TECHNISCHE UNIVERSITÄT DRESDEN

DRESDEN concept

SFB 1143

Solid State Theory (SS2020)

Lecture 6: Second quantization & free electron gas at $T > 0$

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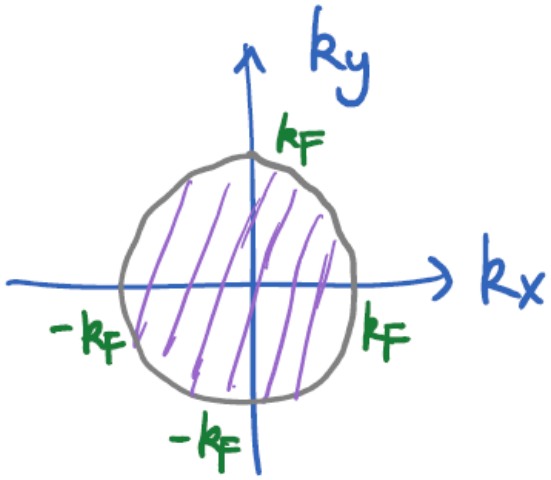
§ 2.1 Free electron gas

- Last lecture: free electron gas at $T = 0$

$$H = -\frac{\hbar^2}{2m}\sum_{j=1}^{N_e}\vec{\nabla}_j^2$$

  - Ground state: Fermi sphere

$$|FS\rangle = \prod_{|\vec{k}|<k_F}\prod_{\sigma=\uparrow,\downarrow} c^\dagger_{\vec{k},\sigma}|0\rangle$$



  - Ground-state energy:

$$E = 2\sum_{|\vec{k}|<k_F}\frac{\hbar^2|\vec{k}|^2}{2m}$$

  - Density of states (DOS): $D(\varepsilon) = 2\sum_{\vec{k}}\delta(\varepsilon-\varepsilon_{\vec{k}})$

§ 2.2 Second quantization

- Second quantization vs. first quantization:

Electron creation / annihilation operators:

$$c^{\dagger}_{\vec{k},\sigma} \quad , \quad c_{\vec{k},\sigma}$$

$$\{ c_{\vec{k},\sigma} , c_{\vec{k}',\sigma'} \} = \{ c^{\dagger}_{\vec{k},\sigma} , c^{\dagger}_{\vec{k}',\sigma'} \} = 0$$

$$\{ c_{\vec{k},\sigma} , c^{\dagger}_{\vec{k}',\sigma'} \} = \delta_{\vec{k},\vec{k}'} \delta_{\sigma\sigma'}$$

Fermi sphere $$|FS\rangle = \prod_{|\vec{k}|<k_F} \prod_{\sigma=\uparrow,\downarrow} c^{\dagger}_{\vec{k},\sigma} |0\rangle$$

§ 2.2 Second quantization

- Second quantization vs. first quantization:

One electron state:

first-quantized form

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \quad \Longleftrightarrow \quad C^{+}_{\vec{k},\sigma}|0\rangle$$

Second-quantized form

§ 2.2 Second quantization

- Second quantization vs. first quantization:

One electron state:

first-quantized form $\phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$ $\Leftrightarrow$ second-quantized form $c^{\dagger}_{\vec{k},\sigma}|0\rangle$

$$c^{\dagger}_{\vec{k},\sigma} = \frac{1}{\sqrt{V}} \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, \psi^{\dagger}_{\sigma}(\vec{r})$$

$$= \int d\vec{r}\, \phi_{\vec{k}}(\vec{r})\, \psi^{\dagger}_{\sigma}(\vec{r})$$

Creation of an electron with spin σ at position $\vec{r}$

- First-quantized wave functions appear as expansion coefficients of second-quantized operators.

§ 2.2 Second quantization

- Second quantization vs. first quantization:

Many-electron state :

first-quantized form

"Slater determinant"

$$\Psi(\{\vec{r}\}) = \det\begin{pmatrix} \phi_{\vec{k}_1}(\vec{r}_1) & \cdots & \phi_{\vec{k}_1}(\vec{r}_{N_e/2}) \\ \vdots & \ddots & \vdots \\ \cdots & \cdots & \cdots \end{pmatrix} \times (\text{spin-}\downarrow \text{ part})$$

$\Leftrightarrow$

second-quantized form

$$|FS\rangle = \prod_{\substack{|\vec{k}|<k_F \\ \sigma=\uparrow,\downarrow}} C^{+}_{\vec{k},\sigma}|0\rangle$$

