I. Fundamentals

1) Invertibility Theorem

The mapping $G: \{V(r,t) + C(t)\} \rightarrow n(r,t)$ is one-to-one, and therefore is invertible,

where $V(r,t)$ is an external potential, $C(t)$ a time-dependent constant, and $n(r,t)$ the density.

\textbf{Proof 1} \hspace{1cm} [Runge & Gross, PRL 52, 997 (1984)]

When $V(t,t)$ can be expanded into a Taylor series at $t = t_0$, RG proved that if $(\partial / \partial t)^k [V(t,t) - V(t,t)]_{t=t_0} \neq C(t)$ for some $k$, then $(\partial / \partial t)^k [n(t,t) - n(t,t)]_{t=t_0} \neq 0$. Therefore, $G$ is one-to-one.

\textbf{Proof 2} \hspace{1cm} [Ng & Singwi, PRL 59, 2627 (1987)]

In the linear-response scheme by the short-time expansion of density response function, NgS showed that, for short-time domain, if $\int_{t_0}^{t} dt (t-t') [V(t,t') - V(t,t')] \neq C(t)$ for some $t$, then $n(t,t) - n(t,t)$ \neq 0 at the time.

2) Density Functional Theorem [Runge & Gross (1984)]

As a consequence of the invertibility theorem,

The expectation value of an arbitrary operator is a functional of $n(r,t)$. 
The mapping,
\[ \vec{\mathcal{N}}(t) \mapsto \{ \vec{\mathcal{N}}(t) + C(t) \} \mapsto \{ \exp[-i\vec{\mathcal{A}}(t)/\hbar] |\psi(t)\rangle \} \]

\[ \mapsto \langle \Psi(t) | \text{arbitrary operator} | \Psi(t)\rangle \]
specifies the expectation value uniquely, where \( N \) is the total number of electrons.

\[ 3. \textbf{Action Principle [Runge & Gross (84)]} \]

The action integral
\[ A_{\psi}[n(t)] = \int_{t_0}^{t_1} dt \langle \Psi(t) | i\hbar \hat{\rho} \hat{\sigma} + T - U \Psi(t) \rangle - \int_{t_0}^{t_1} dt \int d\sigma n(t) \Psi(t) \Psi(t)^\ast \]  
\[ (1) \]
is stationary at the exact density, i.e.,
\[ S A_{\psi} / S n(t) = 0 \quad \text{at} \quad n(t) = G \cdot \nabla n(t) \]  
\[ (2) \]
where \( T \) and \( U \) are the kinetic and Coulomb-interaction parts of the Hamiltonian.

\[ 4. \textbf{Time-dependent Kohn-Sham Scheme [Runge & Gross (84)]} \]

We define the exchange-correlation (xc) action as
\[ A_{xc} = - \int_{t_0}^{t_1} dt \langle \Psi(t) | i\hbar \hat{\rho} \hat{\sigma} + T - U \Psi(t) \rangle + \int_{t_0}^{t_1} dt \langle \Psi(t) | i\hbar \hat{\rho} \hat{\sigma} + T - U \Psi(t) \rangle e^2 = 0 \]
\[ - \frac{e^2}{2} \int_{t_0}^{t_1} dt \int d\sigma d\sigma' \int |r-r'| n(\vec{r},t) n(\vec{r}',t) \]  
\[ (3) \]
Then the Euler equation (2) for \( n(\vec{r},t) \) is equivalent to calculating \( n(\vec{r},t) \) as follows:

\[ \left[ i\hbar \partial \nabla^2 m - V(\vec{r},t) - \sum_{\vec{r}'} d\sigma' (\delta(\vec{r'} - \vec{r}) n(\vec{r},t) - U_{xc}(\vec{r},t)) \right] \psi(\vec{r},t) = 0 \]  
\[ (4) \]
\[ n(\vec{r},t) = \sum_{\vec{r}_i} |\psi_i(\vec{r},t)|^2 \]  
\[ (5) \]
where the xc potential \( U_{xc}(r,t) \) is given by

\[
U_{xc}(r,t) = \frac{\delta A_{xc}}{\delta n(r,t)}.
\]  

(6)

Combination of KS eq. and noneq. GF theory \( \rightarrow \) calc. of any physical quantity.

\[\text{II. Density-functional Dynamics}\]

Though the Kohn-Sham (KS) states, \( \psi_i(r,t) \) in Eq. (4), do not represent the physical single-particle properties, they are very useful tools for calculating physical quantities accurately; rigorous algorithms can be derived for calculating the single-particle Green's functions (GF) \( G(i,i') \), the xc action \( A_{xc} \), and the xc potential \( U_{xc}(i) \), through a many-body theory based on the KS states. For treat time-dependent situations, we invoke Keldysh's closed time-path formalism. The unperturbed GF in which is given by

\[
G_0(i,i') = -i [\Theta_p(t-t') \Sigma \psi_i(1) \psi_{i'}(1) f_i - \Theta_p(t'-t) \Sigma \psi_i(1) \psi_{i'}(1) (1-f_i)]
\]  

(7)

where \( \Theta_p(t) \) is a step function on the closed time path, and \( f_i \) is the occupation number of the \( i \)-th KS state.

