ELEMENTARY INTRODUCTION TO NON-ELEMENTARY METHODS IN QUANTUM MECHANICS

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1. ELEMENTARY INTRODUCTION TO SECOND QUANTIZATION

1.1. QUANTUM OSCILLATOR AS A SIMPLE MODEL OF MANY-BODY PROBLEM. BOSE QUANTA

$$
\begin{aligned}
a &:= \frac{1}{\sqrt{2}}\left(\xi + \frac{\partial}{\partial \xi}\right), \\
a^{\dagger} &:= \frac{1}{\sqrt{2}}\left(\xi - \frac{\partial}{\partial \xi}\right).
\end{aligned}
$$

Main commutator relations for the algebra of creation and annihilation operators

$$
\begin{aligned}
\left[a, a^{\dagger}\right] &= I, & (1)\\
\hat{N} &= a^{\dagger} a, & (2)\\
\hat{H} &= h\omega\left(a^{\dagger} a + \frac{1}{2}\right), & (3)\\
\left[\hat{N}, a^{\dagger}\right] &= a^{\dagger}, & (4)\\
\left[\hat{N}, a\,\right] &= -a. & (5)
\end{aligned}
$$

In Eqs.(2) - (5):
$\hat{N}$ **- the number-of-quanta operator,**
$\hat{H}$ **- the Hamiltonian.**
Using the identity (Leibnitz):

$$
[a, bc] = [a, b]\, c + b\, [a, c]\,,
$$

we get

$$
\left[a, a^{\dagger n}\right] = \left[a, a^{\dagger}\right] a^{\dagger(n-1)} + \ldots + \left[a, a^{\dagger}\right] = n\left(a^{\dagger}\right)^{n-1}. \tag{6}
$$

We define the vacuum state vector $\mid 0\rangle$ as a solution of the following equation

$$
a \mid 0\rangle = 0 \tag{7}
$$

and the state vector

$$| \, n\rangle = \frac{1}{\sqrt{n!}} \left(a^{\dagger}\right)^{n} | \, 0\rangle. \tag{8}$$

Using the identities (2)-(7) we obtain then

$$\begin{aligned}
a^{\dagger} \mid n\rangle &= \sqrt{n+1} \mid n+1\rangle, & (9)\\
a \mid n\rangle &= \sqrt{n} \mid n-1\rangle, & (10)\\
\hat{N} \mid n\rangle &= n \mid n\rangle, & (11)\\
\hat{H} \mid n\rangle &= h\omega \left(n+\frac{1}{2}\right) \mid n\rangle, & (12)\\
\langle n \mid n\rangle &= 1. & (13)
\end{aligned}$$

As a consequence of (8)-(10) we call:
a **-the annihilation operator,**
$a^{\dagger}$ **- the creation operator and**
$| \, n\rangle$ **- the state vector with** n **particle (** n **quanta).**
Using the definitions (7) and (8) and Eqs.(9) and (10), we obtain the matrix elements

$$< k|a^{\dagger}|n >= \sqrt{n+1}\delta_{kn+1},$$
$$< k|a|n >= \sqrt{n}\delta_{kn-1}$$

and the corresponding matrices

$$\hat{a} = \{a_{kn}\}, \quad \hat{a}^{\dagger} = \{a^{\dagger}_{kn}\}$$

which we write as following infinite tables

$$\hat{a} = \{a_{kn}\} = \left(\begin{array}{cccccc}
 & (n=0) & (n=1) & (n=2) & (n=3) & \\
(k=0) & 0 & \sqrt{1} & 0 & 0 & \dots \\
(k=1) & 0 & 0 & \sqrt{2} & 0 & \dots \\
(k=2) & 0 & 0 & 0 & \sqrt{3} & \dots \\
 & \dots & \dots & \dots & \dots & \dots
\end{array}\right),$$

$$
\hat{a}^\dagger = \{a^\dagger_{kn}\} = \begin{array}{c} \\ (k=0) \\ (k=1) \\ (k=2) \\ (k=3) \\ \end{array} \begin{pmatrix} (n=0) & (n=1) & (n=2) & (n=3) & \\ 0 & 0 & 0 & 0 & \dots \\ \sqrt{1} & 0 & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & 0 & \dots \\ 0 & 0 & \sqrt{3} & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}.
$$

From these tables we see that they are hermitian conjugate

$$
\{a^\dagger_{kn}\} = \{a^\star_{nk}\}.
$$

We can also see that the matrix of the number-of-quanta operator is diagonal:

$$
\hat{N} = \{N_{kn}\} = \begin{array}{c} \\ (k=0) \\ (k=1) \\ (k=2) \\ (k=3) \\ \end{array} \begin{pmatrix} (n=0) & (n=1) & (n=2) & (n=3) & \\ 0 & 0 & 0 & 0 & \dots \\ 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & 2 & 0 & \dots \\ 0 & 0 & 0 & 3 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}.
$$

1.2. HEISENBERG PICTURE FOR QUANTUM OSCILLATOR, COHERENT STATES.

The Heisenberg picture is defined as the following transformation of operators and the state vectors

$$
\hat{A}_H = e^{i\hat{H}t/h}\hat{A}e^{-i\hat{H}t/h}, \tag{14}
$$

$$
|\rangle_{Schr} = e^{-i\hat{H}t/h}\,|\rangle_H. \tag{15}
$$

For the creation and annihilation operators in the Heisenberg picture we get

$$
a^\dagger_H(t) = e^{iHt/h}a^\dagger e^{-iHt/h}, \tag{16}
$$

$$
a_H(t) = e^{iHt/h}ae^{-iHt/h}. \tag{17}
$$

They satisfy the equations-of-motion

$$i\hbar\frac{\partial}{\partial t}a_H^\dagger(t) \;=\; [a_H^\dagger(t), H], \tag{18}$$

$$i\hbar\frac{\partial}{\partial t}a_H(t) \;=\; [a_H(t), H]. \tag{19}$$

The commutator relation (1) for operators which are taken at the same time and the Hamiltonian (12) remain unchanged:

$$\left[a_H(t), a_H^\dagger(t)\right] = I,$$
$$\hat{H}\,(t) = \hat{H}.$$

Then the equations-of-motion for the creation and annihilation operators is written as

$$\begin{aligned}\left[a_H^\dagger(t), \hat{H}\right] \;&=\; \left[a_H^\dagger(t), \hat{H}(t)\right] = \\ = \hbar\omega[a_H^\dagger(t), a_H^\dagger(t)a_H(t)] \;&=\; -\hbar\omega a_H^\dagger(t),\end{aligned} \tag{20}$$

$$\begin{aligned}\left[a_H(t), \hat{H}\right] \;&=\; \left[a_H(t), \hat{H}(t)\right] = \\ = \hbar\omega\left[a_H(t), a_H^\dagger(t)a_H(t)\right] \;&=\; \hbar\omega a_H(t)\end{aligned} \tag{21}$$

and we obtain a trivial solution of Eqs.(20) and (21)

$$i\hbar\frac{\partial}{\partial t}a_H^\dagger(t) = -\hbar\omega a_H^\dagger(t) \Rightarrow a_H^\dagger(t) = a^\dagger e^{+i\omega t}, \tag{22}$$

$$i\hbar\frac{\partial}{\partial t}a_H(t) = \hbar\omega a_H(t) \Rightarrow a_H(t) = a e^{-i\omega t}. \tag{23}$$

We define the coordinate and the momentum operators:

$$\hat{x} \;:=\; \frac{1}{\sqrt{2}}\sqrt{\frac{\hbar}{m\omega}}\left(a + a^\dagger\right), \tag{24}$$

$$\hat{p} \;:=\; -i\frac{1}{\sqrt{2}}\sqrt{\hbar m\omega}\left(a - a^\dagger\right). \tag{25}$$

In the Heisenberg representation they are written

$$\hat{x}(t) = \frac{1}{\sqrt{2}}\sqrt{\frac{h}{m\omega}}\left(ae^{-i\omega t} + a^\dagger e^{i\omega t}\right), \quad (26)$$

$$\hat{p}(t) = -i\frac{1}{\sqrt{2}}\sqrt{hm\omega}\left(ae^{-i\omega t} - a^\dagger e^{i\omega t}\right), \quad (27)$$

$$\Delta\hat{X} := X - \bar{X} \quad , \quad \overline{\Delta X^2} := \overline{X^2} - \bar{X}^2,$$

$$\begin{aligned} \Delta\hat{x}(t) &= \hat{x}(t) - \bar{\hat{x}(t)}, \\ \Delta\hat{p}(t) &= \hat{p}(t) - \bar{\hat{p}(t)}, \end{aligned}$$

$$\begin{aligned} \langle\Delta x^2(t)\rangle &= \frac{h}{2m\omega}\Big(\langle\Delta a^{\dagger 2}\rangle e^{2i\omega t} + \langle\Delta a^2\rangle e^{-2i\omega t} + \\ &+ \big(\langle\{a, a^\dagger\}\rangle - 2\langle a\rangle\langle a^\dagger\rangle\big)\Big), \quad (28) \\ \langle\Delta p^2(t)\rangle &= \frac{hm\omega}{2}\Big(\langle\Delta a^{\dagger 2}\rangle e^{2i\omega t} + \langle\Delta a^2\rangle e^{-2i\omega t} - \\ &- \big(\langle\{a, a^+\}\rangle - 2\langle a\rangle\langle a^\dagger\rangle\big)\Big), \quad (29) \end{aligned}$$

$$\begin{aligned} \langle\Delta x^2(t)\rangle\langle\Delta p^2(t)\rangle &= \frac{1}{4}h^2\Big(\big(\langle\Delta a^2\rangle e^{-2i\omega t} + \langle\Delta a^{+2}\rangle e^{2i\omega t}\big)^2 \\ &- \big(\langle\{a, a^\dagger\}\rangle - 2\langle a\rangle\langle a^\dagger\rangle\big)^2\Big) \geq \frac{1}{4}h^2. \quad (30) \end{aligned}$$

From a simple analysis of the Heisenberg unequality (30) we come to a definition of coherent states of Bose oscillators, for which the unequality achieves it's low boundary:

$$a \mid \alpha\rangle = \alpha \mid \alpha\rangle \quad (31)$$

and conclude that the vacuum state $\mid 0\rangle$ Eq.(7) is also an eigenstate of Eq.(31) with the eigenvalue which is equal to zero:

$$a \mid 0\rangle = \alpha \mid 0\rangle, \ \alpha = 0.$$

Proceeding in this way, we get for coherent sates the equation

$$\langle\Delta x^2(t)\rangle\langle\Delta p^2(t)\rangle = \frac{1}{4}h^2,$$

Now we will find eigenvectors of the coordinate operator (24) and we introduce first the basis set $\{\psi_n(\xi)\}$:

$$\begin{aligned} H_n(\xi) &= (-1)^n e^{\xi^2}(\frac{\partial}{\partial\xi})^n e{-}\xi^2, & (32)\\ \psi_n(\xi) &= \frac{1}{\sqrt{2^n n!}}\cdot\frac{1}{(\pi)^{1/4}}e^{-\xi^2/2}H_n(\xi). & (33)\end{aligned}$$

which satisfies the recursive relations:

$$\left(\xi+\frac{\partial}{\partial\xi}\right)\psi_n(\xi) = \sqrt{2n}\psi_{n-1}(\xi), \qquad (34)$$

$$\left(\xi-\frac{\partial}{\partial\xi}\right)\psi_n(\xi) = \sqrt{2(n+1)}\psi_{n+1}(\xi), \qquad (35)$$

$$\xi\psi_n(\xi) = \sqrt{\frac{n}{2}}\psi_{n-1}(\xi) + \sqrt{\frac{(n+1)}{2}}\psi_{n+1}(\xi), \qquad (36)$$

$$\frac{\partial}{\partial\xi}\psi_n(\xi) = \sqrt{\frac{n}{2}}\psi_{n-1}(\xi) - \sqrt{\frac{(n+1)}{2}}\psi_{n+1}(\xi). \qquad (37)$$

