An Aside: 2nd quantization

when particle numbers are not conserved, as in QFT or in a grand canonical ensemble it is advantageous, to work in "second quantization"

The somewhat strange name originates from the time when physicists realized that forces between particles, i.e. interactions, are mediated by exchange of bosons - quantized particles.

The indistinguishability of identical particles forces us to be noncommittal when writing down many-particle wave-functions in QM: we cannot say which particle is in which state as the particles are indistinguishable.

The CPT theorem (valid for Lorentz-invariant field theories) demands that the many-particle wave-function must be either symmetric (bosons) or anti-symmetric under exchange:

<u>Bosons:</u> $\Psi^B(r_1, \dots, r_i \dots r_j, \dots r_N) = \Psi^B(r_1 \dots, r_j \dots r_i, \dots r_N)$

<u>Fermions:</u> $\Psi^F(r_1 \dots, r_i \dots r_j, \dots r_N) = -\Psi^F(r_1 \dots r_j \dots r_i, \dots r_N)$

For example, the wavefunction for 2 electrons in state a and b has to be

$$\Psi(\underline{r}_1, \underline{r}_2) = A[\psi_a(\underline{r}_1)\psi_b(\underline{r}_2) - \psi_a(\underline{r}_2)\psi_b(\underline{r}_1)]$$

This is the determinant of a matrix

$$\begin{pmatrix} \psi_a(r_1) & \psi_a(r_2) \\ \psi_b(r_1) & \psi_b(r_2) \end{pmatrix}$$

A completely anti-symmetric (fermionic) wave-function is called a Slater determinant

$$\Psi_{n_1, n_2, \dots n_{max}}(\underline{r}_1 \dots r_N) = \sqrt{\frac{1}{N!}} \begin{vmatrix} \phi_{n_1}(\underline{r}_1) & \dots & \phi_{n_{max}}(\underline{r}_1) \\ \phi_{n_2}(\underline{r}_2) & \dots & \phi_{n_{max}}(\underline{r}_2) \\ \vdots & & \vdots \\ \phi(\underline{r}_N) & \dots & \phi_{n_{max}}(\underline{r}_N) \end{vmatrix}$$

In 2^{nd} quantization, we can describe a particle by a field operator

$$\hat{\Psi}(\underline{r}) = \sum_i \hat{a}_i \phi_{n_i}(\underline{r}).$$

where i runs over the quantum numbers associated with the set of eigenstates ϕ, the coefficient a_i is an operator and ϕ_{n_i} is a (1^{st}-quantized) Schrödinger wave-function.

(22)

Commutation relations:

$$[\hat{\Psi}(\underline{r}), \hat{\Psi}^+(\underline{r}')]_\pm = \delta(\underline{r}-\underline{r}')$$

$$[\hat{\Psi}(\underline{r}), \hat{\Psi}(\underline{r}')]_\pm = [\hat{\Psi}^+(\underline{r}), \hat{\Psi}^+(\underline{r}')]_\pm = 0$$

which implies

$$[a_i, a_j^+]_\pm = \delta_{ij}, \quad [a_i, a_j]_\pm = [a_i^+, a_j^+]_\pm = 0$$

The upper sign is for fermions and the lower one is for bosons.

Many-body states are constructed from the vacuum state

$$|0\rangle$$

a is called annihilation operator

a^+ is called creation operator

The annihilation operator annihilates the vacuum

$$a_i|0\rangle = 0$$

The creation operator creates states.

E.g. one particle in state i: $a_i^+|0\rangle = |1\rangle_i$

The anti-commutation relation for fermions encode the Pauli principle:

$$a^2 = (a^+)^2 = 0 \quad \rightsquigarrow \quad \begin{array}{ll} a^+|0\rangle = |1\rangle & a|1\rangle = |0\rangle \\ a^+|1\rangle = 0 & a|0\rangle = 0 \end{array}$$

- many-particle state:

$$(a_1^+)^{n_1}(a_2^+)^{n_2} \dots |0\rangle = |n_1 n_2 \dots\rangle$$

Homework: study the mini-review on 2^{nd} quantization on the website (ccm.zju.edu.cn/?page_id=1058) and work out exercise sheet 1.