Solution in this scheme leads to the following density-functional dynamics: The KS one-body Schrödinger equation is solved concurrently with the many-body equations for \( G(i,i') \) and \( U_{xc}(i) \). Because of causality, we can calculate \( \psi_i(r,t), G(i,i') \), and \( U_{xc}(i) \), at each time step only with the knowledge of these functions in previous time steps.

\[\text{also some other physical quantities if necessary!}\]
(1) Self-Energy Formula for $\mathcal{U}_{xc}(t,t')$

With the closed-time path expression for the action and the ordinary nonequilibrium GF theory, we can derive the following expression for $\mathcal{U}_{xc}(t,t')$:

$$\mathcal{U}_{xc}(t,t') = -2i \oint d\zeta \oint d\zeta' \left\{ \sum_{\sigma} G_0^{c}(\zeta,\zeta') \Gamma(\zeta,t') \right\}$$

where $p$ denotes the integration over the closed time path,

$$G_0^{c}(\zeta,t') = -i \sum_{\xi} \mathcal{U}_{\xi}(\zeta,t')$$

and $\Sigma_{xc}(1,1')$ is the self-energy excluding the Hartree term.

Equation (8b) clearly guarantee the causality; for the calculation of $\mathcal{U}_{xc}(t,t')$, we need only the previous time-step information.
Equation (8) is a straightforward generalization of the expression for $v_{xc}(r)$ in the static DFT derived by Sham [PRB 32, 3876 (1985)]. The formulation of $Ax_c$ in terms of the Keldysh closed time path has been suggested by Peuckert [J. Phys. C 11, 4945 (1978)].

(2) Other Formulas for $v_{xc}(r, t)$

(i) Correlation-function Formula [Ng, PRB 39, 9947 (1989), for the static case.]

$$v_{xc}(r) = -\frac{1}{2} \int_0^1 d\lambda \int d^3r \int d^3r' \frac{e^2}{(r-r')^2} \chi_{\alpha}^{(\beta, \lambda)}(r_1, r_2; \beta, \beta'; 4, 1) \chi_{\alpha}^{(\beta, \lambda)}(4, 1) \tag{11}$$

(ii) Linear Response Scheme [Gross & Kohn, PRL 55, 2850 (1985)]]

$$v_{xc}(r, \omega) = \int d\omega' f_{xc}(r, \omega'; \omega) \Delta N(r, \omega)$$

$$\left\{ \begin{align*}
  f_{xc}^{\uparrow}(r, \omega) &= \chi_{\alpha\beta}(r, \omega) - \chi_{\alpha\beta}(r', \omega) - e^2 / (r-r') \\
  \chi_{\alpha\beta}(r, \omega) &= \sum_{i,j} \frac{\psi_i^*(r) \psi_j^*(r) \psi_i(r') \psi_j(r')}{\omega - (\epsilon_j - \epsilon_i) + i\delta} (f_i - f_j) \tag{14}
\end{align*} \right.$$ (Local-density Approximation)

$$f_{xc}^{\uparrow}(r, \omega) = \delta(r-r') f_{xc}^{\uparrow}(q=0, \omega; n(r)) \tag{15}$$

where $f_{xc}$ is the function in homogeneous electron liquids.