§ 2.2 Second quantization

- Second quantization vs. first quantization:

$$|FS\rangle = \left(C^{\dagger}_{\vec{k}_1,\uparrow} C^{\dagger}_{\vec{k}_2,\uparrow} \cdots C^{\dagger}_{\vec{k}_{Ne/2},\uparrow} \right) \left(C^{\dagger}_{\vec{k}_1,\downarrow} C^{\dagger}_{\vec{k}_2,\downarrow} \cdots C^{\dagger}_{\vec{k}_{Ne/2},\downarrow} \right) |0\rangle$$

§ 2.2 Second quantization

- Second quantization vs. first quantization:

$$|FS\rangle = \left(c^{\dagger}_{\vec{k}_1,\uparrow} c^{\dagger}_{\vec{k}_2,\uparrow} \cdots c^{\dagger}_{\vec{k}_{N_e/2},\uparrow} \right) \left(c^{\dagger}_{\vec{k}_1,\downarrow} c^{\dagger}_{\vec{k}_2,\downarrow} \cdots c^{\dagger}_{\vec{k}_{N_e/2},\downarrow} \right) |0\rangle$$

$$\| \text{ use inverse Fourier transform}$$

$$\int d\vec{r}_1 \cdots d\vec{r}_{N_e/2} \left[\phi_{\vec{k}_1}(\vec{r}_1) \cdots \phi_{\vec{k}_{N_e/2}}(\vec{r}_{N_e/2}) \right] \psi^{\dagger}_{\uparrow}(\vec{r}_1) \cdots \psi^{\dagger}_{\uparrow}(\vec{r}_{N_e/2})$$

$$\| \text{ sum over all permutations of } \vec{r}_1, \ldots, \vec{r}_{N_e/2}$$

$$\left(\tfrac{N_e}{2}\right)! \int d\vec{r}_1 \cdots d\vec{r}_{N_e/2} \sum_{\sigma \in S_{N_e/2}} \mathrm{sgn}(\sigma)\, \phi_{\vec{k}_1}(\vec{r}_{\sigma(1)}) \cdots \phi_{\vec{k}_{N_e/2}}(\vec{r}_{\sigma(N_e/2)})$$

$$\times \psi^{\dagger}_{\uparrow}(\vec{r}_1) \cdots \psi^{\dagger}_{\uparrow}(\vec{r}_{N_e/2})$$

$$\| \det(\cdots)$$

"Slater determinant"!

§ 2.2 Second quantization

- Second quantization vs. first quantization:

$$|FS\rangle \propto \int d\vec{r}_1 \cdots d\vec{r}_{N_e} \det\begin{pmatrix} \phi_{\vec{k}_1}(\vec{r}_1) & \cdots & \phi_{\vec{k}_1}(\vec{r}_{N_e/2}) \\ \vdots & \ddots & \vdots \end{pmatrix} \det\begin{pmatrix} \phi_{\vec{k}_1}(\vec{r}_{N_e/2+1}) & \cdots & \phi_{\vec{k}_1}(\vec{r}_{N_e}) \\ \vdots & \ddots & \vdots \end{pmatrix}$$

$$\times \psi_\uparrow^+(\vec{r}_1) \cdots \psi_\uparrow^+(\vec{r}_{N_e/2}) \psi_\downarrow^+(\vec{r}_{N_e/2+1}) \cdots \psi_\downarrow^+(\vec{r}_{N_e}) |0\rangle$$

$$= \int d\vec{r}_1 \cdots d\vec{r}_{N_e} \; \Psi(\vec{r}_1, \cdots, \vec{r}_{N_e}) \psi_\uparrow^+(\vec{r}_1) \cdots \psi_\uparrow^+(\vec{r}_{N_e/2}) \psi_\downarrow^+(\vec{r}_{N_e/2+1}) \cdots \psi_\downarrow^+(\vec{r}_{N_e}) |0\rangle$$

First-quantized Slater determinant wave function

§ 2.2 Second quantization

- Second quantization vs. first quantization:

Hamiltonian :

first-quantized form

$$H = -\sum_{j=1}^{N_e} \frac{\hbar^2}{2m} (\vec{\nabla}_j)^2$$

$\Leftrightarrow$

second-quantized form

$$H = \sum_{\vec{k},\sigma} \varepsilon_{\vec{k}} C^{\dagger}_{\vec{k},\sigma} C_{\vec{k},\sigma}$$

$$= \int d\vec{r} \sum_{\sigma=\uparrow,\downarrow} \psi^{\dagger}_{\sigma}(\vec{r}) \left(-\frac{\hbar^2}{2m}\vec{\nabla}^2\right) \psi_{\sigma}(\vec{r})$$

use $\psi_{\sigma}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} C_{\vec{k},\sigma} e^{i\vec{k}\cdot\vec{r}}$

