Problem set 4

Phy-801

February 2026

1. **Particle hole symmetry at the Fermi surface and the Mott relation**: this question will help demonstrate the importance of particle hole symmetry at the Fermi surface.

   (a) Consider Sommerfeld electrons with the usual $p^2/2m$ dispersion. Show that

   $$g(\varepsilon_{\rm F}) = \frac{3n}{2\varepsilon_{\rm F}} \tag{1}$$

   where n is the electron density. Further show that

   $$g'(\varepsilon_{\rm F}) = \frac{g(\varepsilon_{\rm F})}{2\varepsilon_{\rm F}} \tag{2}$$

   and hence argue why each higher order derivative $g^{(n)}(\varepsilon_{\rm F})$ should be smaller by a further factor $\varepsilon_{\rm F}$.

   (b) The Sommerfeld expansion allows us to evaluate integrals of the following form, which arise frequently in linear response theory

   $$\int_{-\infty}^{\infty} d\varepsilon \lambda(\varepsilon)\left(-\frac{\partial f_0}{\partial \varepsilon}\right) = \lambda(\mu) + \tfrac{1}{6}(\pi k_{\rm B}T)^2\lambda''(\mu) + \tfrac{7}{360}(\pi k_{\rm B}T)^4\lambda^{(4)}(\mu) + \dots \tag{3}$$

   where $f_0 = f_{\rm FD}(\beta(\varepsilon-\mu))$ is the equilibrium distribution function.
   Note that $\partial f/\partial\epsilon$ is even at the Fermi surface, that

   $$\left.\frac{\partial f_0}{\partial \varepsilon}\right|_{\varepsilon=\mu+\delta\varepsilon} = \left.\frac{\partial f_0}{\partial \varepsilon}\right|_{\varepsilon=\mu-\delta\varepsilon} \tag{4}$$

   Consequently, if λ is odd at the Fermi surface, specifically (also known as "particle hole anti-symmetric")

   $$\lambda(\mu+\delta\varepsilon) = -\lambda(\mu-\delta\varepsilon) \tag{5}$$

   this integral is strictly zero. Such a situation would however be fine tuned, and is not generically expected to occur when considering physically relevant observables. Functions which are even $\lambda(\mu+\delta\varepsilon) = \lambda(\mu-\delta\varepsilon)$ are know as particle-hole symmetric, and functions which are odd $\lambda(\mu+\delta\varepsilon) = -\lambda(\mu-\delta\varepsilon)$ are particle-hole anti-symmetric.
   Nevertheless, in thermoelectrics integrals of the form $\lambda(\varepsilon) = \sigma(\varepsilon)(\varepsilon-\mu)^k$ appear, which are "close" to odd/even for integer k. Show that these integrals have an odd-even effect where for k even, the leading order term is proportional to $\sigma(\mu)$, whereas for k odd it is proportional to $\sigma'(\mu)$.

   (c) Consider the Boltzmann equation for electrons in an electric field with an energy dependent relaxation rate

   $$\frac{\partial f}{\partial t} + \boldsymbol{v}\cdot\nabla_{\boldsymbol{r}} f + \frac{1}{\hbar}\boldsymbol{F}\cdot\nabla_{\boldsymbol{k}} f = \frac{f_0 - f}{\tau(\varepsilon_{\boldsymbol{k}})} \tag{6}$$

   where $|\boldsymbol{v}| = v(\varepsilon_{\boldsymbol{k}})$ is the velocity and $\boldsymbol{F} = -e\boldsymbol{E}$ is the coulomb force, and f_0 is the equilibrium state. A simple ansatz for the solution is obtained by including a drift momentum $\boldsymbol{q}$

   $$f = f_{\rm FD}(\beta(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \mu)). \tag{7}$$

i. Show that expanding to linear order in $\boldsymbol{q}$ this yields

$$\delta f = -\hbar \boldsymbol{v} \cdot \boldsymbol{q} \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \tag{8}$$

where $\boldsymbol{v} = \frac{1}{\hbar} \nabla_{\boldsymbol{k}} \varepsilon_{\boldsymbol{k}}$ is the ($\boldsymbol{k}$-dependent) velocity.

