Electronic structure of solid matter

MSc course 2019

Problem set 2

Exercise 1

Considering a system of independent electrons the expectation value of a Hermitean operator $\mathcal{A}$ is given by

$$A = \sum_n f(\varepsilon_n) \langle \varphi_n | \mathcal{A} | \varphi_n \rangle \,, \tag{1}$$

where $f(\varepsilon) = 1/\left(1 + e^{(\varepsilon-\mu)/k_BT}\right)$ is the Fermi distribution, μ is the chemical potential, and $|\varphi_n\rangle$ are the eigenfunctions of the one-electron Hamiltonian,

$$\mathcal{H} |\varphi_n\rangle = \varepsilon_n |\varphi_n\rangle \,. \tag{2}$$

Prove that A can be expressed as

$$A = -\frac{1}{\pi} \mathrm{Im} \int_{\curvearrowright} dz\, f(z)\, Tr\left(\mathcal{A}\mathcal{G}(z)\right) - 2k_BT \sum_{\mathrm{Im}\, z_k > 0} \mathrm{Re}\, Tr\left(\mathcal{A}\mathcal{G}(z_k)\right) \,, \tag{3}$$

where $\mathcal{G}(z) = (z - \mathcal{H})^{-1}$ is the resolvent operator, $\curvearrowright$ denotes a contour in the upper complex semiplane with the endpoints $-\infty$ and ∞, and $z_k = \mu + i\,(2k+1)\,\pi k_BT \quad (k \in \mathbb{Z})$ are the poles of $f(z)$ (fermionic Matsubara poles) lying between the real axis and $\curvearrowright$.

Exercise 2

Let the tight-binding Hamiltonian matrix $\underline{\underline{H}} = \left\{\underline{H}_{ij}\right\}$ describe the electrons in a solid. The atom at a given site n is replaced by an other atom, characterized by the on-site matrix, $\underline{H}'_n$, while the off-site blocks of the Hamiltonian are supposed to be unchanged.
(a) Prove that the site-diagonal block of the resolvent matrix related to site n is

$$\underline{G}'^{nn}(z) = \underline{G}^{nn}(z) \left(\underline{I} - \Delta\underline{H}_n \underline{G}^{nn}(z)\right)^{-1} \,, \tag{4}$$

where $\Delta\underline{H}_n = \underline{H}'_n - \underline{H}_n$ and $\underline{G}^{nn}(z)$ is the site-diagonal block of the resolvent matrix of the host system.
(b) Show that in case of a disordered binary alloy the single-site CPA condition for the t-matrices is equivalent with the following condition for the resolvent matrices,

$$\underline{G}_c^{nn}(z) = c\underline{G}_A^{nn}(z) + (1-c)\underline{G}_B^{nn}(z) \,, \tag{5}$$

where $\underline{G}_\alpha^{nn}(z)$ denotes the site-diagonal block of the resolvent matrix when a single impurity of type $\alpha \in \{A, B\}$ is embedded into the effective medium at site n. *(This exercize was in fact discussed in the course.)*

Exercise 3

Consider the case when two atoms at sites n and m are replaced in Exercise 2. Prove that the corresponding site-off-diagonal block of the resolvent matrix can be expressed as

$$\underline{G}'^{nm} = \underline{\tilde{D}}_n \left(\underline{I} - \underline{G}^{nm}\underline{t}_m\underline{G}^{mn}\underline{t}_n\right)^{-1}\underline{G}^{nm}\underline{D}_m \,, \tag{6}$$

where

$$\underline{D}_m = \left(\underline{I} - \Delta\underline{H}_m\underline{G}^{mm}\right)^{-1} \;,\; \underline{\tilde{D}}_n = \left(\underline{I} - \underline{G}^{nn}\Delta\underline{H}_n\right)^{-1} \;,\; \underline{t}_n = \Delta\underline{H}_n\underline{\tilde{D}}_n = \underline{D}_m\Delta\underline{H}_m \,!$$

