Theory of finite Fermi systems

Summary

- Second quantization
  - Annihilation and creation operators
  - One and two-body operators
  - Vacuum, normal product and contractions
  - Expectation value and Wick theorem
- Hartree-Fock equations
  - The variational principle
  - Hartree-Fock method

❑ Theory of finite systems: second quantization

"Second quantization" formalism

systems of indistinguishable (identical) particles

We consider N Fermions in states $\{\varphi_i, i = 1, 2 \ldots, N\}$

❑ Creation-annihilation operators

State of *N* Fermions

$$\mathit{First\ quantization} \qquad\qquad \mathit{Second\ quantization}$$

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \ldots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \ldots & \varphi_2(N) \\ \ldots & \ldots & \ldots & \ldots \\ \varphi_N(1) & \varphi_N(2) & \ldots & \varphi_N(N) \end{vmatrix} \equiv a_N^+ \ldots a_2^+ a_1^+ |0\rangle$$

State without particles (vacuum)

a_i^+ "Creates" **one** particle in single particle state φ_i

Labels: state, particle

We avoid particle labels

For Fermions: $\{a_k^+, a_l^+\} = 0, \qquad \{a_k, a_l\} = 0, \qquad \{a_k, a_l^+\} = \delta_{kl}$

Representation using "occupation numbers"

$$|n_1, n_2, \ldots\rangle$$

$$N_i = a_i^+ a_i, \qquad \langle n_1, n_2, \ldots | N_i | n_1, n_2, \ldots\rangle = n_i$$

Fermions: $n_i = 0, 1$

❑ Operators in second quantization

$$\text{Arbitrary basis of single particle states } \{\varphi_\alpha\}$$

One body

1st quant. $T = \sum_{i=1}^{N} t_i$ (for instance, kinetic energy $T = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$)

2nd quant. $T = \sum_{\alpha\beta} \langle\alpha|t|\beta\rangle \; a_\alpha^+ a_\beta \equiv \sum_{\alpha\beta} t_{\alpha\beta} \; a_\alpha^+ a_\beta$

$$t_{\alpha\beta} = \sum_{\eta=\uparrow\downarrow} \int d^3r \; \varphi_\alpha^*(\vec{r}, \eta) \; t(\vec{r}) \; \varphi_\beta(\vec{r}, \eta)$$

Sum over all basis

N not used for the operator definition

if the operator does not depend on spin

Two body

1st quant. $V = \sum_{i>j=1}^{N} v_{ij}$ (for instance, Coulomb potential energy) $V = \sum_{i>j=1}^{N} \frac{e^2}{r_{ij}}$

2nd quant. $V = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | v | \gamma\delta \rangle \; a_\alpha^+ a_\beta^+ a_\delta a_\gamma \equiv \frac{1}{2} \sum_{\alpha\beta\gamma\delta} v_{\alpha\beta\gamma\delta} \; a_\alpha^+ a_\beta^+ a_\delta a_\gamma$

Reversed ordering

$$v_{\alpha\beta\gamma\delta} = \sum_{\eta_1\eta_2} \int d^3r_1 d^3r_2 \; \varphi_\alpha^*(\vec{r}_1, \eta_1) \; \varphi_\beta^*(\vec{r}_2, \eta_2) \; v(\vec{r}_1, \vec{r}_2) \; \varphi_\gamma(\vec{r}_1, \eta_1) \varphi_\delta(\vec{r}_2, \eta_2)$$

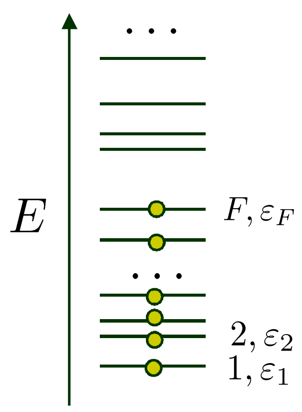
Again: Sum over all basis
N not used for the operator definition

Justification: matrix elements with N particle states are the same in first and second quantization

❑ The“renormalized vacuum”

We are interested in matrix elements with a particular state of the N particle system, the reference state or renormalized vacuum:

$$|v\rangle = a_N^+ \dots a_2^+ a_1^+ \; |0\rangle$$



Ordered single particle states $\{\varepsilon_1, \varepsilon_2, \dots, \varepsilon_N, \dots\}$

Fermi level $\varepsilon_N \equiv \varepsilon_F$

Obviously, for Fermions it is

$$a_\beta |v\rangle = 0 \quad \text{si} \quad \beta > F \quad (\varepsilon_\beta > \varepsilon_F)$$

$$a_\beta^+ |v\rangle = 0 \quad \text{si} \quad \beta \leq F \quad (\varepsilon_\beta \leq \varepsilon_F)$$