ii. Show that for non-zero $\boldsymbol{E}$, $\nabla_{\boldsymbol{r}} T$ and $\nabla_{\boldsymbol{r}} \mu$ the linear response correction to the steady state distribution of (6) is described by the ansatz (8) with $\boldsymbol{q} = \boldsymbol{q}_1 + \boldsymbol{q}_2$

$$\boldsymbol{q}_1 = \frac{e\tau}{\hbar} \boldsymbol{\mathcal{E}}, \qquad \boldsymbol{q}_2 = \frac{(\varepsilon - \mu)\tau}{\hbar T} \nabla_{\boldsymbol{r}} T, \tag{9}$$

where $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ are the drift momenta induced by the electrochemical force $\boldsymbol{\mathcal{E}} = \boldsymbol{E} + \frac{1}{e} \nabla_{\boldsymbol{r}} \mu$ and temperature gradient $\nabla_{\boldsymbol{r}} T$.

(d) Consider the case of weak $\boldsymbol{\mathcal{E}}$, and $\nabla \mu = 0$, $\nabla T = 0$. Calculate the electric current

$$\boldsymbol{j} = \frac{1}{4\pi^3} \int d^3k (-e\boldsymbol{v}) \delta f \tag{10}$$

and hence show that to leading order in T, that the conductivity is $\boldsymbol{j} = \sigma \boldsymbol{E}$

$$\sigma = \sigma(\mu), \quad \text{where} \quad \sigma(\varepsilon) = \frac{e^2}{3} g(\varepsilon) \tau(\varepsilon) v(\varepsilon)^2 \tag{11}$$

(e) Subsequently obtain the thermoelectric response coefficients L^{ij}

$$\begin{pmatrix} \boldsymbol{j} \\ \boldsymbol{j}_q \end{pmatrix} = \begin{pmatrix} L^{11} & L^{12} \\ L^{21} & L^{22} \end{pmatrix} \begin{pmatrix} \boldsymbol{\mathcal{E}} \\ -\nabla T \end{pmatrix}. \tag{12}$$

where the heat current $\boldsymbol{j}_q$ is given by

$$\boldsymbol{j}_q = \frac{1}{4\pi^3} \int d^3k (\varepsilon - \mu) \boldsymbol{v} \delta f \tag{13}$$

express each of the L^{ij} in terms of the integrals

$$I_k = \int_{-\infty}^{\infty} d\varepsilon \sigma(\varepsilon) (\varepsilon - \mu)^k \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \tag{14}$$

where k is an integer.

(f) Using that the scattering time τ is slowly varying with ε, estimate the scale of

$$\sigma'(\varepsilon)/\sigma(\varepsilon) \tag{15}$$

and with reference to your result to part (1b), explain why L^{12} and L^{21} are much further suppressed from their Drude values than L^{11} and L^{22}.

(g) Subsequently show that the Seebeck coefficient (defined by $\boldsymbol{\mathcal{E}} = S \nabla T$ under open-circuit conditions $\boldsymbol{j} = 0$) is given by the Mott relation

$$S = S_0 \, k_{\mathrm{B}} T \left. \frac{d \ln \sigma(\varepsilon)}{d\varepsilon} \right|_{\varepsilon = \mu} \tag{16}$$

and calculate the value of S_0.

2. **The exchange hole and the thermal coherence length:** Even before accounting for interactions, the non-interacting many electron ground state has correlation effects due to exchange statistics.

(a) Consider a gas of non-interacting spin degenerate electrons, in its Slater determinant ground state $|\Psi\rangle$. Show that the expectation of a single body operator $A = \sum_i a(\boldsymbol{r}_i)$ is given by

$$\langle\Psi| A |\Psi\rangle = \sum_{(i,\sigma)\,\in\,\mathrm{occ}} \int d^3\boldsymbol{r}\, |\psi_i(\boldsymbol{r},\sigma)|^2\, a(\boldsymbol{r}) \tag{17}$$

where i denotes an orbital index, and $\sigma =\uparrow,\downarrow$ a spin state, and the sum is taken over occupied states (i,σ).