The Hamiltonian in 2^{nd} quantization can now be written as

$$\hat{H} = \sum_{i,j} a_i^+ \langle i|T|j\rangle a_j + \frac{1}{2}\sum_{i,j,k,l} a_i^+ a_j^+ \langle ij|V|kl\rangle a_l a_k$$

$$= \int d^3r\, \hat{\Psi}^+(\underline{r})\, T(\underline{r}, \vec{\nabla}_r)\, \hat{\Psi}(\underline{r}) + \frac{1}{2}\int d^3r \int d^3r'\, \hat{\Psi}^+(\underline{r})\, \hat{\Psi}^+(\underline{r}')\, V(\underline{r}, \underline{r}')\, \hat{\Psi}(\underline{r}')\, \hat{\Psi}(\underline{r})$$

and in particular

$$H_0 = \sum_{k,\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma}$$

$c^+_{\underline{k}\sigma} c_{\underline{k}\sigma}$ is the number operator (see exercise sheet 1) that counts the number of particles in state $\underline{k}\sigma$

$\uparrow$
good quantum numbers of state $\underline{k}\sigma$

Therefore $H_0 = \sum_{k,\sigma} \varepsilon_k c^+_{k\sigma} c_{k\sigma}$ just adds up the kinetic energy of all occupied states.

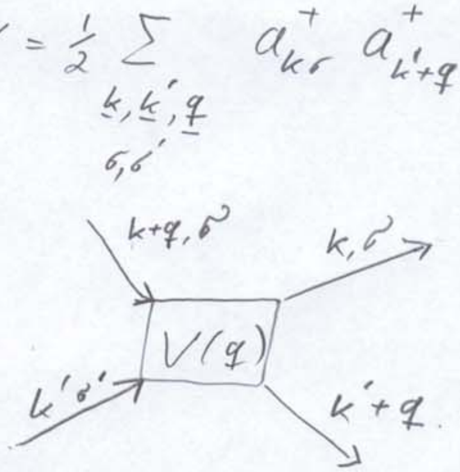
For a translational invariant system, momentum is a good quantum number.

For a general two-body interaction V, we have in that case $V(\underline{r}, \underline{r}') = V(\underline{r} - \underline{r}')$ or, in terms of the Fourier transform

$$V(\underline{q}) = \frac{1}{V} \int d^3\underline{r} \; e^{i\vec{q}\cdot\vec{r}} \, V(\underline{r})$$

$\uparrow$
volume

we have $\hat{V} = \frac{1}{2} \sum_{\substack{\underline{k},\underline{k}',\underline{q} \\ \sigma,\sigma'}} a^+_{k\sigma} \, a^+_{k'+q,\sigma'} \, V(\vec{q}) \, a_{k'\sigma'} \, a_{k+q\sigma}$



$\rightsquigarrow$ scattering of two particles with momentum transfer $\vec{q}$ from particle (with σ) to another (with σ')

(25)

Pauli paramagnetism of conduction electrons

In our previous treatment of Curie paramagnetism we assumed localized (imobile) moments associated with atoms or ions.
Now, we want to study the opposite limit of delocalized, mobile moments: conduction electrons are itinerant and carry spin and thus a magnetic moment.
Therefore, we expect that the conduction electrons contribute to the paramagnetism of a metal.

We consider a model that only contains the coupling of the magnetic field to the electron spin:

$$\mathcal{H} = \underbrace{\sum_{k,\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma}}_{\sum_k \varepsilon_k (c_{k\uparrow}^+ c_{k\uparrow} + c_{k\downarrow}^+ c_{k\downarrow})} + \mu_B B \sum_k (c_{k\uparrow}^+ c_{k\uparrow} - c_{k\downarrow}^+ c_{k\downarrow})$$

$$= \sum_k (\varepsilon_k + \mu_B B) c_{k\uparrow}^+ c_{k\uparrow} + \sum_k (\varepsilon_k - \mu_B B) c_{k\downarrow}^+ c_{k\downarrow}$$

→ electrons in a magnetic field continue to be free but possess slightly shifted single-particle energies $\varepsilon_k \pm \mu_B B$

- $c_{k\uparrow}^+$ generates a state with quantum numbers $\underline{k}$ and $\sigma = \uparrow$
- $c_{k\uparrow}$ destroys " " " "
- $c_{k\sigma}^+ c_{k\sigma}$ counts the number of particles in state $(\underline{k}, \sigma)$

Note, that we used

$$S_z = \frac{\hbar}{2} \sum_R \left(c_{R\uparrow}^+ c_{R\uparrow} - c_{R\downarrow}^+ c_{R\downarrow} \right) = \frac{\hbar}{2} \sum_k \left(c_{k\uparrow}^+ c_{k\uparrow} - c_{k\downarrow}^+ c_{k\downarrow} \right)$$

so that

$$\mu_z = g \frac{e}{2mc} S_z = -\mu_B \sum_k \left(c_{k\uparrow}^+ c_{k\uparrow} - c_{k\downarrow}^+ c_{k\downarrow} \right)$$

