Take $d = 0.350$, $R_c = 0.943$, and $U_0 = -31.30$ (the units are angstroms and electron volts). These numbers are appropriate for aluminum and are the subject of Problem 2. The task is to compute

$$U(\vec{r}) = \sum_{\vec{K}} e^{i\vec{K}\cdot\vec{r}} U_{\vec{K}}, \tag{10.58}$$

taking $\vec{K}$ to be the reciprocal lattice vectors of an fcc lattice of spacing $a = 4.05$ (Å).

(a) Find $U_{\vec{K}=0}$.

(b) Use Eq. (2.3) to construct the primitive vectors of the reciprocal lattice.

(c) Consult Appendix A.6 for guidance on the use of the fast Fourier transform. Obtain a routine capable of performing the transform for $N \times N \times N$ arrays of numbers; the problems will use $N = 4$, 5, 8, and 12. If such a routine cannot be located, the problems can be performed for $N = 4$, 8 only.

(d) For a given value of N, for what values of $\vec{r}$ will a fast Fourier transform routine compute $U(\vec{r})$, and how will they be indexed?

(e) Use the routine to evaluate Eq. (10.58), taking $N = 5$, and printing the 125 values of $U(\vec{r})$ and $\vec{r}$ in the Wigner–Seitz cell. Here are some of the values. The first three numbers are x, y, and z coordinates of $\vec{r}$ in angstrons, and the final number is the value of the potential $U(\vec{r})$ in Rydbergs.

```
0.     0.     0.    ( 0.201763183,0.)
0.     0.405  0.405 (-0.201839209,0.)
0.     0.810  0.810 (-0.757843018,0.)
0.     1.215  1.215 (-0.757843018,0.)
0.     1.620  1.620 (-0.201839209,0.)
0.405  0.     0.405 (-0.201839194,0.)
0.405  0.405  0.810 (-0.658886611,0.)
0.405  0.810  1.215 (-0.718343496,0.)
0.405  1.215  1.620 (-0.734894872,0.)
```

If only $N = 4$ is possible, then U does not come out to be real; the first values are

```
0.       0.       0.        ( 0.166458577, 0.         )
0.       0.50625  0.50625   (-0.265354961, 0.240282357)
0.       1.01250  1.01250   (-0.911596537, 0.         )
0.       1.51875  1.51875   (-0.265354961,-0.240282357)
0.50625  0.       0.50625   (-0.265354931, 0.240282387)
0.50625  0.50625  1.01250   (-0.591810703,-0.186816186)
0.50625  1.01250  1.51875   (-0.781587422, 0.103971817)
```

5. **Plane wave band structure, part III:** Consider Schrödinger's equation in the form of Eq. (7.59).

The task is to find the lowest-lying eigenvalue $\mathcal{E}$ and eigenfunction ψ solving this equation with the potential given by Eq. (10.57). Look for a solution with Bloch index $\vec{k} = 0$; essentially, this means that one sets $\vec{q} = 0$ in Eq. (7.59). Restrict all calculations to the $5 \times 5 \times 5$ set of $\vec{K}$ considered in the previous portion of the problem.

(a) Define a $5 \times 5 \times 5$ complex array $\psi(\vec{K})$. Let $\mathcal{E}_{\max}$ be $\mathcal{E}^0_{K_{\max}}$, where $K_{\max}$ is the largest value of $\vec{K}$ under consideration. Write a routine to compute

$$\psi'(\vec{K}) \equiv (\mathcal{E}^0_{\vec{K}} - \mathcal{E}_{\max})\psi(\vec{K}) + \sum_{\vec{K}'} U_{\vec{K}'}\psi(\vec{K} - \vec{K}'). \tag{10.59}$$

The hard part of the computation is the convolution $\sum_{\vec{K}'} U_{\vec{K}'}\psi(\vec{K} - \vec{K}')$. To perform the convolution, use the fact that

$$\sum_{\vec{K}'} U_{\vec{K}'}\psi(\vec{K} - \vec{K}') = \frac{1}{N^3}\mathcal{F}[\mathcal{F}^{-1}[U_{\vec{K}}] \times \mathcal{F}^{-1}[\psi(\vec{K})]]; \tag{10.60}$$

that is, take the inverse Fourier transforms of U and ψ, form a new array by multiplying together each element of U and ψ, take the Fourier transform of the result, and divide by N^3. This procedure is vastly faster than performing the sums described by the convolution directly.

