GW approximation

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(Dated: August 9, 2020)

1. GW

A. Motivation

We want now to investigate theoretically, the so called one particle spectroscopy experiments. Two of them are *Photoemission* (PES) and the *inverse photoemission* (IPE).

In photoemission, a photon with energy $\hbar\omega$ is absorbed by an electron in a partially occupied energy band, and this increase in energy allows the electron to escape from the system. In inverse photoemission, an electron is injected into the system and occupies an unoccupied state $|\psi_\beta\rangle$. The energy is released in form of a photon with energy $\hbar\omega$.

We start with the N-electron ground state that can be written as:

$$|N\rangle = \frac{1}{\sqrt{N!}} |\varphi_{\alpha_1}, \varphi_{\alpha_2}, \cdots, \varphi_{\alpha_N}\rangle . \tag{1.1}$$

This state represents a many electrons wave function composed of single electron states: φ_{α_i} corresponding to the single particle Hilbert spaces $\mathcal{H}_i$

The vacuum state is when there are no electrons in the system

$$|0\rangle . \tag{1.2}$$

One can start to populate the system by introducing the creation operator $\hat{a}^\dagger_\alpha$

$$\hat{a}^\dagger_{\alpha_1} |0\rangle = \sqrt{1} |\varphi_{\alpha_1}\rangle \tag{1.3}$$

$$\hat{a}^\dagger_{\alpha_2} |\varphi_{\alpha_1}\rangle = \sqrt{2} |\varphi_{\alpha_2}\varphi_{\alpha_1}\rangle \tag{1.4}$$

from which one can derive the general formula:

$$\hat{a}^\dagger_\alpha |N\rangle = \sqrt{N+1} |\varphi_{\alpha_1}, \varphi_{\alpha_2}, \cdots \varphi_{\alpha_N}\rangle \tag{1.5}$$

Special attention has to be put in the order of the creation operators, since we are working with Fermions and the wave function has to be antisymmetric with respect to an exchange of a pair of particles; in other words:

$$\left|\varphi^1_{\alpha_1}, \varphi^2_{\alpha_2}, \cdots, \varphi^i_{\alpha_i}, \varphi^j_{\alpha_j}, \cdots, \varphi^N_N\right\rangle = -1 \left|\varphi^1_{\alpha_1}, \varphi^2_{\alpha_2}, \cdots, \varphi^j_{\alpha_i}, \varphi^i_{\alpha_j}, \cdots, \varphi^N_N\right\rangle \tag{1.6}$$

where to explicitely take into account that fermions are indistinguishable particles, we labelled the particles with a superindex $1, 2, \cdots, N$ that we leave out for the sake of notation.

The annihilation operator $\hat{a}_\beta$ destroys a particle in state β

$$\hat{a}_\beta |N\rangle = \hat{a}_\beta |\varphi_{\alpha_1}, \varphi_{\alpha_2}, \ldots, \varphi_{\alpha_i}, \ldots, \varphi_{\alpha_N}\rangle = (-1)^p \delta_{\beta,\alpha_i} \frac{1}{\sqrt{N}} \left|\varphi_{\alpha_1}, \varphi_{\alpha_2}, \ldots, \varphi_{\alpha_{i-1}}, \varphi_{\alpha_{i+1}}, \ldots, \varphi_{\alpha_N}\right\rangle \tag{1.7}$$

where p indicates the number of permutations that took to place the state φ_{α_i} to the left side of the state ket $|N\rangle$.