Using the functions (32) and (33), Eqs.(9) and (10) and the recursive relations (34)-(37), we show that the state vector

$$\mid\xi_0\rangle = \sum_n \psi_n^\star(\xi_0)\mid n\rangle \qquad (38)$$

is an eigenvector of the operator:

$$\begin{aligned}\frac{1}{\sqrt{2}}\left(a+a^\dagger\right)\mid\xi_0\rangle = \frac{1}{\sqrt{2}}\left(a+a^\dagger\right)\sum_n \psi_n^\star(\xi_0)\mid n\rangle = \\ = \xi_0\mid\xi_0\rangle \qquad (39)\end{aligned}$$

and we prove the representation

$$-i\frac{1}{\sqrt{2}}\left(a-a^{\dagger}\right)\mid\xi_0\rangle=-i\frac{1}{\sqrt{2}}\left(a-a^{\dagger}\right)\sum_n\psi_n^{\star}(\xi_0)\mid n\rangle=$$
$$=i\frac{\partial}{\partial\xi_0}\mid\xi_0\rangle. \qquad (40)$$

From Eqs.(39) and (40) we conclude that

$$\langle\xi_0\mid\frac{1}{\sqrt{2}}\left(a+a^{\dagger}\right)\mid n\rangle=\xi_0\langle\xi_0\mid n\rangle, \qquad (41)$$

$$\langle\xi_0\mid -i\frac{1}{\sqrt{2}}\left(a-a^{\dagger}\right)\mid n\rangle=-i\frac{\partial}{\partial\xi_0}\langle\xi_0\mid n\rangle. \qquad (42)$$

Thus, we come to the wave function

$$\Psi\left(\xi\right)=\langle\xi\mid n\rangle$$

and to the coordinate and the momentum operators of the quantum oscillator:

$$\hat{p}_{\xi}\Psi\left(\xi\right)=-i\frac{\partial}{\partial\xi}\Psi\left(\xi\right), \qquad (43)$$
$$\hat{\xi}\Psi\left(\xi\right)=\xi\Psi\left(\xi\right). \qquad (44)$$

These formulas (43) and (44) and the definitions (39), (40) lead to the coordinate representation for the creation and annihilation operators - first formulas of the 1.1.Subsection. Finally we explicitly solve Eq.(31) by writing

$$\mid\alpha\rangle=\sum_l\frac{\alpha^l}{\sqrt{l!}}\mid l\rangle=$$
$$=\sum_l\frac{\alpha^l}{l!}a^{\dagger l}\mid 0\rangle=e^{\alpha\, a^{\dagger}}\mid 0\rangle. \qquad (45)$$

This solution is non-normalized, the corresponding normalization factor is $\frac{1}{(\pi)^{\frac{1}{4}}}e^{-\frac{|\alpha|^2}{2}}$.

Using rather obvious transformations, we write also the wave function for the coherent state

$$\langle \xi \mid e^{\alpha\, a^{\dagger}} \mid 0 \rangle \;=\; e^{\frac{\alpha}{\sqrt{2}}\left(\xi - \frac{\partial}{\partial \xi}\right)} e^{-\frac{\xi^2}{2}} =$$
$$= e^{\frac{\xi^2}{2}} e^{\frac{-\alpha}{\sqrt{2}}\frac{\partial}{\partial \xi}} e^{-\xi^2} \;=\; e^{\frac{\xi^2}{2}} e^{-\left(\xi - \frac{\alpha}{\sqrt{2}}\right)^2}$$

and the wave function of normalized coherent states is written as follows

$$\Psi_c\left(\xi\right) = \frac{1}{\left(\pi\right)^{\frac{1}{4}}} e^{-\frac{|\alpha|^2}{2}} e^{\frac{\xi^2}{2}} e^{-\left(\xi - \frac{\alpha}{\sqrt{2}}\right)^2}.$$

2. SECOND QUANTIZATION OF FERMI OSCILLATOR

2.1. FERMI QUANTUM OSCILLATOR AS ONE-BODY PROBLEM.

Main commutator relations for the Grassman algebra of creation and annihilation Fermi operators:

$$\left(\begin{array}{rcl} \{a, a^{\dagger}\} & = & I, \\ \{a, a\} & = & 0, \\ \{a^{\dagger}, a^{\dagger}\} & = & 0, \end{array} \right. \tag{46}$$

$$\hat{N} = a^{\dagger} a, \tag{47}$$
$$\hat{H}_0 = \epsilon a^{\dagger} a, \tag{48}$$
$$\left[\hat{N}, a^{\dagger}\right] = a^{\dagger}, \tag{49}$$
$$\left[\hat{N}, a\,\right] = -a, \tag{50}$$

where
$\hat{N}$ - the number-of-particle operator

$\hat{H}_0$ **- the Hamiltonian**

Main identities for commutators and anticommutators:

$$\begin{aligned} [a,bc] &= \{a,b\}c - b\{a,c\}, &(51)\\ [a,bcd] &= \{a,b\}cd - b\{a,c\}d + \\ & \quad bc\{a,d\} - 2bcda, &(52)\\ [a,bcdf] &= \{a,b\}cdf - b\{a,c\}df \\ &+ bc\{a,d\}f - bcd\{a,f\}. &(53)\end{aligned}$$

We define again the vacuum state vector $\mid 0\rangle$ **for Fermi oscillators as a non-degenerate solution of the following equation**

$$a \mid 0\rangle = 0, \qquad (54)$$

and the state vector

$$\mid 1\rangle = a^\dagger \mid 0\rangle,\ \langle 1 \mid 1\rangle. \qquad (55)$$

Using the definitions (46)-(50), we conclude that for the Fermi oscillator

$$a^{\dagger^n} = 0, \quad \textbf{if} \ \ n \geq 2.$$

Hence, for the Fermi oscillator only two state vectors exist: $\mid 0\rangle, \mid 1\rangle$ **. With this restriction we rewrite Eqs. (9) - (13) as follows**

$$\begin{aligned} a^\dagger \mid n\rangle &= \sqrt{n+1} \mid n+1\rangle \delta_{n0}, &(56)\\ a \mid 1\rangle &= \sqrt{n} \mid n-1\rangle \delta_{n1}, &(57)\\ \hat{N} \mid n\rangle &= n \mid n\rangle \ (n=0,1)\,, &(58)\\ \hat{H}_0 \mid n\rangle &= \epsilon \mid n\rangle \delta_{n0} \ (n=0,1)\,, &(59)\\ \langle n \mid n\rangle &= 1 \ (n=0,1)\,. &(60)\end{aligned}$$

As a consequence of Eqs.(47),(48) and (55)-(57) in the case of the Fermi oscillator we also call

a -the annihilation operator,
$a^\dagger$ - the creation operator and
$\mid 1\rangle$ - the one-particle Fermi state vector.
Using the definitions (56), (57) and (58), we obtain the matrix elements

$$< k|a^\dagger|n >= \sqrt{n+1}\delta_{kn+1}\delta_{n0}\delta_{k1},$$
$$< k|a|n >= \sqrt{n}\delta_{kn-1}\delta_{n1}\delta_{k0}$$

and the corresponding matrices $\hat{a} = \{a_{kn}\}, \hat{a}^\dagger = \{a^\dagger_{kn}\}$ which we write as following tables

$$\hat{a} = \{a_{kn}\} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix},$$

$$\hat{a}^\dagger = \{a^\dagger_{kn}\} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

From these tables we see that they are hermitian conjugate: $\{a^\dagger_{kn}\} = \{a^\star_{nk}\}$. We can also see that the matrix of the number-of-quanta operator is diagonal:

$$\hat{N} = \{N_{kn}\} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

2.2. HEISENBERG PICTURE FOR FERMI OSCILLATOR.

The Heisenberg picture is again defined as transformations of operators and the state vectors which were written in Eqs.(15) - (17) and they satisfy the equations-of-motion (18), (19). We rewrite these transformations and equations for Fermi operators:

$$\hat{A}_H = e^{i\hat{H}_0 t/h}\hat{A}e^{-i\hat{H}_0 t/h}, \quad (61)$$
$$|\rangle_{Schr} = e^{-i\hat{H}_0 t/h}\ |\rangle_H, \quad (62)$$

$$a_H^\dagger(t) = e^{i\hat{H}_0 t/h} a^\dagger e^{-i\hat{H}_0 t/h}, \quad (63)$$

$$a_H(t) = e^{i\hat{H}_0 t/h} a e^{-i\hat{H}_0 t/h}, \quad (64)$$

$$ih\frac{\partial}{\partial t} a_H^\dagger(t) = [a_H^\dagger(t), \hat{H}_0], \quad (65)$$

$$ih\frac{\partial}{\partial t} a_H(t) = [a_H(t), \hat{H}_0] \quad (66)$$

with the anticommutator relation (46) and the Hamiltonian (57) which remains unchanged if the operators are taken at the same time:

$$\{a_H(t), a_H^\dagger(t)\} = I, \; \hat{H}_0\,(t) = \hat{H}_0.$$

Then the right-hand side of equations-of-motion for the creation and annihilation operators is written as

$$\begin{aligned}\left[a_H^\dagger(t), \hat{H}_0\right] &= \left[a_H^\dagger(t), \hat{H}_0(t)\right] = \epsilon\left[a_H^\dagger(t), a_H^\dagger(t) a_H(t)\right] = \\ = \epsilon\left(\{a_H^\dagger(t), a_H^\dagger(t)\} a_H(t) \right. &- \left. a_H^\dagger(t)\{a_H^\dagger(t), a_H(t)\}\right) = \\ &= -\epsilon a_H^\dagger(t), \end{aligned} \tag{67}$$

$$\begin{aligned}\left[a_H(t), \hat{H}_0\right] &= \left[a_H(t), \hat{H}_0(t)\right] = \epsilon\left[a_H(t), a_H^\dagger(t) a_H(t)\right] = \\ \epsilon\left(\{a_H(t), a_H^\dagger(t)\} a_H(t) \right. &- \left. a_H(t)\{a_H^\dagger(t), a_H(t)\}\right) = \\ = \epsilon a_H(t) & \end{aligned} \tag{68}$$

and we obtain a trivial solution of Eqs.(67) and (68)

$$i\hbar\frac{\partial}{\partial t} a_H^\dagger(t) = -\epsilon a_H^\dagger(t) \Rightarrow a_H^\dagger(t) = a^\dagger e^{+i\frac{\epsilon t}{\hbar}}, \tag{69}$$

$$i\hbar\frac{\partial}{\partial t} a_H(t) = \epsilon a_H(t) \Rightarrow a_H(t) = a e^{-i\frac{\epsilon t}{\hbar}}. \tag{70}$$

2.3. WAVE FUCTION OF FERMI OSCILLATOR. COORDINATE, MOMENTUM AND INTERACTION OPERATORS.

Here we notice that the operators (24) and (25) do not commute with the corresponding number-of-particle operator $\hat{N}$, therefore the coordinate and the momentum of one Bose oscillator is not defined. This is not the case for Fermi oscillators. In order to write expressions for the coordinate and the momentum operators which commute with the number-of-particle operator we introduce a set of mutually anticommuting creation and mutually anticommuting annihilation operators

$$\{a_j\},\ \{a_j^\dagger\}\,(j = 1, 2, \ldots N)\,.$$

and we suppose that there is a non-degenerate vacuum state-vector $\mid 0\rangle$, $\langle 0 \mid 0\rangle = 1$. Then the vacuum state is

simultaneous vacuum sate for all annihilation operators:

$$a_j \mid 0\rangle = 0. \tag{71}$$

Now, we define the algebra:

$$\{a_j, a_k^\dagger\} = \delta_{jk}, \{a_j, a_k\} = 0, \{a_j^\dagger, a_k^\dagger\} = 0 \tag{72}$$

and the operators

$$\hat{N} = \sum_j a_j^\dagger a_j, \tag{73}$$

$$\hat{H}_0 = \sum_j \epsilon_j a_j^\dagger a_j, \tag{74}$$

$$\left[\hat{N}, a_j^\dagger\right] = a_j^\dagger, \tag{75}$$

$$\left[\hat{N}, a_j\right] = -a_j, \tag{76}$$

which are an extension of (46) -(50). 2^N **state vectors**

$$\mid 0\rangle,\ a_j^\dagger \mid 0\rangle, \ldots,\ a_{j'}^\dagger a_j^\dagger \mid 0\rangle, \ldots,\ a_{j''}^\dagger a_{j'}^\dagger a_j^\dagger \mid 0\rangle, \ldots$$

are mutually orthogonal and normalized. They are eigenstates of the operator $\hat{N}$ **(73) and the corresponding eigenvalue is equal to the total number of creation operators in a state vector. These numbers are not bigger than** N**. We introduce now an orthonormal basis set of** N **functions** $\phi_{j\sigma_j}(\hat{r})$ **and the following linear combinations of the creation and annihilation operators:**

$$\hat{\psi}_\sigma(\vec{r}) = \sum_j \phi_{j\sigma}(\vec{r})\, a_{j\sigma}, \tag{77}$$

$$\hat{\psi}_\sigma^\dagger(\vec{r}) = \sum_j \phi_{j\sigma}^\star(\vec{r})\, a_{j\sigma}^\dagger. \tag{78}$$