§ 2.2 Second quantization

- Second quantization vs. first quantization:

Particle-number operator for an electron with wave-vector $\vec{k}$ and spin σ:

$$n_{\vec{k},\sigma} = c^{+}_{\vec{k},\sigma} c_{\vec{k},\sigma}$$

$$\begin{cases} n_{\vec{k},\sigma}|0\rangle = 0 \\ n_{\vec{k},\sigma} c^{+}_{\vec{k},\sigma}|0\rangle = c^{+}_{\vec{k},\sigma}|0\rangle \end{cases} \Rightarrow$$

$n_{\vec{k},\sigma}$ has eigenvalue 0 and 1.

Pauli's exclusion principle!

§ 2.2 Second quantization

- Second quantization vs. first quantization:

$$H|FS\rangle = \sum_{\vec{k}} \sum_{\sigma=\uparrow,\downarrow} \varepsilon_{\vec{k}}\, n_{\vec{k},\sigma} \prod_{|\vec{k}'|<k_F,\ \sigma'=\uparrow,\downarrow} c^{+}_{\vec{k}',\sigma'}|0\rangle$$

$$= \sum_{|\vec{k}|<k_F} \sum_{\sigma=\uparrow,\downarrow} \varepsilon_{\vec{k}} \prod_{|\vec{k}'|<k_F,\ \sigma'=\uparrow,\downarrow} c^{+}_{\vec{k}',\sigma'}|0\rangle$$

$$= 2\sum_{|\vec{k}|<k_F} \varepsilon_{\vec{k}}\,|FS\rangle$$

$$= E$$

✓

§ 2.2 Second quantization

- Second quantization vs. first quantization:

General idea on the derivation of second-quantized operators from first-quantized forms:

"match matrix elements"

§ 2.2 Second quantization

- Second quantization vs. first quantization:

General idea on the derivation of second-quantized operators from first-quantized forms:

"match matrix elements"

- Example: Coulomb interaction

$$\sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|} \Longleftrightarrow \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \sum_{\sigma_1,\sigma_2} \psi^+_{\sigma_1}(\vec{r}_1) \psi^+_{\sigma_2}(\vec{r}_2) \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \psi_{\sigma_2}(\vec{r}_2) \psi_{\sigma_1}(\vec{r}_1)$$

§ 2.3 Free electron gas at $T > 0$

- Partition function:

$$Z = \mathrm{Tr}\, e^{-\beta(H-\mu n)} \qquad \beta = \frac{1}{k_B T}$$

$$n = \sum_{\vec{k},\sigma} n_{\vec{k},\sigma} = \sum_{\vec{k},\sigma} c^{+}_{\vec{k},\sigma} c_{\vec{k},\sigma}$$

  - Grand canonical ensemble:

It's more convenient to control the particle number N_e with a chemical potential μ.

μ has to be determined!

§ 2.3 Free electron gas at $T > 0$

- Partition function:

$$
\begin{aligned}
Z &= \mathrm{Tr}\; e^{-\beta \sum_{\vec{k},\sigma} (\varepsilon_{\vec{k}} - \mu) c^{+}_{\vec{k},\sigma} c_{\vec{k},\sigma}} \\
&= \mathrm{Tr} \prod_{\vec{k},\sigma} e^{-\beta(\varepsilon_{\vec{k}} - \mu) n_{\vec{k},\sigma}} \\
&\quad \rightarrow \sum_{\{n_{\vec{k},\sigma}\}} \langle \{n_{\vec{k},\sigma}\} | \cdots | \{n_{\vec{k},\sigma}\} \rangle \\
&= \prod_{\vec{k},\sigma} \sum_{n_{\vec{k},\sigma}=0,1} e^{-\beta(\varepsilon_{\vec{k}} - \mu) n_{\vec{k},\sigma}} \\
&= \prod_{\vec{k},\sigma} \left[1 + e^{-\beta(\varepsilon_{\vec{k}} - \mu)} \right] \\
&= \prod_{\vec{k}} \left[1 + e^{-\beta(\varepsilon_{\vec{k}} - \mu)} \right]^2
\end{aligned}
$$

§ 2.3 Free electron gas at $T > 0$

- Electron distribution function:

$$\langle n_{\vec{k},\sigma} \rangle_T = \frac{1}{\mathcal{Z}} \mathrm{Tr}\left[n_{\vec{k},\sigma} e^{-\beta(H-\mu N)} \right]$$

$$= \cdots$$ (mostly repeat the steps for $\mathcal{Z}$, except for one mode: $n_{\vec{k},\sigma}$.)

$$= \frac{1}{e^{\beta(\varepsilon_{\vec{k}}-\mu)}+1}$$

Fermi-Dirac distribution!