The anti-commutation relations are not being proved here, but they are:

$$\left\{\hat{a}_\alpha^\dagger, \hat{a}_\beta^\dagger\right\} = \left\{\hat{a}_\alpha, \hat{a}_\beta\right\} = 0 \tag{1.8}$$

$$\left\{\hat{a}_\alpha^\dagger, \hat{a}_\beta\right\} = \left\{\hat{a}_\alpha, \hat{a}_\beta^\dagger\right\} = \delta_{\alpha,\beta} \tag{1.9}$$

Now we introduce the so called *Field-operators*: their action is to create/annihilate a particle at time t and position $\mathbf{r}$ in a quantum state α

$$\hat{\psi}^\dagger(\mathbf{r},t) = \sum_\alpha \langle \mathbf{r}|\varphi_\alpha(t)\rangle^\dagger \hat{a}_\alpha^\dagger = \sum_\alpha \varphi^*(\mathbf{r},t)\hat{a}_\alpha^\dagger \tag{1.10}$$

$$\hat{\psi}(\mathbf{r},t) = \sum_\alpha \langle \mathbf{r}|\varphi_\alpha(t)\rangle \hat{a}_\alpha = \sum_\alpha \varphi(\mathbf{r},t)\hat{a}_\alpha \tag{1.11}$$

$$\tag{1.12}$$

They follow the same anticommutation rules as in 1.9

$$\left\{\hat{\psi}_\alpha^\dagger, \hat{\psi}_\beta^\dagger\right\} = \left\{\hat{\psi}_\alpha, \hat{\psi}_\beta\right\} = 0 \tag{1.13}$$

$$\left\{\hat{\psi}_\alpha^\dagger, \hat{\psi}_\beta\right\} = \left\{\hat{\psi}_\alpha, \hat{\psi}_\beta^\dagger\right\} = \delta_{\alpha,\beta} \tag{1.14}$$

With this definitions we can write an arbitrary operator $\hat{A}$ containing one and two particle parts, in second quantization formalism

$$\hat{A} \equiv \sum_{\alpha,\beta} \langle \varphi_\alpha|\hat{A}|\varphi_\beta\rangle \hat{a}_\alpha^\dagger \hat{a}_\beta + \sum_{\alpha,\beta,\gamma,\delta} \langle \varphi_\alpha\varphi_\beta|\hat{A}|\varphi_\delta\varphi_\gamma\rangle \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma \hat{a}_\delta \tag{1.15}$$

Here we have re-arranged the creation and annihilation operators in normal ordering (just using commutation relations to place all the creation operators to the far left and the annihilation operators to the far right)

B. One particle Green's function

We have obtain some Green's functions in past lectures (they were the result of a perturbation to a system, or a solution of Schrödinger equation, etc.) Here, we write down the Causal one particle Green's function (or time ordered Green's function, or simply Green's function)

$$G(\mathbf{r}_1,t_1;\mathbf{r}_1',t_1') = -i\left\langle N\middle|\hat{T}\left[\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\right]\middle|N\right\rangle$$

$$= -i\Theta(t_1 - t_1')\left\langle N\middle|\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\middle|N\right\rangle + i\Theta(t_1'-t_1)\left\langle N\middle|\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\hat{\psi}(\mathbf{r}_1,t_1)\middle|N\right\rangle. \quad (1.16)$$

The physical interpretation of this Green's function is as follows:

1. if $t_1 > t_1'$ an electron is created at time t' at position $\mathbf{r}_1'$ and it gets propagated to position $\mathbf{r}_1$ and destroyed at time t_1.

2. if $t_1' > t_1$ a hole is created at time t at position $\mathbf{r}_1$ and it propagates to position $\mathbf{r}_1'$ and destroyed at time t_1'.