For infinite number of particles they satisfy the anticommutator relation:

$$\begin{aligned}
\{\hat{\psi}_\sigma(\vec{r}), \hat{\psi}_{\sigma'}^\dagger(\vec{r}')\} &= \delta(\vec{r} - \vec{r}')\,\delta_{\sigma\sigma'}, \\
\{\hat{\psi}_\sigma(\vec{r}), \hat{\psi}_{\sigma'}(\vec{r}')\} &= 0, \\
\{\hat{\psi}_\sigma^\dagger(\vec{r}), \hat{\psi}_{\sigma'}^\dagger(\vec{r}')\} &= 0
\end{aligned} \tag{79}$$

and we show that the state vector

$$\mid \vec{r}\rangle_\sigma = \hat{\psi}^\dagger_\sigma(\vec{r}) \mid 0\rangle \tag{80}$$

is an eigenstate of the coordinate operator for Fermi particles:

$$\hat{\vec{R}} = \sum_\sigma \int d^3r \hat{\psi}^\dagger_\sigma(\vec{r})\, \vec{r} \hat{\psi}_\sigma(\vec{r})\,. \tag{81}$$

With the simple algebra it is then obtained

$$\hat{\vec{R}} \mid \vec{r}\rangle_\sigma = \sum_{\sigma'} \int d^3r' \hat{\psi}^\dagger_{\sigma'}(\vec{r}')\, \vec{r}' \{\hat{\psi}_{\sigma'}(\vec{r}')\,, \hat{\psi}^\dagger_\sigma(\vec{r})\} \mid 0\rangle = \vec{r} \mid \vec{r}\rangle_\sigma. \tag{82}$$

Here the anticommutator (79) has been used. The same algebra leads to the similar representation for the momentum operator

$$\hat{\vec{P}} = \sum_\sigma \int d^3r \hat{\psi}^\dagger_\sigma(\vec{r}) \left(-ih\vec{\nabla}_{\vec{r}}\right) \hat{\psi}_\sigma(\vec{r}) \tag{83}$$

and

$$\begin{aligned} \hat{\vec{P}} \mid \vec{r}\rangle_\sigma = \sum_{\sigma'} \int d^3r' \hat{\psi}^\dagger_{\sigma'}(\vec{r}') \left(-ih\vec{\nabla}_{\vec{r}'}\right) \{\hat{\psi}_{\sigma'}(\vec{r}') \quad , \quad \hat{\psi}^\dagger_\sigma(\vec{r})\} \mid 0\rangle \\ = \; i \;\, h\vec{\nabla}_{\vec{r}} \mid \vec{r}\rangle_\sigma. \end{aligned} \tag{84}$$

The number-of-particle operator (47) and the Hamiltonian (48) are written as

$$\begin{aligned} \hat{N} &= \sum_{j\sigma} a^\dagger_{j\sigma} a_{j\sigma} = \sum_{\sigma'} \int d^3r' \hat{\psi}^\dagger_{\sigma'}(\vec{r}')\, \hat{\psi}_{\sigma'}(\vec{r}')\,, \\ \hat{H}_0 &= \sum_{j\sigma} a^\dagger_{j\sigma} \epsilon_{j\sigma} a_{j\sigma} = \sum_{\sigma'} \int d^3r' \hat{\psi}^\dagger_{\sigma'}(\vec{r}')\, \hat{h}(\vec{r}')\, \hat{\psi}_{\sigma'}(\vec{r}') \equiv \\ &\equiv \sum_{\sigma'} \int d^3r' \hat{\psi}^\dagger_{\sigma'}(\vec{r}') \left(-\frac{h^2}{2m}\Delta_{\vec{r}'} + v(\vec{r}')\right) \hat{\psi}_{\sigma'}(\vec{r}')\,. \end{aligned} \tag{85}$$

Following commutator equations can be easily proved:

$$\left[\hat{N}, \hat{\vec{R}}\right] \; = \; 0,$$

$$\left[\hat{N},\hat{\vec{P}}\right] = 0,$$
$$\left[\hat{N},\hat{H}_0\right] = 0 \tag{86}$$

and we can write the one-particle wave function as the matrix element:

$$\Psi_\sigma\left(\vec{r}\right) = \langle 0 \mid \hat{\psi}_\sigma\left(\vec{r}\right) \mid l\rangle_\sigma. \tag{87}$$

If the one-particle state (55) is specified as

$$\mid l\rangle_\sigma = a^\dagger_{l\sigma} \mid 0\rangle, \tag{88}$$

then

$$\Psi_\sigma\left(\vec{r}\right) = \phi_{l\sigma}\left(\vec{r}\right). \tag{89}$$

Eq.(86) is interpreted as number of particles conservation in a system with the Hamiltonian (86) and Eqs.(83), (84) and (87)-(89) give us

$$_\sigma\langle\vec{r} \mid \hat{\vec{R}} \mid l\rangle_\sigma = \vec{r}\Psi_\sigma\left(\vec{r}\right), \tag{90}$$
$$_\sigma\langle\vec{r} \mid \hat{\vec{P}} \mid l\rangle_\sigma = -i\hbar\vec{\nabla}_{\vec{r}}\Psi_\sigma\left(\vec{r}\right). \tag{91}$$

Thus, we have obtained the conventional representation of the coordinate and the momentum operators in the space of one-particle wave functions.

2.4. MANY-BODY SYSTEM OF QUANTUM OSCILLATORS.

A state vector of n-body system of identical Fermi particles is usually expanded by state vectors

$$\mid n_{\{\mathcal{M}\}}\rangle \equiv \prod_{j\in\{\mathcal{M}\}} a^\dagger_{j\sigma_j} \mid 0\rangle, \tag{92}$$

where $\mathcal{M}$ is a set of n indexes or by state vectors

$$\mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle \equiv \prod_{j=1,\ldots,n} \hat{\psi}^{\dagger}_{\sigma_j}\left(\vec{r}_j\right) \mid 0\rangle, \tag{93}$$

which are obviously n-particle generalization of the sate vector (80). If we apply operators (81), (83) and (85) to the state vector (93), we get

$$\hat{\vec{R}} \mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle = \left(\sum_{j=1,\ldots,n} \vec{r}_j\right) \mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle, \tag{94}$$

$$\hat{\vec{P}} \mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle = \left(\sum_{j=1,\ldots,n} i\hbar \vec{\nabla}_{\vec{r}_j}\right) \mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle, \tag{95}$$

$$\hat{N} \mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle = n \mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle, \tag{96}$$

$$\hat{H}_0 \mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle = \left(\sum_{j=1,\ldots,n} \hat{h}\left(\vec{r}_j\right)\right) \mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle. \tag{97}$$

These expressions (94)-(96) lead to coordinate representations of corresponding operators in the space of wave functions:

$$\langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \hat{\vec{R}} \mid \rangle = \sum_{j=1,\ldots,n} \vec{r}_j \langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \rangle, \tag{98}$$

$$\langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \hat{\vec{P}} \mid \rangle = \\ = \sum_{j=1,\ldots,n} -i\hbar \vec{\nabla}_{\vec{r}_j} \langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \rangle, \tag{99}$$

$$\langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \hat{N} \mid \rangle = n \langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \rangle, \tag{100}$$

$$\langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \hat{H}_0 \mid \rangle = \\ = \sum_{j=1,\ldots,n} \hat{h}\left(\vec{r}_j\right) \langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \rangle. \tag{101}$$

Using Eqs.(93) and (94), we calculate the wave function

$$\langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \rangle = \langle 0 \mid \prod_{j=1,\ldots,n} \hat{\psi}_{\sigma_j}\left(\vec{r}_j\right) \prod_{k\in\{\mathcal{M}\}} a^{\dagger}_{k\sigma_k} \mid 0\rangle. \tag{102}$$

We write first the identity:

$$\langle 0 \mid \prod_{j\in\{\mathcal{M}\}} a_{j\sigma_j} \prod_{k\in\{\mathcal{M}\}} a^{\dagger}_{k\sigma_k} \mid 0\rangle = det\{\delta_{j\sigma_j\, k\sigma_k}\}, \tag{103}$$

which is in fact a simple variant of the Wick's theorem and the right-hand side of Eq.(103) is an antisymmetrized product of the Kronecker deltas $\delta_{j\sigma_j\, k\sigma_k}$ (Slater determinant). This identity can be proved if we write the left-hand side of as a mean value of the commutator

$$\langle 0 \mid a_{j_1\sigma_{j_1}} \ldots a_{j_{n-1}\sigma_{j_{n-1}}} \left[a_{j_n\sigma_{j_n}}, \prod_{k\in\{\mathcal{M}\}} a^{\dagger}_{k\sigma_k} \right] \mid 0\rangle$$

and use an expansion for the commutator as a set of anti-commutators which is similar to Eq.(52). The wave function (102) is written then as the Slater determinant:

$$det\{\phi_{j\sigma_j}(\vec{r}_k)\, \delta_{\sigma_j\sigma_k}\}.$$

Concluding this Subsection, we introduce the two-particle interaction operator in the second quantization representation. It is written as:

$$\hat{V} = \frac{1}{2} \sum_{ijkl\sigma\sigma'} \langle ij \mid\mid kl\rangle a^{\dagger}_{i\sigma} a^{\dagger}_{j\sigma'} a_{l\sigma'} a_{k\sigma} =$$

$$= \frac{1}{2} \sum_{\sigma\sigma'} \int\int d^3r d^3r' V\left(\mid \vec{r} - \vec{r}' \mid\right) \hat{\psi}^{\dagger}_{\sigma}(\vec{r})\, \hat{\psi}^{\dagger}_{\sigma'}(\vec{r}')\, \hat{\psi}_{\sigma'}(\vec{r}')\, \hat{\psi}_{\sigma}(\vec{r}) \tag{104}$$

and an application of this operator to the state vector (93) results in

$$\hat{V} \mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle =$$

$$= \frac{1}{2} \sum_{\sigma\sigma'} \int\int d^3r d^3r' V\left(\mid \vec{r} - \vec{r}' \mid\right) \hat{\psi}^{\dagger}_{\sigma}(\vec{r})\, \hat{\psi}^{\dagger}_{\sigma'}(\vec{r}')\, \hat{\psi}_{\sigma'}(\vec{r}')$$

$$\times \left[\hat{\psi}_{\sigma}(\vec{r}), \prod_{j=1,\ldots,n} \hat{\psi}^{\dagger}_{\sigma_j}(\vec{r}_j) \right] \mid 0\rangle =$$

$$= \frac{1}{2} \sum_{i\neq j=1,\ldots,n} V\left(\mid \vec{r}_i - \vec{r}_j \mid\right) \mid \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n\rangle. \tag{105}$$

In the space of the wave functions this interaction is written as multiplication operator

$$
\begin{aligned}
&\langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \hat{V} \mid \rangle = \\
&= \frac{1}{2} \sum_{i \neq j = 1, \ldots, n} V\left(\mid \vec{r}_i - \vec{r}_j \mid\right) \quad \langle \vec{r}_1, \sigma_1, \ldots, \vec{r}_n, \sigma_n \mid \rangle. \qquad (106)
\end{aligned}
$$

This expression is obtained when we expand the commutator in (105) in a set of anticommutators recursively using the identities (51) - (53).