❑ "Normal" operator product

Annihilation or creation operators.
Is that in which operators that annihilate the reference state are on the right.
Each inversion "carries a minus sign".
Examples:

$$\alpha, \beta, \gamma > F \quad \Rightarrow \quad \mathcal{N}(a_\alpha a_\beta^+ a_\gamma) = -a_\beta^+ a_\alpha a_\gamma$$

$$\alpha, \beta > F, \gamma \leq F \quad \Rightarrow \quad \mathcal{N}(a_\alpha a_\beta^+ a_\gamma) = a_\beta^+ a_\gamma a_\alpha$$

Expectation value with $|v\rangle$

$$\langle v|\mathcal{N}(ABC\ldots)|v\rangle = 0$$

❑ Contraction of two operators

$$\underbracket{AB} = AB - \mathcal{N}(AB)$$

A and *B* are creation or annihilation operators.
It is a number (constant 0 or 1) due to the commutation rules.
It is always zero, except in two cases:

notation

$$\underbracket{a_\alpha a_\beta^+} = \overset{>}{\delta}_{\alpha\beta} \quad (\alpha, \beta > F)$$

$$\underbracket{a_\alpha^+ a_\beta} = \overset{<}{\delta}_{\alpha\beta} \quad (\alpha, \beta \le F)$$

Other cases

$$\underbracket{a_\alpha a_\beta^+} = 0 \quad (\alpha > F, \beta \le F)$$

$$\underbracket{a_\alpha^+ a_\beta^+} = 0 \quad (\alpha, \beta \le F)$$

$$\cdots$$

❑ Expectation values

With the reference state

Since $AB = \underbracket{AB} + \mathcal{N}(AB)$

$$\boxed{\langle v|AB|v\rangle = \langle v|\underbrace{\underbracket{AB}}_{\text{a number}}|v\rangle + \underbrace{\langle v|\mathcal{N}(AB)|v\rangle}_{\text{zero}} = \underbracket{AB}}$$

❑ Wick theorem

The expectation value with the reference state $|v\rangle$ of an arbitrary product of creation and annihilation operators is equal to the sum of all combinations fully contracted in pairs.

Conditions for a non vanishing expectation value:

A.- Equal number of creation and annihilation operators

B.- Equal number of creation and annihilation operators above and below the Fermi level

C.- Each 'crossing of contractions' carries a minus sign

Examples

One body $$\langle v|T|v\rangle = \sum_{\alpha\beta} t_{\alpha\beta}\, \langle v|a^+_\alpha a_\beta|v\rangle = \sum_{\alpha\beta} t_{\alpha\beta}\, \overset{<}{\delta}_{\alpha\beta} = \sum_{i\leq F} t_{ii}$$

$$= \sum_{i\leq F}\left(\sum_\eta \int d^3r\; \varphi_i^*(\vec{r},\eta)\; t(\vec{r})\; \varphi_i(\vec{r},\eta)\right)$$

If operator does not depend on spin

Two body

$$\langle v|V|v\rangle = \frac{1}{2}\sum_{\alpha\beta\gamma\delta} v_{\alpha\beta\gamma\delta}\,\Big(\langle v|a^+_\alpha a^+_\beta a_\delta a_\gamma|v\rangle + \langle v|a^+_\alpha a^+_\beta a_\delta a_\gamma|v\rangle\Big)$$

$$= \frac{1}{2}\sum_{\alpha\beta\gamma\delta} v_{\alpha\beta\gamma\delta}\,\big(-\overset{<}{\delta}_{\alpha\delta}\,\overset{<}{\delta}_{\beta\gamma} + \overset{<}{\delta}_{\alpha\gamma}\,\overset{<}{\delta}_{\beta\delta}\big)$$

$$= \frac{1}{2}\sum_{i,j\le F}\left(v_{ijij} - v_{ijji}\right) \qquad \text{(direct-exchange)}$$

$$= \sum_{i>j=1}^{F}\left(v_{ijij} - v_{ijji}\right) \qquad \text{(pairs)}$$

$$= \sum_{i>j=1}^{F}\left(\sum_{\eta_1\eta_2}\int d^3r_1 d^3r_2\ \varphi_i^*(\vec{r}_1,\eta_1)\ \varphi_j^*(\vec{r}_2,\eta_2)\ v(\vec{r}_1,\vec{r}_2)\ \varphi_i(\vec{r}_1,\eta_1)\varphi_j(\vec{r}_2,\eta_2)\right.$$

$$\left. - \sum_{\eta_1\eta_2}\int d^3r_1 d^3r_2\ \varphi_i^*(\vec{r}_1,\eta_1)\ \varphi_j^*(\vec{r}_2,\eta_2)\ v(\vec{r}_1,\vec{r}_2)\ \varphi_j(\vec{r}_1,\eta_1)\varphi_i(\vec{r}_2,\eta_2)\right)$$

