Lecture on First-principles Computations (21)
Introduction to the Green Function Theory

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Computational schemes beyond LDA and GGAs

LDA/ GGAs

+ Wave function methods → Hybrids, double hybrids, Random-phase approximation, …

+ vdW corrections → DFT+ $\sum_{ij} f\left(R_{ij}\right)\frac{C_6^{ij}}{R_{ij}^6}$, vdW-DF

+ Green function methods → The *GW* method

+ model Hamiltonian approach → LDA+U, LDA+DMFT …

Why bother?

- Green function is a useful quantity; many physical observables can be directly obtained if the Green function of a system is known.

  One-particle Green function →
  1. the expectation value of any single-particle operator within the ground state
  2. the ground-state energy
  3. the excitation spectrum of the system

- Many-body theories, which are required in many situations, can be most conveniently expressed in terms of Green function

- The Feynman rule for carrying out the many-body perturbation expansion is simpler for Green function than for other quantities.

Second quantization for fermionic systems

Define an orthonormal single-particle orbital :

$$|i\rangle = |\phi_i\rangle, \qquad i = 1,2,\cdots, M \qquad \text{(ordered in certain way)}$$

N-body (*N*<=*M*) wave function can be expanded as :

$$\Psi(x_1,\cdots,x_N,t) = \sum_{n_1,\cdots,n_M=0}^{1} f(n_1,\cdots,n_{\mathrm{M}},t)\Phi_{n_1,\cdots,n_M}(x_1,\cdots,x_N)$$

$$x = (\mathbf{r},\sigma)$$

$$\Phi_{n_1,\cdots,n_{\mathrm{M}}}(x_1,\cdots,x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_{j_1}(x_1) & \cdots & \phi_{j_1}(x_N) \\ \dots & \vdots & \dots \\ \phi_{j_N}(x_1) & \cdots & \phi_{j_N}(x_N) \end{vmatrix} (j_1 < j_2 < \cdots < j_N)$$

Formally we can write

$$|\Psi(t)\rangle = \sum_{n_1,\cdots,n_{\mathrm{M}}} f(n_1,n_2,\cdots,n_{\mathrm{M}},t)|n_1,n_2,\cdots,n_{\mathrm{M}}\rangle, \qquad n_i = 0,1$$

Second quantization for fermionic systems

$$|\Psi(t)\rangle = \sum_{n_1,\cdots,n_\mathrm{M}} f\,(n_1, n_2, \cdots, n_\mathrm{M}, t)\big|n_1, n_2, \cdots, n_\mathrm{M}\big\rangle, \quad n_i = 0,1$$

Define creation and annihilation operators:

$$\hat{c}_k^\dagger\big|n_1, n_2, \cdots, n_k, \cdots, n_\mathrm{M}\big\rangle = C_+(k)\big|n_1, n_2, \cdots, n_k + 1, \cdots, n_\mathrm{M}\big\rangle,$$

$$\hat{c}_k\big|n_1, n_2, \cdots, n_k, \cdots, n_\mathrm{M}\big\rangle = C_-(k)\big|n_1, n_2, \cdots, n_k - 1, \cdots, n_\mathrm{M}\big\rangle$$

$C_+(k), C_-(k)$ can be chosen to be 1.

Note:

$$\hat{c}_k^\dagger| \cdots, n_k = 1, \cdots \rangle = 0$$
$$\hat{c}_k^\dagger| \cdots, n_k = 0, \cdots \rangle = | \cdots, n_k = 1, \cdots \rangle$$
$$\hat{c}_k| \cdots, n_k = 1, \cdots \rangle = | \cdots, n_k = 0, \cdots \rangle$$
$$\hat{c}_k| \cdots, n_k = 0, \cdots \rangle = 0$$

Second quantization for fermionic systems

$$\hat{c}_k^\dagger|0\rangle_k = |1\rangle_k\,,\ \ \hat{c}_k^\dagger|1\rangle_k = 0; \qquad \hat{c}_k|0\rangle_k = 0\,,\ \ \hat{c}_k|1\rangle_k = |0\rangle_k$$

Hence: $\hat{c}_k\hat{c}_k^\dagger + \hat{c}_k^\dagger\hat{c}_k = 1,\ \ (\hat{c}_k)^2 = 0,\ \ (\hat{c}_k^\dagger)^2 = 0$