"Feasibility of the Density-functional Dynamics"

(i) So far, no approx is included; everything is exact.
(ii) Sham & Schlüter applied the static version of Eq. (8) with the lowest-order $\Sigma_x = \Sigma_0$ to semiconductors and have solved it approximately. In the same level of approx, DFD will be also feasible.
Time-dependent Density-functional Theory:

Fundamentals

8. System

The Hamiltonian of the system is given by

\[ H(t) = T + U + V(t) \quad (1) \]

\[ T = \sum_{\sigma} \int d^3 r \, \frac{1}{2m} (\mathbf{p}^\sigma)^2 \psi^\dagger_\sigma (\mathbf{r}) \psi_\sigma (\mathbf{r}) \quad (2) \]

\[ U = \frac{1}{2} \sum_{\sigma_1, \sigma_2} \int d^3 r_1 d^3 r_2 \, \psi^\dagger_\sigma_1 (\mathbf{r}_1) \psi^\dagger_\sigma_2 (\mathbf{r}_2) \, U(\mathbf{r}_1 - \mathbf{r}_2) \psi_{\sigma_1} (\mathbf{r}_1) \psi_{\sigma_2} (\mathbf{r}_2) \quad (3) \]

\[ V(t) = \int d^3 r \, \rho(\mathbf{r}) \mathcal{U}(\mathbf{r}, t) \quad (4) \]

where \( \psi^\dagger_\sigma (\mathbf{r}) \) and \( \psi_\sigma (\mathbf{r}) \) are the creation and annihilation operators for an electron with spin \( \sigma \); \( \rho(\mathbf{r}) = \sum \psi^\dagger_\sigma (\mathbf{r}) \psi_\sigma (\mathbf{r}) \), \( U(\mathbf{r}) = e^2/r \), and \( \mathcal{U}(\mathbf{r}, t) \) is an external field.

We define a mapping \( G \) such that

\[ G: \mathcal{U}(\mathbf{r}, t) \rightarrow \eta(\mathbf{r}, t) = \langle \psi(t) | \rho(\mathbf{r}) | \psi(t) \rangle \quad (5) \]

where \( | \psi(t) \rangle \) is the state which satisfies

\[ [i\hbar \partial / \partial t - H(t)] | \psi(t) \rangle = 0 \quad (6) \]

with a fixed initial condition,

\[ | \psi(t=t_0) \rangle = | \psi_0 \rangle. \quad (7) \]

8. Invertibility Theorem

The mapping

\[ G: \{ \mathcal{U}(\mathbf{r}, t) + C(t) \} \rightarrow \eta(\mathbf{r}, t) \quad (8) \]

is one-to-one, and therefore is invertible. Here, \( C(t) \) is a time dependent constant.
(1) Proof \cite{Runge&Gross, PRL 52, 997 (1984)}

This proof states if the potential can be expanded into a Taylor series and if \( V(r,t) - V'(r,t) \neq C(t) \), then the corresponding densities \( n(r,t) - n'(r,t) \neq 0 \).

\[ (\partial / \partial t)^{k+2} [ n(r,t) - n'(r,t) ] = (i \hbar / m) \nabla \cdot \left\{ n(r,t) \nabla (\partial / \partial t)^{k} [ V(r,t) - V'(r,t) ] \right\}_{t=t_0} \tag{9} \]

(2) The following relation can be derived.

First, consider the equation of motion for the current:

\[ j(r,t) = \langle \psi(t) | j(r) | \psi(t) \rangle \tag{10} \]

Where

\[ j(r) = \frac{1}{2} \sum \{ \psi^*_a(r) \frac{i \hbar}{m} \nabla \psi_a(r) - \frac{i \hbar}{m} \nabla \psi^*_a(r) \} \psi_a(r) \]. \tag{11} \]

The equation for the difference in current is given by

\[ \frac{\partial}{\partial t} [ j(r,t) - j'(r,t) ] = -\frac{i}{\hbar} \langle \psi | j(r) | V(r,t) - V'(t) | \psi \rangle \psi(t) \]

\[ = \frac{\hbar}{im} n(r,t_0) \nabla \frac{\partial}{\partial t} [ V(r,t) - V'(r,t) ] \]

because \( n(r,t_0) = \langle \psi_{r'} | n(r) | \psi \rangle \) is common by assumption. Higher order derivatives are derived as

\[ \left( \frac{\partial}{\partial t} \right)^2 [ j(r,t) - j'(r,t) ] = -\frac{i}{\hbar} \langle \psi | j(r) | V(r,t) - V'(t) | \psi \rangle \psi(t) \nabla^2 [ V(r,t) - V'(t) ] \]

\[ + \frac{\hbar}{im} n(r,t_0) \nabla \left( \frac{\partial}{\partial t} \right)^2 [ V(r,t) - V'(r,t) ] \]

and so on. The result is

\[ (\partial / \partial t)^{k+1} [ j(r,t) - j'(r,t) ] = \frac{\hbar}{im} n(r,t_0) \nabla \left( \frac{\partial}{\partial t} \right)^k [ V(r,t_0) - V'(r,t_0) ] \] \tag{12} \]

Combining Eq. (12) and the continuity equation,

\[ \frac{\partial}{\partial t} n(r,t) = -\nabla \cdot j(r,t), \tag{13} \]

we get Eq. (9) //
(2) The l.h.s., $(\partial/\partial t)^{k+2}[n(r,t)-n'(r,t)]$, of Eq. (9) cannot vanish if $(\partial/\partial t)^k[u(r,t)-u'(r,t)] \neq C(t)$.

