Empirical Pseudopotential Method

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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:

\[
\left( \frac{\hbar^2}{2m} \nabla^2 + E \right) \varphi(r) = 0
\]

The solutions form the basis of plane waves:

\[
\varphi_k(r) = C_k e^{ik \cdot r}
\]

with:

\[
k^2 = k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2}
\]
The velocity, \( \mathbf{v} \), of a particle represented by a wave packet centered around the crystal momentum, \( \mathbf{k} \), is obtained from the dispersion relation between \( \mathbf{k} \) and the energy \( E \) as

\[
E_k = \frac{\hbar^2 k^2}{2m} \quad \therefore \quad \mathbf{v} = \left\langle \frac{\hbar}{i} \nabla \right\rangle = \frac{1}{\hbar} \nabla_k E_k = \frac{\hbar \mathbf{k}}{m}
\]

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

\[
\varphi_k(x, y, z) = \varphi_k(x + L, y + L, z + L); \quad V = L^3
\]

\[
k_x = \frac{2\pi}{L} n_x, \quad k_y = \frac{2\pi}{L} n_y, \quad k_z = \frac{2\pi}{L} n_z; \quad n_{x,y,z} = 0, \pm 1, \pm 2, \ldots
\]

Thus, \( \mathbf{k} \), takes on discrete values, with a volume per cell in \( \mathbf{k} \)-space of

\[
V_K = \frac{8\pi^3}{V}
\]

Normalization of the wavefunction in the volume \( V \) requires:

\[
\int d\mathbf{r} \varphi_k^*(\mathbf{r}) \varphi_k(\mathbf{r}) = \delta_{k,k'}
\]

\[
\therefore \quad \varphi_k(\mathbf{r}) = V^{1/2} e^{i\mathbf{k} \cdot \mathbf{r}}
\]

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

\[
D(E)dE = \frac{2m^{3/2} E^{1/2}}{\sqrt{2\pi^2 \hbar^3}} dE = \frac{(2)V}{8\pi^3} dk
\]

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 macroscopic systems, summations over \( k \) may be replaced by the coarse grain integral:

\[
\sum_k \rightarrow \frac{V}{8\pi^3} \int dk
\]
B. Bloch Functions and Reciprocal Space

Translational symmetry in a crystal implies that

\[ V_l(r) = V_l(r + a); \quad a = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3 \]

where \( l, m, n \) 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

\[ \varphi_{n,k}(r) = e^{ikr}u_{n,k}(r); \quad u_{n,k}(r) = u_{n,k}(r + a) \]

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

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

Reciprocal Space

For a 1D periodic function: \( f(x) = f(x + l); \quad l = na \)

We may expand it in a Fourier series

\[ f(x) = \sum_n A_n e^{i2\pi nx/a} = \sum_g A_g e^{i2\pi x/a} = \sum_g A_g e^{igx}; \quad g = \frac{2\pi n}{a} \]

The Fourier components are defined on a discrete set of periodically arranged points (analogy: frequencies) in a reciprocal space to coordinate space.

3D Generalization

\[ u_{n,k}(r) = \sum_G f_G^n(k)e^{iG \cdot r}; \quad G = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \]

\( G \perp a \) where \( hkl \) are integers. \( G = \) Reciprocal lattice vector
Due to the periodicity requirement of cell-periodic part

\[ u_{n,k}(r) = u_{n,k}(r + a) ; \quad e^{iG \cdot (r + a)} = e^{iG \cdot r} e^{i2\pi n} = e^{iG \cdot r} \]

The basis vectors of reciprocal space are given by

\[ b_1 = \frac{2\pi a_1 \times a_3}{a_1 \cdot a_2 \times a_3} ; \quad b_2 = \frac{2\pi a_1 \times a_1}{a_1 \cdot a_2 \times a_3} ; \quad b_3 = \frac{2\pi a_1 \times a_2}{a_1 \cdot a_2 \times a_3} \]

The total Bloch function may be expanded as

\[ \varphi_{n,k}(r) = e^{ik \cdot r} \sum_{G} f_{G}^{n}(k)e^{iG \cdot r} = \left| n, k \right> \]

With associated properties:

\[ \varphi_{n,k+G}(r) = \varphi_{n,k}(r) \]
\[ E_{n,k+G} = E_{n,k} \]

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**C. Band Structure in Diamond (IV) and Zinc-Blende (III-V) Crystals**

- Tetrahedral coordination (sp³ orbitals)
- Interpenetrating FCC lattices (1/4 1/4 1/4)
- 2 atom basis
- Diamond Structure (Si, Ge)- Same atom in basis (inversion symmetry)
- Zinc-Blende (GaAs, InP)- Opposite atoms form basis, partially ionic bonding
The periodic set of allowed points corresponding to the Fourier (reciprocal) space associated with the real (space) lattice form a periodic lattice.