For $k \neq k'$, $\quad |\cdots, n_k = 1, \cdots, n_{k'} = 1, \cdots\rangle = -|\cdots, n_{k'} = 1, \cdots, n_k = 1, \cdots\rangle$

$$\hat{c}_k^\dagger\hat{c}_{k'}^\dagger = -\hat{c}_{k'}^\dagger\hat{c}_k^\dagger, \qquad \hat{c}_k\,\hat{c}_{k'} = -\,\hat{c}_{k'}\,\hat{c}_k$$

In summary, the anti-commutation rule:

$$\left[\hat{c}_k, \hat{c}_{k'}^\dagger\right]_+ = \hat{c}_k\hat{c}_{k'}^\dagger + \hat{c}_{k'}^\dagger\hat{c}_k = \delta_{kk'}$$

$$[\hat{c}_k, \hat{c}_{k'}]_+ = \left[\hat{c}_k^\dagger, \hat{c}_{k'}^\dagger\right]_+ = 0$$

$\hat{n}_k = \hat{c}_k^\dagger\hat{c}_k$: Particle number operator

$$\hat{n}_k\left|n_1, n_2, \cdots, n_M\right\rangle = n_k\left|n_1, n_2, \cdots, n_M\right\rangle$$

The operators in second-quantization representation

Single-particle operators:

$$\hat{Q} = \sum_{k=1}^{N} \hat{q}\,(x_k) \quad e.g., \quad \hat{T} = -\sum_{k=1}^{N} \frac{\nabla_k^2}{2}$$

Under second quantization:

$$\hat{Q} = \sum_{ij} q_{ij}\, \hat{c}_i^\dagger \hat{c}_j, \quad q_{ij} = \langle i \mid \hat{q} \mid j \rangle$$

The Hamiltonian operator:

$$\hat{H} = \sum_{ij} h_{ij}^0\, \hat{c}_i^\dagger \hat{c}_j + \frac{1}{2} \sum_{ijkl} V_{ijkl}\, \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_l \hat{c}_k$$

$$V_{ijkl} = \langle ij \mid V \mid kl \rangle = \int\int d\,x_1 dx_2 \phi_i^*(x_1) \phi_j^*(x_2) V(x_1 - x_2) \phi_k(x_1) \phi_l(x_2)$$

The Field operators

$$\hat{\psi}^\dagger(x) = \sum_i \hat{c}_i^\dagger \, \phi_i^*(x); \quad \hat{\psi}(x) = \sum_i \hat{c}_i \, \phi_i(x)$$

Field operators are real-space representation of the creation and annihilation operators!

For fermions, the anti-commutation rule

$$\left[\hat{\psi}(x), \hat{\psi}^\dagger(x')\right]_+ = \delta(x - x')$$

$$\left[\hat{\Psi}(x), \hat{\Psi}(x')\right]_+ = \left[\hat{\Psi}^\dagger(x), \hat{\Psi}^\dagger(x')\right]_+ = 0$$

The density operator:

$$\hat{n}(x) = \hat{\Psi}^\dagger(x)\hat{\Psi}(x) \qquad n(x) = \langle\Psi \mid \hat{\Psi}^\dagger(x)\hat{\Psi}(x) \mid \Psi\rangle / \langle\Psi|\Psi\rangle$$

The Hamiltonian operator:

$$\hat{H} = \int d\,x \hat{\Psi}^\dagger(x) h^0(x) \hat{\Psi}(x) + \frac{1}{2}\int\int dx\,dx' \hat{\Psi}^\dagger(x)\hat{\Psi}^\dagger(x') V(x,x') \hat{\Psi}(x')\hat{\Psi}(x)$$

Schrödinger picture vs Heisenberg picture

Schrödinger picture:

$$i\frac{\partial|\Psi_S(t)\rangle}{\partial t} = \hat{H}|\Psi_S(t)\rangle$$

$$|\Psi_S(t)\rangle = e^{-i\hat{H}(t-t_0)}|\Psi_S(t_0)\rangle, \qquad O(t) = \langle\Psi_S(t) \mid \hat{O}_s \mid \Psi_S(t)\rangle$$

