Band structure
(read Kittel, ch. 7)

Now we include the crystal potential $V(\mathbf{r})$. This will lead to a more complicated dispersion for the electron states. First consideration is that the potential is periodic in the space lattice:

We then expect the electron density is also periodic.

Note, it is not necessarily $\Psi(\mathbf{r})$ that is periodic in the space lattice. Based on the above, we can write:

$$\Psi(\mathbf{r}) = \lambda \Psi(\mathbf{r} + \mathbf{a}_i)$$

where $\mathbf{a}_i$ is primitive lattice vector, and $\lambda$ is an arbitrary phase.

for 1D, periodic BC’s, $\lambda^N = 1$, so

$$n = 1, 2, \ldots, N$$

So we can write:

$$\Psi(x) = U_k(x)e^{i2\pi nx/Na}$$

This is called a Bloch function.

$$k = \frac{2\pi n}{L}$$

with $U_k(x + a) = U_k(x)$, $L \equiv Na$.

General 3D crystal case

Since $V(\mathbf{r})$ periodic in lattice, make a Fourier analysis:

G: reciprocal lattice vectors
The sum over $G$ only goes over reciprocal lattice vectors, as proven previously.

Now make a Fourier analysis of $\Psi(\hat{r})$:

$$
\Psi(\hat{r}) = \sum_k C(k) e^{i\hat{k} \cdot \hat{r}}
$$

here $k$ goes over all values allowed by the BC’s; $\Psi(\hat{r})$ is not periodic in the lattice.

Writing down the Schrodinger equation:

plugging in the Fourier series for $\Psi(\hat{r})$:

$$
\sum_k \left[ \frac{\hbar^2 k^2}{2m} C(k) + \sum_G U_G C(k) e^{i\hat{G} \cdot \hat{r}} - E C(k) \right] e^{i\hat{k} \cdot \hat{r}} = 0
$$

multiply by $e^{-i\hat{k} \cdot \hat{r}}$ and integrate over $V$:

[use $\int_V e^{-i\hat{k} \cdot \hat{r}} e^{i\hat{k} \cdot \hat{r}} dV = V \delta_{kk'}$ and $\int_V e^{-i\hat{k} \cdot \hat{r}} e^{i(\hat{G} + \hat{k}) \cdot \hat{r}} dV = V \delta_{kk' - G}$]

then change dummy variable $k'$ back to $k$. Define kinetic energy

This is called the central equation. It provides the starting point for all band structure theory. It actually describes a set of simultaneous equations for a set of coefficient for wavevector $k$, $C(k)$. Notice that $C(k)$ is only coupled to the set of vectors $C(k-G)$. 
The wavefunction corresponding to a particular value of \( k \) is similarly composed of a superposition of all components with wavevectors \( k + G \), where we sum over all \( G \) vectors:

\[
\Psi_k(\mathbf{r}) = \sum_{G} C(k - G) e^{i(k - G) \cdot \mathbf{r}}
\]

\[
= \left[ \sum_{G} C(k - G) e^{-iG \cdot \mathbf{r}} \right] e^{i k \cdot \mathbf{r}}
\]

We can thus write:

The electron wavefunction representing a particular \( k \) vector is written as a product of the function \( u_k \), which is periodic in the lattice, times a plane-wave factor. This result is known as the Bloch theorem.

**Reduced zone scheme**

The \( k \) label is not unique. It actually labels a superposition of wavevectors separated by all possible \( G \) vectors. We can choose any one of these as the label for this wavefunction. We make the convention to choose \( k \) in 1st BZ.