2.5. WICK'S THEOREM.

The normal-ordered product or normal product is defined as an antisymmetric product

$$
: ABCD \ldots : \qquad (107)
$$

of the creation and annihilation operators with all creation operators been moved to the left side of the product. For two operators difference between the normal product and the ordinary product is called a contraction

$$
AB =: AB : + A'B'. \qquad (108)
$$

Normal-ordered product is obtained from the ordinary product by subsequent use of the anticommutators (72). A simple example of Eq.(108) the first anticommutator in (72) when it is written as

$$
a_{j\sigma_j} a^{\dagger}_{k\sigma_k} =: a_{j\sigma_j} a^{\dagger}_{k\sigma_k} : + \delta_{j\sigma_j \, k\sigma_k}, \qquad (109)
$$

where we have used the antisymmetry of the normal product

$$
: a_{j\sigma_j} a^{\dagger}_{k\sigma_k} : = - a^{\dagger}_{k\sigma_k} a_{j\sigma_j}.
$$

From Eq. (109) we get then a contraction

$$a'_{j\sigma_j} a^{\dagger\prime}_{k\sigma_k} = \delta_{j\sigma_j\ k\sigma_k} \tag{110}$$

and , obviously, the contraction

$$a^{\dagger\prime}_{k\sigma_k} a'_{j\sigma_j} = 0. \tag{111}$$

Any product of operators can be transformed to the normal product plus normal products with single, double, and maybe fully contracted products:

$$\begin{aligned} ABCDF\ldots =&: ABCDF\ldots : + : A'B'CDF\ldots : + \\ &: A'CD'F\ldots : + \ldots + : A'B''C'DF''\ldots + \ldots : \end{aligned} \tag{112}$$

- Wick's theorem. An example of a fully contarcted product is the Slater determinant of Kronecker deltas in the right-hand side of Eq.(103). It is a product of all possible contractions in the operator

$$\prod_{j\in\{\mathcal{M}\}} a_{j\sigma_j} \prod_{k\in\{\mathcal{M}\}} a^{\dagger}_{k\sigma_k}.$$

Now we prove a lemma which states that the following equation is valid:

$$\begin{aligned} :\ldots ABCD : F \ &= \ :\ldots ABCDF : + :\ldots ABCD'F' : + \\ + :\ldots ABC'DF' : \ &+ \ :\ldots AB'CDF' : + \ldots \\ &+ :\ldots A'BCDF' : + \ldots \end{aligned} \tag{113}$$

It is clear that the only non-trivial case when Eq.(113) has to be proved is the case of F being a creation operator and all $\ldots ABCD$ an annihilation operator. Then we can omit the symbol of the normal product in the left-hand side of Eq.(113) and using anticommutators (72),

we subsequently write

$$
\begin{aligned}
\dots ABCDF = -\dots ABCFD + :\dots ABC\{D,F\}:= \\
= \dots ABFCD - :\dots AB\{C,F\}D: + :\dots ABC\{D,F\}:= \\
= \dots FABCD - :\dots \{A,F\}BCD: + :\dots A\{B,F\}CD: - \\
- :\dots AB\{C,F\}D: + :\dots ABC\{D,F\}:.
\end{aligned} \tag{114}
$$

In order to compensate the alternating signs in Eq.(114) we introduce a normal product with contractions and preserve the order of normal-ordered operators, writing, for example, the following expression for the normal product

$$
:\dots ABC'DF': \stackrel{\text{def}}{=} -:\dots AB\{C,F\}D: .
$$

The last equation in (114) together with this definition turns to Eq.(113) and we have proved the lemma.

The Wick's theorem is now easily proved by mathematical induction. It is valid for two operators (Eq.(109)). We make a supposition that is also valid for n operators. Then for $n+1$ operators it is valid according to Eq.(113).

2.6. PARTICLE-HOLE REPRESENTATION FOR CREATION AND ANNIHILATION OPERATORS.

In the previous subsection the Wick's theorem has been proved for any product of creation-annihilation operators. A simple consequence of this proof is the Wick's theorem for any separate linear combination of creation operators and annihilation operators, for example, the combinations (77) and (78). In this case the contraction (110) is written as

$$
\hat{\psi}'_{\sigma}\left(\vec{r}\right)\hat{\psi}^{\dagger\prime}_{\sigma'}\left(\vec{r}'\right) = \delta\left(\vec{r}-\vec{r}'\right)\delta_{\sigma\sigma'} \tag{115}
$$

and

$$\hat{\psi}_{\sigma}^{\dagger\prime}(\vec{r})\,\hat{\psi}_{\sigma'}^{\prime}(\vec{r}') = 0. \tag{116}$$

Simultaneous linear combinations of both creation and annihilation operators can also be normal-ordered, but in this case the normal ordering corresponds to a new vacuum state vector. An example of these transformation is the particle-hole transformation. The annihilation operators of the one-particle states which are occupied in the new vacuum $|\rangle$ create hole states in the new vacuum and they are in fact hole creation operators and the corresponding

$$a_{j\sigma_j} = b_{j\sigma_j}^{\dagger} \tag{117}$$

and the corresponding creation operators annihilate the hole state and therefore they are hole annihilation operators

$$a_{j\sigma_j}^{\dagger} = b_{j\sigma_j} \tag{118}$$

for all $\{j\sigma_j\}$ which are occupied in the new vacuum state $|\rangle$.

These new creation-annihilation operators satisfy the anticommutator relations (72), the linear combinations (117) and (118) are canonical transformations and they, obviously, have the contractions

$$\begin{aligned} a_{j\sigma_j}^{\prime} a_{k\sigma_k}^{\dagger\prime} &= \delta_{j\sigma_j\,k\sigma_k}, & (119)\\ a_{j\sigma_j}^{\dagger\prime} a_{k\sigma_k}^{\prime} &= 0, & (120)\\ b_{j\sigma_j}^{\prime} b_{k\sigma_k}^{\dagger\prime} &= \delta_{j\sigma_j\,k\sigma_k}, & (121)\\ b_{j\sigma_j}^{\dagger\prime} b_{k\sigma_k}^{\prime} &= 0. & (122) \end{aligned}$$

We denote as $\mathcal{N}$ manifold of indexes of all occupied one-particle states of an spin-unrestricted state vector $|\rangle$ and introduce the occupation-number-function

$$n(j\sigma_j) = \left(\begin{array}{ll} 1 & \textbf{if } j\sigma_j \in \mathcal{N} \\ 0 & \textbf{if } j\sigma_j \notin \mathcal{N} \end{array} \right. . \tag{123}$$

Using (118)- (121), we obtain contractions

$$\begin{aligned} \hat{\psi}'_{\sigma}(\vec{r})\,\hat{\psi}^{\dagger\prime}_{\sigma'}(\vec{r}') &= \sum_{j\sigma_j} \phi_{j\sigma_j}(\vec{r})\,\delta_{\sigma_j\,\sigma} \\ &\qquad \phi^{\star}_{j\sigma_j}(\vec{r}')\,\delta_{\sigma_j\,\sigma'}\left(1 - n(j\sigma_j)\right), \qquad (124) \\ \hat{\psi}^{\dagger\prime}_{\sigma'}(\vec{r}')\,\hat{\psi}'_{\sigma}(\vec{r}) &= \sum_{j\sigma_j} \phi_{j\sigma_j}(\vec{r})\,\delta_{\sigma_j\,\sigma}\phi^{\star}_{j\sigma_j}(\vec{r}')\,\delta_{\sigma_j\,\sigma'} n(j\sigma_j). \qquad (125) \end{aligned}$$

A summation of (124) and (125) gives, obviously (115).

The conventional many-body perturbation theory in the time-dependent form can be formulated in terms of integrals with the Wick's time-ordered integrands. This formulation is conveniently used for partial summation of perturbation expansions. The operators (77) and (78) of this formulation are transformed to the interaction picture (Dirac picture) by the unitary operator

$$e^{-i\frac{\hat{H}_0 t}{h}}$$

(the following formulas we write in atomic units, where $h = 1$). For the one-electron Hamiltonian (85) this transformation gives

$$\begin{aligned} \hat{\psi}_{\sigma}(\vec{r}, t) &= \sum_{j} \phi_{j\sigma} e^{-i\epsilon_j t}(\vec{r})\, a_{j\sigma}, \qquad (126) \\ \hat{\psi}^{\dagger}_{\sigma}(\vec{r}, t) &= \sum_{j} \phi^{\star}_{j\sigma}(\vec{r})\, e^{i\epsilon_j t} a^{\dagger}_{j\sigma}. \qquad (127) \end{aligned}$$

These expressions ((126) and (127)) are again linear combinations of the creation-annihilation operators and for the basis set of spin-orbitals $\{\phi_j(\vec{r})\}$ which is chosen as the set of the eigenfunctions of the operator $\hat{h}\left(\vec{r}'\right)$ in (85) their contractions in the Wick's normal-ordered expansion of a product of operators $\hat{\psi}_\sigma\left(\vec{r},t\right)$ and $\hat{\psi}^\dagger_\sigma\left(\vec{r},t\right)$ are written as follows

$$\begin{aligned}
\hat{\psi}'_\sigma\left(\vec{r},t\right)\hat{\psi}^{\dagger\prime}_{\sigma'}\left(\vec{r}',t'\right) &= \sum_{j\sigma_j}\phi_{j\sigma_j}\left(\vec{r}\right)\delta_{\sigma_j\,\sigma} \\
&\times\ \phi^\star_{j\sigma_j}\left(\vec{r}'\right)\delta_{\sigma_j\,\sigma'}e^{-i\epsilon_j(t-t')}\left(1-n(j\sigma_j)\right), \quad (128)\\
\hat{\psi}^{\dagger\prime}_{\sigma'}\left(\vec{r}',t'\right)\hat{\psi}'_\sigma\left(\vec{r},t\right) &= \sum_{j\sigma_j}\phi_{j\sigma_j}\left(\vec{r},t\right)\delta_{\sigma_j\,\sigma} \\
&\times\ \psi^\star_{j\sigma_j}\left(\vec{r}'\right)\delta_{\sigma_j\,\sigma'}e^{-i\epsilon_j(t-t')}n(j\sigma_j). \quad (129)
\end{aligned}$$

Other contractions of binary products of operators (126) and (127) are equal to zero.