This is the reason why 1.16 is also called a *Propagator.*

As we already know from the last topic on TDDFT, we can find some properties from the Green's function (like the Density of States). The way to proceed in this case, is to write down the equation of motion for the Propagator 1.16, in other words, take the time derivative of it

$$\begin{aligned}
\frac{\partial}{\partial t_1}G(\mathbf{r}_1,t_1;\mathbf{r}_1',t_1') =& \frac{\partial}{\partial t_1}\left\langle N\middle|\theta(t_1-t_1')\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1') - \theta(t_1'-t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\hat{\psi}(\mathbf{r}_1,t_1)\middle|N\right\rangle \\
\frac{\partial}{\partial t_1}G(\mathbf{r}_1,t_1;\mathbf{r}_1',t_1') =& \left\langle N\middle|\delta(t_1-t_1')\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1') + \theta(t_1-t_1')\left(\frac{\partial}{\partial t_1}\hat{\psi}(\mathbf{r}_1,t_1)\right)\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\middle|N\right\rangle \\
&+ \left\langle N\middle|\delta(t_1-t_1')\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\hat{\psi}(\mathbf{r}_1,t_1) - \theta(t_1'-t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1)\left(\frac{\partial}{\partial t_1}\hat{\psi}(\mathbf{r}_1,t_1)\right)\middle|N\right\rangle
\end{aligned} \quad (1.17)$$

Where we have used the chain rule on the time derivative and also the definition of the derivative of the step function

$$\frac{\partial}{\partial t}\theta(t-t') = -\frac{\partial}{\partial t'}\theta(t-t') = \delta(t-t'). \quad (1.18)$$

As we can see from Eq.(1.17), we need to find out the expression of the time derivative of the field operator $\hat{\psi}(\mathbf{r}_1,t_1)$. To do so, we use the Heisenberg equation of motion

$$i\frac{\partial\hat{\psi}(\mathbf{r}_1,t_1)}{\partial t_1} = \left[\hat{\psi}(\mathbf{r}_1,t_1),\hat{H}\right] \quad (1.19)$$

We consider a Hamiltonian consisting on two terms: a single particle term that encloses the kinetic energy plus some any local external field, and an interacting part. We can use the form of a general two particle operator in second quantization 1.15 (we consider in the rest o the calculation, $\hbar = 2m = 1$):

$$\hat{H} = \int d^3r\ h_0\hat{\psi}^\dagger(\mathbf{r},t)\hat{\psi}(\mathbf{r},t) + \int d^3r\int d^3r' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r},t)\hat{\psi}^\dagger(\mathbf{r}',t')\hat{\psi}(\mathbf{r}',t')\hat{\psi}(\mathbf{r},t) \quad (1.20)$$

in Eq.(1.20) we have denoted the two particle potential with $w(\mathbf{r}_1-\mathbf{r}_1')$. From now on we can assume that the interaction is of the Coulomb type, i.e. $w(\mathbf{r}_1-\mathbf{r}_1') = \dfrac{1}{|\mathbf{r}_1-\mathbf{r}_1'|}$

The equation of motion for $\hat{\psi}(\mathbf{r}_1,t_1)$ is lenghty and here we just present the final result; details on the calculation can be found in Appendix (A)

$$\theta(t_1-t_1')\left(\frac{\partial}{\partial t_1}\hat{\psi}(\mathbf{r}_1,t_1)\right)=i\theta(t_1-t_1')\left(h_0\hat{\psi}(\mathbf{r}_1,t_1)+\int d\mathbf{r}'w(\mathbf{r}_1-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}',t_1)\ \hat{\psi}(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}_1,t_1)\right)$$

$$\begin{aligned}\theta(t_1-t_1')\left(\frac{\partial}{\partial t_1}\hat{\psi}(\mathbf{r}_1,t_1)\right)&=i\theta(t_1-t_1')h_0\hat{\psi}(\mathbf{r}_1,t_1)\\&\quad+i\theta(t_1-t_1')\int d\mathbf{r}'w(\mathbf{r}_1-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}',t_1')\end{aligned}\tag{1.21}$$