To see how this works, consider free-electron (empty lattice): \( V(\mathbf{r}) = 0 \)

For \( \mathbf{k} \) outside 1st BZ, find \( \mathcal{G} \) so that \( \mathbf{k}' = \mathbf{k} - \mathcal{G} \) is in 1st BZ. Drop the prime and define the band index, \( n \).

\[
\text{then}
\]
\[ E_n(k_x, k_y, k_z) = \frac{\hbar^2}{2m} [(k_x + G_{nx})^2 + (k_y + G_{ny})^2 + (k_z + G_{nz})^2] \]

Display entire band-structure in 1st BZ

<table>
<thead>
<tr>
<th>Label</th>
<th>Ga/2π</th>
<th>2mE(000)/\hbar^2</th>
<th>2mE(k_x,0,0)/\hbar^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>000</td>
<td>0</td>
<td>( k_x^2 )</td>
</tr>
<tr>
<td>2,3</td>
<td>100, \bar{1}00</td>
<td>( (2\pi/a)^2 \equiv G_o^2 )</td>
<td>((k_x \pm G_o)^2)</td>
</tr>
<tr>
<td>4-7</td>
<td>010, 0\bar{1}0, 001, 00\bar{1}</td>
<td>( G_o^2 )</td>
<td>( k_x^2 + G_o^2 )</td>
</tr>
<tr>
<td>8-11</td>
<td>110,101, 1\bar{1}0, 10\bar{1}</td>
<td>2( G_o^2 )</td>
<td>((k_x + G_o)^2 + G_o^2)</td>
</tr>
<tr>
<td>12-15</td>
<td>\bar{1}0, \bar{1}01, \bar{1}\bar{1}0, \bar{1}\bar{0}\bar{1}</td>
<td>2( G_o^2 )</td>
<td>((k_x - G_o)^2 + G_o^2)</td>
</tr>
</tbody>
</table>
Band Gaps

Bands cross at zone boundary, i.e.: \( k = \frac{1}{2} G = \frac{\pi}{a} \) crosses \( k' = k - G = -\frac{\pi}{a} \)

The corresponding free-electron wavefunction is:

\[
|\Psi_+|^2 = \frac{2}{a} \cos^2 \left( \frac{\pi x}{a} \right) \quad |\Psi_-|^2 = \frac{2}{a} \sin^2 \left( \frac{\pi x}{a} \right) \quad (\text{normalized to one cell})
\]

\( |\Psi_+|^2 \) peaks at \( x = na \): on the atoms

\( |\Psi_-|^2 \) peaks at \( x = \left( n + \frac{1}{2} \right) a \): between the atoms

Put in the crystal potential - this will split the energies of \( \Psi_\pm \).

Using:

\[
\Delta E = \Psi_+ - \Psi_-
\]

Make a very simple model potential, taking only 2 terms: \( G = \pm 2\pi/a \), \( U_G = -U \). Thus:

\[
\Delta E = -\frac{4U}{a} \int_0^a \cos \left( \frac{2\pi x}{a} \right) \cos \left( \frac{\pi x}{a} \right) dx = -U
\]

Similarly, \( \Delta E_+ = U \). Energy lowered for \( \Psi_+ \) “bonding” orbital, raised for \( \Psi_- \) “antibonding” orbital. A gap opens up of 2U.
Now let’s use the central eqn. to find behavior near the zone boundary.

Two components $\Psi(x) = C(k)e^{ikx} + C(k-G)e^{i(k-G)x}$ are strongly coupled by the $G = \frac{2\pi}{a}$ term in $V(x)$. We will only consider the coupling of these two components, taking a simple 2x2 portion of the infinite matrix. Near the zone boundary, we take: $k \approx \frac{1}{2} G$, $k - G \approx -\frac{1}{2} G$, and again $V(x) = 2U_G \cos \frac{2\pi x}{a}$, with $U_G = -U$. The 2x2 system we have to solve is:

$$
\begin{align*}
(\varepsilon_k - E)C(k) + U_G C(k - G) &= 0 \\
U_G C(k) + (\varepsilon_{k-G} - E)C(k - G) &= 0
\end{align*}
$$

Recall that

Solve for $E$:

$$
E = \frac{\varepsilon_k + \varepsilon_{k-G}}{2} \pm \left[ \left( \frac{\varepsilon_k - \varepsilon_{k-G}}{2} \right)^2 + U_G^2 \right]^{1/2}
$$

At the zone edge $\varepsilon_k = \varepsilon_{k-G}$, so $E = \varepsilon_{k-G} \pm U_G$, and we find a gap of $2U$, as before.