Heisenberger Picture:

$$|\Psi_H(t)\rangle = e^{i\hat{H}t}|\Psi_S(t)\rangle, \qquad i\frac{\partial|\Psi_H(t)\rangle}{\partial t} = 0$$

$$O(t) = \langle\Psi_H \mid \hat{O}_H(t) \mid \Psi_H\rangle, \qquad \hat{O}_H(t) = e^{i\hat{H}t}\hat{O}_S e^{-i\hat{H}t}$$

$$\hat{H}_H(t) = \hat{H}_S = \hat{H}$$

Definition of the Green function

Time-ordered Green function:

Time-ordered operator

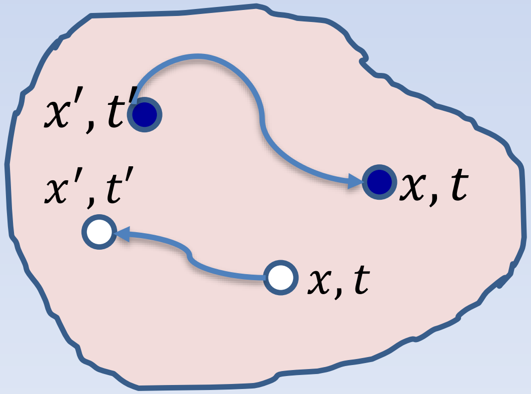
$$G(x,t;x',t') = \frac{-i\langle\Psi_0 \mid T\hat{\psi}(x,t)\hat{\psi}^\dagger(x',t') \mid \Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}$$

Many-body ground state

$$T\hat{\psi}(x,t)\hat{\psi}^\dagger(x',t') = \begin{cases} \hat{\psi}(x,t)\hat{\psi}^\dagger(x',t'), & t > t' \\ -\hat{\psi}^\dagger(x',t')\hat{\psi}(x,t), & t < t' \end{cases}$$

Time-dependent field operator:

$$\hat{\psi}(x,t) = e^{i\hat{H}t}\hat{\psi}(x)e^{-i\hat{H}t}$$



One-particle properties from the Green function

$$G(x,t;x',t') = G(x,x';t-t') =$$

$$\begin{cases} -ie^{iE_0(t-t')}\langle\Psi_0 \mid \hat{\psi}(x)e^{-i\hat{H}(t-t')}\hat{\psi}^\dagger(x') \mid \Psi_0\rangle / \langle\Psi_0|\Psi_0\rangle, & t > t' \\ ie^{-iE_0(t-t')}\langle\Psi_0 \mid \hat{\psi}^\dagger(x')e^{i\hat{H}(t-t')}\hat{\psi}(x) \mid \Psi_0\rangle / \langle\Psi_0|\Psi_0\rangle, & t < t' \end{cases}$$

Density matrix: $x = (\mathbf{r}, \sigma)$

$$\rho_\sigma(\boldsymbol{r},\boldsymbol{r}') = -i \lim_{t'\to t^+} G(\boldsymbol{r},\sigma,t;\boldsymbol{r}',\sigma,t') = -i \lim_{t-t'\to 0^-} G(\boldsymbol{r},\sigma;\boldsymbol{r}',\sigma;t-t')$$
$$= -iG(\boldsymbol{r},\sigma;\boldsymbol{r}',\sigma;0^-)$$

Spin-polarized electron density:

$$n_\sigma(\boldsymbol{r}) = \rho_\sigma(\boldsymbol{r},\boldsymbol{r}) = G(\boldsymbol{r},\sigma;\boldsymbol{r},\sigma;0^-)$$

The kinetic energy density:

$$\epsilon_k(\boldsymbol{r}) = -i \lim_{\boldsymbol{r}'\to\boldsymbol{r}} \sum_\sigma \left(-\frac{\nabla_r^2}{2}\right) G(\boldsymbol{r},\sigma;\boldsymbol{r}',\sigma;0^-)$$

The ground-state energy

$$E_0 = \langle \hat{H} \rangle = \langle \widehat{H_0} \rangle + \langle \hat{V} \rangle$$

$$\hat{H} = \int d\,x \hat{\psi}^{\dagger}(x) h^0(x) \hat{\psi}(x) + \frac{1}{2}\int\int dx\, dx' \hat{\psi}^{\dagger}(x) \hat{\psi}^{\dagger}(x') V(x,x') \hat{\psi}(x') \hat{\psi}(x)$$

$$\langle \widehat{H}_0 \rangle = \int dx\, \langle \hat{\psi}^{\dagger}(x) h^0(x) \hat{\psi}(x) \rangle = -i \int dx \lim_{x' \to x} h^0(x) G(x,x';0^-)$$

$$\langle \hat{V} \rangle = \frac{1}{2}\int\int dx\, dx' V(x,x') \langle \hat{\psi}^{\dagger}(x) \hat{\psi}^{\dagger}(x') \hat{\psi}(x') \hat{\psi}(x) \rangle$$

How to obtain the expectation value of the product of 4 fermion operators?