Substituting Eq.(1.21) into Eq.(1.17) we get

$$\begin{aligned}\frac{\partial}{\partial t_1}G(\mathbf{r}_1,t_1;\mathbf{r}_1',t_1')&=\delta(t_1-t_1')\left\langle N\middle|\left\{\hat{\psi}(\mathbf{r}_1,t_1),\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\right\}\middle|N\right\rangle\\&\quad+i\left\langle N\middle|\theta(t_1-t_1')h_0\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1')-\ \theta(t_1'-t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1')h_0\hat{\psi}(\mathbf{r}_1,t_1)\middle|N\right\rangle\\&\quad+i\left\langle N\middle|\theta(t_1-t_1')\int d\mathbf{r}'w(\mathbf{r}_1-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\right.\\&\quad\left.-\theta(t_1'-t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\int d\mathbf{r}'w(\mathbf{r}_1-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}_1,t_1)\middle|N\right\rangle\\\left(i\frac{\partial}{\partial t_1}-h_0\right)\mathbf{G}(\mathbf{r}_1,t_1;\mathbf{r}_1',t_1')&=\delta(t_1-t_1')\delta(\mathbf{r}_1-\mathbf{r}_1')\\&\quad+i\left\langle N\middle|\theta(t_1-t_1')\int d\mathbf{r}'w(\mathbf{r}_1-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\right.\\&\quad\left.-\theta(t_1'-t_1)\int d\mathbf{r}'w(\mathbf{r}_1-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\hat{\psi}^\dagger(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}_1,t_1)\middle|N\right\rangle\end{aligned}$$

$$\left(i\frac{\partial}{\partial t_1}-h_0\right)G(\mathbf{r}_1,t_1;\mathbf{r}_1',t_1')=\delta(t_1-t_1')\delta(\mathbf{r}_1-\mathbf{r}_1')-i\int d^3r'w(\mathbf{r}_1-\mathbf{r}')G_2\left(\mathbf{r}_1,t_1,\mathbf{r}',t_1^+;\mathbf{r}_1',t_1',\mathbf{r}',t_1^{'+}\right)\tag{1.22}$$

Where the terms: $t_1^+=\lim_{\eta\to0}t_1+\eta$ and $t_1^{'+}=\lim_{\eta\to0}t_1'+\eta$ are added to ensure the correct time ordering of the operators (earlier times have to be on the left).

We have defined here the **two particle Green's function** G_2 that is a correlation between to electrons under the action of the potential $w(\mathbf{r}_1-\mathbf{r}')$. Nonentheless, equation 1.22 defines a three particle Green's function arising from the equation of motion for G_2 and so on and so forth, this is called the BBGKY hierarchy e.o.m.

Before procceding, let us use a short hand notation for the quantities in 1.22

$$(\mathbf{r}_1,t_1)=1\tag{1.23}$$

$$(\mathbf{r}_1',t_1')=1'\tag{1.24}$$

$$\left(\mathbf{r}',t_1^+\right)=2\tag{1.25}$$

$$\left(\mathbf{r}', t_1^{'+}\right) = 2^+ \tag{1.26}$$

and the Dyson-equation becomes

$$\left(i\frac{\partial}{\partial t_1} - h_0\right)G(1,1') = \delta(1-1') - i\int d2\; w(\mathbf{r}_1 - \mathbf{r}')G_2\left(1,2;1',2^+\right) \tag{1.27}$$

Instead of trying to solve 1.27 to all orders of the equations of motion, we can truncate the series and define all the possible higher order terms as the so-called *self-energy* $\Sigma(1,2)$, and then the equation for the one particle Green's function becomes

$$\left(i\frac{\partial}{\partial t_1} - h_0\right)G(1,1') + i\int d2\; \Sigma(1,2)G_2\left(1,2;1',2^+\right) = \delta(1-1') \tag{1.28}$$

C. Hedin's equations

Our task now is to find an approximate expression for the self energy $\Sigma(1,2)$. This can be done in two approaches: using Wick's theorem or by the functional derivate technique developed by Hedin, we present here a rough explanation.

First we consider a time dependent field $\phi(\mathbf{r},t)$ that is just a mathematical tool for the evaluation of the self energy. At the end, the field will can be taken equal to 0.

