSe ZnTe CdTe	$\begin{array}{c} -0.21 \\ -0.23 \\ -0.20 \\ -0.22 \\ -0.23 \\ -0.21 \\ -0.23 \\ -0.22 \\ -0.22 \\ -0.22 \\ -0.22 \\ -0.22 \\ -0.23 \\ -0.22 \\ -0.23 \\ -0.22 \\ -0.20 \end{array}$	$\begin{array}{c} +0.04\\ +0.01\\ 0.00\\ +0.03\\ +0.01\\ +0.02\\ +0.01\\ 0.00\\ 0.00\\ +0.03\\ +0.01\\ 0.00\\ 0.00\\ 0.00\\ \end{array}$	$\begin{array}{r} +0.08 \\ +0.06 \\ +0.04 \\ +0.06 \\ +0.06 \\ +0.05 \\ +0.05 \\ +0.04 \\ +0.07 \\ +0.06 \\ +0.05 \\ +0.04 \end{array}$	$\begin{array}{c} 0 \\ 0 \\ +0.12 \\ +0.07 \\ +0.06 \\ +0.07 \\ +0.06 \\ +0.08 \\ +0.06 \\ +0.24 \\ +0.13 \\ +0.13 \\ +0.15 \end{array}$	$\begin{array}{c} 0 \\ 0 \\ 0 \\ +0.07 \\ +0.05 \\ +0.05 \\ +0.05 \\ +0.05 \\ +0.05 \\ +0.14 \\ +0.12 \\ +0.10 \\ +0.09 \end{array}$	$\begin{array}{c} 0 \\ 0 \\ +0.02 \\ +0.01 \\ +0.01 \\ +0.01 \\ +0.03 \\ +0.01 \\ +0.04 \\ +0.04 \end{array}$		

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Numerical Solution

NCN

Assume we chose $|\mathbf{G}|^2=19$ to be sufficiently accurate to represent the bands. There are then 89 set of simultaneous equations which form the matrix eigenvalue equation:

$\overline{\mathbf{H}} \bullet \mathbf{U} = E\mathbf{U}$

where **H** is an 89x89 array, **U** is an 89 element column vector representing the eigenvectors, and E is an eigenvalue corresponding to one of the eigenvectors.

Using a standard linear algebra subroutines in for example EISPACK, the eigenvalues and eigenvectors are obtained for each **k**. Sorting the lowest eight eigenvalues corresponds to the lowest 4 valence bands, and the first 4 conduction bands.