(reductio ad absurdum)

Assume $\nabla \cdot [n(r,t)\nabla U(r)] = 0$ with $U(r) \neq \text{const}$. Then,

$$0 = \int_{\text{surf}} U(r) \nabla \cdot [n(r,t)\nabla U(r)]$$

$$= \frac{1}{2} \int_{\text{surf}} \nabla U(r) \cdot \nabla U(r) = \int_{\text{surf}} n(r,t)[\nabla U(r)]^2$$

If $\nabla U(r)$ falls off rapidly, the first term is zero. The second term cannot vanish. //

(3) If $u(r,t) - u'(r,t) \neq C(t)$, there is some $k$ where $(\partial/\partial t)^k[u(r,t_0) - u'(r,t_0)] \neq C(t)$. Then, from Eq. (9), $(\partial/\partial t)^{k+2}[n(r,t_0)-n'(r,t_0)] \neq 0$. We have thus proved the one-to-one correspondence. //

(2) Proof [Ng & Singwi, PRL 59, 2627 (1982)]

We divide the density into $n(r) + \delta n(r,t)$. In short time after $t_0$, $\delta n(r,t)$ is small and can be treated in linear-response scheme,

$$\delta n(r,t) = \int_{\text{surf}} \int_{t_0}^t dt' \chi(r,t; r', t') U(r,t')$$

(14)

where

$$\chi(r,t; r', t') = -i\hbar^{-1} \langle [\rho(r,t), \rho'(r,t')] \rangle.$$  

(15)

In the short-time region, we can also use short-time expansions,

$$\chi(r,t; r', t') = \sum_{n=1}^{\infty} \frac{(t-t')^n}{n!} \left(-\frac{i}{\hbar}\right)^n \langle [\ldots [\rho(r,H), \rho'(H), \ldots, H], \rho'(t')] \rangle.$$  

(16)
Using the continuity equation (13), the first term of the expansion is

\[ \chi(r,t'; r',t') = \frac{\hbar}{i} (t-t') \nabla \cdot <[\psi(r), \rho(r')] > \]

\[ = -\frac{tt'}{2m} \nabla \cdot < \rho(r) \delta(r'-r) + \frac{\hbar^2}{\sqrt{4\pi}} (t-t') \nabla \delta(r'-r) > \]

Substituting Eq. (17) in Eq. (14) and subtracting the same for \( \nu'(r,t) \), we get

\[ \n(r,t) - \n'(r,t) = \frac{1}{\hbar} \nabla \cdot \left\{ \rho(r) \nabla \int_{t_0}^{t} dt(t-t') [\nu(r,t') - \nu'(r,t')] \right\} \tag{18} \]

Therefore, unless \( \int_{t_0}^{t} dt(t-t') [\nu(r,t') - \nu'(r,t')] = c(t) \) for all small \( t \), where this expansion is valid, \( \n(r,t) - \n'(r,t) \neq 0 \) for some \( t \). (See (1) for the proof.) \( \nabla [\psi(r,t) - \psi'(r,t)] \) cannot be zero at all time \( t \) and all space point \( r \). Because if we assume it identically zero, then

\[ \nabla \frac{\partial^2}{\partial t^2} \psi(r,t) = \nabla [\psi(r,t) - \psi'(r,t)] = 0 \] for all space-time points; this contradicts the assumption \( \nabla [\psi(r,t) - \psi'(r,t)] \neq 0 \) at some time \( t \).

**S. Density Functional**

As a consequence of the invariability,

An arbitrary physical quantity is a functional of \( \n(r,t) \).

\[ \nott \rightarrow \{ \psi(r,t) + c(t) \} \] specifies an external field within time-dependent constant, and the Hamiltonian within a factor \( NC(t) \), where \( N \) is the total number of electrons. It therefore specifies the state within a phase factor, i.e.,

\[ \{ \psi(r,t) + c(t) \} \rightarrow \{ \exp[-i\hat{H}t/\hbar] \psi(t') | \psi(t) = NC(t) \} \tag{19} \]

This phase factor does not enter the expectation value of any quantity; thus, \( \nott \) specifies any expectation value uniquely. //
S. Action Principle

The action integral
\[ A_{2}[n] = \int_{t_0}^{t_f} dt \langle \psi(t)|i\hbar \partial_t - H\rangle - \int_{t_0}^{t_f} dt' \int d\mathbf{r} n(t') v(t') \]  
(20)

is stationary at the exact density, i.e.,
\[ \frac{\delta A_{2}}{\delta n(t')} = 0 \quad \text{for} \quad n(t') = G \cdot v(t') \]  
(21)

(\because \text{Action integral is stationary at the state satisfies Eq. (6), so})

that is stationary at the corresponding \( n(t) \).  