Since we are going to work in the dirac representation, then we need the expression for the time-evolution operator and the Dirac representation of the wave function:

$$|\psi_D(\mathbf{r},t)\rangle = \hat{U}_D(t,t_0)\,|\psi_D(\mathbf{r},t_0)\rangle \tag{1.29}$$

where

$$\hat{U}_D(t,t_0) = T\exp\left(-i\int_{t_0}^{t} d\tau\hat{\phi}(\tau)\right) \tag{1.30}$$

and we have used again the formalism of second quantization to write down the operator $\hat{\phi}(\tau)$

$$\hat{\phi}(\tau) = \int d^3r\phi(\mathbf{r},\tau)\hat{\psi}_D^\dagger\hat{\psi}_D \tag{1.31}$$

We can write the Dirac equation of motion for the field operator $\hat{\psi}_D(r)$

$$i\frac{\partial}{\partial t}\hat{\psi}_D(\mathbf{r}) = \left[\hat{\psi}_D(\mathbf{r}), \hat{H}_0\right] \tag{1.32}$$

We also define the term

$$\hat{S} = \hat{U}_D(\infty,-\infty) = T\exp\left(-i\int_{-\infty}^{\infty} d\tau\hat{\phi}(\tau)\right) \tag{1.33}$$

The general form of a one particle and two particle Green's functions in the Dirac picutre are given by

$$iG(1,2) = \frac{\left\langle N\middle|\hat{T}\left[\hat{S}\hat{\psi}_D(1)\hat{\psi}_D^\dagger(2)\right]\middle|N\right\rangle}{\left\langle N\middle|\hat{S}\middle|N\right\rangle} \tag{1.34}$$

$$G_2(1,2,3,4) = i^2\frac{\left\langle N\middle|\hat{T}\left[\hat{S}\hat{\psi}_D(1)\hat{\psi}_D(3)\hat{\psi}_D^\dagger(4)\hat{\psi}_D^\dagger(2)\right]\middle|N\right\rangle}{\left\langle N\middle|\hat{S}\middle|N\right\rangle} \tag{1.35}$$

The proof for 1.34 and 1.35 is far from trivial and the reader should find a good discussion on [2] (pp.83).

In the precence of an external field, the Green's function 1.34 equation of motion is expressed in terms of its functional derivative:

$$\left(i\frac{\partial}{\partial t_1} - H^0(1) - V(1)\right)G(1,2) - i\int v(1^+3)\frac{\delta G(1,2)}{\delta\phi(3)}d(1,2) = \delta(1,2) \tag{1.36}$$

where

$$V(1) = \phi(1) - i\int d(3)v(13)G(33^+). \tag{1.37}$$

The second term is the so called *direct term of the Hartree-Fock Potential.* It is called direct term because it doesn't take into consideration the indistinguishability of electrons. (another way to understand this term is by considering the approximation of the two particle Green's function as a product of two single particle Green's function or *Hartree Approximation* ([1] pp.285):

$$G_2(1,2,3,4) = G(12)G(34) \tag{1.38}$$

The two particle Green's function describes then, two particles propagating independently, i.e. no correlations between them.

This descomposition into single particle Green's functions allows us to obtain an approximate expresion for $G(12)$ (or also $G(1,2)$) in terms of a screened Coulomb potential $W(1,2)$ which at the same time is written in terms of the Polarization function $P(1,2)$.

$W(1,2)$ describes the effective potential that an electron at point 1 feels due to an electron at point 2 including the polarization of the rest of the electrons (*Screening*).

The information that the Polarization function contains, can be understood as the value of all the scattering events between electrons and holes in the screening cloud. This is the role of the *Vertex function* $\Lambda(1,2,3)$, which once again, it is written in terms of the *Self energy* term $\Sigma(1,2)$ that contains information about the exchange and correlation beyond the mean-field (i.e. Hartree-Fock).