The key is the equation of motion of the Green function!

The Galitskii-Migdal formula

$$G(x,t;x',t') = -i\langle \Psi_0 \mid T\widehat{\psi}(x,t)\widehat{\psi}^\dagger(x',t') \mid \Psi_0\rangle \quad \text{(assuming } \langle \Psi_0|\Psi_0\rangle = 0)$$

$$i\frac{\partial}{\partial t}G(x,t;x',t') = -i\,\langle \Psi_0 \mid T\left(i\frac{\partial}{\partial t}\widehat{\psi}(x,t)\right)\widehat{\psi}^\dagger(x',t') \mid \Psi_0\rangle$$

$$i\frac{\partial}{\partial t}\widehat{\psi}(x,t) = \left[\widehat{\psi}(x,t),\widehat{H}\right] = h_0(x)\widehat{\psi}(x,t) + \int d\,x'\widehat{\psi}^\dagger(x',t)V(x,x')\widehat{\psi}(x',t)\widehat{\psi}(x,t)$$

$$\Longrightarrow \langle \hat{V}\rangle = -\frac{i}{2}\int dx \lim_{t'\to t^+}\lim_{x'\to x}\left(\mathrm{i}\frac{\partial}{\partial \mathrm{t}} - \mathrm{h}_0(\mathrm{x})\right)G(x,t;x,t')$$

The Galitskii-Migdal formula

$$E_0 = \langle \widehat{H}_0\rangle + \langle \hat{V}\rangle = -\frac{i}{2}\int dx \lim_{\mathrm{t}'\to t^+}\lim_{\mathrm{x}'\to \mathrm{x}}\left(\mathrm{i}\frac{\partial}{\partial \mathrm{t}} + \mathrm{h}_0(\mathrm{x})\right)G(x,t;x,t')$$

The Lehmann representation

Variable replacement : $t - t' \to t$

$$G(x,x';t) = -i\theta(t)\langle\Psi_0 \mid \hat{\psi}(x,t)\hat{\psi}^\dagger(x',0) \mid \Psi_0\rangle$$
$$+i\theta(-t)\langle\Psi_0 \mid \hat{\psi}^\dagger(x',0)\hat{\psi}(x,t) \mid \Psi_0\rangle$$

Denoting $|\Psi_0\rangle = |\Psi_0^N\rangle$ $\quad \sum_s \left|\Psi_s^{N+1}\right\rangle\langle\Psi_s^{N+1}| = 1$, $\sum_r \left|\Psi_r^{N-1}\right\rangle\langle\Psi_r^{N-1}| = 1$

$$G(x,x';t) = -i\theta(t)\sum_s \langle\Psi_0^N \mid \hat{\psi}(x,t) \mid \Psi_s^{N+1}\rangle\langle\Psi_s^{N+1} \mid \hat{\psi}^\dagger(x',0) \mid \Psi_0\rangle$$
$$+i\theta(-t)\sum_r \langle\Psi_0^N \mid \hat{\psi}^\dagger(x',0) \mid \Psi_r^{N-1}\rangle\langle\Psi_r^{N-1} \mid \hat{\psi}(x,t) \mid \Psi_0\rangle$$
$$= -i\theta(t)\sum_s e^{i(E_0^N - E_s^{N+1})t}\langle\Psi_0^N \mid \hat{\psi}(x) \mid \Psi_s^{N+1}\rangle\langle\Psi_s^{N+1} \mid \hat{\psi}^\dagger(x') \mid \Psi_0\rangle$$
$$+i\theta(-t)\sum_r e^{i(E_r^{N-1} - E_0^N)t}\langle\Psi_0^N \mid \hat{\psi}^\dagger(x') \mid \Psi_r^{N-1}\rangle\langle\Psi_r^{N-1} \mid \hat{\psi}(x) \mid \Psi_0\rangle$$