Concluding this subsection we derive Wick's expansion for the Wick's time-ordered product of operators (126) and (127) as a sum of normal-ordered products. Using contractions (128) and (129), we write

$$\begin{aligned}
T\left(\hat{\psi}_\sigma\left(\vec{r},t\right)\hat{\psi}^\dagger_{\sigma'}\left(\vec{r}',t'\right)\right) &\overset{def}{=} \hat{\psi}_\sigma\left(\vec{r},t\right)\hat{\psi}^\dagger_{\sigma'}\left(\vec{r}',t'\right)\theta\left(t-t'\right)\ - \\
&-\ \hat{\psi}^\dagger_{\sigma'}\left(\vec{r}',t'\right)\hat{\psi}_\sigma\left(\vec{r},t\right)\theta\left(t'-t\right)\ = \\
=: \hat{\psi}_\sigma\left(\vec{r},t\right)\hat{\psi}^\dagger_{\sigma'}\left(\vec{r}',t'\right): + &\ \hat{\psi}'_\sigma\left(\vec{r},t\right)\hat{\psi}^{\dagger\prime}_{\sigma'}\left(\vec{r}',t'\right)\theta\left(t-t'\right)\ + \\
&-\ \hat{\psi}^{\dagger\prime}_{\sigma'}\left(\vec{r}',t'\right)\hat{\psi}'_\sigma\left(\vec{r},t\right)\theta\left(t'-t\right)\ = \\
=: \hat{\psi}_\sigma\left(\vec{r},t\right)\hat{\psi}^\dagger_{\sigma'}\left(\vec{r}',t'\right): + &\quad T\left(\hat{\psi}'_\sigma\left(\vec{r},t\right)\hat{\psi}^{\dagger\prime}_{\sigma'}\left(\vec{r}',t'\right)\right), \quad (130)
\end{aligned}$$

where

$$\begin{aligned}
T\left(\hat{\psi}'_\sigma\left(\vec{r},t\right)\hat{\psi}^{\dagger\prime}_{\sigma'}\left(\vec{r}',t'\right)\right) &\overset{def}{=} \hat{\psi}'_\sigma\left(\vec{r},t\right)\hat{\psi}^{\dagger\prime}_{\sigma'}\left(\vec{r}',t'\right)\theta\left(t-t'\right)\ + \\
&-\ \hat{\psi}^{\dagger\prime}_{\sigma'}\left(\vec{r}',t'\right)\hat{\psi}'_\sigma\left(\vec{r},t\right)\theta\left(t'-t\right) \quad (131)
\end{aligned}$$

is a definition of the time-ordered contraction and Eq.(130) is the Wick's theorem for time-ordered product of two operators (126) and (127). In order to prove the theorem for

any product we use again the mathematical induction and suppose that this statement is valid for for time-ordered product n operators

$$\underbrace{T\left(ABCDF\ldots\right)}_{n} =: ABCDF\ldots : + : A'B'CDF\ldots : + \\ : A'CD'F\ldots : + \ldots + : A'B''C'DF''\ldots + \ldots : \quad (132)$$

with time-ordered contractions:

$$\begin{aligned} A'B' &\equiv T\left(A'B'\right), \\ A'D' &\equiv T\left(A'D'\right), \\ &\ldots, \\ B''F'' &\equiv T\left(B''F''\right), \\ &\ldots . \end{aligned}$$

For $n+1$ time-ordered operators we find an operator with the minimal time (M) and write

$$\underbrace{T\left(ABCDF\ldots M\ldots\right)}_{n+1} = (-1)^{[P]}\underbrace{T\left(ABCDF\ldots\right)}_{n} M \quad (133)$$

where $[P]$ is the pairity of permutation of the product $ABCDF\ldots M\ldots$ to $ABCDF\ldots M$. For $\underbrace{T\left(ABCDF\ldots\right)}_{n}$ we can use Eq.(130) (Wick's theorem for n time-ordered operators and with time-ordered contractions). For products

$$\begin{aligned} : ABCDF\ldots : M, \\ : A'B'CDF\ldots : M, \\ : A'CD'F\ldots : M, \\ : A'B''C'DF''\ldots : M, \\ \ldots \end{aligned}$$

with time-ordered contractions (132) we use the lemma Eq.(113) with ordinary contractions, but the time of M is minimal and we can write

$$\begin{aligned} A'M' &= T\left(A'M'\right), \\ B'M' &= T\left(B'M'\right), \\ C'M' &= T\left(C'M'\right), \\ D'M' &= T\left(D'M'\right), \\ &\ldots . \end{aligned} \tag{134}$$

Thus, we have proved the Wick's theorem for time-ordered products. Finally we write the time-ordered contractions for $a^{\dagger}_{j\sigma_j}, a_{k\sigma_k}$

$$\begin{aligned} a'_{k\sigma_k}(t)\, a^{\dagger\prime}_{l\sigma_l}(t') &= \sum_{j\sigma_j} \delta_{kj}\delta_{\sigma_k\sigma_j}(\vec{r}) \\ &\times\ \delta_{lj}\delta_{\sigma_l\sigma_j} e^{-i\epsilon_j(t-t')}\left(1-n(j\sigma_j)\right), \end{aligned} \tag{135}$$

$$\begin{aligned} a^{\dagger\prime}_{l\sigma_l}(t')\, a'_{k\sigma_k}(t) &= \sum_{j\sigma_j} \delta_{kj}\delta_{\sigma_k\sigma_j}(\vec{r}) \\ &\times\ \delta_{lj}\delta_{\sigma_l\sigma_j} e^{-i\epsilon_j(t-t')} n(j\sigma_j) \end{aligned} \tag{136}$$

and

$$\begin{aligned} T\left(a'_{k\sigma_k}(t)\, a^{\dagger\prime}_{l\sigma_l}(t')\right) &= \sum_{j\sigma_j} \delta_{kj}\delta_{\sigma_k\sigma_j}(\vec{r})\, \delta_{lj}\delta_{\sigma_l\sigma_j} e^{-i\epsilon_j(t-t')} \\ &\times\left(\left(1-n(j\sigma_j)\right)\theta\left(t-t'\right) - n(j\sigma_j)\theta\left(t'-t\right)\right). \end{aligned} \tag{137}$$

3. ONE-PARTICLE GREEN'S FUNCTIONS IN THE MANY-BODY THEORY

3.1. GREEN'S FUNCTION OF NON-INTERACTING PARTICLES

From Eqs.(128), (129), (131), (135) - (137) we get equations for expectation values

$$\langle| \, T\left(\hat{\psi}_{\sigma}\left(\vec{r},t\right)\hat{\psi}^{\dagger}_{\sigma'}\left(\vec{r}',t'\right)\right)|\rangle = \sum_{j\sigma_j} e^{-i\epsilon_j(t-t')}\delta_{\sigma_j\,\sigma}\delta_{\sigma_j\,\sigma'}$$
$$\times\phi_{j\sigma_j}\left(\vec{r}\right)\phi^{\star}_{j\sigma_j}\left(\vec{r}'\right)$$
$$\left(\left(1-n(j\sigma_j)\right)\theta\left(t-t'\right)-n(j\sigma_j)\theta\left(t'-t\right)\right) \tag{138}$$

and

$$\langle| \, T\left(a_{k\sigma_k}\left(t\right)a^{\dagger}_{l\sigma_l}\left(t'\right)\right)|\rangle = \sum_{j\sigma_j} e^{-i\epsilon_j(t-t')}\delta_{kj}\delta_{\sigma_k\sigma_j}\left(\vec{r}\right)\delta_{lj}\delta_{\sigma_l\sigma_j}$$
$$\times\left(\left(1-n(j\sigma_j)\right)\theta\left(t-t'\right)-n(j\sigma_j)\theta\left(t'-t\right)\right). \tag{139}$$

These expectation values satisfy the following equations:

$$\left(i\frac{\partial}{\partial t}-\hat{h}\right)\langle| \, T\left(\hat{\psi}_{\sigma}\left(\vec{r},t\right)\hat{\psi}^{\dagger}_{\sigma'}\left(\vec{r}',t'\right)\right)|\rangle =$$
$$= i\delta^{(3)}\left(\vec{r}-\vec{r}'\right)\delta\left(t-t'\right)\delta_{\sigma\,\sigma'}, \tag{140}$$
$$\sum_m\left(i\frac{\partial}{\partial t}\delta_{k\,m}-\{\hat{h}\}_{k\,m}\right)\langle| \, T\left(a_{m\sigma}\left(t\right)a^{\dagger}_{l\sigma'}\left(t'\right)\right)|\rangle =$$
$$= i\delta_{k\,l}\delta\left(t-t'\right)\delta_{\sigma\,\sigma'}, \tag{141}$$

where in Eqs. (140) and (141) $\hat{h}$ and $\{\hat{h}\}_{k,m}$ is the operator from (85) and it's matrix in the basis of spin-orbitals $\{\phi_j(\vec{r})\}$. These expectation values are usually multiplied by $-i$ and called one-particle Green's functions of the system of non-interacting particles with the Hamiltonian (74)

$$\begin{aligned} G^{(0)}_{k\sigma_k,l\sigma_l}\left(t,t'\right) &\stackrel{def}{=} \\ -i\langle| \, T\left(a_{k\sigma_k}\left(t\right)a^{\dagger}_{l\sigma_l}\left(t'\right)\right)|\rangle &= -i\sum_{j\sigma_j} e^{-i\epsilon_j(t-t')}\delta_{kj}\delta_{\sigma_k\sigma_j}\left(\vec{r}\right)\delta_{lj}\delta_{\sigma_l\sigma_j} \\ \times\left(\left(1-n(j\sigma_j)\right)\theta\left(t-t'\right)\right. &- \left.n(j\sigma_j)\theta\left(t'-t\right)\right). \end{aligned} \tag{142}$$

3.2. ONE-PARTICLE GREEN'S FUNCTION OF INTERACTING PARTICLES

For system of interaction particles (electrons) with the Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{143}$$

in the Heisenberg picture the transformation of Schrödinger operators is done by

$$e^{-i\hat{H}t},$$

which defines the corresponding Heisenberg creation -annihilation operators

$$\begin{aligned} a_{H\,p}\left(t\right) &= e^{i\hat{H}t} a_p e^{-i\hat{H}t}, \\ a^{\dagger}_{H\,q}\left(t\right) &= e^{i\hat{H}t} a^{\dagger}_q e^{-i\hat{H}t}. \end{aligned} \tag{144}$$

Here and in the following subsections we will also use indexes $p, q, r, s, \ldots$ **. instead of indexes** $j\sigma_j, k\sigma_k, l\sigma_l, \ldots$ **. The one-particle Green's function is then defined as the expectation value of the time-ordered product of operators (143):**

$$G_{p,q}\left(t,t'\right) \stackrel{def}{=} -i\langle|\, T\left(a_p\left(t\right) a^{\dagger}_q\left(t'\right)\right) |\rangle, \tag{145}$$

where brackets $|\rangle$ **or** $\langle|$ **in (145) represent an eigenstate vector of the Hamiltonian (143). In an explicit form this definition of the one-particle Green's function is written**

$$\begin{aligned} G_{p,q}\left(t,t'\right) &\stackrel{def}{=} -i\langle|\, a_p(t)a^{\dagger}_q(t') \,|\rangle\theta(t-t') + i\langle|\, a^{\dagger}_q(t')a_p(t) \,|\rangle\theta(t'-t) \\ &= G^{(A)}_{p,q}\left(t,t'\right)\theta(t-t') + G^{(R)}_{p,q}\left(t,t'\right)\theta(t'-t), \end{aligned} \tag{146}$$

and the Hamiltonian in these notations is

$$\hat{H} = \sum_{p,q} h_{p,q} a^{\dagger}_p a_q + \frac{1}{2}\sum_{p,q,r,s}\left(p,q \mid r,s\right) a^{\dagger}_p a^{\dagger}_r a_s a_q. \tag{147}$$

Equations for the one-particle Green's functions are obtained from the equations-of-motion (65) and (66) after the substitution $\hat{H}_0 \to \hat{H}$

$$i\frac{\partial}{\partial t}G^{(A)}_{p,q}\left(t,t'\right) \;=\; -i\langle|\left[a_p(t),\hat{H}\right]a^{\dagger}_q(t')\,|\rangle, \tag{148}$$

$$i\frac{\partial}{\partial t}G^{(R)}_{p,q}\left(t,t'\right) \;=\; i\langle|\,a^{\dagger}_q(t')\left[a_p(t),\hat{H}\right]|\rangle, \tag{149}$$

with the Hamiltonian (147) they give

$$i\frac{\partial}{\partial t}G_{p,q}(t,t') = \sum_{p'} h_{p,p'}G_{p',q}(t,t') - i\sum_{p',r,s}(p,p'\mid r,s) \times\langle|\,\mathbf{T}\left(a^{\dagger}_r\left(t\right)a_s\left(t\right)a_{p'}\left(t\right)a^{\dagger}_q\left(t'\right)\right)|\rangle + \delta\left(t-t'\right)\delta_{pq}, \tag{150}$$

where again T is the chronological ordering symbol of Wick.