Now look at the behavior as we move away from zone edge. Take $k = \frac{G}{2} - \delta$, and consider small $\delta$.

$$
\varepsilon_{k-G} = \frac{\hbar^2}{2m} \left( \frac{G^2}{4} + \delta G + \delta^2 \right)
$$
Plug into the expression for $E$:

$$E(\delta) = \epsilon_{G/2} + \frac{\hbar^2 \delta^2}{2m} \pm \left[ 4 \epsilon_{G/2} \frac{\hbar^2 \delta^2}{2m} + U_G \right]^{1/2}$$

$$\approx \epsilon_{G/2} + \frac{\hbar^2 \delta^2}{2m} \pm U_G \left[ 1 + 2 \frac{\epsilon_{G/2} \hbar^2 \delta^2}{U_G^2} \right], \text{ for } \delta \ll \frac{2m|U_G|}{G \hbar^2}$$

To see that this represents two parabolic bands, let $E_+ = \epsilon_{G/2} + U_G = \epsilon_{G/2} - U$, and $E_- = \epsilon_{G/2} - U_G = \epsilon_{G/2} + U$. The two solutions for $E$ can then be expressed as:

$$E_a = E_- + \frac{\hbar^2 \delta^2}{2m} \left( 1 + \frac{2 \epsilon_{G/2}}{U} \right)$$

$$E_b = E_+ + \frac{\hbar^2 \delta^2}{2m} \left( 1 - \frac{2 \epsilon_{G/2}}{U} \right)$$

Note that the two bands have unequal effective masses.
**k•p Theory**

This is a perturbation theory approach that can give good results for describing semiconductor bands near the band edges.

Take the Bloch function:

\[ \Psi_k(\hat{r}) = u(k, \hat{r}) e^{i \hat{k} \cdot \hat{r}} \]

Insert this into the Schrödinger equation:

\[
\hat{p} \Psi_k(\hat{r}) = \left( \frac{-\hbar^2}{2m} \nabla \right) \Psi_k(\hat{r}) = \left( \frac{-\hbar^2}{2m} \nabla \right) u(k, \hat{r}) e^{i \hat{k} \cdot \hat{r}}
\]

where \( \hat{p} \equiv -i\hbar \nabla \). Expand:

\[
\frac{-\hbar^2}{2m} \Psi_k(\hat{r}) = \left[ \frac{-\hbar^2}{2m} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2 k \cdot \hat{p}}{m} \right] u(k, \hat{r}) e^{i \hat{k} \cdot \hat{r}}
\]

So we can write a new Schrödinger equation for the Bloch lattice function \( u(k, \hat{r}) \):

\[
\left\{ \left( \frac{-\hbar^2}{2m} + V(\hat{r}) \right) + \frac{\hbar^2 k \cdot \hat{p}}{m} \right\} u(k, \hat{r}) = E(k) u(k, \hat{r})
\]

Suppose we have solved for, or know, or have a good guess for the eigenvalues at \( k=0 \) (the band edges). We treat the \( k \cdot p \) term as a perturbation and do perturbation theory. In 1st order perturbation theory the energy shift is (labelling by a band index, \( n \)):

\[
\Delta E = \frac{\hbar}{m} \langle u_n(0, \hat{r}) | \hat{k} \cdot \hat{p} | u_n(0, \hat{r}) \rangle + \frac{\hbar^2 k^2}{2m}
\]

Keep in mind that here \( m \) is the free electron mass. For direct bandgap semiconductors at \( k=0 \), the wavefunctions are either symmetric or anti-symmetric in space, that is:

\[
\langle \hat{k} \cdot \hat{p} | u_n(0, \hat{r}) \rangle = 0
\]

The matrix element of \( p \) must therefore be zero. Thus, at the band edge, we have no term in the energy that is linear in \( k \).