(b) To find the ground state of Eq. (7.59),

i. Choose some random initial normalized $\psi(\vec{K})$, such as $\psi(0) = 1$, with all other components zero.
ii. Find ψ' according to Eq. (10.59).
iii. Normalize ψ'.
iv. Put ψ' back into the right-hand side of Eq. (10.59), and find ψ''.
v. Normalize ψ''.
vi. Continue in this fashion until the process converges. One should be left with the lowest-energy eigenstate of Schrödinger's equation.
vii. What is the eigenvalue $\mathcal{E}$ of this state from Eq. (7.59)?

6. **Plane wave band structure, part IV:** Consider again the potential given in Eq. (10.57). The new task is to compute the lowest-lying six eigenvalues $\mathcal{E}_{n\vec{k}}$ of

$$(\mathcal{E}^0_{\vec{q}} - \mathcal{E})\psi(\vec{q}) + \sum_{\vec{K}'} U_{\vec{K}'}\psi(\vec{q} - \vec{K}') \tag{10.61}$$

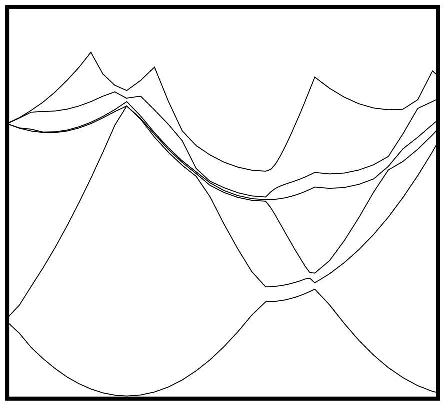
for $\vec{k} = [2\pi/a](.4\ .4\ .4)$, and $a = 4.05$Å. Combine the routine for computing action of the Hamiltonian on wave functions with the orthogonalization routine Problem 3. Use an $8 \times 8 \times 8$ grid for $\vec{K}$.

For the first four eigenvalues, on $8 \times 8 \times 8$ and $12 \times 12 \times 12$ grids one has the following in Rydbergs:

$8 \times 8 \times 8$	$12 \times 12 \times 12$
−0.27	−0.27
0.13	0.13
1.17	1.17
1.17	1.17

7. **Plane wave band structure, part V:**

(a) By adding an outer loop to the program produced in the previous problem, calculate the band structure of aluminum. Use a $4 \times 4 \times 4$ grid. Carry out the calculation along the trajectory L to Γ, Γ to X, X to U, U to Γ. Use about ten k points for each leg of the trajectory. Plot the first six bands. Do not expect the results to be perfect; the energy levels do not always appear in the correct order, and sometimes the convergence is slow. With a cutoff of around 10,000 on iterations for each energy level, one obtains the following figure:



The task is to produce a graph of roughly similar quality, with energies indicated on the y axis in electron volts. Compare with the energy bands of aluminum shown in Figure 10.7.

(b) Suppose that energies in Figure 10.7 were reported relative to the Fermi level. Outline in words the calculations needed to determine the Fermi level.

References

O. K. Andersen (1973), Simple approach to the band-structure problem, *Solid State Communications*, **13**, 133–136.

N. W. Ashcroft (1966), Electron-ion pseudopotentials in metals, *Physics Letters*, **23**, 48–50.

G. B. Bachelet, D. R. Hamann, and M. Schluter (1982), Pseudopotentials that work: From H to Pu, *Physical Review B*, **26**, 4199–4228.

D. W. Bullett (1980), The renaissance and quantitative development of the tight-binding method, *Solid State Physics: Advances in Research and Applications*, **35**, 129–214.

R. Car and M. Parrinello (1985), Unified approach for molecular dynamics and density-functional theory, *Physical Review Letters*, **55**, 2471–2474.

M. L. Cohen (1979), The pseudopotential panacea, *Physics Today*, **32**(7), 40–47.

M. L. Cohen and V. Heine (1970), The fitting of pseudopotentials to experimental data and their subsequent application, *Solid State Physics: Advances in Research and Applications*, **24**, 37–248.

J. O. Dimmock (1971), Calculation of electronic energy bands by the augmented plane wave method, *Solid State Physics: Advances in Research and Applications*, **26**, 103–274.

H. Ehrenreich and L. M. Schwartz (1976), The electronic structure of alloys, *Solid State Physics: Advances in Research and Applications*, **31**, 149–286.