- The \textit{Wigner-Seitz} unit cell corresponding to the reciprocal lattice is the First Brillouin Zone.

- \textit{\Gamma} is zone center, \textit{L} is on zone face in (111) direction, \textit{X} is on face in (100) direction.

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

Empirical Pseudopotential Method

- Popular, straightforward technique for calculating the bandstructure in semiconductors is the \textit{empirical pseudopotential method} (EPM).\textsuperscript{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.


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 \( r_b/2\).

\[
r_b = a_o \left( \frac{1}{4} \frac{1}{4} \frac{1}{4} \right)
\]

The Hamiltonian is of the form:

\[
H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})
\]

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

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)

Expand:

\[
V(\mathbf{r}) = \sum_G V(G)e^{iG\cdot\mathbf{r}}; \quad G = hb_1 + kb_2 + lb_3
\]

The Fourier coefficient is:

\[
V(G) = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} V(\mathbf{r})e^{-iG\cdot\mathbf{r}}
\]

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 portions

\[
= \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} \left[ V_1 \left( \mathbf{r} + \frac{r_b}{2} \right) + V_2 \left( \mathbf{r} - \frac{r_b}{2} \right) \right] e^{-iG\cdot\mathbf{r}}
\]

where \( V_1 \) and \( V_2 \) represent the atomic-like potentials centered at \( \pm r_b/2 \) (pseudopotentials which are smooth compared to the actual rapidly varying core potential)
(a) Constant effective potential in the core region:

\[ V(r) = \begin{cases} 
-\frac{Z e^2}{4 \pi \epsilon_0} r & r > r_C \\
-\frac{Z e^2}{4 \pi \epsilon_0} & r \leq r_C 
\end{cases} \]

(b) Empty core model:

\[ V(r) = \begin{cases} 
-\frac{Z e^2}{4 \pi \epsilon_0} r & r > r_C \\
0 & r \leq r_C 
\end{cases} \]

(c) Model potential due to Heine and Aharenkov:

\[ V(r) = \begin{cases} 
-\frac{Z e^2}{4 \pi \epsilon_0} r & r > r_C \\
A & r \leq r_C 
\end{cases} \]

(d) Lin and Kleinman model potentials:

\[ V(r) = \begin{cases} 
-\frac{Z e^2}{4 \pi \epsilon_0} \exp[-\beta(r-r_C)] & r > r_C \\
0 & r \leq r_C 
\end{cases} \]

Using the displacement property of Fourier series

\[ V(\mathbf{r}) = \sum_G \left( e^{i \mathbf{G} \cdot \mathbf{r}_b / 2} V_1(\mathbf{G}) + e^{-i \mathbf{G} \cdot \mathbf{r}_b / 2} V_2(\mathbf{G}) \right) e^{i \mathbf{G} \cdot \mathbf{r}} \]

Split into symmetric and anti-symmetric parts

\[ = \sum_G \left( e^{i \mathbf{G} \cdot \mathbf{r}_b / 2} \left[ \frac{V_1}{2} + \frac{V_1}{2} \right] + e^{-i \mathbf{G} \cdot \mathbf{r}_b / 2} \left[ \frac{V_1}{2} - \frac{V_1}{2} \right] \right) e^{i \mathbf{G} \cdot \mathbf{r}} \]

\[ + \sum_G \left( e^{i \mathbf{G} \cdot \mathbf{r}_b / 2} \left[ \frac{V_2}{2} - \frac{V_2}{2} \right] + e^{-i \mathbf{G} \cdot \mathbf{r}_b / 2} \left[ \frac{V_2}{2} + \frac{V_2}{2} \right] \right) e^{i \mathbf{G} \cdot \mathbf{r}} \]

\[ = \sum_G \left( \cos \left( \frac{\mathbf{G} \cdot \mathbf{r}_b}{2} \right) V_1(\mathbf{G}) + i \sin \left( \frac{\mathbf{G} \cdot \mathbf{r}_b}{2} \right) V_1(\mathbf{G}) \right) e^{i \mathbf{G} \cdot \mathbf{r}} \]

\[ + \sum_G \left( \cos \left( \frac{\mathbf{G} \cdot \mathbf{r}_b}{2} \right) V_2(\mathbf{G}) - i \sin \left( \frac{\mathbf{G} \cdot \mathbf{r}_b}{2} \right) V_2(\mathbf{G}) \right) e^{i \mathbf{G} \cdot \mathbf{r}} \]
For covalent materials, $V_1=V_2$ so that $V_a=0$