So we need to go to second order perturbation theory to get the correction beyond \( \frac{\hbar^2 k^2}{2m} \).

The result is:
We can write this as:

\[ E_n(k) = E_n(0) + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{m \neq n} \frac{\langle u_n(0, \mathbf{r})|\hat{\mathbf{k}} \cdot \hat{\mathbf{p}}|u_m(0, \mathbf{r})\rangle^2}{E_n(0) - E_m(0)} \]

Only the nearest bands interact, due to the influence of the energy denominator. So we can approximate the sum with only one term arising from the closest band (valence or conduction band respectively):

\[ \frac{1}{m^*} = \frac{1}{m} \left[ 1 + \frac{2}{mk^2} \frac{\langle u_n(0, \mathbf{r})|\hat{\mathbf{k}} \cdot \hat{\mathbf{p}}|u_m(0, \mathbf{r})\rangle^2}{E_n(0) - E_m(0)} \right] \]

For the conduction band effective mass, we then have:

\[ P \]

\( P \) is always a positive number so the valence band states “push up” the conduction band states, causing the effective mass to be lighter, and vice versa. The \( \hat{\mathbf{p}} \) operator is a derivative so it primarily picks out the \( k \) value of the state it acts on. The band edge states in common semiconductors are folded in from the second Brillouin zone. So \( k = \frac{2\pi}{a} \), where \( a \) is the lattice constant. So we can estimate \( P = \hbar \cdot 2\frac{\pi}{a} \). Then,

\[ 2\frac{P^2}{m} \approx \frac{8\pi^2 \hbar^2}{ma^2} \approx 22 \text{eV} \], for typical \( a \approx 0.5nm \). Finally,

\[ m_e^* = \frac{mc^*}{m} \]

For GaAs, \( E_g = 1.4 \text{eV} \), so \( m_e^* \approx 0.06m \), very close to the correct value (0.0665m). The plot below shows the bandgap dependence of \( m_e^* \), a rather good job, indicating that \( P \) for most semiconductors is remarkably constant.
More realistic bandstructure calculations  (reading: Kittel pp. 232-242, Handouts:)

Many methods, approximations, sophistications

Zoology:

- OPW: orthogonalized plane wave method
- LAPW: linearized augmented plane wave
- LMTO: linear muffin-tin orbitals
- LCAO: linear combination of atomic orbitals
- EPM: empirical pseudo-potential method
- DFT: density functional theory
- LDA: local-density approximation (to DFT)

... most beyond our scope.

We will explore one relatively easy method in detail to get a full sense of what a realistic bandstructure calculation is like, the LCAO method, also known as the Tight Binding Method.

This method starts with the free atom wavefunctions, and describes the bonding among atoms, where the wavefunctions of adjacent atoms overlap, by making a correction. The corrected wavefunctions are formed by taking linear combinations of atomic wavefunctions corresponding to neighboring atoms.
\( \psi_i(r - r_j) \): normalized atomic wf, quantum #s t, on j\textsuperscript{th} atom.

We will focus on outer valence states of atoms, i.e., 3s for Na; 3s3p for Si, etc.

Make the expansion: \( \Psi = \sum_j c_j \psi_i(\hat{r} - \hat{r}_j) \).

\( \Psi \) must satisfy the Bloch theorem. Thus, if we construct a wavefunction with a definite value of \( k \), (band picture) we must have:

\[
\Psi_{k,\ell}(\hat{r}) = \frac{1}{\sqrt{N}} \sum_j \psi_i(\hat{r} - \hat{r}_j) e^{i \mathbf{k} \cdot \mathbf{r}_j},
\]

for \( \mathbf{T} \) a lattice vector.

This is satisfied by:

\[
\Psi_{k,\ell}(\hat{r}) = \frac{1}{\sqrt{N}} \sum_j \psi_i(\hat{r} - \hat{r}_j) e^{i \mathbf{k} \cdot \mathbf{r}_j}.
\]

This assumes 1 band is formed from each atomic state.

