Cohen and Bergstresser empirical pseudopotentials

Andrea Dal Corso

International School for Advanced Studies (SISSA),

Via Bonomea 265, 34136, Trieste, Italy and

IOM - CNR, Via Bonomea 265, 34136, Trieste, Italy

(Dated: October 30, 2026)

Abstract

These notes extend the previous code developed for the free-electron model to incorporate a local pseudopotential accounting for ionic and core-electron effects. Comprehensive details are provided for calculating the electronic band structures of diamond, silicon, tin, and selected III-V and II-VI semiconductors.

I. PLANE WAVES SOLUTION OF THE ELECTRONIC PROBLEM

We can now return to our Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi_{\mathbf{k}v}(\mathbf{r}) = \epsilon_{\mathbf{k}v}\psi_{\mathbf{k}v}(\mathbf{r}), \tag{1}$$

for a generic potential possessing the periodicity of the Bravais lattice $V(\mathbf{r}+\mathbf{R}_\mu) = V(\mathbf{r})$. We attempt to expand the Bloch functions in plane waves. Since $\psi_{\mathbf{k}v}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{k}v}(\mathbf{r})$ with $u_{\mathbf{k}v}(\mathbf{r}+\mathbf{R}_\mu) = u_{\mathbf{k}v}(\mathbf{r})$ being periodic with respect to the Bravais lattice, the function $u_{\mathbf{k}v}(\mathbf{r})$ can be expanded in plane waves $f_{\mathbf{G}}(\mathbf{r})$. Therefore,

$$\psi_{\mathbf{k}v}(\mathbf{r}) = \frac{1}{\sqrt{V}}\sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}v}e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}. \tag{2}$$

Substituting this equation into Eq. 1, we obtain an equation for the expansion coefficients $c_{\mathbf{k}+\mathbf{G}v}$:

$$\sum_{\mathbf{G}'}\left[\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2\delta_{\mathbf{G}\mathbf{G}'} + V(\mathbf{G}-\mathbf{G}')\right]c_{\mathbf{k}+\mathbf{G}'v} = \epsilon_{\mathbf{k}v}c_{\mathbf{k}+\mathbf{G}v}, \tag{3}$$

where

$$V(\mathbf{G}) = \frac{1}{\Omega}\int_\Omega d^3r V(\mathbf{r})e^{-i\mathbf{G}\mathbf{r}} \tag{4}$$

is the Fourier transform of the periodic potential.

This is an algebraic eigenvalue equation, but the size of the matrix (the number of $\mathbf{G}$ vectors) is infinite. We could solve it using standard linear algebra techniques if we could make the matrix size finite. As we did for the free-electron case, we could choose a cut-off energy E_{cut} and restrict the $\mathbf{G}$ vectors to those satisfying

$$\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 < E_{cut}. \tag{5}$$

As in the free-electron case, we express $\mathbf{k}$ and $\mathbf{G}$ in units of $\frac{2\pi}{a}$ and write this equation as

$$\frac{\hbar^2}{2ma_B^2}\left(\frac{2\pi}{\bar{a}}\right)^2|\mathbf{k}+\mathbf{G}|^2 < E_{cut}, \tag{6}$$

or

$$\frac{E_H}{2}\left(\frac{2\pi}{\bar{a}}\right)^2|\mathbf{k}+\mathbf{G}|^2 < E_{cut}, \tag{7}$$

so if we express E_{cut} in Rydberg we obtain the equation

$$\left(\frac{2\pi}{\bar{a}}\right)^2|\mathbf{k}+\mathbf{G}|^2 < E_{cut}. \tag{8}$$

This equation is usually written

$$|\mathbf{k}+\mathbf{G}|^2 < E_{cut}. \tag{9}$$

with $|\mathbf{k}+\mathbf{G}|^2$ expressed in $\frac{1}{a_B}$.

We can also estimate how the number of $\mathbf{G}$ vectors increases with the cut-off. A sphere of radius $\sqrt{E_{cut}}$ has a volume in reciprocal space of $\frac{4\pi}{3}\left(E_{cut}\right)^{\frac{3}{2}}$, while each $\mathbf{G}$ vector occupies a volume equal to that of the Brillouin zone $\frac{(2\pi)^3}{\Omega}$. The number of $\mathbf{G}$ vectors is therefore

$$N_{\mathbf{G}} = \frac{4\pi}{3}\left(E_{cut}\right)^{3/2}\frac{\Omega}{(2\pi)^3}. \tag{10}$$

It is proportional to the volume and to the cut-off energy raised to the power of 1.5.