As it is seen from Eq.(146) the retarded part of the one-particle Green's function in the limit $t'-t\to+0$ is proportional to the one-particle density matrix

$$\lim_{t'-t\to+0} G_{p,q}\left(t,t'\right) \;=\; \lim_{t'-t\to+0} G^{(R)}_{p,q}\left(t,t'\right) = \;=\; iD_{p,q} \tag{151}$$

and, therefore, it can be used in calculations of mean values of the one-particle physical quantities. It can also be used for a calculation of the total energy of the interacting particles. We can write, for example,

$$E = -\frac{i}{2}\sum_{p,p\prime,q}\delta_{pq}\lim_{t'\to t^+}\left(i\frac{\partial}{\partial t}\delta_{pp'}+h_{pp'}\right)G^{(R)}_{p'q}\left(t,t'\right). \tag{152}$$

If we multiply the interaction operator $\hat{V}$ by a coupling constant λ and use the Hellmann-Feynman theorem then the energy is expressed as

$$E = E_0 - \frac{i}{2}\int\limits_0^1\frac{d\lambda}{\lambda}\sum_{p,p\prime,q}\delta_{pq}\lim_{t'\to t^+}\left(i\frac{\partial}{\partial t}\delta_{pp'}-h_{pp'}\right)$$

$$\times \left(G_{p'q}\,(t,t') - G^{(0)}_{p'q}\,(t,t') \right). \qquad (153)$$

In Eqs.(152) and (153) $t' \to t^{+} = t' \to t + 0.$

3.3. KÄLLÉN - LEHMANN DECOMPOSITION OF THE ONE-PARTICLE GREEN'S FUNCTION

Green's functions of interacting particles can not be written in the form the spectral resolutions for non-interacting particles (138) and (139) with eigenvalues $e^{-i\epsilon_j\left(t-t'\right)}$**. For Green's functions of interacting particles there is also a canonical decomposition, which can be used in different approximations. One of such approximations is written below. In order to obtain this decomposition we write two resolutions of unity in subspaces of** $n-1$ **and** $n+1$ **particles**

$$\sum_j \mid n-1, j\rangle\langle n-1, j \mid = \hat{I}_{n-1},$$

$$\sum_j \mid n+1, j\rangle\langle n+1, j \mid = \hat{I}_{n+1}$$

for eigenstates of corresponding Hamiltonians

$$\hat{H}_{n-1},\ \hat{H}_{n+1}.$$

Then the following expansions are obvious

$$\begin{aligned} G_{p,q}\,(t,t') \;&=\; -i\sum_j \langle \mid a_p(t) \mid n+1, j\rangle\langle n+1, j \mid a^{\dagger}_q(t') \mid\rangle \theta(t-t') + \\ &\quad +i\sum_j \langle \mid a^{\dagger}_q(t') \mid n-1, j\rangle\langle n-1, j \mid a_p(t) \mid\rangle \theta(t'-t) \\ &=\; G^{(A)}_{p,q}\,(t,t')\,\theta(t-t') + G^{(R)}_{p,q}\,(t,t')\,\theta(t'-t), \end{aligned} \qquad (154)$$

$$G^{(A)}_{p,q}\,(t,t') = -i\sum_j \langle \mid a_p \mid n+1, j\rangle exp^{-i(E^{n+1}_j - E_0)(t-t')}$$
$$\times \langle n+1, j \mid a^{\dagger}_q \mid\rangle, \qquad (155)$$

$$G^{(R)}_{p,q}(t,t') = i\sum_j \langle | \, a^\dagger_q \mid n-1,j\rangle exp^{-i(E^{n-1}_j - E_0)(t'-t)}$$
$$\times \langle n-1,j \mid a_p \, |\rangle. \tag{156}$$

The one-electron overlaps

$$\begin{aligned} &\langle n+1,j \mid a^\dagger_q \, |\rangle, \\ &\langle n-1,j \mid a_p \, |\rangle \end{aligned} \tag{157}$$

compose rectangular matrices with non-orthogonal rows.

The same decomposition is also valid for the one-particle density function

$$D^{(A)}_{p,q} = \sum_j \langle | \, a_p \mid n+1,j\rangle\langle n+1,j \mid a^\dagger_q \, |\rangle, \tag{158}$$

$$\begin{aligned} D_{p,q} = D^{(R)}_{p,q} &= \delta_{pq} - D^{(A)}_{p,q} = \\ &= \sum_j \langle | \, a^\dagger_q \mid n-1,j\rangle\langle n-1,j \mid a_p \, |\rangle. \end{aligned} \tag{159}$$

Equations (154)-(155) resemble transformation of two matrices to diagonal matrices, which can be done by a non-orthogonal transformation. The transformation is obtained from the generalized eigenvalue equation. It is simple to get this transformation for small values of $t-t'$ up to the first order in this difference. For the retarded Green's function we need to solve the equation

$$\sum_{p'} \langle | \, a^\dagger_q \left[a_{p'}, \hat{H}\right] \, |\rangle \phi^j_{p'} = \epsilon_j \sum_{p'} D^{(R)}_{q,p'} \phi^j_{p'}. \tag{160}$$

The set $\{\Phi^j_p = \hat{D}^{\frac{1}{2}}\phi^j_p\}$ is mutually orthogonal and it is then used for pseudospectral resolution of matrices in both sides of Eq.(160):

$$\langle | \, a^\dagger_q \left[a_p, \hat{H}\right] \, |\rangle = \sum_j \hat{D}^{\frac{1}{2}}\Phi^j_q \epsilon_j (\hat{D}^{\frac{1}{2}}\Phi^j_p)^\star,$$
$$D_{q,p} = \sum_j \hat{D}^{\frac{1}{2}}\Phi^j_q (\hat{D}^{\frac{1}{2}}\Phi^j_p)^\star \tag{161}$$

$$G_{p,q}^{(R)}\left(t,t'\right) = \sum_j D^{\frac{1}{2}}\Phi_q^j exp^{-i(E_j^{n-1}-E_0)(t'-t)}(\hat{D}^{\frac{1}{2}}\Phi_p^j)^\star + \dots \tag{162}$$

An ellipses in Eq.(162) denotes terms of the second and higher orders. A similar expansion is also valid for the advanced Green's function and it can be shown that this algorithm gives the exact energy of the state function $|\rangle$ which is obtained from a variation principle. Actually, for any MCSCF function if the formula (153) for the energy is used.

In the CAS decomposition without the inactive subspace the exact Green's function is obtained according to the Källén-Lehmann formulas (154) and (155) when the states $\mid n-1,j\rangle$ are positive ionic CAS states built of active orbitals and the ones $\mid n+1,j\rangle$ are negative ionic CAS states built of active orbitals and the CAS states with one virtual (secondary) orbital. In this case the CAS energy is obtained using both Eqs.(152) and (153).

3.4. PERTURBATION EXPANSION FOR GREEN'S FUNCTION

A perturbation expansion for one-particle Green's function is obtained in the Dirac picture

$$\begin{aligned} a_{H\,p}\left(t\right) &= e^{i\hat{H}t}e^{-i\hat{H}_0t}a_{I\,p}e^{i\hat{H}_0t}e^{-i\hat{H}t}, \\ a_{H\,q}^{\dagger}\left(t\right) &= e^{i\hat{H}t}e^{-i\hat{H}_0t}a_{I\,q}^{\dagger}e^{i\hat{H}_0t}e^{-i\hat{H}t}, \end{aligned} \tag{163}$$

where

$$\begin{aligned} e^{i\hat{H}t}e^{-i\hat{H}_0t} &= \hat{S}\left(0,t\right), \\ e^{i\hat{H}_0t}e^{-i\hat{H}t} &= \hat{S}\left(t,0\right) \end{aligned} \tag{164}$$

evolution operators in the Dirac picture. The general expression for the evolution operator is

$$e^{i\hat{H}_0 t} e^{-i\hat{H}\left(t-t'\right)} e^{-i\hat{H}_0 t'} = \hat{S}\left(t, t'\right), \tag{165}$$

which is expanded in the perturbation series

$$\hat{S}\left(t, t'\right) = \sum_l \frac{1}{i^l l!} \int_t^{t'} \dots \int_t^{t'} T\left(\hat{V}(t_1)\hat{V}(t_2)\dots\hat{V}(t_l)\right) dt_1 \dots dt_l \tag{166}$$

with the interaction in the Dirac picture

$$\hat{V}(t_l) = e^{i\hat{H}_0 t}\hat{V}e^{-i\hat{H}_0 t}. \tag{167}$$

In the perturbation expansion limiting values of $\hat{S}\left(t, t'\right)$ are used:

$$\hat{S}_\gamma\left(0, -\infty \mid \lambda\right), \hat{S}_\gamma\left(\infty, 0 \mid \lambda\right)$$

and

$$\hat{S}_\gamma\left(\infty, -\infty \mid \lambda\right) \overset{def}{=} \hat{S}_\gamma\left(\infty, 0 \mid \lambda\right)\hat{S}_\gamma\left(0, -\infty \mid \lambda\right)$$

- the complete S_γ- matrix. If we redefine time-ordered products in integrands of (166) according to the rule

$$T\left(\hat{V}\left(t_1\right)\dots\hat{V}\left(t_j\right)\dots\hat{V}\left(t_l\right) exp^{-\gamma|t_{min}|}\right) \tag{168}$$

we obtain

$$\begin{aligned}\hat{S}_\gamma^{(l)}\left(0, -\infty\right) &= \int \frac{1}{E - \hat{H}_0 + i\gamma}\hat{V} \\ &\dots \frac{1}{E - \hat{H}_0 + i\gamma}\hat{V}\delta\left(\hat{H}_0 - E\right) dE\end{aligned} \tag{169}$$

and with

$$T\left(\hat{V}\left(t_1\right)\dots\hat{V}\left(t_j\right)\dots\hat{V}\left(t_l\right) exp^{-\gamma|t_{max}|}\right), \tag{170}$$

$$\begin{aligned}\hat{S}_\gamma^{(l)}\left(\infty, 0\right) &= \int \delta\left(\hat{H}_0 - E\right)\hat{V}\frac{1}{E - \hat{H}_0 + i\gamma} \\ &\dots \hat{V}\frac{1}{E - \hat{H}_0 + i\gamma} dE\end{aligned} \tag{171}$$

for the l-th order of the series

$$\hat{S}_\gamma(0,\pm\infty) = \hat{I} + \sum_{l=1}^{\infty} \hat{S}_\gamma^{(l)}(0,\pm\infty). \tag{172}$$

If we apply Eq.(169) to an eigenstate $\mid E_0\rangle$ of $\hat{H}_0$ (101) and Eq.(171) to $\langle E_0 \mid$ we then obtain

$$\hat{S}_\gamma^{(l)}(0,-\infty) \mid E_0\rangle =$$
$$i\gamma \frac{1}{E_0 - \hat{H}_0 + i\gamma}\left[\hat{V}\frac{1}{E_0 - \hat{H}_0 + i\gamma}\right]^l \mid E_0\rangle,$$
$$\langle E_0 \mid \hat{S}_\gamma^{(l)}(\infty,0) =$$
$$i\gamma\langle E_0 \mid \left[\frac{1}{E_0 - \hat{H}_0 + i\gamma}\hat{V}\right]^l \frac{1}{E_0 - \hat{H}_0 + i\gamma}. \tag{173}$$

Then from the expansion (172) for small γ it follows that $\hat{S}_\gamma(0,-\infty) \mid E_0\rangle$ and $\langle E_0 \mid \hat{S}_\gamma(\infty,0)$ are equal to first-order-pole contributions to the contour integral in $\oint_{E_0} dz \frac{1}{z-\hat{H}} \mid E_0\rangle$ and $\frac{1}{2\pi}\langle E_0 \mid \oint_{E_0} \frac{1}{z-\hat{H}} dz$. They do not exist when γ tends to zero, but one can easily check that

$$\lim_{\gamma\to 0} \frac{\hat{S}_\gamma(0,-\infty) \mid E_0\rangle}{\langle E_0 \mid \hat{S}_\gamma(0,-\infty) \mid E_0\rangle} = \frac{|\rangle}{\langle E_0 \, |\rangle}$$

and

$$\lim_{\gamma\to 0} \frac{\langle E_0 \mid \hat{S}_\gamma(\infty,0)}{\langle E_0 \mid \hat{S}_\gamma(\infty,0) \mid E_0\rangle} = \frac{\langle|}{\langle| \, E_0\rangle}.$$

Hence, we can write

$$\hat{S}_\gamma(0,-\infty) \mid E_0\rangle = c \, |\rangle + \ldots, \ \langle E_0 \mid \hat{S}_\gamma(\infty,0) = c'\langle| + \ldots. \tag{174}$$

