

Computational Electronics

Empirical Pseudopotential Method

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The Empirical Pseudopotential Method

The concept of pseudopotentials was introduced by Fermi [1] to study high-lying atomic states. Afterwards, Hellman proposed that pseudopotentials be used for calculating the energy levels of the alkali metals [2]. The wide spread usage of pseudopotentials did not occur until the late 1950s, when activity in the area of condensed matter physics began to accelerate. The main advantage of using pseudopotentials is that only valence electrons have to be considered. The core electrons are treated as if they are frozen in an atomic-like configuration. As a result, the valence electrons are thought to move in a weak one-electron potential.

The pseudopotential method is based on the orthogonalized plane wave (OPW) method due to Herring. In this method, the crystal wavefunction $\psi_{\mathbf{k}}$ is constructed to be orthogonal to the core states. This is accomplished by expanding $\psi_{\mathbf{k}}$ as a smooth part of symmetrized combinations of Bloch functions $\varphi_{\mathbf{k}}$, augmented with a linear combination of core states. This is expressed as

$$\psi_{\mathbf{k}} = \varphi_{\mathbf{k}} + \sum_t b_{\mathbf{k},t} \Phi_{\mathbf{k},t} , \quad (1)$$

where $b_{\mathbf{k},t}$ are orthogonalization coefficients and $\Phi_{\mathbf{k},t}$ are core wave functions. For Si-14, the summation over t in Eq. (1) is a sum over the core states $1s^2 2s^2 2p^6$. Since the crystal wave function is constructed to be orthogonal to the core wave functions, the orthogonalization coefficients can be calculated, thus yielding the final expression

$$\psi_{\mathbf{k}} = \varphi_{\mathbf{k}} - \sum_t \langle \Phi_{\mathbf{k},t} | \varphi_{\mathbf{k}} \rangle \Phi_{\mathbf{k},t} . \quad (2)$$

To obtain a wave equation for $\varphi_{\mathbf{k}}$, the Hamiltonian operator

$$H = \frac{p^2}{2m} + V_C , \quad (3)$$

is applied to Eq. (2), where V_C is the attractive core potential, and the following wave equation results

$$\left(\frac{p^2}{2m} + V_C + V_R \right) \varphi_{\mathbf{k}} = E \varphi_{\mathbf{k}}, \quad (3)$$

where V_R represents a short-range, non-Hermitian repulsion potential, of the form

$$V_R = \sum_t \frac{(E - E_t) \langle \Phi_{\mathbf{k},t} | \varphi_{\mathbf{k}} \rangle \Phi_{\mathbf{k},t}}{\varphi_{\mathbf{k}}}. \quad (4)$$

E_t in Eq. (5) represents the atomic energy eigenvalue, and the summation over t represents a summation over the core states. The result given in Eq. (4) can be thought of as wave equation for the pseudo-wave function, $\varphi_{\mathbf{k}}$, but the energy eigenvalue E corresponds to the true energy of the crystal wave function $\psi_{\mathbf{k}}$. Furthermore, as a result of the orthogonalization procedure, the repulsive potential V_R , which serves to cancel the attractive potential V_C , is introduced into the pseudo-wave-function Hamiltonian. The result is a smoothly varying pseudopotential $V_p = V_C + V_R$. This result is known as the Phillips-Kleinman cancellation theorem [3] which provides justification why the electronic structure of strongly-bound valence electrons can be described using a nearly-free electron model and weak potentials.

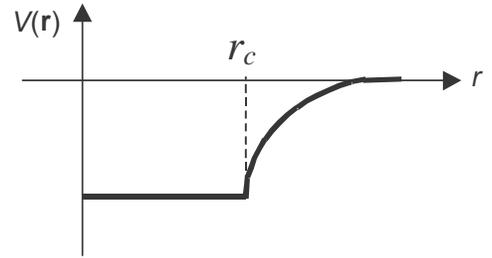
To simplify the problem further, model pseudopotentials are used in place of the actual pseudopotential. Figure 1 summarizes the various models employed. Note that the 3D Fourier transforms (for bulk systems) of each of the above-described model potentials are of the following general form

$$V(q) \sim \frac{Ze^2}{\epsilon_0 q^2} \cos(qr_c). \quad (5)$$

This q -dependent pseudopotential is then used to calculate the energy band structure along different crystallographic directions, using the procedure outlined in the following section.