S. Time-dependent Kohn-Sham Scheme

We define the exchange-correlation (xc) action through the relation,
\[ \int_{t_0}^{t_f} dt \langle \psi(t)|i\hbar \partial_t - H\rangle = \int_{t_0}^{t_f} dt \langle \psi(t)|i\hbar \partial_t - T + V_{\text{xc}}(t)\rangle e^2 = 0 \]
\[ -\frac{1}{2} \int_{t_0}^{t_f} dt' \int d\mathbf{r} n(t') n(t) - A_{xc} \]  
(22)

Then, the Euler equation (21) becomes
\[ \frac{\delta}{\delta n(t')} \int_{t_0}^{t_f} dt \langle \psi(t)|i\hbar \partial_t - T + V_{\text{xc}}(t)\rangle e^2 = 0 - V_{\text{eff}}(n(t)) = 0 \]  
(23)

where
\[ V_{\text{eff}}(n(t)) = V_{\text{e}}(n(t)) + \int d\mathbf{r}' n(t') + V_{\text{xc}}(n(t)) \]  
(24)

and the xc potential \( V_{\text{xc}}(n(t)) \) is defined by
\[ V_{\text{xc}}(n(t)) = \frac{\delta A_{\text{xc}}}{\delta n(t)} \]  
(25)
Equation (23) is the same equation for determining \( n(x,t) \) of a non-interacting system in a field \( \psi(x,t) \). Therefore, \( n(x,t) \) is given by solving the following equations, supposing that \( \ket{e_0} = \sum_{i=1}^{N} \alpha_i \ket{\psi_i(0)} \), vacuum>:

\[
\begin{align*}
\left[ i \frac{\hbar}{\partial t} + \frac{\hbar^2 V^2}{2m} - V_{\text{eff}}(x,t) \right] \psi_i(x,t) &= 0 \\
\mathcal{N}(x,t) &= \sum_{i=1}^{N} |\psi_i(x,t)|^2
\end{align*}
\]
S. Definitions

The Hamiltonian of the system is given by

\[ H(t) = T + U + V(t) \]  

\[ T = \frac{\hbar^2}{2m} \sum \int d^3r \left( \psi^*_\sigma(r) (-i\hbar \nabla^2/2m) \psi_\sigma(r) \right) \]  

\[ U = \frac{1}{2} \sum \sum \int d^3r \int d^3r' \psi^*_\sigma(r) \psi^*_\sigma(r') U(r-r') \psi_\sigma(r) \psi_\sigma(r') \]  

\[ V(t) = \int d\mathbf{r} \rho(r) U(r,t) \]  

where \( \psi_\sigma(r) \) and \( \psi^*_\sigma(r) \) are the creation and annihilation operators of an electron with spin \( \sigma \), \( \rho(r) = \sum \psi^*_\sigma(r) \psi_\sigma(r) \), \( U(r) = e^2/r \), and \( U(r,t) \) is an external field.

We split the Hamiltonian (1) into two parts,

\[ H(t) = [ T + V_{\text{eff}}(t) ] + [ U + V(t) - V_{\text{eff}}(t) ] \]  

\[ = H_0(t) + H_1(t) \]  

Here,

\[ V_{\text{eff}}(t) = \int d^3r \rho(r) U_{\text{eff}}(r,t) \]  

\[ U_{\text{eff}}(r,t) = U(r,t) + \int d^3r' U(r',t)n(r',t) + U_{\text{xc}}(r,t) \]  

where the exchange-correlation (xc) potential \( U_{\text{xc}}(r,t) \) is given by

\[ U_{\text{xc}}(r,t) = \frac{\delta A_{\text{xc}}}{\delta n(r,t)} \]  

with the xc action \( A_{\text{xc}} \) defined through the relation

\[ A = \int_{t_i}^{t_f} dt \langle \psi(t) | i \hbar \alpha \partial_t - H(t) | \psi(t) \rangle \]  

\[ = \int_{t_i}^{t_f} dt \langle \psi(t) | i \hbar \alpha \partial_t - T | \psi(t) \rangle \mathcal{E}_2 - \int_{t_i}^{t_f} dt \int d^3r n(r,t) U(r,t) \]  

\[ - \frac{1}{2} \int_{t_i}^{t_f} dt \int d^3r_1 \int d^3r_2 U(r_1-r_2) n(r_1,t)n(r_2,t) - A_{\text{xc}}. \]
\[ n(r,t) = \langle \psi(t)| \rho(r) | \psi(t) \rangle \text{ is the density expectation value.} \]