❑ Hartree-Fock equations

They determine the single particle states $\{\varepsilon_k, \varphi_k, k = 1, 2 \ldots\}$
Variational method

$$\langle v|H|v\rangle \text{ minimal with respect to basis variations}$$

Hamiltonian

$$H = \underbrace{T + V_{\text{ext}}}_{\text{1 body}} + V = H_0 + V$$

2 bodies

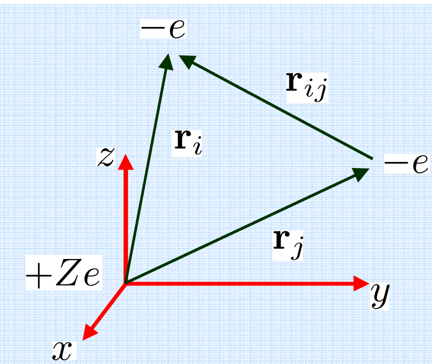
1st quantization

$$H_0 = \sum_{i=1}^{N} h(i) \qquad h = \frac{\vec{p}^{\,2}}{2m} + v_{\text{ext}}(\vec{r})$$

$$V = \sum_{i>j=1}^{N} v(i,j)$$

Example, the atomic Hamiltonian

$$H = \sum_{i=1}^{N} \left(\frac{\vec{p}^{\,2}}{2m} - \frac{Ze^2}{r} \right)_i + \sum_{i>j=1}^{N} \frac{e^2}{r_{ij}}$$



Variational principle (Rayleigh-Ritz)

$$\langle v| \longrightarrow \langle v| + \langle \delta v|$$ variation

$$\frac{\langle v|H|v\rangle}{\langle v|v\rangle} \longrightarrow \frac{\langle v+\delta v|H|v\rangle}{\langle v+\delta v|v\rangle} = \frac{\langle v|H|v\rangle}{\langle v|v\rangle + \langle \delta v|v\rangle} + \frac{\langle \delta v|H|v\rangle}{\langle v|v\rangle + \langle \delta v|v\rangle}$$

$$= \frac{\langle v|H|v\rangle}{\langle v|v\rangle}\left(1 - \frac{\langle \delta v|v\rangle}{\langle v|v\rangle} + \ldots\right) + \frac{\langle \delta v|H|v\rangle}{\langle v|v\rangle}(1 - \ldots)$$

$$\left[\begin{array}{r} \langle v|v\rangle = 1 \\ \langle v|H|v\rangle \equiv E \end{array}\right]$$

$$= E + \underbrace{\langle \delta v|H - E|v\rangle}_{\delta E}$$

Stationary

$$\delta E = 0 \quad \Rightarrow \quad \langle \delta v|H - E|v\rangle = 0 \quad \Rightarrow \quad (H - E)|v\rangle = 0$$

Diverse forms for $|v\rangle$ and for $|\delta v\rangle$ give rise to different theories

The Hartree-Fock method

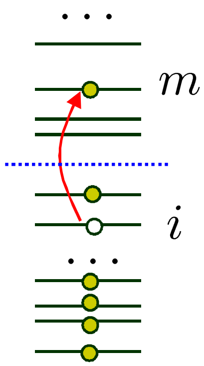
$$\langle \delta v | H - E | v \rangle = 0$$

$$H = \sum_{\alpha\beta} h_{\alpha\beta}\; a_\alpha^+ a_\beta + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} v_{\alpha\beta\gamma\delta}\; a_\alpha^+ a_\beta^+ a_\delta a_\gamma$$

$$|v\rangle = a_N^+ \dots a_2^+ a_1^+ \; |0\rangle$$

$$|\delta v\rangle \approx a_m^+ a_i |v\rangle \quad (m > F, i \leq F)$$

Set of particle-hole transitions



Note that $\langle \delta v | v \rangle = \langle v | a_i^+ a_m | v \rangle = 0$

$$\langle \delta v | H - E | v \rangle = 0 \Rightarrow \langle \delta v | H | v \rangle = 0$$