The Lehmann representation

$$G(x,x';t) = -i\theta(t)\sum_s e^{i(E_0^N - E_s^{N+1})t}\langle\Psi_0^N \mid \hat{\psi}(x) \mid \Psi_s^{N+1}\rangle\langle\Psi_s^{N+1} \mid \hat{\psi}^\dagger(x') \mid \Psi_0\rangle$$

$$+i\theta(-t)\sum_r e^{i(E_r^{N-1} - E_0^N)t}\langle\Psi_0^N \mid \hat{\psi}^\dagger(x') \mid \Psi_r^{N-1}\rangle\langle\Psi_r^{N-1} \mid \hat{\psi}(x) \mid \Psi_0\rangle$$

$$\theta(t) = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\frac{e^{-i\omega t}}{\omega + i\eta}$$

$$G(x,x';\omega) = \int_{-\infty}^{\infty} G(x,x';t)e^{i\omega t}dt =$$

$$\sum_s \frac{\langle\Psi_0^N \mid \hat{\psi}(x) \mid \Psi_s^{N+1}\rangle\langle\Psi_s^{N+1} \mid \hat{\psi}^\dagger(x') \mid \Psi_0\rangle}{\omega - (E_s^{N+1} - E_0^N) + i\eta} +$$

$$\sum_r \frac{\langle\Psi_0^N \mid \hat{\psi}^\dagger(x') \mid \Psi_r^{N-1}\rangle\langle\Psi_r^{N-1} \mid \hat{\psi}(x) \mid \Psi_0\rangle}{\omega - (E_0^N - E_r^{N-1}) - i\eta}$$

Green function for non-interacting systems

The Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{H}_{int} \quad \text{where} \quad \hat{H}_{int} = 0$$

$$\hat{H}_0 = \sum_n \epsilon_n \, \hat{c}_n^\dagger \hat{c}_n \quad \Longrightarrow \quad \left[\hat{c}_n, \hat{H}_0\right]_+ = \epsilon_n \hat{c}_n$$

$$\hat{c}_n(t) = e^{i\hat{H}_0 t} \hat{c}_n e^{-i\hat{H}_0 t}$$

$$i\frac{\partial}{\partial t}\hat{c}_n(t) = e^{i\hat{H}_0 t}[\hat{c}_n, H_0]_+ \, e^{-i\hat{H}_0 t} = \epsilon_n \hat{c}_n(t) \quad \Longrightarrow \quad \hat{c}_n(t) = e^{-i\epsilon_n t}\hat{c}_n$$

The field operator:

$$\hat{\psi}(x,t) = \sum_n \hat{c}_n\,(t)\phi_n(x) = \sum_n e^{-i\epsilon_n t}\,\phi_n(x)\hat{c}_n$$

Green function for non-interacting systems

The field operator:

$$\widehat{\psi}(x,t) = \sum_n \hat{c}_n(t)\phi_n(x) = \sum_n e^{-i\epsilon_n t}\,\phi_n(x)\hat{c}_n$$

$$\widehat{\psi}^\dagger(x') = \sum_n \phi_n^*(x')\hat{c}_n^\dagger$$

The non-interacting Green function:

$$G(x,x';t) = -i\langle\Phi_0 \mid T\widehat{\psi}(x,t)\widehat{\psi}^\dagger \mid \Phi_0\rangle$$

$$= -i\sum_{nn'} \phi_n(x)\phi_n{}'(x')e^{-i\epsilon_n t}\left[\theta(t)\langle\Phi_0 \mid \hat{c}_n\hat{c}_{n'}^\dagger \mid \Phi_0\rangle - \theta(-t)\langle\Phi_0 \mid \hat{c}_{n'}^\dagger\hat{c}_n \mid \Phi_0\rangle\right]$$

$$= -i\sum_n \phi_n(x)\phi_n(x')e^{-i\epsilon_n t}[\theta(t)\theta(\epsilon_n - \epsilon_\mathrm{F}) - \theta(-t)\theta(\epsilon_\mathrm{F} - \epsilon_n)]$$