In these asymptotic relations the ellipsis stands for the terms which vanish in the limit $\gamma \to 0$. From Eqs.(174) for the normalization constants we obtain

$$cc' = \langle E_0 \mid \hat{S}_\gamma(\infty,-\infty) \mid E_0\rangle + \ldots \tag{175}$$

and from the definition (145) we receive the formula for the one-particle Green's function in the Dirac picture:

$$G_{p,q}(t,t') = \frac{1}{i}\langle E_0 \mid \hat{S}_\gamma(\infty,0)\,T\,(S_\gamma(0,t)$$

$$\frac{\times a_{Ip}(t)\,S_\gamma(t,t')\,a^\dagger_{Iq}(t')\,S_\gamma(t',0)\Big)\,\hat{S}_\gamma(0,-\infty) \mid E_0\rangle}{\langle E_0 \mid \hat{S}_\gamma(\infty,-\infty) \mid E_0\rangle} + \ldots . \quad (176)$$

The right-hand side of Eq.(176) is usually written in the following compact form

$$G_{p,q}(t,t') =$$

$$\frac{1}{i}\frac{\langle E_0 \mid T\left(a_{Ip}(t)\,a^\dagger_{Iq}(t')\,\hat{S}_\gamma(\infty,-\infty)\right) \mid E_0\rangle}{\langle E_0 \mid \hat{S}_\gamma(\infty,-\infty) \mid E_0\rangle} + \ldots . \qquad (177)$$

Eq.(177) is in fact a series. If it converges uniformly, we can go to the limit $\gamma \to 0$ and write

$$G_{p,q}(t,t') =$$

$$\frac{1}{i}\frac{\langle E_0 \mid T\left(a_{Ip}(t)\,a^\dagger_{Iq}(t')\,\hat{S}(\infty,-\infty)\right) \mid E_0\rangle}{\langle E_0 \mid \hat{S}(\infty,-\infty) \mid E_0\rangle}. \qquad (178)$$

This formula together with the series (166) is used for perturbation expansions of the one-particle Green's function. Here we make several remarks. The asymptotic formulas (174) and (175) are equivalent to the adiabatic theorem by Born and Fock and the limit $\gamma \to 0$ exists only for a non-degenerate state vector $\mid E_0\rangle$. For a degenerate state vector we can distinguish two cases:
1. $\mid E_0\rangle$ is degenerate and $|\rangle$ is non-degenerate. Then the convergency can achieved by a suitable change of the Hamiltonian $\hat{H}_0$.
2. Both $\mid E_0\rangle$ and $|\rangle$ are degenerate - open-shell case - then the state vector $\mid E_0\rangle$ projects out other state vectors of

the open shell and the formula (178) is valid again. A perturbation expansion for the one-particle Green's function is usually obtained from the representation (178) and the series (166). In a straightforward application of this formula one has to reexpand the series in the denominator of Eq.(178), but for a one-configuration reference state vector $\mid E_0\rangle$ one can factorize the nominator and cancel $\langle E_0 \mid \hat{S}\left(\infty,-\infty\right) \mid E_0\rangle$ - vacuum terms cancellation theorem. This factorization is done with help of the Wick's theorem. According to the theorem the integrand of

$$
\begin{aligned}
&\langle E_0 \mid T\left(a_p\left(t\right) a_q^\dagger\left(t'\right) \hat{S}\left(\infty,-\infty\right)\right) \mid E_0\rangle = \\
&\sum_l \frac{1}{i^l l!} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \langle E_0 \mid T\left(a_p\left(t\right) a_q^\dagger\left(t'\right)\right. \\
&\left. \times \hat{V}(t_1)\hat{V}(t_2)\ldots\hat{V}(t_l)\right) \mid E_0\rangle dt_1 \ldots dt_l
\end{aligned}
\tag{179}
$$

is expanded in the sum of fully contracted products. Working out possible contractions we collect the terms with fully contracted products of creation-annihilation operators within the different groups of interaction operators $V(t_{l_1})V(t_{l_2})...V(t_{l_k})$. Remaining $l-k$ interaction operators in the l-th order of the expansion are connected by contractions altogether and and with the operators $a_p\left(t\right) a_q^\dagger\left(t'\right)$ of the time ordered product in Eq.(179). We will call this group of operators connected. Due to the permutation symmetry of the interaction operators in the time ordered product we finally obtain in the l-th order $\frac{l!}{k!m!}$, $m = l-k$ different cases. Hence, making summation over all possible values of k, we get the factorization

$$\langle E_0 \mid T\left(a_p(t)\, a_q^{\dagger}(t')\, \hat{S}(\infty,-\infty)\right) \mid E_0\rangle =$$
$$\sum_m \frac{1}{i^m m!}\int_{-\infty}^{\infty}\dots\int_{-\infty}^{\infty}\langle E_0 \mid T\left(a_p(t)\, a_q^{\dagger}(t')\right.$$
$$\left.\times\, \hat{V}(t_1)\dots\hat{V}(t_m)\right) \mid E_0\rangle_c dt_1\dots dt_m$$
$$\times \sum_k \frac{1}{i^k k!}\int_{-\infty}^{\infty}\dots\int_{-\infty}^{\infty}\langle E_0 \mid T\left(\hat{V}(t_1)\dots\hat{V}(t_k)\right) \mid E_0\rangle dt_1\dots dt_k \quad (180)$$

and

$$G_{p,q}(t,t') = \sum_l \frac{1}{i i^l l!}\int_{-\infty}^{\infty}\dots\int_{-\infty}^{\infty}\langle E_0 \mid T\left(a_p(t)\, a_q^{\dagger}(t')\right.$$
$$\left.\times\, \hat{V}(t_1)\dots\hat{V}(t_l)\right) \mid E_0\rangle_c dt_1\dots dt_l. \qquad (181)$$

3.5. DIAGRAM TECHNIQUES FOR GREEN'S FUNCTIONS

A diagrammatic representation for the contractions of creation-annihilation operators in the perturbation expansion is a simple and expedient way to distinguish a topological structure of the Wick's pairings of the operators. In the diagrams each contraction is denoted by a solid line (two-index electron- hole line) and the interaction is denoted by the wavy line (four-index vertex). In the first order we get two diagrams Fig.1,2 of Appendix, which are associated with the following fully contracted terms of Eq.(181)

$$-i\sum_{k,l,m,n}\int_\tau G_{p,k}(t,\tau)\,(k,l\mid m,n)\, G_{l,q}(\tau,t')\, G_{n,m}(\tau,\tau^+)\, d\tau$$
$$i\sum_{k,l,m,n}\int_\tau G_{p,k}(t,\tau)\,(k,l\mid m,n)\, G_{n,q}(\tau,t')\, G_{l,m}(\tau,\tau^+)\, d\tau. \quad (182)$$

The analytical expression (182)is written according to the correspondence rule: each solid line is associated with the

Green's function, each wavy line with the four-index two-electron integral, which is time-independent; the total product is integrated over the time variable, which corresponds to the time of the interaction operator in Eq.(181), and it is summed up over the indexes of the contractions which correspond to the creation-annihilation operators in the interaction operator; whole expression is multiplied by the phase-factor $i^l(-1)^\Sigma$ where l-is the order of the perturbation expansion and Σ is the number of the closed electron loops in the diagram. Using the Wick's theorem in the second order for the one-particle Green's function, we obtain the diagrams Fig.3. The complete perturbation series is expressed by the connected Feynman diagrams with two external solid lines. A diagram is compact if it has not parts connected by one solid line and a diagram is irreducible if it does not contain diagrams of lower order as its parts. For example, from all connected diagrams of the second order Fig.3 only last two diagrams are compact and irreducible. The first diagram in this figure is reducible and the second one is non-compact. From the diagrams Fig.1,2,3 it is seen that they can be written as integrals for operators $\hat{G}^{(0)}(t,t'), \hat{G}(t,t'), \hat{G}^{(A,R)}(t,t')$ which correspond to matrices $\{G^{(0)}_{p,q}(t,t')\}, \{G_{p,q}(t,t')\}, \{G^{(A,R)}_{p,q}(t,t')\}$ with the self-energy operator $\hat{\Sigma}(\tau,\tau')$ which corresponds to the self-energy matrix $\{\Sigma_{p,q}(t,t')\}$

$$\int d\tau d\tau' \hat{G}^{(0)}(t,\tau)\hat{\Sigma}(\tau,\tau')\hat{G}^{(0)}(\tau',t'), \tag{183}$$

where

$$\hat{G}^{(0)}(t,t') = \left(i\frac{\partial}{\partial t} - \hat{h}\right)^{-1} \hat{I}\delta(t-t') \tag{184}$$

is the operator with the core from Eq.(140) A compact self-energy operator is called mass-operator. In the first order two diagrams for the mass operator are represented on Fig.4 of Appendix. Using the mass-operator we can write the Dyson equation

$$\begin{aligned} \hat{G}(t,t') &= \hat{G}^{(0)}(t,t') + \\ \int d\tau d\tau' \hat{G}^{(0)}(t,\tau)\, \hat{M}^{(c)}(\tau,\tau')\, \hat{G}(\tau',t'). \end{aligned} \tag{185}$$

Iterations of Eq.(185) give a relation between the mass-operator $\hat{M}^{(c)}$ and the self-energy operator $\hat{\Sigma}$

$$\begin{aligned} \hat{G} &= \hat{G}^{(0)} + \hat{G}^{(0)}\hat{M}^{(c)}\hat{G} \\ &= \hat{G}^{(0)} + \hat{G}^{(0)}\hat{M}^{(c)}\hat{G}^{(0)} + \hat{G}^{(0)}\hat{M}^{(c)}\hat{G}^{(0)}\hat{M}^{(c)}\hat{G}^{(0)} + \ldots \\ &= \hat{G}^{(0)} + \hat{G}^{(0)}\hat{\Sigma}\hat{G}^{(0)}. \end{aligned} \tag{186}$$

The mass-operator and the self-energy operator depend in their turn on $\hat{G}^{(0)} : \hat{M}^{(c)} = \hat{M}^{(c)}\left(\hat{G}^{(0)}\right)$, but performing internal summations we can write a Dyson equation with an irreducible mass-operator which depends on $\hat{G}$

$$\hat{G} = \hat{G}^{(0)} + \hat{G}^{(0)}\hat{M}^{(irr)}\left(\hat{G}\right)\hat{G}, \tag{187}$$

where the irreducible mass-operator $\hat{M}^{(irr)}\left(\hat{G}\right)$ is represented by a perturbation expansion. The first order terms of this expansion are in Fig.4 and the second order terms are in Fig.9. If, for example, we use only the first order terms for $\hat{M}^{(irr)}\left(\hat{G}\right)$ Fig.4,5, we get the HF-Dyson equation for the Green's function in the Hartree-Fock approximation Fig.6. A graphical representation for the Dyson equation (187) is given in Fig.10. It is in fact an exact equation for the one-particle Green's function which can be used in model applications.