We now form the Hamiltonian matrix, using these basis functions:

\[
\langle \Psi_{k,\ell} | H | \Psi_{k,\ell} \rangle = \frac{\int \Psi_{k,\ell}^*(r) \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \Psi_{k,\ell}(r) d^3 r}{\int \Psi_{k,\ell}^*(r) \Psi_{k,\ell}(r) d^3 r}.
\]

Take a superposition of potentials of individual atoms:

since \( \psi_i \) is an atomic wf:

\( \varepsilon_i \): free atom eigenvalue

Then:
Finally:

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V \right) \Psi_{k,i} = \frac{1}{\sqrt{N}} \sum_{j} \left[ \varepsilon_i + \sum_{i \neq j} v(\hat{r} - \hat{r}_i) \psi_i(\hat{r} - \hat{r}_j)e^{ik \cdot \hat{r}_j} \right].
\]

\( i=j \) term

\[
\langle \Psi_{k,i} | H | \Psi_{k,i} \rangle = \varepsilon_i + \frac{1}{N} \sum_{i,j} e^{ik \cdot (\hat{r}_j - \hat{r}_i)} \int \psi_i^*(\hat{r} - \hat{r}_j) \sum_{i \neq j} v(\hat{r} - \hat{r}_i) \psi_i(\hat{r} - \hat{r}_j) d^3r
\]

\[
\frac{\int \Psi_{k,i}^* \Psi_{k,i} d^3r}{\int \Psi_{k,i}^* \Psi_{k,i} d^3r}
\]

Treat w.f. overlap as a small correction.

1. drop overlap in denom. Denom → 1
2. drop ‘3-center’ integrals:
   
   keep only \( l = i \), \( l = j \) terms

\( l=j \) terms:

\[
\frac{1}{N} \sum_j \int \psi_i^*(\hat{r} - \hat{r}_j) \sum_{i \neq j} v(\hat{r} - \hat{r}_i) \psi_i(\hat{r} - \hat{r}_j) d^3r
\]

This is the expectation at each ion, of the potential due to all neighbors. It is independent of j. The sum = \( N \cdot (\text{one term}) \). It is also independent of \( \hat{k} \). We can lump this into \( \varepsilon_i \).

\( l = i \) terms:

\[
\frac{1}{N} \sum_{i,j} e^{ik \cdot (\hat{r}_j - \hat{r}_i)} \int \psi_i^*(\hat{r} - \hat{r}_j) v(\hat{r} - \hat{r}_i) \psi_i(\hat{r} - \hat{r}_j) d^3r
\]

All j terms are equivalent again. Pick origin at a given \( \hat{r}_j \):
This term is $k$-dependent, and gives rise to band-structure.

**Simple example:**

1. Take simple cubic crystal.
2. Atomic 3s - state, which is totally symmetric.

then

$$\sum_{\hat{r}_i \neq 0} e^{-i\hat{k} \cdot \hat{r}_i} \int \psi_i^*(\hat{r} - \hat{r}_i) v(\hat{r} - \hat{r}_i) \psi_i(\hat{r}) d^3 r$$

$(E_{ss}$ is ordinarily negative, since $v$ is attractive.)

This has the same value for all neighbors, $i$, due to the symmetry of both the wavefunction and the potential.

So:

**Energy band diagram:**

- Simple cubic Brillouin zone
- Symmetry lines and points
Tight-binding for diamond: zinc-blende semiconductors

1) correct lattice structure, 4 nearest neighbors at tetrahedral positions

2) sp³ hybridization: s-state and 3-fold degenerate p-state considered together. Must diagonalize Hamiltonian matrix within this sub-space.

3) 2-different atoms: A,B. Nearest neighbor interactions are always A-B or B-A.