Exercise 4

The nearest neighbor tight-binding Hamiltonian for a single-band system on a simple one-dimensional lattice is given by

$$H_{ij} = \varepsilon_0\,\delta_{ij} + V\,\left(\delta_{i,j+1} + \delta_{i,j-1}\right) \;, \tag{7}$$

where i and j denote sites of the lattice ($V > 0$). Prove that, for $\operatorname{Im} z > 0$ and $\varepsilon_0 - 2V < \varepsilon \equiv \operatorname{Re} z < \varepsilon_0 + 2V$, the resolvent matrix can be expressed as

$$G^{ij}\left(z\right) = \frac{\left(\frac{z-\varepsilon_0}{2V} - \sqrt{\left(\frac{z-\varepsilon_0}{2V}\right)^2 - 1}\right)^{|i-j|}}{2V\sqrt{\left(\frac{z-\varepsilon_0}{2V}\right)^2 - 1}} \;, \tag{8}$$

consequently,

$$G^{ii}\left(z\right) = \frac{1}{\sqrt{\left(z-\varepsilon_0\right)^2 - 4V^2}} \;, \tag{9}$$

and the density of states per lattice site is

$$n\left(\varepsilon\right) = \frac{1}{\pi\sqrt{4V^2 - \left(\varepsilon-\varepsilon_0\right)^2}} \,! \tag{10}$$

Exercise 5

Show that the single-site CPA condition for the above mentioned system can be written in the form,

$$\varepsilon_c = c\varepsilon_A + \left(1-c\right)\varepsilon_B - \left(\varepsilon_A - \varepsilon_c\left(z\right)\right)\left(\varepsilon_B - \varepsilon_c\left(z\right)\right)G_c^{00}\left(z\right) \;, \tag{11}$$

where c is the concentration of component A, ε_A and ε_B are the on-site energies for components A and B, $\varepsilon_c\left(z\right)$ is the self-energy for the effective medium and

$$G_c^{00}\left(z\right) = \frac{1}{\sqrt{\left(z - \varepsilon_c\left(z\right)\right)^2 - 4V^2}} \,! \tag{12}$$

Exercise 6

Let us fix the on-site energies in the above example as

$$\varepsilon_A = \varepsilon_0 \quad \varepsilon_B = -\varepsilon_0 \tag{13}$$

and introduce the variables

$$x_0 = \frac{\varepsilon_0}{2V} , \quad x_c = \frac{\varepsilon_c(z)}{2V} , \quad \omega = \frac{z}{2V} . \tag{14}$$

Eq. (11) can then be written as

$$x_c = (2c-1)\, x_0 + \frac{x_0^2 - x_c^2}{\sqrt{(\omega - x_c)^2 - 1}} . \tag{15}$$

Solve this equation numerically by writing a corresponding computer code!
(a) An iterative solution can start with $x_c^{(1)} = (2c-1)\, x_0$ (in fact, this is the virtual crystal approximation). Apply a small positive imaginary part for ω ($\mathrm{Im}\,\omega \simeq 0.01 - 0.05$) and use a linear mixing scheme,

$$x_c^{(n+1),in} = \alpha\, x_c^{(n),out} + (1-\alpha)\, x_c^{(n),in} \tag{16}$$

with a suitable value of α ($\alpha \simeq 0.1 - 0.5$)!

Important note: from the two possible values of $\sqrt{(\omega - x_c)^2 - 1}$ *the one with negative imaginary part should be chosen!*
(b) More preferably, the well-coverging iterative process proposed in the course should be used. Start again with $x_c^{(0)} = (2c-1)\, x_0$, then follow the steps:

$$1: \quad G_c^{00(n)}(z) = \frac{1}{\sqrt{\left(\omega - x_c^{(n)}\right)^2 - 1}} \tag{17}$$

$$\Downarrow$$

$$2: \quad t_c^{(n)} = \frac{c\left(x_0 - x_c^{(n)}\right)}{1 - \left(x_0 - x_c^{(n)}\right) G_c^{00(n)}} - \frac{(1-c)\left(x_0 + x_c^{(n)}\right)}{1 + \left(x_0 + x_c^{(n)}\right) G_c^{00(n)}} \tag{18}$$

$$\Downarrow$$

$$3: \quad x_c^{(n+1)} = x_c^{(n)} + \frac{t_c^{(n)}}{1 + t_c^{(n)} G_c^{00(n)}} \tag{19}$$

$$\text{repeat from step 1 until convergence} \tag{20}$$

After getting the self-consistent solution for x_c, plot the dimensionless averaged density of states,

$$n_c(\omega) = -\,\mathrm{Im}\,\frac{1}{\sqrt{(\omega - x_c)^2 - 1}} , \tag{21}$$

for *(i)* $c = 0.5$ and $x_0 = 1$, *(ii)* for $c = 0.5$ and $x_0 = 2$, and *(iii)* for $c = 0.1$ and $x_0 = 2$!