(b) Now consider a two body operator $B = \frac{1}{2}\sum_{i\neq j} b(\boldsymbol{r}_i,\boldsymbol{r}_j)$. The expectation value has both Hartree and Fock (i.e. exchange) terms

$$\langle\Psi| B |\Psi\rangle = B_{\mathrm{H}} - B_{\mathrm{F}} \tag{18}$$

i. Give expressions for the two terms B_{H} and B_{F} in terms of the occupied orbitals $\psi_i(\boldsymbol{r})$.

ii. Show that for a special case of a two body operator of the form $C = \frac{1}{2}\sum_{i\neq j} c(\boldsymbol{r}_i)c(\boldsymbol{r}_j)$ these terms simplify and we obtain

$$C_{\mathrm{H}} = \frac{1}{2}\Big(\sum_{i\sigma}\gamma^{\sigma}_{ii}\Big)^2, \qquad C_{\mathrm{F}} = \frac{1}{2}\sum_{ij\sigma}|\gamma^{\sigma}_{ij}|^2 \tag{19}$$

where

$$\gamma^{\sigma}_{ij} = \int d^3\boldsymbol{r}\, c(\boldsymbol{r})\psi^*_i(\boldsymbol{r},\sigma)\psi_j(\boldsymbol{r},\sigma) \tag{20}$$

(c) Assume that $|\Psi\rangle$ is the ground state of non-interacting electrons, with Hamiltonian $H = \frac{p^2}{2m}$, in three dimensions. Consider the electron density-density correlator

$$\rho^{(2)}(\boldsymbol{r},\boldsymbol{r}') = \langle\Psi| \sum_{i\neq j}\delta(\boldsymbol{r}_i-\boldsymbol{r})\delta(\boldsymbol{r}_j-\boldsymbol{r}') |\Psi\rangle \tag{21}$$

this object is useful to calculate, as it allows us to evaluate any two-body operator that may be defined in real space via the relation

$$\langle\Psi| B |\Psi\rangle = \tfrac{1}{2}\int d^3\boldsymbol{r}\int d^3\boldsymbol{r}'\, b(\boldsymbol{r},\boldsymbol{r}')\rho^{(2)}(\boldsymbol{r},\boldsymbol{r}'). \tag{22}$$

Using your result from 2b calculate the electron density-density correlator $\rho^{(2)}(\boldsymbol{r},\boldsymbol{r}')$. Show that it takes the form

$$\rho^{(2)}(\boldsymbol{r},\boldsymbol{r}') = n^2 F(k_{\mathrm{F}}|\boldsymbol{r}-\boldsymbol{r}'|) \tag{23}$$

and give a closed form expression for $F(x)$ in terms of standard trigonometric functions.

(d) Sketch $\rho^{(2)}(\boldsymbol{r},\boldsymbol{r}')$ as a function of $k_{\mathrm{F}}|\boldsymbol{r}-\boldsymbol{r}'|$ labelling the asymptotic behaviour (small r and large r). The "hole" at small r is known as the exchange hole, or correlation hole, and arises as particle positions are anti-correlated in space due to exchange statistics. The oscillations in this function are known as Friedel oscillations.

(e) When we evaluate the Coulomb energy it is necessary to include the positive charge of the ions to get non-divergent results. In the "jellium" approximation we assume that the ions form a uniform background of positive charge. In this approximation the average charge density operator is defined as

$$\hat{\rho}_q(\boldsymbol{r}) = en - e\sum_i \delta(\boldsymbol{r}_i-\boldsymbol{r}). \tag{24}$$

One finds that, as expected, its expectation value is uniformly zero

$$\rho_q(\boldsymbol{r}) = \langle\Psi| [en - e\sum_i \delta(\boldsymbol{r}_i-\boldsymbol{r})] |\Psi\rangle = en - en = 0 \tag{25}$$

while the charge density-density correlator is given by

$$\rho^{(2)}_q(\boldsymbol{r},\boldsymbol{r}') = e^2\left[\rho^{(2)}(\boldsymbol{r},\boldsymbol{r}') - n^2\right] \tag{26}$$

i.e. the background exactly cancels the Hartree term leaving only the Fock term. The total Coulomb energy is given by

$$U_{\rm C} = \tfrac{1}{2}\int d^3\boldsymbol{r}\int d^3\boldsymbol{r}' \left(\frac{1}{4\pi\epsilon_0|\boldsymbol{r}-\boldsymbol{r}'|}\right)\rho_q^{(2)}(\boldsymbol{r},\boldsymbol{r}'). \tag{27}$$