Coordinates of nearest neighbors in diamond:

\[ \hat{r}_1 = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z}) \quad \hat{r}_2 = \frac{a}{2}(\hat{x} - \hat{y} - \hat{z}) \]

\[ a = \text{edge of primitive cell} = \frac{a_0}{2}. \]

For the s-states (neglecting the constant terms):

\[ \langle s^A | H | s^B \rangle = \sum_{r_i \neq 0} e^{-i\hat{k} \cdot \hat{r}_i} \int \Psi^*_s(\hat{r} - \hat{r}_i) v(\hat{r} - \hat{r}_i) \Psi_s(\hat{r}) \, d^3r \]

\[ \equiv E_{ss} (e^{-i\hat{k} \cdot \hat{r}_1} + e^{-i\hat{k} \cdot \hat{r}_2} + e^{-i\hat{k} \cdot \hat{r}_3} + e^{-i\hat{k} \cdot \hat{r}_4}) \]

\[ B_o(k) = e^{\frac{-ia}{2}(k_x + k_y + k_z)} + e^{\frac{-ia}{2}(k_x - k_y - k_z)} + e^{\frac{-ia}{2}(-k_x + k_y - k_z)} + e^{\frac{-ia}{2}(-k_x + k_y + k_z)} \]
p - p interactions pointing in same direction also involve $B_o(k)$:

$$\langle p_x^A | H | p_x^B \rangle = \langle p_y^A | H | p_y^B \rangle = \langle p_z^A | H | p_z^B \rangle = E_{xx} B_o(k)$$

The s - p interactions are more complicated. Consider an s orbital on A, and a $p_x$ orbital on B. At $r_1, r_2$, $p_x$ points away from A. At $r_3, r_4$, $p_x$ points toward A.

$s_x$ is odd, so:

$$\langle s^A | H | p_x^B \rangle = E_{sp}^{AB} \left( e^{-i \vec{k} \cdot \vec{r}_1} + e^{-i \vec{k} \cdot \vec{r}_2} - e^{-i \vec{k} \cdot \vec{r}_3} - e^{-i \vec{k} \cdot \vec{r}_4} \right)$$

Similarly,

$$\langle s^A | H | p_y^B \rangle = E_{sp}^{AB} B_2(k)$$
$$\langle s^A | H | p_z^B \rangle = E_{sp}^{AB} B_3(k)$$

And the off diagonal p - p interactions are:

$$\langle p_x^A | H | p_y^B \rangle = E_{xy} B_3(k)$$

Semi-Empirical Tight Binding Method: SETBM

Parameters: $\varepsilon_s^A, \varepsilon_s^B, \varepsilon_p^A, \varepsilon_p^B, E_{ss}, E_{xx}, E_{xy}, E_{sp}^{AB}, E_{sp}^{BA}$

Use these as fitting parameters. Gaps between bands can be obtained from optical spectra, and this can be used to obtain empirical values for the fit parameters. The full band structure can then be obtained from the theory.
Tight Binding Summary:

Matrix elements of Hamiltonian:

\[ \langle \Psi_{k,t} | H | \Psi_{k,t} \rangle = \varepsilon_t + \sum_{r_i \neq 0} e^{i \mathbf{k} \cdot \mathbf{r}} \int \psi_i^*(\mathbf{r} - \mathbf{r}_i) v(\mathbf{r} - \mathbf{r}_i) \psi_t(\mathbf{r}) d^3 r \]

for diamond, zinc-blend semiconductors, include 4 states: 1s, and 3p states on each atom \( \rightarrow 8 \times 8 \) Hamiltonian matrix

Bloch sums:

\[ \langle s | H | p \rangle, \quad \text{and} \quad \langle p_i | H | p_j \rangle \] matrix elements are related by symmetry for each site.