Accordingly, \( H_1(t) \) is given by
\[ \begin{aligned}
H_1(t) &= U - \int d^3r \rho(r) w(r,t) \\
w(r,t) &= \int d^3r' n(r',t) + U_{xc}(r,t)
\end{aligned} \tag{10} \tag{11}

\section{Action Integral}

To analyze the structure of action, it is convenient to extend the time region \( (t_i \rightarrow t_f) \) to the Keldysh closed time path \( (t_i \rightarrow t_f \rightarrow t_i) \). [For the closed time path formalism, see for example, Chou et al. Phys. Rep. 118, 1 (1985).] Accordingly, the extended action is given by
\[ A = \int_p dt \langle \psi(t)| i \hbar \partial / \partial t - H(t) | \psi(t) \rangle \tag{12} \]

where \( p \) denotes the integration over the closed time path.

We here introduce a dimensionless coupling constant \( \lambda \) such that
\[ H(t) = H_0(t) + \lambda H_1(t) \tag{13} \]
then we can show that [Peucker, J. Phys. C11, 4945 (1978)]
\[ A - A_{\lambda=0} = \int_0^1 d\lambda \int_p dt \langle \psi(t)| H_1(t) | \psi(t) \rangle \tag{14} \]
\[ \text{(Generating Functional)} \]

To proceed further, we introduce the generating functional \( W \) as [see for example, Chou et al. (85)],
\[ W = - (\hbar/2) \ln Z \tag{15} \]
\[ Z = \text{tr}(S \hat{\rho}) \] (16)

Here, \( \hat{\rho} \) is the statistical operator, and the scattering matrix \( S \) is given by

\[ S = T_p \exp \left[ -i \int_{\mathcal{C}} \psi_i^\dagger \psi_f \right] \]

where \( T_p \) is the time-ordering operator on the closed time path, and the subscript \( H \) indicates the Heisenberg representation.

We can derive the following expression for \( W \),

\[ W - W_{\lambda=0} = \frac{i}{2} \int_0^t dt \int_p \Delta_p < H_f(t) > \]

where the expectation value here is given by

\[ < H_f(t) > = Z^{-1} \text{tr} \{ T_p [ \theta_H(t) S ] \hat{\rho} \} \]

thus coincides the physical expectation value when \( \Phi(t, t') = 0 \).

Comparing Eqs. (14) and (18),

\[ A - A_{\lambda=0} = 2i ( W - W_{\lambda=0} ) \]

S. Analysis of the Generating Functional

The single-particle Greens function (GF),

\[ G(t, t') = -\frac{i}{2} \sum_\phi < T_p [ \psi_i^\dagger \psi_f ] > \]

is generated from \( W \) by the functional derivative,

\[ \frac{\delta W}{\delta \Phi(t, t')} = G(t, t') \]

The vertex functional \( \Gamma \) is then defined as

\[ \Gamma[\phi] = W[\phi] - \int_p dh \int_p \psi_i^\dagger G(t, t') \psi_f \phi(t, t') \]
Then, using Eq. (22),
\[
\frac{\delta \Gamma}{\delta g(1,1)} = -\phi(1,1)
\]  \hspace{1cm} (24)

(Functional Representation for \( W \))

Using the equation of motion for \( g \), we can derive the Dyson equation,
\[
\Sigma^{-1}(1,1') = \Sigma^{-1}_0(1,1') - \hbar^{-1} \phi(1,1') - \Sigma(1,1')
\]  \hspace{1cm} (25)