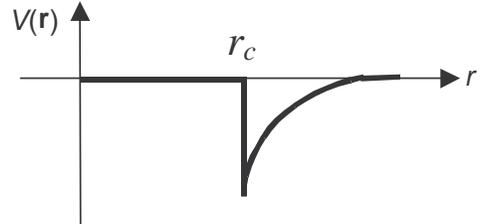
(a) Constant effective potential in the core region:

$$V(r) = \begin{cases} \frac{-Ze^2}{4\pi\epsilon_0 r}; & r > r_C \\ \frac{-Ze^2}{4\pi\epsilon_0 r_C}; & r \leq r_C \end{cases}$$



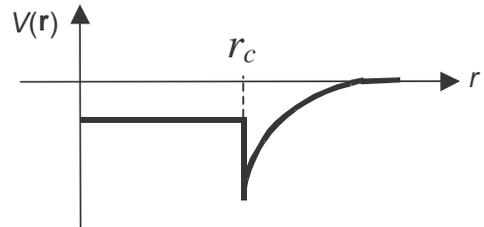
(b) Empty core model:

$$V(r) = \begin{cases} \frac{-Ze^2}{4\pi\epsilon_0 r}; & r > r_C \\ 0; & r \leq r_C \end{cases}$$



(c) Model potential due to Heine and Abarenkov:

$$V(r) = \begin{cases} \frac{-Ze^2}{4\pi\epsilon_0 r}; & r > r_C \\ A; & r \leq r_C \end{cases}$$



(d) Lin and Kleinman model potentials:

$$V(r) = \begin{cases} 2 \frac{-Ze^2}{4\pi\epsilon_0 r} \{1 - \exp[-\beta(r - r_C)]\}; & r > r_C \\ 0; & r \leq r_C \end{cases}$$

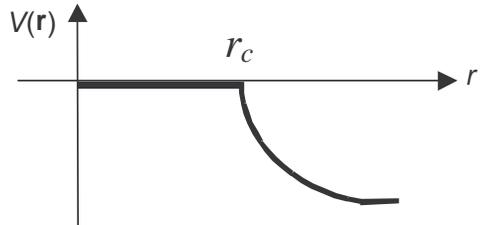


Figure 1. Various model potentials.

Description of the Empirical Pseudopotential Method

Recall from the previous section that the Phillips-Kleinman cancellation theorem provides a means for the energy band problem to be simplified into a one-electron-like problem. For this purpose, Eq. (4) can be re-written as

$$\left(\frac{p^2}{2m} + V_p \right) \phi_{\mathbf{k}} = E \phi_{\mathbf{k}} , \quad (6)$$

where V_p is the smoothly varying crystal pseudopotential. In general, V_p is a linear combination of atomic potentials, V_a , which can be expressed as summation over lattice translation vectors \mathbf{R} and atomic basis vectors $\boldsymbol{\tau}$ to arrive at the following expression

$$V_p(\mathbf{r}) = \sum_{\mathbf{R}} \sum_{\boldsymbol{\tau}} V_a(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}) . \quad (7)$$

To simplify further, the inner summation over $\boldsymbol{\tau}$ can be expressed as the total potential, V_0 , in the unit cell located at \mathbf{R} . Eq. (8) then becomes

$$V_p(\mathbf{r}) = \sum_{\mathbf{R}} V_0(\mathbf{r} - \mathbf{R}) . \quad (8)$$

Because the crystal potential is periodic, the pseudopotential is also a periodic function and can be expanded into a Fourier series over the reciprocal lattice to obtain

$$V_p(\mathbf{r}) = \sum_{\mathbf{G}} V_0(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} , \quad (9)$$

where the expansion coefficient is given by

$$V_0(\mathbf{G}) = \frac{1}{\Omega} \int d^3r V_0(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} , \quad (10)$$

and Ω is the volume of the unit cell.