\[ \langle s^A | H | s^B \rangle = E_{ss} B_o(k) \]
\[ \langle p_x^A | H | p_x^B \rangle = \langle p_y^A | H | p_y^B \rangle = \langle p_z^A | H | p_z^B \rangle = E_{xx} B_o(k) \]

\[ \langle s^A | H | p_y^B \rangle = E_{sp}^A B_2(k) \]
\[ \langle s^A | H | p_z^B \rangle = E_{sp}^A B_3(k) \]

\[ \langle p_x^A | H | p_z^B \rangle = E_{xy} B_2(k) \]
\[ \langle p_y^A | H | p_z^B \rangle = E_{xy} B_1(k) \]

\[ \langle p_i^B | H | p_j^A \rangle = B_{ji}(k) E_{xy} \]
For the full zone calculation, we need to diagonalize an 8 x 8 system - 4 levels each on 2 atoms. The H matrix may be written

\[
H = \begin{bmatrix}
[E^A] & [AB] \\
[BA] & [E^B]
\end{bmatrix}
\]

\[
[BA] = [AB]^\dagger \equiv [AB]^T
\]

The 8 energy eigenvalues are found by:

\[
\begin{bmatrix}
\varepsilon_s & 0 & 0 & 0 \\
0 & \varepsilon_p & 0 & 0 \\
0 & 0 & \varepsilon_p & 0 \\
0 & 0 & 0 & \varepsilon_p
\end{bmatrix}
\]

diagonal

Different \([E^A], [E^B]\)

if \(A \neq B\) i.e. GaAs

\[
[AB] =
\begin{bmatrix}
E_{ss}B_0 & E_{sp}^AB_1 & E_{sp}^AB_2 & E_{sp}^AB_3 \\
-E_{sp}^AB_1 & E_{xx}B_0 & E_{xy}B_3 & E_{xy}B_2 \\
-E_{sp}^AB_2 & E_{xy}B_3 & E_{xx}B_0 & E_{xy}B_1 \\
-E_{sp}^AB_3 & E_{xy}B_2 & E_{xy}B_1 & E_{xx}B_0
\end{bmatrix}
\]

At \(k = 0\) (Γ point), consider the main band gap. By symmetry, the problem simplifies. All \(B_j = 0\), except \(B_0(k) = 4\). Only remaining interaction s - s and diagonal p - p. Separately diagonalize s - s and p - p energy matrices:

\[
\begin{vmatrix}
\varepsilon_s - E & 4E_{ss} \\
4E_{ss} & \varepsilon_s - E
\end{vmatrix} = 0
\]
Each have bonding (- sign) and antibonding (+ sign) states.

\[
E_s = \frac{\varepsilon_s^A + \varepsilon_s^B}{2} \pm \sqrt{\left(\frac{\varepsilon_s^A - \varepsilon_s^B}{2}\right)^2 + 16E_{ss}^2}
\]

\[
E_p = \frac{\varepsilon_p^A + \varepsilon_p^B}{2} \pm \sqrt{\left(\frac{\varepsilon_p^A - \varepsilon_p^B}{2}\right)^2 + 16E_{xx}^2}
\]

usual order

\[\begin{align*}
E_p^+ & \quad E_s^+ \\
E_s^- & \quad E_p^- \\
\text{Bottom of CB} & \quad \text{s-like} \\
\text{Top of VB} & \quad \text{p-like}
\end{align*}\]
Review

Periodic potential: 

Bloch function \( \Psi_k(\mathbf{r}) = \left[ \sum_G C(k-G) e^{iG \cdot \mathbf{r}} \right] e^{ik \cdot \mathbf{r}} \)

Central equation \( \left( \frac{\hbar^2 k^2}{2m} - E \right) C(k) + \sum_G U_G C(k-G) = 0 \)

Band Gaps arise at zone boundaries: Bragg diffraction

Main problem is to find self-consistent \( V(\mathbf{r}) \) and solve many-body problem.

LCAO method: work from free atom states consider near-neighbors.

Example Bandstructure Diagrams

Free electron bands in the empty diamond lattice
Figure 8.10: Energy bands of Si, Ge, GaAs, and InSb in subfigures (A)–(D), respectively, as calculated with empirical nonlocal pseudopotentials. Energy scale in eV (after Chelikowsky and Cohen, 1976).