Recall the expansion of the wavefunction in Bloch states:

$$\psi_{n,k}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \psi_{n,k}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} U_{G}^{n}(\mathbf{k}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

Set of simultaneous equations for $U(\mathbf{G})$
*In the empirical method, the form factors, \(V(G)\), for discrete values of \(G\) are treated as adjustable constants which are tabulated. Assuming the series converges, only the first few terms are important.

Must specify possible values of \(G\)

For the FCC real lattice, the reciprocal lattice is the BCC lattice with primitive unit vectors

\[
\mathbf{b}_1 = \frac{2\pi}{a_0} (\hat{x} + \hat{y} + \hat{z})
\]

\[
\mathbf{b}_2 = \frac{2\pi}{a_0} (-\hat{x} + \hat{y} + \hat{z})
\]

\[
\mathbf{b}_3 = \frac{2\pi}{a_0} (\hat{x} - \hat{y} + \hat{z})
\]

Reciprocal Vectors

In terms of the unit Cartesian vectors, nearest neighbor sites in reciprocal space correspond to

| \(G\) group \(\text{(units } 2\pi/a_0)\) | # permutations | Total number of elements | \(|G|^2 \text{ (} 2\pi/a_0)^2\text{) 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 \(G^2=11\).
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>
<thead>
<tr>
<th>Material</th>
<th>$V_{k^0}$</th>
<th>$V_{k^0}$</th>
<th>$V_{k^1}$</th>
<th>$V_{k^2}$</th>
<th>$V_{k^3}$</th>
<th>$V_{k^4}$</th>
<th>$V_{k^5}$</th>
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<tr>
<td>Si</td>
<td>-0.21</td>
<td>+0.04</td>
<td>+0.08</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Ge</td>
<td>-0.23</td>
<td>+0.01</td>
<td>+0.06</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Sn</td>
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<td>0.00</td>
<td>+0.04</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GaP</td>
<td>-0.22</td>
<td>+0.03</td>
<td>+0.07</td>
<td>-0.12</td>
<td>+0.07</td>
<td>+0.02</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>-0.23</td>
<td>+0.01</td>
<td>+0.06</td>
<td>+0.07</td>
<td>+0.05</td>
<td>+0.01</td>
<td></td>
</tr>
<tr>
<td>AlSb</td>
<td>-0.21</td>
<td>+0.02</td>
<td>+0.05</td>
<td>+0.05</td>
<td>+0.04</td>
<td>+0.02</td>
<td></td>
</tr>
<tr>
<td>InP</td>
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<td>+0.01</td>
<td>+0.06</td>
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<td>+0.05</td>
<td>+0.01</td>
<td></td>
</tr>
<tr>
<td>GeSb</td>
<td>-0.22</td>
<td>0.00</td>
<td>+0.05</td>
<td>-0.05</td>
<td>+0.05</td>
<td>+0.01</td>
<td></td>
</tr>
<tr>
<td>InAs</td>
<td>-0.22</td>
<td>0.00</td>
<td>+0.05</td>
<td>+0.08</td>
<td>+0.05</td>
<td>+0.03</td>
<td></td>
</tr>
<tr>
<td>InSb</td>
<td>-0.23</td>
<td>0.00</td>
<td>+0.04</td>
<td>+0.06</td>
<td>+0.05</td>
<td>+0.01</td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>-0.22</td>
<td>+0.03</td>
<td>+0.07</td>
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<td>+0.18</td>
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<tr>
<td>ZnSe</td>
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<td>+0.06</td>
<td>-0.18</td>
<td>+0.12</td>
<td>+0.03</td>
<td></td>
</tr>
<tr>
<td>ZnTe</td>
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<td>0.00</td>
<td>+0.05</td>
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<td>+0.04</td>
<td>+0.15</td>
<td>+0.09</td>
<td>+0.04</td>
<td></td>
</tr>
</tbody>
</table>

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

$$\mathbf{H} \cdot \mathbf{U} = \mathbf{E} \mathbf{U}$$

where $\mathbf{H}$ is an 89x89 array, $\mathbf{U}$ is an 89 element column vector representing the eigenvectors, and $\mathbf{E}$ 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.
Sample Simulation Results

Silicon

Germanium