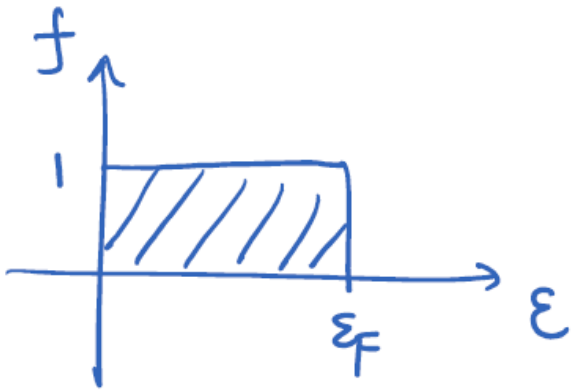
(as expected ...)

$$f(\varepsilon, \mu, T) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}$$

§ 2.3 Free electron gas at $T > 0$

- Determination of chemical potential μ:

$T = 0$: $f(\varepsilon, \mu, T) = \begin{cases} 1, & 0 < \varepsilon < \mu \\ 0, & \varepsilon > \mu \ \& \ \varepsilon < 0 \end{cases}$

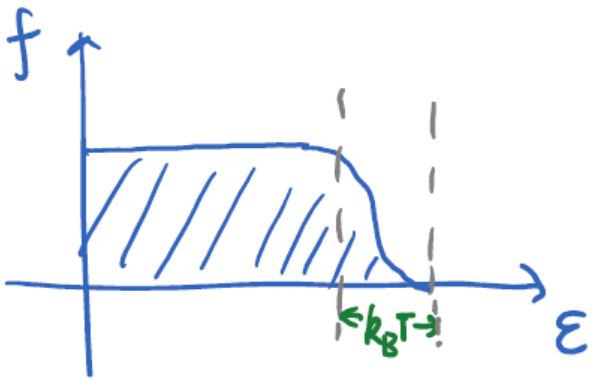


$\Rightarrow \quad \mu(T=0) = \varepsilon_F$

§ 2.3 Free electron gas at $T > 0$

- Determination of chemical potential μ:

$T > 0$ and $T \ll T_F = \frac{\varepsilon_F}{k_B}$ ($10^4 \sim 10^5$ K in metals)



μ has a weak dependence on T.
(close to ε_F)

§ 2.3 Free electron gas at $T > 0$

- Determination of chemical potential μ:

$$N_e = \sum_{\vec{k},\sigma} \langle n_{\vec{k},\sigma} \rangle_T = \sum_{\vec{k},\sigma} \frac{1}{e^{\beta(\varepsilon_{\vec{k}} - \mu)} + 1}$$

$$= \sum_{\vec{k},\sigma} \int_{-\infty}^{\infty} d\varepsilon \; \delta(\varepsilon - \varepsilon_{\vec{k}}) \frac{1}{e^{\beta(\varepsilon_{\vec{k}} - \mu)} + 1}$$

$$\delta(\varepsilon - \varepsilon_{\vec{k}}) \rightarrow D(\varepsilon)$$

$$= \int_{-\infty}^{\infty} d\varepsilon \; D(\varepsilon) \, f(\varepsilon, \mu, T)$$

  - Sommerfeld expansion (low T):

$$\int_{-\infty}^{\infty} d\varepsilon \; f(\varepsilon, \mu, T) \, g(\varepsilon) = \int_{-\infty}^{\mu} d\varepsilon \; g(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 \, g'(\mu) + O(T^4)$$

§ 2.3 Free electron gas at $T > 0$

- Determination of chemical potential μ:

$$N_e \simeq \int_{-\infty}^{\mu} d\varepsilon\, D(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 D'(\mu)$$

§ 2.3 Free electron gas at $T > 0$

- Determination of chemical potential μ:

$$N_e \simeq \int_{-\infty}^{\mu} d\varepsilon\, D(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 D'(\mu)$$

Differentiate with respect to T:

$$D(\mu)\frac{d\mu}{dT} + \frac{\pi^2}{3} k_B^2 T\, D'(\mu) = 0$$

$$\Rightarrow \quad \frac{d\mu}{dT} = -\frac{\pi^2}{3} k_B^2 T \frac{D'(\mu)}{D(\mu)}$$

§ 2.3 Free electron gas at $T > 0$

- Determination of chemical potential μ:

$$N_e \simeq \int_{-\infty}^{\mu} d\varepsilon\, D(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 D'(\mu)$$

$$\Rightarrow \quad \frac{d\mu}{dT} = -\frac{\pi^2}{3} k_B^2 T \frac{D'(\mu)}{D(\mu)}$$

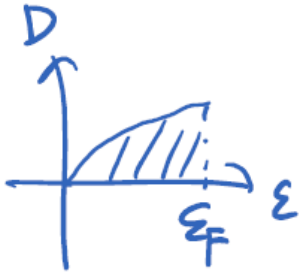
If $D(\varepsilon)$ increases with ε for $\varepsilon \simeq \varepsilon_F$ (i.e. $D'(\varepsilon_F) > 0$)

μ decreases when T increases !