Here,
\[
\Sigma^{-1}_0(1,1') = \left[ \frac{\partial^2}{\partial t \partial t'} + \hbar^2 q^2/2m - \hbar^{-1} V_{\text{eff}}(1) \right] \delta p(1,1')
\]  \hspace{1cm} (26)
\[
\Sigma(1,1') = \Sigma_{xc}(1,1') - \hbar^{-1} \left[ \omega(1') - \mathcal{U}(1,2) \mathcal{N}(2) \right] \delta p(1,1')
\]  \hspace{1cm} (27)
\[
\Sigma_{xc}(1,1') = -\hbar^{-1} \mathcal{U}(1,2) \chi^{(2)}(3,1';2,\bar{2}) \Gamma^{-1}(3,1')
\]  \hspace{1cm} (28)

where \( \delta p(1,1') = \delta(q_{1-1'}) \delta(p_{1-1'}) \) is the delta function on the closed time path, \( \mathcal{U}(1,2) = \mathcal{U}(1_{-2}) \delta p(1,1') \),
\[
\chi^{(2)}(1,1';2,2') = \frac{\delta^{-1}}{\delta \phi(1,1) \ldots \delta \phi(2,2')} \langle \tau \left[ \psi^+_0(1) \psi_0(1') \right] \rangle
\]  \hspace{1cm} (29)

and the bars indicate the integration over the indices.

Comparing Eqs. (24) and (25), we get
\[
\Gamma = \hbar \text{tr} \left[ \ln g - \Sigma^{-1}_0 g + 1 \right] + \hbar \Xi
\]  \hspace{1cm} (30)

where \( \text{tr} \alpha = \alpha(T, \Gamma) \) and
\[
\frac{\delta \Xi}{\delta g(1,1)} = \Sigma(1,1')
\]  \hspace{1cm} (31)

Using Eqs. (23) and (30),
\[
W = \hbar \text{tr} \left[ \ln g - \Sigma g \right] + \hbar \Xi
\]  \hspace{1cm} (32)
where we have used Eq. (25). Subtracting from Eq. (32) the corresponding expression with $\lambda = 0$, and decomposing the self-energy according to Eq. (27), we obtain for $\Phi(1,1') = 0$,

$$ W - W_{\lambda=0} = \hbar \text{Tr} \left[ \ln(G/G_0) - G_0^{-1}G + 1 \right] - \frac{1}{2} W(\bar{\tau}) \Pi(\bar{\tau}) + \frac{i}{\hbar} W(\bar{\tau},\bar{\tau}) \Pi(\bar{\tau}) \Pi(\bar{\tau}) + \Xi_{xc} $$

(33)

where

$$ rac{\delta \Xi_{xc}}{\delta G(1,1')} = \Sigma_{xc}(1,1'). $$

(34)

S. The Exchange Correlation Action

The xc action

$$ A_{xc} = -A + \int dt \langle \phi(t) | i \hbar \partial_t - T + \Sigma(t) \rangle \xi^2 = 0 - \gamma(1) \Pi(1) - \frac{1}{2} u(1,2) \Pi(1) \Pi(2) $$

(35)

is calculated from Eqs. (33), (20), and noting that

$$ A_{\lambda=0} = \int dt \langle \phi(t) | i \hbar \partial_t - T + \Sigma(t) \rangle \xi^2 = 0 - \gamma(1) \Pi_{\text{eff}}(1) $$

(36)

as

$$ A_{xc} = -2i \text{Tr} \left[ \ln(G/G_0) - G_0^{-1}G + 1 \right] - 2i \Xi_{xc} $$

(37)

Diagrammatically, $\Xi_{xc}$ corresponds to all the closed, connected, skeleton graphs, excluding the $W$-field and Hartree terms, i.e.,

$$ \begin{array}{c}
\text{ } \hspace{1cm} \text{ } \hspace{1cm} \text{ } \hspace{1cm}
\hspace{1cm} \text{ } \hspace{1cm} \text{ } \hspace{1cm}
\hspace{1cm} \text{ } \hspace{1cm} \text{ } \hspace{1cm}
\hspace{1cm} \text{ } \hspace{1cm} \text{ } \hspace{1cm}
\end{array} + \begin{array}{c}
\text{ } \hspace{1cm} \text{ } \hspace{1cm} \text{ } \hspace{1cm}
\hspace{1cm} \text{ } \hspace{1cm} \text{ } \hspace{1cm}
\hspace{1cm} \text{ } \hspace{1cm} \text{ } \hspace{1cm}
\hspace{1cm} \text{ } \hspace{1cm} \text{ } \hspace{1cm}
\end{array}.$$

This expression is a generalization of that for $\Sigma_{xc}$ in the static case by Sham [PRB 32, 3876 (1985)].
S. The Exchange Correlation Potential