4. IMAGINARY SHIFTS AND S-MATRIX BASED CALCULATIONS FOR THE ENERGY

4.1. S-MATRIX AND RIESZ-KATO PERTURBATION THEORY

The Riesz-Kato perturbation expansion is based on the contour integral representation of the energy shift:

$$E - E_0 = A/B, \tag{188}$$

with

$$A = \frac{1}{2\pi i} \sum_{l=0,1,\ldots} \oint_{E_0} \langle E_0 \mid \left[\hat{V}_{int} \frac{1}{z - \hat{H}_0} \right]^l \mid E_0 \rangle dz, \tag{189}$$

$$B = \frac{1}{2\pi i} \sum_{l=0,1,\ldots} \oint_{E_0} \langle E_0 \mid \left[\frac{1}{z - \hat{H}_0} \hat{V}_{int} \frac{1}{z - \hat{H}_0} \right]^l \mid E_0 \rangle dz. \tag{190}$$

As it was demonstrated in the Subsection 3.4. we can write for expectation values of the

$$\langle E_0 \mid \hat{S}^{(l)}_\gamma \mid E_0 \rangle \equiv \langle E_0 \mid \hat{S}^{(l)}_\gamma (0, -\infty) \mid E_0 \rangle =$$
$$= \langle E_0 \mid \hat{S}^{(l)}_\gamma (\infty, 0) \mid E_0 \rangle = \langle E_0 \mid \left[\hat{V}_{int} \frac{1}{E_0 - \hat{H}_0 + i\gamma} \right]^l \mid E_0 \rangle. \tag{191}$$

Therefore,

$$\frac{1}{2\pi} \oint_L \langle E_0 \mid \hat{S}^{(l)}_\gamma \mid E_0 \rangle d\gamma = \frac{1}{2\pi i} \oint_{E_0} \langle E_0 \mid \left[\hat{V}_{int} \frac{1}{z - \hat{H}_0} \right]^l \mid E_0 \rangle dz, \tag{192}$$

$$\frac{1}{2\pi i} \oint_L \frac{1}{\gamma} \langle E_0 \mid \hat{S}^{(l)}_\gamma \mid E_0 \rangle d\gamma =$$
$$= \frac{1}{2\pi i} \oint_{E_0} \langle E_0 \mid \frac{1}{z - \hat{H}_0} \left[\hat{V}_{int} \frac{1}{z - \hat{H}_0} \right]^l \mid E_0 \rangle dz \tag{193}$$

and

$$A=\sum_l \frac{1}{2\pi}\oint_L \langle E_0 \mid \hat{S}_\gamma^{(l)} \mid E_0\rangle d\gamma = \frac{1}{2\pi}\oint_L \langle E_0 \mid \hat{S}_\gamma \mid E_0\rangle d\gamma \qquad (194)$$

and

$$B=\sum_l \frac{1}{2\pi i}\oint_L \frac{1}{\gamma}\langle E_0 \mid \hat{S}_\gamma^{(l)} \mid E_0\rangle d\gamma = \frac{1}{2\pi i}\oint_L \frac{1}{\gamma}\langle E_0 \mid \hat{S}_\gamma \mid E_0\rangle d\gamma. \qquad (195)$$

For the complete S_γ-matrix

$$\hat{S}_\gamma(\infty,-\infty)=\hat{S}_\gamma(\infty,0)\,\hat{S}_\gamma(0,-\infty) \qquad (196)$$

we can write

$$\begin{aligned}
A' &= \frac{1}{2\pi}\oint_L \langle E_0 \mid \hat{S}_\gamma(\infty,-\infty) \mid E_0\rangle d\gamma = \\
&= \frac{1}{\pi}\oint_L \langle E_0 \mid \hat{S}_\gamma \mid E_0\rangle d\gamma \\
&- \frac{1}{2\pi}\oint_L \frac{\partial}{\partial\gamma}(\gamma\langle E_0 \mid \hat{S}_\gamma \mid E_0\rangle) d\gamma, \qquad (197)\\
B' &= \frac{1}{2\pi i}\oint_L \frac{1}{\gamma}\langle E_0 \mid \hat{S}_\gamma(\infty,-\infty) \mid E_0\rangle d\gamma = \\
&= \frac{1}{2\pi i}\oint_L \frac{1}{\gamma}\langle E_0 \mid \hat{S}_\gamma \mid E_0\rangle d\gamma \\
&- \frac{1}{2\pi i}\oint_L \frac{\partial}{\partial\gamma}\langle E_0 \mid \hat{S}_\gamma \mid E_0\rangle d\gamma. \qquad (198)
\end{aligned}$$

For isolated energy levels the second terms in Eqs.(197) and (198) are equal to zero. Hence, we come to the formula

$$E-E_0=\frac{1}{2}A'/B'. \qquad (199)$$

Sucher (1957)

From Eqs.(173)-(175) of Subsection 3.4. it follows that the enegy shift can be also expressed as an adiabatic limit of the fraction A_γ/B_γ with

$$A_\gamma = \langle E_0 \mid \hat{V}\hat{S}_\gamma\,(0,-\infty) \mid E_0\rangle = \langle E_0 \mid \hat{S}_\gamma\,(\infty,0)\,\hat{V} \mid E_0\rangle, \quad (200)$$

$$B_\gamma = \langle E_0 \mid \hat{S}_\gamma\,(0,-\infty) \mid E_0\rangle = \langle E_0 \mid \hat{S}_\gamma\,(\infty,0) \mid E_0\rangle \quad (201)$$

and

$$E - E_0 = \lim_{\gamma\to 0} A_\gamma/B_\gamma. \quad (202)$$

Therefore the asymptotic formulas are valid

$$E - E_0 = A_\gamma/B_\gamma + \ldots \quad (203)$$

$$\frac{|\rangle}{\langle E_0 \,|\rangle} = \frac{\hat{S}_\gamma\,(0,-\infty) \mid E_0\rangle}{\langle E_0 \mid \hat{S}_\gamma\,(0,-\infty) \mid E_0\rangle} + \ldots$$

and

$$\frac{\langle|}{\langle| \, E_0\rangle} = \frac{\langle E_0 \mid \hat{S}_\gamma\,(\infty,0)}{\langle E_0 \mid \hat{S}_\gamma\,(\infty,0) \mid E_0\rangle} + \ldots\;,$$

which gives a justification for complex shifts in the perturbation expansions for energy shifts and for wave functions.

The Riesz-Kato perturbation expansions are not very sensitive to reference states in our case it is $\mid E_0\rangle$. Generally speaking this reference can be changed if we change H_0 Hamiltonian. An estimate for a proper reference state may be obtained from Eqs. (172) and (173):

$$i\gamma\frac{1}{E_0 - \hat{H}_0 + i\gamma}\sum_{l=1}^{\infty}\left[\hat{V}\frac{1}{E_0 - \hat{H}_0 + i\gamma}\right]^l \mid E_0\rangle =$$

$$= \hat{S}_\gamma(0,-\infty) \mid E_0\rangle = i\gamma \frac{1}{E_0 - \hat{H} + i\gamma} \mid E_0\rangle,$$

$$i\gamma\langle E_0 \mid \sum_{l=1}^{\infty}\left[\frac{1}{E_0 - \hat{H}_0 + i\gamma}\hat{V}\right]^l \frac{1}{E_0 - \hat{H}_0 + i\gamma} =$$

$$= \langle E_0 \mid \hat{S}_\gamma(\infty,0) = i\gamma\langle E_0 \mid \frac{1}{E_0 - \hat{H} + i\gamma} \tag{204}$$

and for

$$\langle E_0 \mid \hat{S}_\gamma(\infty,-\infty) \mid E_0\rangle = (i\gamma)^2 \langle E_0 \mid \left(\frac{1}{E_0 - \hat{H} + i\gamma}\right)^2 \mid E_0\rangle. \tag{205}$$

$$G_{p,q}(t,t') = \frac{1}{i}\langle E_0 \mid \hat{S}_\gamma(\infty,0)\, T\,(S_\gamma(0,t)$$

$$\frac{\times a_{Ip}(t)\, S_\gamma(t,t')\, a^\dagger_{Iq}(t')\, S_\gamma(t',0)\big)\, \hat{S}_\gamma(0,-\infty) \mid E_0\rangle}{\langle E_0 \mid \hat{S}_\gamma(\infty,-\infty) \mid E_0\rangle} + \ldots =$$

$$= \frac{1}{i}\langle E_0 \mid \frac{1}{E_0 - \hat{H} + i\gamma} T\,(S_\gamma(0,t)$$

$$\frac{\times a_{Ip}(t)\, S_\gamma(t,t')\, a^\dagger_{Iq}(t')\, S_\gamma(t',0)\big)\, \frac{1}{E_0 - \hat{H} + i\gamma} \mid E_0\rangle}{\langle E_0 \mid \left(\frac{1}{E_0 - \hat{H} + i\gamma}\right)^2 \mid E_0\rangle} + \ldots\ . \tag{206}$$

Eqs.(204),(205) and (206) are used later in order to define the Green's function which is obtained after a partial summation.

4.3. PARTIAL SUMMATION IN EXPECTATION VALUES OF S_γ-MATRICES

We consider now an exact (FCI) solution in a model subspace $\mathcal{N}_\mathcal{C}$ with energy $\mathcal{E}_\mathcal{C}$ which satisfies the Brillouin's conditions:

$$\langle \mathcal{E}_\mathcal{C} \mid a_p a_q^\dagger \hat{H} \mid \mathcal{E}_\mathcal{C}\rangle = \mathcal{E}_\mathcal{C}\langle \mathcal{E}_\mathcal{C} \mid a_p a_q^\dagger \mid \mathcal{E}_\mathcal{C}\rangle$$

then the one-particle Green's function

$$G_{p,q}\left(t,t'\right)=\frac{1}{i}\langle\mathcal{E}_{\mathcal{C}}\mid T\left(a_p\left(t\right)a_q^{\dagger}\left(t'\right)\right)\mid\mathcal{E}_{\mathcal{C}}\rangle=$$
$$-i\langle\mathcal{E}_{\mathcal{C}}\mid a_p e^{-i\hat{H}(t-t')}a_q^{\dagger}\mid\mathcal{E}_{\mathcal{C}}\rangle\theta(t-t')+$$
$$+i\langle\mathcal{E}_{\mathcal{C}}\mid a_q^{\dagger}e^{-i\hat{H}(t'-t)}a_p\mid\mathcal{E}_{\mathcal{C}}\rangle\theta(t'-t), \tag{207}$$

where $e^{-i\hat{H}(t'-t)}$ acts in the subspace of all $(N-1)$-particle positive ionic states of the model subspace $\mathcal{N}_{\mathcal{C}}$. The operator $e^{-i\hat{H}(t-t')}$ acts in the subspace all $(N+1)$-particle negative ionic states of the model subspace $\mathcal{N}_{\mathcal{C}}$ with admixture of $(N+1)$-particle negative ionic states with one virtual spin-orbital. A corresponding contraction of the complete Hamiltonian to this subspaces we denote $\hat{H}_C=\hat{h}_C+\hat{V}_C$. For the complete Hamiltonian we have:

$$\hat{H}=\hat{h}_C+\hat{V}_C+\hat{h}_1+\hat{V}_1, \tag{208}$$

where $\hat{h}_C$ is the one-particle operator $\hat{H}_0$ which was used previously in thr perturbation expansion for the one-particle Green's function. A multiple perturbation expansion for the S_γ-matrix is written the as the series:

$$\langle E_0\mid\hat{S}_\gamma\mid E_0\rangle=\sum_{l,m,n}\frac{1}{l!i^l m!i^m n!i^n}\int\ldots\int\langle E_0\mid T\,(\tag{209}$$
$$\hat{V}_C(t_1)\hat{V}_C(t_2)\ldots\hat{V}_C(t_l)\hat{V}_1(\tau_1)\hat{V}_1(\tau_2)\ldots\hat{V}_1(\tau_m)\ldots \tag{210}$$
$$\times\hat{h}_1(\sigma_1)\ldots\hat{h}_1(\sigma_n)\Big)\mid E_0\rangle dt_1\ldots dt_l d\tau_1\ldots d\tau_m d\sigma_1\ldots d\sigma_n. \tag{211}$$

From this series we see that the diagrams with all possible insertions with contractions of $\hat{V}_C$ lead to a substitute of all solid lines by the Green's function:

$$
\begin{aligned}
&\frac{1}{i}\langle E_0 \mid \frac{1}{E_0-\hat{H}_C+i\gamma} T\left(S_\gamma\left(0,t\right)\right. \\
&\frac{\left.\times a_{Ip}\left(t\right) S_\gamma\left(t,t'\right) a^\dagger_{Iq}\left(t'\right) S_\gamma\left(t',0\right)\right) \frac{1}{E_0-\hat{H}_C+i\gamma} \mid E_0\rangle}{\langle E_0 \mid \left(\frac{1}{E_0-\hat{H}_C+i\gamma}\right)^2 \mid E_0\rangle} + \ldots = \\
&= -i\langle \mathcal{E}_{\mathcal{C}} \mid a_p e^{-i\hat{H}_C(t-t')} a^\dagger_q \mid \mathcal{E}_{\mathcal{C}}\rangle \theta(t-t') + \\
&+ i\langle \mathcal{E}_{\mathcal{C}} \mid a^\dagger_q e^{-i\hat{H}_C(t'-t)} a_p \mid \mathcal{E}_{\mathcal{C}}\rangle \theta(t'-t) + \ldots = \\
&= G^C_{p,q}\left(t,t'\right). \qquad (212)
\end{aligned}
$$