Calculate $U_{\rm C}$ and give your answer as the ratio $U_{\rm C}/U_{\rm KE}$ in terms of $a_0 k_{\rm F}$ where a_0 is the Bohr radius and $U_{\rm KE}$ is the kinetic energy in the ground state

$$U_{\rm KE} = \langle\Psi|\sum_i \frac{\hbar^2 k_i^2}{2m}|\Psi\rangle\,. \tag{28}$$

Using your result calculate $U_{\rm C}/U_{\rm KE}$ for copper. [You may use: the Bohr radius is given by $a_0 = 0.529$Å standard Sommerfeld electron results—$U_{\rm KE} = \frac{3}{5}NE_F$ and $k_{\rm F}^3 = 3\pi^2 n$, and the properties of copper—Cu is monovalent (one conduction electron per atom), with molar mass $63.55\,{\rm g\,mol^{-1}}$, and at 300 K has density $\rho = 8.96\,{\rm g\,cm^{-3}}$, and an effective electron mass $m^* = m_{\rm e}$]

(f) Note that the charge density-density correlator you previously calculated may be written as

$$\rho_q^{(2)}(\boldsymbol{r},\boldsymbol{r}') = -\frac{e^2}{2}|\rho^{(1)}(\boldsymbol{r},\boldsymbol{r}')|^2 \tag{29}$$

where $\rho^{(1)}(\boldsymbol{r},\boldsymbol{r}')$ is the one body density matrix

$$\rho^{(1)}(\boldsymbol{r},\boldsymbol{r}') = \sum_{(i,\sigma)\,\in\,{\rm occ}} \psi_i(\boldsymbol{r},\sigma)\psi_i^*(\boldsymbol{r}',\sigma) \tag{30}$$

given in the Fermi gas by

$$\rho^{(1)}(\boldsymbol{r},\boldsymbol{r}') = \rho^{(1)}(\boldsymbol{r}-\boldsymbol{r}'),\quad \rho^{(1)}(\boldsymbol{r}) = \frac{1}{4\pi^3}\int_{|\boldsymbol{k}|<k_{\rm F}} d^3k\,{\rm e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} \tag{31}$$

at finite temperatures states are not only filled/empty, but may also take intermediate values

$$\rho^{(1)}(\boldsymbol{r}) = \frac{1}{4\pi^3}\int d^3k\, f_{\rm FD}(\beta(\varepsilon_{\boldsymbol{k}}-\mu)){\rm e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} \tag{32}$$

For $T>0$ the function $\rho^{(1)}(\boldsymbol{r})$ has very different large r behaviour compared to its $T=0$ behaviour

$$\rho^{(1)}(\boldsymbol{r}) \sim \rho^{(1)}_{T=0}(\boldsymbol{r}){\rm e}^{-r/\xi} \tag{33}$$

(where here $\sim$ indicates agreement at large r) obtain an expression for the thermal coherence length ξ in terms of $k_{\rm B}T$ and $v_{\rm F}$, and show that it diverges as $T\to 0$.

Based on the combination of scales, suggest a physical interpretation of this length scale.

Hint: To evaluate (32) (i) perform the angular part of the integral exactly, so that only the radial dk part is left (ii) integrate by parts to get an integrand that depends on $f'_{\rm FD}$ (iii) use that $f'_{\rm FD}$ is sharply peaked at the Fermi surface where you may factor out all slowly varying parts of the integrand—this is a standard trick (iv) approximate $\varepsilon_{\boldsymbol{k}} = \varepsilon_{\rm F} + v_{\rm F}(k-k_{\rm F}) + O(k-k_{\rm F})^2$ (v) make use of the identity

$$\int_{-\infty}^{\infty} ds\frac{{\rm e}^{ist}}{\cosh^2 s} = \pi t\,{\rm csch}(\pi t/2) \tag{34}$$

In class we saw that, surrounding a given electron, screening leads to a depression in the density of other electrons. This is due to electrostatic repulsion. Here we saw that Fermi statistics also leads to a depression, and oscillations. A more detailed theory of screening (due to Lindhard) captures both these effects.