For the magnetization, we can therefore write

$$M = \langle \mu_z \rangle = -\mu_B \sum_k \left(\langle c_{k\uparrow}^+ c_{k\uparrow} \rangle - \langle c_{k\downarrow}^+ c_{k\downarrow} \rangle \right)$$

Therefore, we can express the single particle number expectation values from the Fermi function and find

$$M = -\mu_B \int d\varepsilon \, \rho_0(\varepsilon) \left(f(\varepsilon + \mu_B B) - f(\varepsilon - \mu_B B) \right)$$

where $\rho_0(\varepsilon)$ is the density of states.

For small B, $\rho_0(\varepsilon)$ remains constant over the energy interval $\pm \mu_B B$; using the expansion of the Fermi function, we have

$$M = -2\mu_B^2 B \int d\varepsilon \, \rho_0(\varepsilon) \frac{df}{\partial \varepsilon} = 2\mu_B^2 B \int d\varepsilon \, \rho_0(\varepsilon) \left(-\frac{df}{d\varepsilon} \right)$$

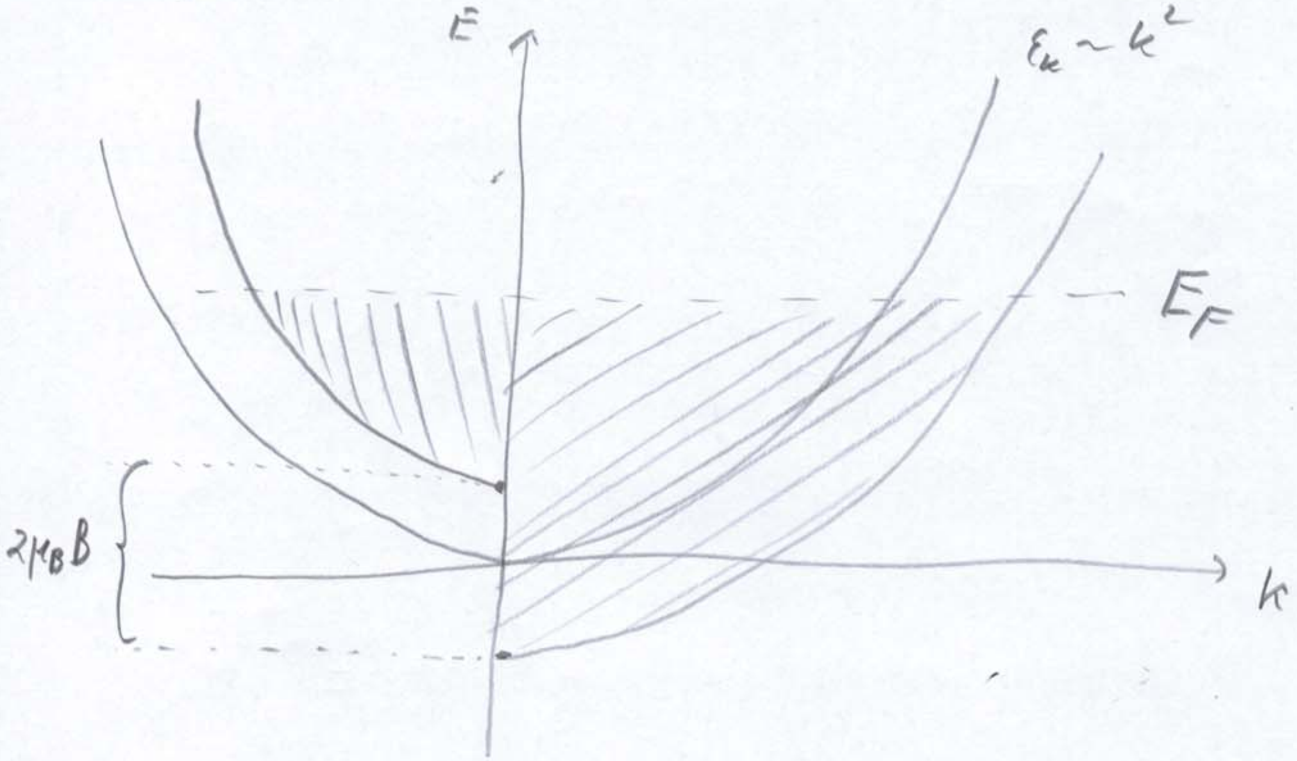
(27) at low temperatures: $-\frac{df}{d\varepsilon} \sim \delta(\varepsilon)$

$\rightarrow \quad M = 2\mu_B^2 B \rho_0(\varepsilon_F)$

and we find (at low T):

<u>Pauli susceptibility</u>: $\boxed{\chi_{Pauli} = 2\mu_B^2 \rho_0(\varepsilon_F)}$

Energy dispersion of free electrons:



(28) Landau diamagnetism of free electrons

Conduction electrons do not only couple via their spin to a magnetic field.