II. THE EMPIRICAL PSEUDOPOTENTIALS

We now assume that the potential can be written as a sum of terms centered on each atom. Moreover, we assume that the potential is spherically symmetric about each atom:

$$V(\mathbf{r}) = \sum_{\mu s} v^s(|\mathbf{r} - \mathbf{R}_\mu - \mathbf{d}_s|). \tag{11}$$

The Fourier transform of the potential is given by:

$$V(\mathbf{G}) = \frac{1}{\Omega} \int_\Omega d^3r \sum_{\mu s} v^s(|\mathbf{r} - \mathbf{R}_\mu - \mathbf{d}_s|) e^{-i\mathbf{G}\mathbf{r}}. \tag{12}$$

By exploiting the periodicity of the potential, we can integrate over the entire volume V. Changing variables in the integral via $\mathbf{r}' = \mathbf{r} - \mathbf{R}_\mu - \mathbf{d}_s$, we obtain:

$$V(\mathbf{G}) = \frac{1}{V} \int_V d^3r' \sum_{\mu s} v^s(|\mathbf{r}'|) e^{-i\mathbf{G}\mathbf{r}'} e^{-i\mathbf{G}\mathbf{R}_\mu} e^{-i\mathbf{G}\mathbf{d}_s}. \tag{13}$$

By definition of the reciprocal lattice vectors, $e^{-i\mathbf{G}\mathbf{R}\mu} = 1$, and the sum over μ yields N, the number of unit cells. The final result is:

$$V(\mathbf{G}) = \sum_s e^{-i\mathbf{G}\mathbf{d}_s} \frac{1}{\Omega} \int_V d^3r' v^s(|\mathbf{r}'|) e^{-i\mathbf{G}\mathbf{r}'}. \tag{14}$$

The term

$$v^s(|\mathbf{G}|) = \frac{1}{\Omega} \int_V d^3r' v^s(|\mathbf{r}'|) e^{-i\mathbf{G}\mathbf{r}'}, \tag{15}$$

is known as the form factor of the potential and depends only on $|\mathbf{G}|$ if the potential is spherically symmetric. Regarding the sum over s, it is convenient to sum over all atomic species γ sharing the same form factor $v^s(|\mathbf{G}|) = v^\gamma(|\mathbf{G})|)$. We can write

$$V(\mathbf{G}) = \sum_\gamma v^\gamma(|\mathbf{G}|) S_\gamma(\mathbf{G}), \tag{16}$$

where $S_\gamma(\mathbf{G}) = \sum_{s\in\gamma} e^{-i\mathbf{G}\mathbf{d}_s}$ is known as the structure factor and depends on the positions of the atoms inside the unit cell.

III. COHEN AND BERGSTRESSER PSEUDOPOTENTIALS

Now suppose that we want to apply this general theory to a zincblende (or a diamond) crystal. This crystal structure possesses an fcc Bravais lattice and two atoms in the unit cell. It is convenient to choose the origin at the midpoint between the two atoms by setting $\mathbf{d}_1 = a(-1/8, -1/8, -1/8)$ and $\mathbf{d}_2 = a(1/8, 1/8, 1/8)$. Let us denote the atom at $\mathbf{d}_1$ as A and the atom at $\mathbf{d}_2$ as B. In this case, by using Euler's formula:

$$e^{-i\mathbf{G}\mathbf{d}_s} = \cos(\mathbf{G}\mathbf{d}_s) - i\sin(\mathbf{G}\mathbf{d}_s), \tag{17}$$

we can write the potential as

$$V(\mathbf{G}) = v^A(|\mathbf{G}|)(\cos(\mathbf{G}\mathbf{d}_2) + i\sin(\mathbf{G}\mathbf{d}_2)) + v^B(|\mathbf{G}|)(\cos(\mathbf{G}\mathbf{d}_2) - i\sin(\mathbf{G}\mathbf{d}_2)), \tag{18}$$

where we used the fact that $\mathbf{d}_1 = -\mathbf{d}_2$. Rewriting this expression in an alternative form:

$$V(\mathbf{G}) = (v^A(|\mathbf{G}|) + v^B(|\mathbf{G}|))\cos(\mathbf{G}\mathbf{d}_2) + i(v^A(|\mathbf{G}|) - v^B(|\mathbf{G}|))\sin(\mathbf{G}\mathbf{d}_2)) \tag{19}$$

Defining the symmetric and the antisymmetric part of the potential as

$$V^S(|\mathbf{G}|) = v^A(|\mathbf{G}|) + v^B(|\mathbf{G}|), \tag{20}$$

$$V^A(|\mathbf{G}|) = v^A(|\mathbf{G}|) - v^B(|\mathbf{G}|), \tag{21}$$

we write the Fourier transform of the potential that has to be inserted in Eq. 3 as

$$V(\mathbf{G}) = V^S(|\mathbf{G}|)\cos(\mathbf{G}\mathbf{d}_2) + iV^A(|\mathbf{G}|)\sin(\mathbf{G}\mathbf{d}_2)). \tag{22}$$

We note that the antisymmetric part vanishes when the two atoms are identical (diamond structure), in which case the Fourier transform of the potential becomes a real quantity.