To apply this formalism to the zincblende lattice, it is convenient to choose a two-atom basis centered at the origin ($\mathbf{R} = 0$). If the atomic basis vectors are given by $\boldsymbol{\tau}_1 = \boldsymbol{\tau} = -\boldsymbol{\tau}_2$, where $\boldsymbol{\tau}$, the atomic basis vector, is defined in terms of the lattice constant a_0 as $\boldsymbol{\tau} = a_0(1/8, 1/8, 1/8)$, $V_0(\mathbf{r})$ can be expressed as

$$V_0(\mathbf{r}) = V_1(\mathbf{r} - \boldsymbol{\tau}) + V_2(\mathbf{r} + \boldsymbol{\tau}) , \quad (11)$$

where V_1 and V_2 are the atomic potentials of the cation and anion. Substituting Eq. (12) into Eq. (11), and using the displacement property of Fourier transforms, $V_0(\mathbf{r})$ can be recast as

$$V_0(\mathbf{G}) = e^{i\mathbf{G}\cdot\boldsymbol{\tau}} V_1(\mathbf{G}) + e^{-i\mathbf{G}\cdot\boldsymbol{\tau}} V_2(\mathbf{G}) . \quad (12)$$

Writing the Fourier coefficients of the atomic potentials in terms of symmetric ($V_s(\mathbf{G}) = V_1 + V_2$) and antisymmetric ($V_a(\mathbf{G}) = V_1 - V_2$) form factors, $V_0(\mathbf{G})$ is given by

$$V_0(\mathbf{G}) = \cos(\mathbf{G} \cdot \boldsymbol{\tau})V_S(\mathbf{G}) + i \sin(\mathbf{G} \cdot \boldsymbol{\tau})V_A(\mathbf{G}) , \quad (13)$$

where the prefactors are referred to as the symmetric and antisymmetric structure factors. The form factors above are treated as adjustable parameters that can be fit to experimental data, hence the name empirical pseudopotential method. For diamond-lattice materials, with two identical atoms per unit cell, the $V_A=0$ and the structure factor is simply $\cos(\mathbf{G} \cdot \boldsymbol{\tau})$. For zinc-blende lattice, like the one in GaAs material system, $V_A \neq 0$ and the structure factor is more complicated.

Now with the potential energy term specified, the next task is to recast the Schrödinger equation in a matrix form. Recall that the solution to the Schrödinger wave equation in a periodic lattice is a Bloch function, which is composed of a plane wave component and a cell periodic part that has the periodicity of the lattice, i.e.

$$\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{G}'} U(\mathbf{G}') e^{i\mathbf{G}' \cdot \mathbf{r}} . \quad (14)$$

By expanding the cell periodic part $u_{\mathbf{k}}(\mathbf{r})$ of the Bloch function appearing in Eq. (15) into Fourier components, and substituting the pseudo-wave function $\varphi_{\mathbf{k}}$ and potential V_0 into the Schrödinger wave equation, the following matrix equation results

$$\sum_{\mathbf{G}} \left\{ \left[\frac{\hbar^2 (\mathbf{k} + \mathbf{G})^2}{2m} - E \right] U(\mathbf{G}) + \sum_{\mathbf{G}'} V_0(\mathbf{G} - \mathbf{G}') U(\mathbf{G}') \right\} = 0 . \quad (15)$$

The expression given in Eq. (16) is zero when each term in the sum is identically zero, which implies the following condition

$$\left[\frac{\hbar^2 (\mathbf{k} + \mathbf{G})^2}{2m} - E \right] U(\mathbf{G}) + \sum_{\mathbf{G}'} V_0(\mathbf{G} - \mathbf{G}') U(\mathbf{G}') = 0 . \quad (16)$$

In this way, the band structure calculation is reduced to solving the eigenvalue problem specified by Eq. (17) for the energy E . As obvious from Eq. (15), $U(\mathbf{G}')$ is the Fourier component of the cell periodic part of the Bloch function. The number of reciprocal lattice vectors used determines both the matrix size and calculation accuracy.