Since electrons are charged, they also couple to the magnetic field via the minimal coupling:

$$\vec{p} \to \vec{p} - \frac{e}{c}\vec{A}$$

For this term we find

$$H = \sum_{i=1}^{N} \frac{1}{2m}\left(\vec{p}_i - \frac{e}{c}\vec{A}(\vec{r}_i)\right)^2 = \sum_i \frac{1}{2m}\left(\vec{p}_i^{\,2} - 2\frac{e}{c}\, p_i \vec{A}(\vec{r}_i) + \frac{e^2}{c^2}\vec{A}^2(\vec{r}_i)\right)$$

For a magnetic field $\parallel \hat{z}$, we write

$$\vec{A} = (0, Bx, 0) \rightsquigarrow \vec{B} = (0,0,B) \quad \text{with} \quad \underbrace{\vec{\nabla}\cdot\vec{A} = 0}_{\text{Landau gauge}}$$

$$\vec{\nabla}\cdot\vec{A} = 0 \Rightarrow \vec{p}\vec{A} = \vec{A}p \quad \text{(used above)}$$

Therefore,

$$H = \sum_i^N \left(\frac{p_{ix}^2}{2m} + \frac{p_{iy}^2}{2m} + \frac{p_{iz}^2}{2m} - \frac{eB}{mc} p_{iy} x_i + \frac{e^2 B^2}{2mc^2} x_i^2\right)$$

There are no interaction terms present

→ sufficient to consider a single term in the sum over i

$$\rightsquigarrow \mathcal{H} = \frac{P_x^2}{2m} + \frac{m}{2}\omega_0\left(X - \frac{P_Y}{m\omega_0}\right)^2 + \frac{P_z^2}{2m}$$

where $\omega_0 = \frac{eB}{mc}$ is the <u>cyclotron</u> frequency.

<u>ansatz:</u> $\Psi = c\,\varphi(x)\,e^{ik_y Y}\,e^{ik_z Z}$

since H does not explicitly depend on Y, Z

$$H\Psi = \left(\frac{P_x^2}{2m} + \frac{m}{2}\omega_0^2\left(X - \frac{\hbar k_y}{m\omega_0}\right)^2 + \frac{\hbar^2 k_z^2}{2m}\right) c\,\varphi(x)\,e^{ik_y Y}e^{ik_z Z}$$

$$= E\,c\,\varphi(x)\,e^{ik_y Y}\,e^{ik_z Z}$$

$\rightsquigarrow$ x-component is a one-dimensional, shifted harmonic oscillator

$$\rightarrow \varphi(x) = \phi_n\left(\frac{x - x_0}{\lambda}\right), \quad x_0 = \frac{\hbar k_y}{m\omega_0} = \frac{\hbar c k_y}{eB}$$

$\uparrow$

Hermite polynomial

$$\lambda = \sqrt{\frac{\hbar}{m\omega_0}} = \sqrt{\frac{\hbar c}{eB}}$$

energy eigenvalues: $E_{n,k_y,k_z} = \hbar\omega_0\left(n + \frac{1}{2}\right) + \frac{\hbar k_z^2}{2m}$

$\rightsquigarrow$ The eigenvalues are degenerate with respect to <u>k_y</u>!

k_y determines the center around which the oscillator swings. To determine the degree of degeneracy, we note that

$$x_0 = \frac{\hbar k_y}{m\omega_0} \leq L_x$$

- assuming periodic boundary conditions: $k_y = \frac{2\pi l_y}{L_y}$ with $l_y \in \mathbb{N}$

$$\rightsquigarrow \quad \frac{2\pi\hbar l_y}{m\omega_0 L_y} \leq L_x \Rightarrow l_y \leq \frac{m\omega_0 L_x L_y}{2\pi\hbar}$$

- degree of degeneracy = number of allowed k_y values of a Landau level

$$\frac{m\omega_0 L_x L_y}{2\pi\hbar} = \frac{|e| B}{c} \; \frac{L_x L_y}{2\pi\hbar}$$

We can now determine M and χ. Instead of free electrons with $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$, we now have non-interacting electrons with single-particle energies E_{n,k_y,k_z}