As a final observation, we can calculate the squared modulus of the $\mathbf{G}$ vectors in units of $\frac{2\pi}{a}$ for the fcc lattice. We find $|\mathbf{G}|^2 = 3$ for $\mathbf{G} = (\pm1, \pm1, \pm1)$, $|\mathbf{G}|^2 = 4$ for $\mathbf{G} = (\pm2, 0, 0)$ and its permutations, $|\mathbf{G}|^2 = 8$ for $\mathbf{G} = (0, \pm2, \pm2)$ and its permutations, and $|\mathbf{G}|^2 = 11$ for $\mathbf{G} = \mathbf{b}_1 + 2\mathbf{b_2} = (1, -1, 3)$ and its permutations. The Cohen and Bergstresser pseudopotentials are listed in Table II of Phys. Rev. **141**, 789 (1966) for carbon, silicon, tin, a few III-V semiconductors (GaP, GaAs, AlSb, InP, GaSb, InAs), and a few II-VI semiconductors (ZnS, ZnSe, ZnTe, CdS). The table contains V_3^S, V_8^S, and V_{11}^S, as well as V_3^A, V_4^A, and V_{11}^A, where the indices correspond to the magnitude of $|\mathbf{G}|^2$. All quantities are given in Rydbergs.

IV. CODE LAYOUT

In order to calculate the band structure of the compounds for which we have empirical potentials, in addition to the quantities already computed in the free-electron code, we need the following additions:

1. We need to encode the table of coefficients defining the potentials, along with the lattice constant $\bar{a}$ for each compound.

2. For each **k**-point along the path in the Brillouin zone, we need to construct an $N_{pw} \times N_{pw}$ matrix containing the free-electron bands on the diagonal and $V(\mathbf{G} - \mathbf{G}')$ for the off-diagonal elements corresponding to $\mathbf{G} - \mathbf{G}'$. N_{pw} varies for each **k** and is the number of plane waves for which $|\mathbf{k} + \mathbf{G}|^2 < E_{cut}$.

3. For each **k**, we need to diagonalize the matrix. Standard LAPACK routines must be used for this purpose, so a routine that calls LAPACK is required. Since the eigenvalues returned by the diagonalization routine are already ordered from lowest to highest, we only need to write the lowest N_b bands requested by the user to disk.

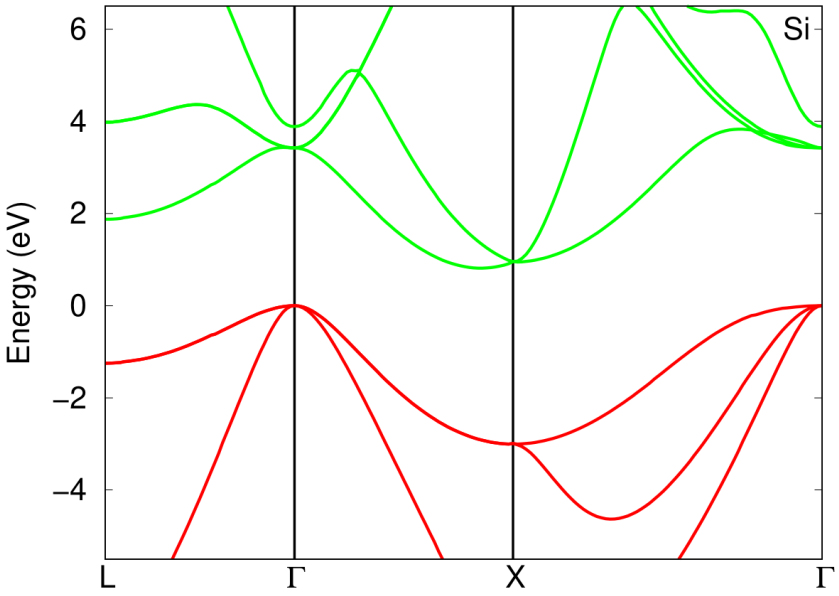


FIG. 1. Electronic band structure of Si obtained with the empirical potentials discussed in the text.

V. RESULTS

An example of the band structure of silicon that can be obtained from the code is given in Fig. 1.