The eigenvalue problem of Eq. (17) can be written in the more familiar form $\mathbf{H}\mathbf{U} = E\mathbf{U}$, where \mathbf{H} is a matrix, \mathbf{U} is a column vector representing the eigenvectors, and E is the energy

eigenvalue corresponding to its respective eigenvector. For the diamond lattice, the diagonal matrix elements of \mathbf{H} are then given by

$$H_{i,j} = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}_i|^2, \quad (17)$$

for $i = j$, and the off-diagonal matrix elements of \mathbf{H} are given by

$$H_{i,j} = V_s(\mathbf{G}_i - \mathbf{G}_j) \cos[(\mathbf{G}_i - \mathbf{G}_j) \cdot \boldsymbol{\tau}], \quad (18)$$

for $i \neq j$. Note that the term $V_s(0)$ is neglected in arriving at Eq. (19), because it will only give a rigid shift in energy to the bands. The solution to the energy eigenvalues and corresponding eigenvectors can then be found by diagonalizing matrix \mathbf{H} .

Implementation of the Empirical Pseudopotential Method for Si and Ge

For a typical semiconductor system, 137 plane waves are sufficient, each corresponding to vectors in the reciprocal lattice, to expand the pseudopotential. The reciprocal lattice of a face-centered cubic (FCC), i.e. diamond or zinc-blende structure, is a body-centered cubic (BCC) structure. Reciprocal lattice vectors up to and including the 10th-nearest neighbor from the origin are usually considered which results in 137 plane waves for the zinc-blende structure. The square of the distance from the origin to each equivalent set of reciprocal lattice sites is an integer in the set $|\mathbf{G}^2| = 0, 3, 4, 8, 11, 12, \dots$ where $|\mathbf{G}^2|$ is expressed in units of $(2\pi/a_0)^2$. Note that the argument of the pseudopotential term V_s in Eq. (19) is the difference between reciprocal lattice vectors. It can be shown that the square of the difference between reciprocal lattice vectors will also form the set of integers previously described. This means that V_s is only needed at discrete points corresponding to nearest-neighbor sites. The pseudopotential, on the other hand, is a continuous quantity. Therefore, its Fourier transform $V_s(q)$ is also a continuous function (see Figure 2). The points corresponding to the first three nearest neighbors are also indicated on this figure.

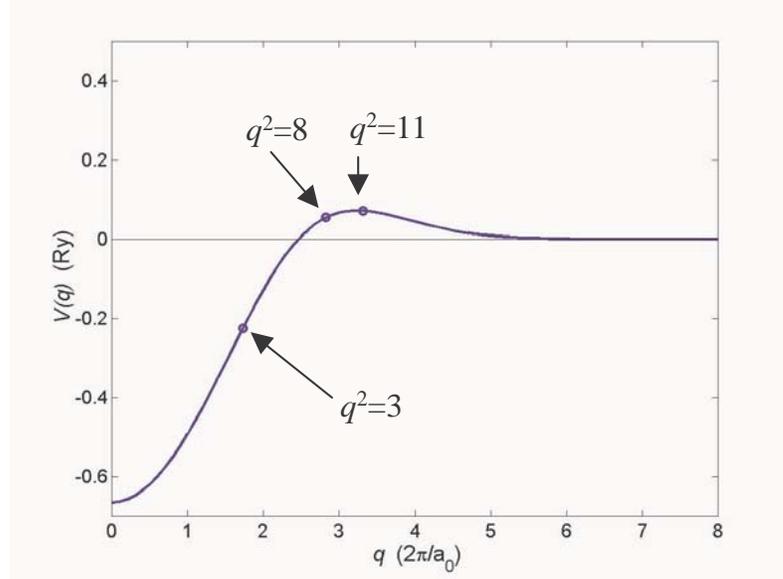


Figure 0. Fourier transform of the pseudopotential. (Note that $q = |\mathbf{G} - \mathbf{G}'|$).

Recall that the pseudopotential is only needed at a few discrete points along the $V(q)$ curve. The discrete points correspond to the q^2 -values that match the integer set described previously. There is some controversy, however, regarding the value of V_s as q vanishes. There are two common values seen in the literature: $V_1(0) = -3/2E_F$ and $V_1(0) = 0$. In most cases, the term $V_s(0)$ is ignored because it only gives a rigid shift in energy to the bands. The remaining form factors needed to compute the band structure for non-polar materials correspond to $q^2 = 3, 8,$ and 11 . For $q^2 = 4$, the cosine term in Eq. (19) will always vanish. Furthermore, for values of q^2 greater than 11 , $V(q)$ quickly approaches zero. This comes from the fact that the pseudopotential is a smoothly varying function, and only few plane waves are needed to represent it. If a function is rapidly varying in space, then many more plane waves would be required. Another advantage of the empirical pseudopotential method is that only three parameters are needed to describe the band structure of non-polar materials.

