PHY 555: Solid–state Physics I
Homework #6
Due: 11/11/2022

> *Homework is due by the end of the due date specified above.* **Late homework will be subject to 3 points off per day past the deadline, please contact me if you anticipate an issue making the deadline.** *It should be turned in via blackboard. For the conceptual and analytical parts, turn in a scan or picture of your answers (please ensure that they are legible) or an electronic copy if done with, e.g., LATEX. For the computational part, turn in your source code and a short description of your results (including plots). The description can be separate (e.g., in LATEX or word), or combined (e.g., in a jupyter notebook). Let me know if you are not sure about the format.*

Conceptual

1. *5 points* What is the problem with the naïve plane-wave expansion for calculating the bandstructure of solids that motivated using the orthogonalization procedure?

Analytical

2. *20 points* *Ab-initio* pseudopotentials are generated by fitting to numerical calculations conducted on isolated atoms. Though not commonly used, we can get a sense of how this is done by analyzing the method of Kerker, J. Phys. C **13** L189 (1980) (See `https://iopscience.iop.org/article/10.1088/0022-3719/13/9/004/pdf`). In this method, We first consider the radial *pseudowavefunction* which is of the form $F_{\text{psp}}(r) = rR_{\text{psp}}(r) = r^{l+1}e^{p(r)}$ where l is the angular quantum number and $p(r) = \alpha r^4 + \beta r^3 + \gamma r^2 + \delta$ with adjustable parameters α, β, γ, and δ.

    The pseudopotential is chosen such that $F_{\text{psp}}(r)$ satisfies a radial Schrödinger equation (using atomic units so $\hbar = m = 1$)

    $$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{\text{psp}}(r) - E_a \right] F_{\text{psp}}(r) = 0 \tag{1}$$

    where E_a is the energy of the atomic radial function, given by the radial Schrödinger equation for the atom

    $$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_a(r) - E_a \right] P_a(r) = 0, \tag{2}$$

    where $P_a(r) = rR_a(r)$ is the "exact" atomic radial wavefunction, which we assume that we can calculate, and V_a is the atomic potential (i.e., $-Z/|r|$).

    (a) Show that Eq. (1) gives $V_{\text{psp}}(r) = E_a + \lambda(2l + 2 + \lambda r^2) + 12\alpha r^2 + 6\beta r + 2\gamma$ where $\lambda = 4\alpha r^2 + 3\beta r + 2\gamma$.

    (b) Show that if $p(r)$ had a term linear in r, $V_{\text{psp}}(r)$ would be singular at $r = 0$.

    (c) The adjustable parameters are determined by placing constraints on the pseudowavefunction. We already constrained the eigenvalues E_a to be the same for both potentials. Now, choose a cutoff radius, outside of which the potentials coincide. I.e.,

    $$V_{\text{psp}}(r) = \begin{cases} E + \lambda(2l + 2 + \lambda r^2) + 12\alpha r^2 + 6\beta r + 2\gamma, & \text{if } r < r_c \\ V_a(r), & \text{if } r > r_c \end{cases} \tag{3}$$

Then, we enforce the following conditions at r_c: (i) $F_{\text{psp}}(r_c) = P_a(r_c)$, (ii) $\frac{d}{dr}F_{\text{psp}}(r_c) = \frac{d}{dr}P_a(r_c)$, and (iii) $\frac{d^2}{dr^2}F_{\text{psp}}(r_c) = \frac{d^2}{dr^2}P_a(r_c)$. Show that these conditions give the three equations for $p(r)$ and its derivatives:

$$\ln\left[\frac{P_a(r_c)}{r_c^{l+1}}\right] = p(r_c) \tag{4}$$

$$r_c\frac{P_a'(r_c)}{P_a(r_c)} = l + 1 + r_c p'(r_c) \tag{5}$$

$$r_c^2 V_a + (l+1)^2 - r_c^2\left[E_a + \left(\frac{P_a'(r_c)}{P_a(r_c)}\right)^2\right] = r_c^2 p''(r_c) \tag{6}$$

where, e.g., $P_a'(r_c) = \frac{dP(r)}{dr}\big|_{r_c}$.

(d) In part (c) we have three equations, but there are four unknowns in $F_{\text{psp}}(r)$. The last unknown is fixed by constraining the total charge within r_c to be that same for the atomic and pseudo wavefunctions. Take Q_a to be the charge inside of the cutoff radius r_c for the exact atomic wavefunction. Write an equation for δ based on this constraint. **Hint:** You will come across an integral involving F_{psp} which cannot be solved analytically, so you can leave it in your expression for δ.