$$\sum_{\alpha\beta} h_{\alpha\beta}\; \langle v | a_i^+ a_m a_\alpha^+ a_\beta | v \rangle + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} v_{\alpha\beta\gamma\delta}\; \langle v | a_i^+ a_m a_\alpha^+ a_\beta^+ a_\delta a_\gamma | v \rangle = 0$$

$$\sum_{\alpha\beta} h_{\alpha\beta}\, \langle v| a_i^+ a_m a_\alpha^+ a_\beta |v\rangle + \frac{1}{2}\sum_{\alpha\beta\gamma\delta} v_{\alpha\beta\gamma\delta}\, \langle v| a_i^+ a_m a_\alpha^+ a_\beta^+ a_\delta a_\gamma |v\rangle = 0$$

$$\sum_{\alpha\beta} h_{\alpha\beta}\, \overset{<}{\delta}_{i\beta} \overset{>}{\delta}_{m\alpha} + \frac{1}{2}\sum_{\alpha\beta\gamma\delta} v_{\alpha\beta\gamma\delta} \left(-\overset{<}{\delta}_{i\delta} \overset{>}{\delta}_{m\alpha} \overset{<}{\delta}_{\beta\gamma} + \overset{<}{\delta}_{i\delta} \overset{>}{\delta}_{m\beta} \overset{<}{\delta}_{\alpha\gamma} + \overset{<}{\delta}_{i\gamma} \overset{>}{\delta}_{m\alpha} \overset{<}{\delta}_{\beta\delta} - \overset{<}{\delta}_{i\gamma} \overset{>}{\delta}_{m\beta} \overset{<}{\delta}_{\alpha\delta}\right) = 0$$

$$h_{mi} + \frac{1}{2}\sum_{t=1}^{F} \left(-v_{mtti} + v_{tmti} + v_{mtit} - v_{tmit}\right) = 0$$

$$h_{mi} + \sum_{t=1}^{F} \left(v_{mtit} - v_{mtti}\right) = 0$$

Rewrite, defining

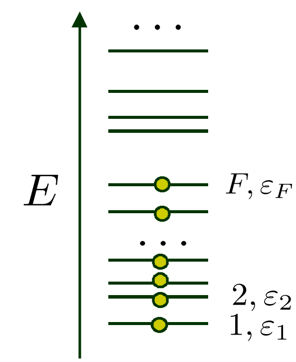
$$H_{HF} = h + \sum_{\alpha\beta} \sum_{t=1}^{F} \left(v_{\alpha t \beta t} - v_{\alpha t t \beta} \right) |\alpha\rangle\langle\beta|$$

$$h_{mi} + \sum_{t=1}^{F} \left(v_{mtit} - v_{mtti} \right) = 0 \quad \Rightarrow \quad \langle m | H_{HF} | i \rangle = 0$$

Does not connect particle states with hole states

Natural choice: HF basis of orbitals $\varphi_k(\vec{r}\eta) \equiv \langle \vec{r}\eta | k \rangle$ diagonalizes H_{HF}

$$H_{HF} |k\rangle = \varepsilon_k |k\rangle$$



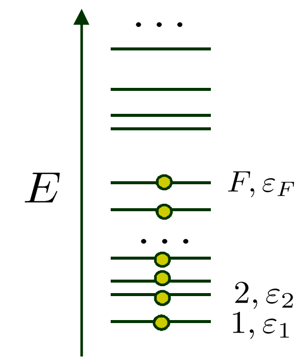
HF equations

$$\boxed{h|k\rangle + \sum_{\alpha} \sum_{t=1}^{F} \left(v_{\alpha t k t} - v_{\alpha t t k} \right) |\alpha\rangle = \varepsilon_k |k\rangle}$$

$$h|k\rangle + \sum_{\alpha} \sum_{t=1}^{F} \left(v_{\alpha tkt} - v_{\alpha ttk}\right) |\alpha\rangle = \varepsilon_k |k\rangle$$

HF eigenvalues
(single particle levels)

$$\boxed{\varepsilon_k = \langle k|h|k\rangle + \sum_{t=1}^{F} \left(v_{ktkt} - v_{kttk}\right)}$$



Total energy of HF state for N particles (reference)

$$\boxed{\begin{aligned} E_v \equiv \langle v|H|v\rangle &= \sum_{k=1}^{F} \langle k|h|k\rangle + \frac{1}{2} \sum_{k,t=1}^{F} \left(v_{ktkt} - v_{kttk}\right) \\ &= \sum_{k=1}^{F} \varepsilon_k - \frac{1}{2} \sum_{k,t=1}^{F} \left(v_{ktkt} - v_{kttk}\right) \end{aligned}}$$