Table 1: Local Pseudopotential Form Factors.

Form Factor (Ry)	Si	Ge
V_3	-0.2241	-0.2768
V_8	0.0551	0.0582

V_{11}	0.0724	0.0152
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Using the form factors listed in **Table 1**, where the Si form factors are taken from [4] and the Ge form factors are taken from [5], the band structures for Si and Ge are plotted in Figure 3 [6]. Note that spin-orbit interaction is not included in these simulations. The lattice constants specified for Si and Ge are 5.43\AA and 5.65\AA , respectively. Si is an indirect band gap semiconductor. Its primary gap, i.e. minimum gap, is calculated from the valence band maximum at the Γ -point to the conduction band minimum along the Δ direction, 85% of the distance from Γ to X. The band gap of Si is calculated to be $E_g^{Si} = 1.08$ eV, in agreement with experimental findings. Ge is also an indirect band gap semiconductor. Its band gap is defined from the top of the valence band at Γ to the conduction band minimum at L. The band gap of Ge is calculated to be $E_g^{Ge} = 0.73$ eV. The direct gap, which is defined from the valence band maximum at Γ to the conduction band minimum at Γ , is calculated to be 3.27 eV and 0.82 eV for Si and Ge, respectively. Note that the curvature of the top valence band of Ge is larger than that of Si. This corresponds to the fact that the effective hole mass of Si is larger than that of Ge. Note that the inclusion of the spin-orbit interaction will lift the triple degeneracy of the bands at the Γ point, leaving doubly-degenerate heavy and light-hole bands and a split-off band moved downward in energy by few 10's of meV (depending upon the material under consideration).

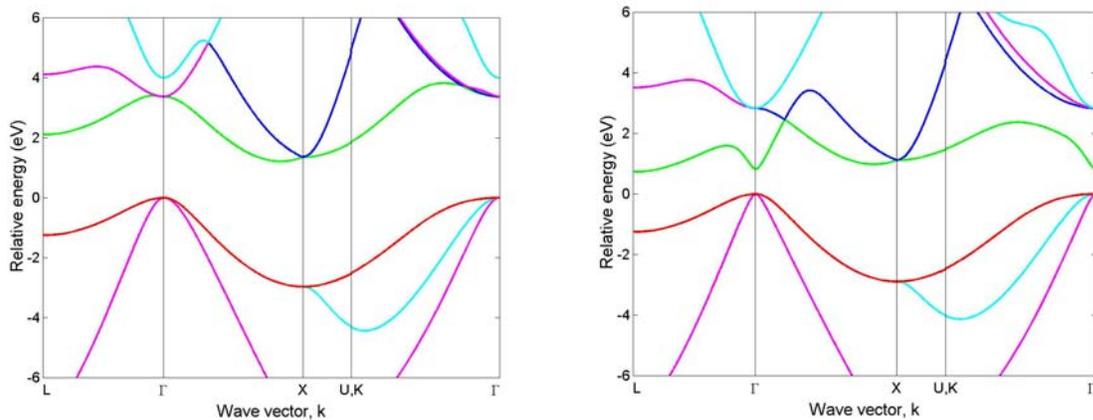


Figure 2. Left panel: band structures of silicon. Right panel: band structure of germanium.

In summary, the local empirical pseudopotential method described in this section is rather good for an accurate description of the optical gaps. However, as noted by Chelikowsky and

Cohen [7], when these local calculations are extended to yield the valence-band electronic density of states, the results obtained are far from satisfactory. The reason for this discrepancy arises from the omission of the low cores in the derivation of the pseudopotential in the previous section. This, as previously noted, allowed the usage of a simple plane wave basis. To correct for the errors introduced, an energy-dependent non-local correction term is added to the local atomic potential. This increases the number of parameters needed but leads to better convergence and more exact band-structure results [8,9].

References

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