→ we can still use the expressions/results of the thermodynamics for the Fermi gas

→ free energy (or grand canonical ensemble allowing for particle and energy fluctuations):

$$\Phi = -2 k_B T \sum_\alpha \ln\left(1 + e^{-\beta(\varepsilon_\alpha - \mu)}\right)$$

(31)

$$\Phi = -2k_B T \sum_\alpha \ln\left(1 + e^{-\beta(\varepsilon_\alpha - \mu)}\right)$$

$$= -2k_B T \frac{L_z}{2\pi\hbar} \int dk_z \, \frac{eB}{c} \, \frac{L_x L_y}{2\pi\hbar} \sum_{n=0}^{\infty} \ln\left(1 + e^{-\beta(\varepsilon_\alpha - \mu)}\right)$$

$$= \frac{e k_B T V}{2\pi^2 \hbar^2} \frac{B}{c} \sum_{n=0}^{\infty} g\left(\mu - \hbar\omega_0 \left(n + \tfrac{1}{2}\right)\right)$$

where $g(\mu - x) = \int dk_z \ln\left(1 + e^{\beta\left(\mu - x - \frac{\hbar^2 k_z^2}{2m}\right)}\right)$

- The sum can be approximated using

$$\sum_{n=0}^{\infty} F\left(n + \tfrac{1}{2}\right) = \int_0^{\infty} dx\, F(x) + \frac{1}{24} F'(0) \quad \text{[Euler-McLaurin formula]}$$

Therefore

$$\sum_{n=0}^{\infty} g\left(\mu - \hbar\omega_0 \left(n + \tfrac{1}{2}\right)\right) = \int_0^{\infty} dx\, g(\mu - \hbar\omega_0 x) + \frac{1}{24} \frac{d}{dx} g(x)\Big|_{x=0}$$

$$= \frac{1}{\hbar\omega_0} \int_{-\infty}^{\mu} dy\, g(y) - \frac{\hbar\omega_0}{24} \frac{d}{dy} g(y)\Big|_{y=\mu}$$

where $y = \mu - \hbar\omega_0 x$

and thus

$$\Phi = \frac{k_B T m}{2\pi^2 \hbar^3} V \left[\int_{-\infty}^{\mu} dy\, g(y) - \frac{(\hbar\omega_0)^2}{24} \frac{d}{dy} g(y)\Big|_{\mu} \right]$$

(32)

The first term in this expression for Φ is independent of B.

We can write $\Phi = \Phi_0(T,\mu) - \frac{\hbar^2 e^2 B^2}{24 m^2 c^2} \frac{\partial^2}{\partial \mu^2} \phi_0(T,\mu)$

where $\Phi_0(T,\mu) = \frac{k_B T m}{2\pi^2 \hbar^3} V \int_{-\infty}^{\mu} dy\, g(y)$

$$= \frac{k_B T m}{2\pi^2 \hbar^3} V \int_{-\infty}^{\mu} dy \int dk_z \ln\left(1 + e^{\beta(y - \frac{\hbar^2 k_z^2}{2m})}\right)$$

For the magnetization, we therefore find

$$M = -\frac{\partial \Phi}{\partial B} = \frac{e^2 \hbar^2}{12 m^2 c^2} B \frac{\partial^2 \Phi_0}{\partial \mu^2}$$

and for the susceptibility:

$$\chi = \frac{\partial M}{\partial B} = \frac{e^2 \hbar^2}{12 m^2 c^2} \frac{\partial^2 \Phi_0}{\partial \mu^2}$$

$$\Rightarrow \chi_{Landau} = \frac{1}{3} \mu_B^2 \frac{\partial^2 \Phi_0}{\partial \mu^2} = -\frac{1}{3} \chi_{Pauli}$$

where Φ_0 denotes the grandcanonical potential without magnetic field: $\Phi_0 = -2 k_B T \sum_k \ln\left(1 + e^{-\beta(\varepsilon_k - \mu)}\right)$

$$\frac{\partial \Phi_0}{\partial \mu} = -2 \sum_k \frac{e^{-\beta(\varepsilon_k - \mu)}}{1 + e^{-\beta(\varepsilon_k - \mu)}} = -2 \sum_k f(\varepsilon_k)$$

$$\frac{\partial^2 \Phi_0}{\partial \mu^2} = -2 \sum_k \frac{df}{d\varepsilon_k} \xrightarrow{T \to 0} -2 \rho_0(\varepsilon_F)$$

$$\boxed{\chi_{total} = \chi_{Pauli} + \chi_{Landau} = \frac{2}{3} \chi_{Pauli}}$$