

Theoretical Material Science: Exercise Sheet 7

Please hand in solutions by: **Tuesday, June 13**, start of the exercise class

Exercise 17 (8 points): *Tight binding approximation: s-levels in an fcc crystal*

In the tight-binding approximation, one expands the crystal (Bloch) eigenfunctions $\varphi_{n,\mathbf{k}}(\mathbf{r})$ into localized atomic eigenfunctions $\hat{\varphi}_\alpha(\mathbf{r} - \mathbf{R}_I)$, with $\hat{h}^{\text{at}}\hat{\varphi}_\alpha = \epsilon_\alpha^{\text{at}}\hat{\varphi}_\alpha$ (\hat{h}^{at} is the atomic Hamiltonian). We consider the case of only a single atomic s orbital $\hat{\varphi}_s$ at each lattice site \mathbf{R}_I .

- a) Show that the expression for the band energy $\epsilon(\mathbf{k})$ (only one band) can be written as:

$$[\epsilon^{\text{at}} - \epsilon(\mathbf{k})]S(\mathbf{k}) + A(\mathbf{k}) = 0, \quad (1)$$

where S is called the overlap and A the potential matrix element:

$$S(\mathbf{k}) = \sum_I e^{i\mathbf{k}\mathbf{R}_I} \int d^3r \hat{\varphi}_s^*(\mathbf{r})\hat{\varphi}_s(\mathbf{r} - \mathbf{R}_I) \quad (2)$$

$$A(\mathbf{k}) = \sum_I e^{i\mathbf{k}\mathbf{R}_I} \int d^3r \hat{\varphi}_s^*(\mathbf{r})\Delta v(\mathbf{r})\hat{\varphi}_s(\mathbf{r} - \mathbf{R}_I)$$

with $\Delta v(\mathbf{r}) = v(\mathbf{r}) - v^{\text{at}}(\mathbf{r})$.

$\Delta v(\mathbf{r})$ is the difference between the atomic potential in \hat{h}^{at} and the full crystal potential $v(\mathbf{r})$. Rewrite Eq. (1) for the band energy by explicitly separating out the “on-site terms” ($\mathbf{R}_I=0$).

- b) Express the band energy $\epsilon(\mathbf{k})$ for an fcc crystal explicitly for the following approximations:
- i) All terms except $\mathbf{R}_I=0$ in $S(\mathbf{k})$ vanish (and $\hat{\varphi}_s$ is normalized to 1).
 - ii) All potential terms in $A(\mathbf{k})$ beyond nearest neighbours vanish.

Hint: Use the notation $\int d^3r \hat{\varphi}_s^(\mathbf{r})\Delta v(\mathbf{r})\hat{\varphi}_s(\mathbf{r}) = -\beta$, $\int d^3r \hat{\varphi}_s^*(\mathbf{r})\Delta v(\mathbf{r})\hat{\varphi}_s(\mathbf{r} - \mathbf{R}_{NN}) = -\gamma(\mathbf{R}_{NN})$, and use the symmetry of the lattice and of the s wave function explicitly to relate $-\gamma(\mathbf{R}_{NN})$ to one another for different nearest neighbours.*

- c) Show that the explicit form of the s bands along the following lines in reciprocal space is:

- i) Along ΓX ($k_y=k_z=0$, $k_x=\frac{2\pi}{a}\zeta$, $0 < \zeta < 1$): $\epsilon = \epsilon^{\text{at}} - \beta - 4\gamma[1 + 2\cos(\pi\zeta)]$
- ii) Along ΓL ($k_y=k_z=k_x=\frac{2\pi}{a}\zeta$, $0 < \zeta < 1/2$): $\epsilon = \epsilon^{\text{at}} - \beta - 12\gamma\cos^2(\pi\zeta)$
- iii) Along ΓK ($k_z=0$, $k_x=k_y=\frac{2\pi}{a}\zeta$, $0 < \zeta < 3/4$): $\epsilon = \epsilon^{\text{at}} - \beta - 4\gamma[\cos^2(\pi\zeta) + 2\cos(\pi\zeta)]$
- iv) Along ΓW ($k_z=0$, $k_x=\frac{2\pi}{a}\zeta$, $k_y=\frac{\pi}{a}\zeta$, $0 < \zeta < 1$):
 $\epsilon = \epsilon^{\text{at}} - \beta - 4\gamma[\cos(\pi\zeta) + \cos(\frac{\pi\zeta}{2}) + \cos(\pi\zeta)\cos(\frac{\pi\zeta}{2})]$

- d) Compute the ratio of “band widths” Θ of the bands along ΓX and ΓL :

$$\Theta = \frac{\epsilon(X) - \epsilon(\Gamma)}{\epsilon(L) - \epsilon(\Gamma)}. \quad (3)$$

Compare the s -wave tight binding result to the result that one would obtain for the lowest-energy bands in the free-electron case.

Please turn over! →

Exercise 18 (4 points): *Lennard-Jones Potential*

As discussed in the lecture, the van der Waals bonding in noble gas crystals can be approximately described using a pairwise Lennard-Jones potential $E^{\text{LJ}}(R) = 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right]$.

a) Identify the attractive and the repulsive term and motivate their functional form.

b) Calculate the energy per atom $\frac{E}{M} = 2\epsilon \sum_{I=2}^M \left[\left(\frac{\sigma}{|\mathbf{R}_I|}\right)^{12} - \left(\frac{\sigma}{|\mathbf{R}_I|}\right)^6 \right]$ in the nearest and next-nearest neighbor shell for a neon fcc crystal with $\sigma = 2.74\text{\AA}$ and $\epsilon = 3.1\text{meV}$.
Can this sum be expected to converge quickly?

c) Assume that the $|\mathbf{R}|^{-6}$ term is replaced by a Coulomb term $\pm 1|\mathbf{R}|^{-1}$, so that the energy per atom is given by $\frac{E}{M} = 2\epsilon \sum_{I=2}^M \left[\left(\frac{\sigma}{|\mathbf{R}_I|}\right)^{12} - \left(\frac{(\pm 1)\sigma}{|\mathbf{R}_I|}\right) \right]$. How does the convergence compare to the convergence of the sum in part b)? Assume that σ in the Coulomb term is positive in the nearest neighbor shell and negative in the next-nearest neighbor shell.