All those equations have to be solved self-consistently to find approximations to the Green's function from which, as we have seen many times, contains useful information about the system (in this case, the quasi-particle energies).

Hedin's equations are

$$\Sigma(1,2) = i\int d(34)G(1,3^+)W(1,4)\Lambda(3,2,4) \tag{1.39}$$

$$G(1,2) = G_0(1,2) + \int d(34) G_0(1,3)\Sigma(3,4)G(4,2) \tag{1.40}$$

$$\Lambda(1,2,3) = \delta(1-2)\delta(2-3) + \int d(4567)\frac{\delta\Sigma(1,2)}{\delta G(4,5)}G(4,6)G(7,5)\Lambda(6,7,3) \tag{1.41}$$

$$P(1,2) = -i\int d3d4 G(1,3)\Lambda(3,4,2)G\left(4,1^{+}\right) \tag{1.42}$$

$$W(1,2) = v(1,2) + \int d(34) v(1,3)P(3,4)W(4,2) \tag{1.43}$$

Appendix A: Equation of motion for the field operator $\hat{\psi}(\mathbf{r}_1, t_1)$

We name the term $\frac{\partial}{\partial t_1}\hat{\psi}(\mathbf{r}_1, t_1) = *$

$$
\begin{aligned}
*i =& \Big[\hat{\psi}(\mathbf{r}_1, t_1), \mathbf{H}\Big] \\
=& \hat{\psi}(\mathbf{r}_1, t_1) \int d\mathbf{r} h_0 \hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}(\mathbf{r}, t) \; - \int d\mathbf{r} h_0 \hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}(\mathbf{r}, t)\hat{\psi}(\mathbf{r}_1, t_1) \\
&+ \hat{\psi}(\mathbf{r}_1, t_1) \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t)\psi(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t) \\
&- \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t)\psi(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t)\hat{\psi}(\mathbf{r}_1, t_1) \\
=& \hat{\psi}(\mathbf{r}_1, t_1) \int d\mathbf{r} h_0 \hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}(\mathbf{r}, t) \; - \int d\mathbf{r} h_0 \hat{\psi}^\dagger(\mathbf{r}, t) \underbrace{\hat{\psi}(\mathbf{r}, t)\hat{\psi}(\mathbf{r}_1, t_1)}_{-\hat{\psi}(\mathbf{r}_1, t_1)\hat{\psi}(\mathbf{r}, t)} \\
&+ \hat{\psi}(\mathbf{r}_1, t_1) \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t)\psi(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t) \\
&- \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t)\psi(\mathbf{r}', t) \underbrace{\hat{\psi}\,(\mathbf{r}, t)\hat{\psi}(\mathbf{r}_1, t_1)}_{-\hat{\psi}(\mathbf{r}_1, t_1)\hat{\psi}(\mathbf{r}, t)} \\
=& \hat{\psi}(\mathbf{r}_1, t_1) \int d\mathbf{r} h_0 \hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}(\mathbf{r}, t) \; + \int d\mathbf{r} h_0 \quad \underbrace{\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}(\mathbf{r}_1, t_1)}_{\delta(t-t_1)\delta(\mathbf{r}-\mathbf{r}_1) - \hat{\psi}(\mathbf{r}_1, t_1)\hat{\psi}^\dagger(\mathbf{r}, t)} \quad \hat{\psi}(\mathbf{r}, t) \\
&+ \hat{\psi}(\mathbf{r}_1, t_1) \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t)\psi(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t) \\
&+ \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t) \underbrace{\hat{\psi}(\mathbf{r}', t)\hat{\psi}(\mathbf{r}_1, t_1)}_{-\hat{\psi}(\mathbf{r}_1, t_1)\psi(\mathbf{r}', t')} \hat{\psi}(\mathbf{r}, t) \\
=& \cancel{\hat{\psi}(\mathbf{r}_1, t_1) \int d\mathbf{r} h_0 \hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}(\mathbf{r}, t)} \; + \int d\mathbf{r} h_0 \delta(t-t_1)\delta(\mathbf{r}-\mathbf{r}_1)\hat{\psi}(\mathbf{r}, t) \; - \cancel{\int d\mathbf{r} h_0 \hat{\psi}(\mathbf{r}_1, t_1)\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}(\mathbf{r}, t)} \\