§ 2.3 Free electron gas at $T > 0$

- Determination of chemical potential μ:

3D electron gas:



$$D(\varepsilon) \propto \sqrt{\varepsilon} \Rightarrow \frac{D'(\mu)}{D(\mu)} = \frac{1}{2\mu}$$

$$\mu(T) = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right]$$

$$= \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right] \qquad T \ll T_F \sim 10^4\,K$$

§ 2.3 Free electron gas at $T > 0$

- Specific heat of the 3D free electron gas:

$$C_V = \left(\frac{dU}{dT}\right)_V$$

Internal energy:

Sommerfeld expansion

$$U(T) = \int_{-\infty}^{\infty} d\varepsilon\, D(\varepsilon)\, f(\varepsilon, \mu, T)\, \varepsilon$$

$$\simeq \int_{-\infty}^{\mu} d\varepsilon\, D(\varepsilon)\, \varepsilon + \frac{\pi^2}{6} (k_B T)^2 \left[D(\mu) + \mu D'(\mu) \right]$$

§ 2.3 Free electron gas at $T > 0$

- Specific heat of the 3D free electron gas:

$$C_V = \left(\frac{dU}{dT}\right)_V$$

$$= \mu D(\mu)\frac{d\mu}{dT} + \frac{\pi^2}{3}k_B^2 T\left[D(\mu) + \mu D'(\mu)\right]$$

$$\frac{\pi^2}{3}k_B^2 T D'(\mu) + D(T)\frac{d\mu}{dT} = 0$$

$$= \frac{\pi^2}{3}k_B^2 T D(\mu)$$

$$\simeq \frac{\pi^2}{3}k_B^2 T D(\varepsilon_F)$$

$$D(\varepsilon) = \frac{3}{2}\frac{N_e}{\varepsilon_F}\left(\frac{\varepsilon}{\varepsilon_F}\right)^{1/2}$$

$$\Downarrow$$

$$D(\varepsilon_F) = \frac{3}{2}\frac{N_e}{\varepsilon_F}$$

$$= \frac{\pi^2}{2}N_e\frac{k_B^2 T}{\varepsilon_F}$$

§ 2.3 Free electron gas at $T > 0$

- Specific heat of the 3D free electron gas:

Specifit heat per unit volume:

$$c_v = \frac{C_v}{V} = \frac{\pi^2}{2} k_B n \cdot \frac{T}{T_F}$$

electron density $n = \frac{N_e}{V}$

$$\Rightarrow \boxed{c_v = \nu T}$$

linear in T !

$$\nu = \frac{\pi^2}{2} \frac{k_B}{T_F} n$$

← Sommerfeld coefficient

§ 2.3 Free electron gas at $T > 0$

- Specific heat of the 3D free electron gas:

Specifit heat per unit volume:

$$c_v = \frac{C_v}{V} = \frac{\pi^2}{2} k_B n \cdot \frac{T}{T_F}$$

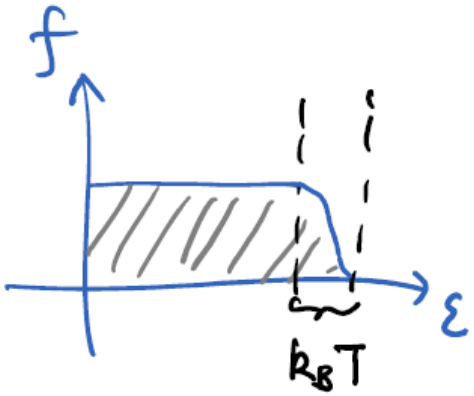
n: electron density $n = \frac{N_e}{V}$

Compare to 3D classical non-interacting particles:

$$C_{v,\,classical} = \frac{3}{2} k_B n$$

§ 2.3 Free electron gas at $T > 0$

- Specific heat of the 3D free electron gas:



very small fraction: $\frac{k_B T}{\varepsilon_F} \ll 1$

Quantum effect !

Only electrons close to the Fermi energy ε_F have substantial contributions to the specific heat.