Green function for non-interacting systems

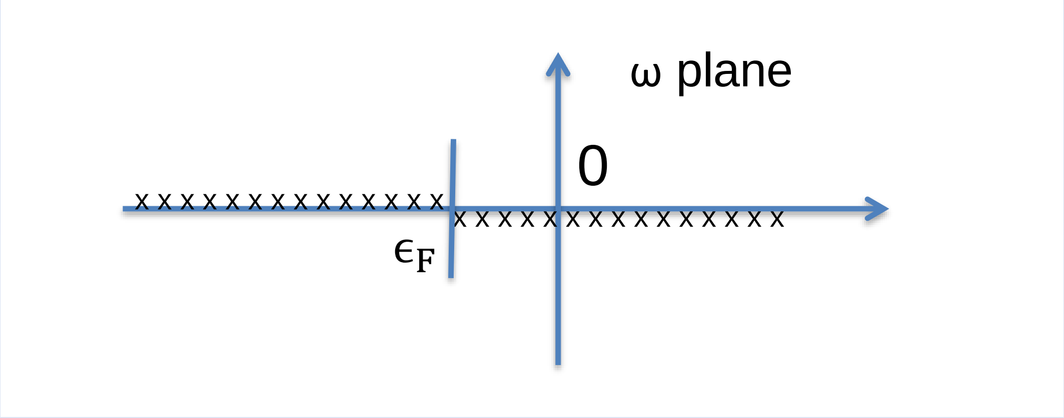
The non-interacting Green function:

$$G(x,x';t) = -i\sum_n \phi_n(x)\phi_n^*(x')e^{-i\epsilon_n t}[\theta(t)\theta(\epsilon_n-\epsilon_F)-\theta(-t)\theta(\epsilon_F-\epsilon_n)]$$

Fourier transform to the frequency domain:

$$G(x,x';\omega) = \int_{-\infty}^{\infty} d\,t G(x,x';t)e^{i\omega t}$$

$$= \sum_n \phi_n(x)\phi_n^*(x')\left[\frac{\theta(\epsilon_n-\epsilon_F)}{\omega+i\eta-\epsilon_n}+\frac{\theta(\epsilon_F-\epsilon_n)}{\omega-i\eta-\epsilon_n}\right]$$



Comparison to the interacting cases

The non-interacting Green function:

$$G(x,x';\omega)=\sum_n \phi_n(x)\phi_n^*(x')\left[\frac{\theta(\epsilon_n-\epsilon_\mathrm{F})}{\omega+i\eta-\epsilon_n}+\frac{\theta(\epsilon_\mathrm{F}-\epsilon_n)}{\omega-i\eta-\epsilon_n}\right]$$

This can be compared to the Lehmann representation in the general case:

$$G(x,x';\omega)=\sum_s \frac{\langle\Psi_0^N \mid \hat{\psi}(x)\mid \Psi_s^{N+1}\rangle\langle\Psi_s^{N+1}\mid \hat{\psi}^\dagger(x')\mid\Psi_0^N\rangle}{\omega-(E_s^{N+1}-E_0^N)+i\eta}+$$

$$\sum_r \frac{\langle\Psi_0^N \mid \hat{\psi}(x)\mid \Psi_r^{N-1}\rangle\langle\Psi_r^{N-1}\mid \hat{\psi}^\dagger(x')\mid\Psi_0^N\rangle}{\omega-(E_0^N-E_r^{N-1})-i\eta}$$

$$\epsilon_s=E_s^{N+1}-E_0^N=\epsilon_s(N+1)+\mu^+;\qquad \mu^+=E_0^{N+1}-E_0^N,\ \epsilon_s(N+1)=E_s^{N+1}-E_0^{N+1}$$

$$\epsilon_r=E_0^N-E_r^{N-1}=-\epsilon_r(N-1)+\mu^-;\qquad \mu^-=E_0^N-E_0^{N-1},\ \epsilon_r(N-1)=E_r^{N-1}-E_0^{N-1}$$

$\mu^+=\mu^-: metal;\quad \mu^+>\mu^-: insulator$

Classical books

- Abrikosov, Gor'kov, Dzyaloshinskii, "*Quantum field theoretical methods in statistical physics*"   (1961, 1963)

- A. Fetter & J. D. Walecka, "*Quantum Theory of Many-particle systems*" (1971)

- G. Mahan, "*Many-particle physics*" (1983) (3rd edition, 2000)