&+ \hat{\psi}(\mathbf{r}_1, t_1) \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t)\psi(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t) \\
&- \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t) \quad \underbrace{\hat{\psi}^\dagger(\mathbf{r}', t)\hat{\psi}(\mathbf{r}_1, t_1)}_{\delta(t-t_1)\delta(\mathbf{r}'-\mathbf{r}_1) - \hat{\psi}(\mathbf{r}_1, t_1)\hat{\psi}^\dagger(\mathbf{r}', t)} \quad \hat{\psi}(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t) \\
=& h_0\hat{\psi}(\mathbf{r}_1, t_1) + \hat{\psi}(\mathbf{r}_1, t_1) \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t)\hat{\psi}(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t) \\
&- \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t)\delta(t-t_1)\delta(\mathbf{r}'-\mathbf{r}_1)\hat{\psi}(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t) \\
&+ \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}') \quad \underbrace{\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}(\mathbf{r}_1, t_1)}_{\delta(t-t_1)\delta(\mathbf{r}-\mathbf{r}_1) - \hat{\psi}(\mathbf{r}_1, t_1)\hat{\psi}^\dagger(\mathbf{r}, t)} \quad \hat{\psi}^\dagger(\mathbf{r}', t)\hat{\psi}(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t) \\
=& h_0\hat{\psi}(\mathbf{r}_1, t_1) + \hat{\psi}(\mathbf{r}_1, t_1) \int d\mathbf{r} \cancel{\int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t)\hat{\psi}(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t)} \\
&- \int d\mathbf{r} w(\mathbf{r}-\mathbf{r}_1)\hat{\psi}^\dagger(\mathbf{r}, t_1)\hat{\psi}(\mathbf{r}_1, t_1)\hat{\psi}(\mathbf{r}, t_1) \\
&+ \int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\delta(t-t_1)\delta(\mathbf{r}-\mathbf{r}_1)\hat{\psi}^\dagger(\mathbf{r}', t)\hat{\psi}(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t) \\
&- \cancel{\int d\mathbf{r} \int d\mathbf{r}' w(\mathbf{r}-\mathbf{r}')\hat{\psi}(\mathbf{r}_1, t_1)\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t)\hat{\psi}(\mathbf{r}', t)\hat{\psi}(\mathbf{r}, t)}
\end{aligned}
\tag{A.1}
$$

$$
\begin{aligned}
i\left(\frac{\partial}{\partial t_1}\hat{\psi}(\mathbf{r}_1,t_1)\right) &= h_0\hat{\psi}(\mathbf{r}_1,t_1) - \int d\mathbf{r} w(\mathbf{r}-\mathbf{r}_1)\hat{\psi}^\dagger(\mathbf{r},t_1)\underbrace{\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}(\mathbf{r},t_1)}_{-\hat{\psi}(\mathbf{r},t)\hat{\psi}(\mathbf{r}_1,t_1)} \\
&\quad + \int d\mathbf{r}' w(\mathbf{r}_1-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}_1,t_1) \\
i\left(\frac{\partial}{\partial t_1}\hat{\psi}(\mathbf{r}_1,t_1)\right) &= h_0\hat{\psi}(\mathbf{r}_1,t_1) + \int d\mathbf{r}' w(\mathbf{r}_1-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}',t_1)\hat{\psi}(\mathbf{r}_1,t_1)
\end{aligned}
\tag{A.2}
$$

where in the last equality we have use the fact that the two particle potential is of the Coulomb type, i.e. symmetic with respect to the particle's position.

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