

## Theoretical Material Science: Exercise Sheet 2

Please hand in solutions by: **Tuesday, May 9**, start of the exercise class

### Exercise 4 (4 points): *Specific heat of metals and electron entropy*

We look at the electron contribution to the specific heat  $c_V$ , where we have defined the Energy and Entropy per volume  $u = U/V$  and  $s = S/V$ . Both parts should be done for Jellium.

$$c_V = T \left( \frac{\partial s}{\partial T} \right)_V = \left( \frac{\partial u}{\partial T} \right)_V \quad (1)$$

a) Determine the electronic contribution to the specific heat (low-temperature expansion):

$$c_V = \left( \frac{\partial u}{\partial T} \right)_V = \frac{\pi^2}{3} k_B^2 T g(\epsilon_F).$$

$g$  denotes the density of electronic levels per unit volume.

For comparison, in a crystal, the low-temperature contribution to  $c_V$  by phonons according to Debye's model (to be derived later in this lecture course) is:

$$c_V^{phonon} = \frac{12\pi^4}{5} n k_B \left( \frac{T}{\Theta_D} \right)^3.$$

$\Theta_D$  is known as the "Debye temperature" of a solid, and  $n$  denotes the number of ions in the solid per volume. Compare the electronic and phononic contributions to the specific heat.

b) Use equation 1 to determine the electron entropy, i.e. derive the equation

$$s = -k_B \sum_i \{ f(\epsilon_i) \ln f(\epsilon_i) + [1 - f(\epsilon_i)] \ln [1 - f(\epsilon_i)] \},$$

where  $f(\epsilon)$  is the Fermi function and the index  $i$  runs over electronic states.

### Exercise 5 (4 points): *Density of states*

Show that the density of energy states for an ideal noninteracting Fermi gas is

a) in one dimension

$$N^{1D}(\epsilon) = \frac{V_g}{\pi \hbar} \sqrt{\frac{m}{2}} \frac{1}{\sqrt{\epsilon}},$$

b) in two dimensions

$$N^{2D}(\epsilon) = \frac{m V_g}{\pi \hbar^2}$$

c) and in three dimensions

$$N^{3D}(\epsilon) = \frac{V_g}{\pi^2} \frac{\sqrt{2m^3}}{\hbar^3} \sqrt{\epsilon}.$$

### Exercise 6 (4 points): *Hartree-Fock approximation*

The energy-functional in the Hartree-Fock approximation is given by the expression

$$E^{HF}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] = T_s[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] + E^{e-nuc}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] + E^{Hartree}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] + E^X[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}],$$

with  $T_s$  and  $E^{Hartree}$  defined as in the Hartree theory and

$$E^X[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{i,j} \delta_{s_i s_j} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\varphi_{o_i s_i}^*(\mathbf{r}) \varphi_{o_j s_j}^*(\mathbf{r}') \varphi_{o_i s_i}(\mathbf{r}) \varphi_{o_j s_j}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

Please turn over! →

**(Exercise 6 continued)** Derive the effective single-particle Hartree-Fock equation by varying  $E^{HF}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}]$  under the constraint that  $\varphi_{o_i s_i}$  is normalized as well as orthogonal. Use the requirement that the total energy assumes its minimum at the ground state, i.e:

$$\frac{\delta}{\delta \varphi_{o_i s_i}^*(\mathbf{r})} \left( E^{HF}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] + \sum_{i,j}^{N_i N_j} \lambda_{o_i s_i, o_j s_j} (\delta_{s_i s_j} - \langle \varphi_{o_i s_i} | \varphi_{o_j s_j} \rangle) \right) = 0.$$

Keep in mind that the coefficients  $\lambda_{o_i s_i, o_j s_j}$  are hermitian in  $i, j$ .