Computational

Table 1: Empirical pseudopotential parameters for selected materials (in Rydbergs) and lattice constants of the conventional cubic cell (in Angstroms).

	a (Å)	$V_{\sqrt{3}}^s$	$V_{\sqrt{4}}^s$	$V_{\sqrt{8}}^s$	$V_{\sqrt{11}}^s$	$V_{\sqrt{3}}^a$	$V_{\sqrt{4}}^a$	$V_{\sqrt{8}}^a$	$V_{\sqrt{11}}^a$
Si	5.43	-0.21	0.0	0.04	0.08	0.0	0.0	0.0	0.0
Ge	5.66	-0.23	0.0	0.01	0.06	0.0	0.0	0.0	0.0
Sn	6.49	-0.20	0.0	0.0	0.04	0.0	0.0	0.0	0.0
GaAs	5.64	-0.23	0.0	0.01	0.06	0.07	0.05	0.0	0.01

3. **25 points** In the previous problem, we discussed *ab initio* pseudopotentials; another approach based on *empirical* pseudopotentials can also be used along with a plane-wave basis to generate band-structures of materials. In Cohen and Bergstresser, Phys. Rev. **141**, 789 (1965) (https://journals.aps.org/pr/pdf/10.1103/PhysRev.141.789), it was shown that the band structure of several semiconductors could be reproduced with very few empirical parameters. The solids that were considered in that work had either the "diamond" or "zincblende" structures. These structures are both based on the face-centered cubic Bravais lattice, with two basis vectors $\mathbf{b}_\pm = \pm\boldsymbol{\tau}$ where $\boldsymbol{\tau} = a(1/8, 1/8, 1/8)$ (a is the lattice constant of the conventional cubic cell). In the diamond structure, e.g., Si, Ge, or Sn, both sublattices are the same atom; in zincblende, e.g., GaAs, they are different atoms. It was shown in Cohen and Bergstresser that the empirical pseudopotential can we written as the Fourier series

$$V(\mathbf{r}) = \sum_{\mathbf{G}}\left[V_G^s\cos(\mathbf{G}\cdot\boldsymbol{\tau}) + iV_G^a\sin(\mathbf{G}\cdot\boldsymbol{\tau})\right]e^{i\mathbf{G}\cdot\mathbf{r}}, \tag{7}$$

where V_G^s and V_G^a are empirical parameters that only depend on the magnitude of $\mathbf{G}$. Consider the first five shells of $\mathbf{G}$ vectors for FCC: $(2\pi/a)(0,0,0)$, $(2\pi/a)(\pm1,\pm1,\pm1)$, $(2\pi/a)(\pm2,0,0)$, $(2\pi/a)(\pm2,\pm2,0)$, and $(2\pi/a)(\pm3,\pm1,1)$ (where we are including all permutations of $\pm$ and x,

y, and z coordinates). The magnitude of these vectors are $(2\pi/a)$ times $0, \sqrt{3}, \sqrt{4}, \sqrt{8}, \sqrt{11}$, respectively. The empirical parameters for these shells for several solids is given in Table 1 (note that V_0^s is just a rigid energy shift, so can be any value).

(a) Write a program that uses the pseudopotential method with the parameters in Table 1 to plot the bandstructures of Si, Ge, Sn, and GaAs along the path $L \rightarrow \Gamma \rightarrow X \rightarrow K \rightarrow \Gamma$ (see Fig. 1 and Table 2 for high-symmetry **k** points/paths) in the energy range from 0 to 0.8 Ha. Compare your results to the corresponding figures in Cohen and Bergstresser.

(b) In these materials, the first four bands are filled, and the rest of the bands are empty. What happens between Si, Ge, and Sn in terms of the gap between filled and empty states?

(c) Qualitatively compare the filled and first empty states of GaAs with those from the tight-binding case you solved in Homework 5. What can you say about the orbital makeup of these states based on the comparison?
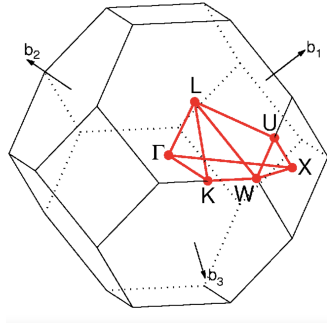

Figure 1: Brillouin zone and high-symmetry points/lines for the face-centered cubic Bravais lattice. (b_1, b_2, b_3 are the reciprocal lattice vectors corresponding to $\mathbf{g}_1$, $\mathbf{g}_2$, and $\mathbf{g}_3$ in the table below.)

Table 2: High-symmetry **k** points of the face-centered cubic lattice.

	$\times\mathbf{g}_1$	$\times\mathbf{g}_2$	$\times\mathbf{g}_3$
Γ	0	0	0
K	3/8	3/8	3/4
L	1/2	1/2	1/2
U	5/8	1/4	5/8
W	1/2	1/4	3/4
X	1/2	0	1/2