We now take the functional derivative of $A_{xc}$ to get $U_{xc}(1)$. To do so, we first note that

$$\frac{\delta}{\delta g(1,1)} [W-W_A=0] = 0$$  \hspace{1cm} (38)

from Eqs. (33), (25), and (27), for the system $\phi(1,1) = 0$. Then, consider the change $S_{\text{eff}}(1); W-W_A=0$ changes only through the explicit dependence of $g_0(1,1)$ on $S_{\text{eff}}(1)$ (see Eq. (26)), because of the variational principle (38), i.e.,

$$S A_{xc} = -2i [g(1,1) - g_0(1,1)] S_{\text{eff}}(1)$$  \hspace{1cm} (32)

$$= [n(1) - n_0(1)] S_{\text{eff}}(1)$$  \hspace{1cm} (39b)

From the definition of $S_{\text{eff}}(1)$, $n(1) = n_0(1)$, so that $S A_{xc} = 0$.

Using the Dyson equation, $S = g_0 + g_0 S G$ (see Eq. (25)), this stationarity is rewritten in the form

$$g_0(1,2) \Sigma(2,3) g(3,1) = 0$$  \hspace{1cm} (40)

or, decomposing $\Sigma(2,3)$ according to Eq. (27),

$$U_{xc}(2) g_0(1,2) g(3,1) = \Sigma_{xc}(2,3) g(3,1)$$  \hspace{1cm} (41)
(Physical Representation of $\mathcal{V}_{xc}(t)$)

We now define the physical GFs,

$$
G_r(1,1') = -\frac{i}{2} \theta(t-t') \sum \langle \psi_0(1), \psi_{z}(1) \rangle
$$

$$
G_a(1,1') = \frac{i}{2} \theta(t'-t) \sum \langle \psi_0(1), \psi^{\dagger}(1) \rangle
$$

$$
G_c(1,1') = -\frac{i}{2} \sum \langle \psi_0(1), \psi^{\dagger}_{z}(1) \rangle
$$

In particular, the zeroth order GFs are expressed in terms of the Kohn-Sham states $\psi_i(n,t)$, as

$$
G_{or}(1,1') = -i \theta(t-t') \sum \psi_{z}(1) \psi^{\dagger}_{z}(1')
$$

$$
G_{oa}(1,1') = i \theta(t'-t) \sum \psi_{z}(1) \psi^{\dagger}_{z}(1')
$$

$$
G_{oc}(1,1') = -i \sum \psi_{z}(1) \psi^{\dagger}_{z}(1') (1-2f_{i})
$$

where $f_i$ is the occupation number of $i$th state.

The rewriting of Eq. (41) using these functions is straightforward; the result is

$$
\mathcal{V}_{xc}(1) = -2i \pi \Pi_{T}(1,2) \left[ g_{0}^{T}(2,3) \sum_{xc}^{T} \left( 3,4 \right) g^{c}(4,2) 
+ g_{0}^{c} \sum_{xc}^{c} g^{a} + g_{0}^{c} \sum_{xc}^{a} g^{a} \right]
$$

where

$$
\Pi_{T}(1,2) = -2i \hbar^{-1} \left[ g_{0}^{T}(1,2) g^{c}(2,1) + g_{0}^{c} g^{a} \right]
$$

Note that the causality is automatically guaranteed, i.e., to calculate $\mathcal{V}_{xc}(1)$, we have only to know the KS states $\psi_i(n,t)$ with $t < t'$. 
8. Correlation-function Representations

From Eqs. (14), (29), and (35), we have

\[
\begin{align*}
A_{xc} &= \frac{\hbar}{2} \int_0^1 d\lambda \ U(\lambda, 1, 2) \chi(1, 2) \\
&\quad - \frac{1}{2} \int_0^1 d\lambda \ U(1, 2) \left[ \eta(\lambda, 2, 2) - \eta(1, 1) \right] \\
&\quad - \int_0^1 d\lambda \ \xi(\lambda) \ [\eta(\lambda) - \eta(1)]  \\
&= \frac{\hbar}{2} \int_0^1 d\lambda \ U(\lambda, 1, 2) \chi(1, 2) \\
&\quad - \frac{1}{2} \int_0^1 d\lambda \ U(1, 2) \left[ \eta(\lambda, 2, 2) - \eta(1, 1) \right] \\
&\quad - \int_0^1 d\lambda \ \xi(\lambda) \ [\eta(\lambda) - \eta(1)]  \\
\end{align*}
\]

(50)

Here, \( \chi(1, 2) = \chi^{(2)}(1, 1, 2, 2) \).

Since \( \eta(\lambda) - \eta(1) = 0 \) both for \( \lambda = 0 \) and \( 1 \), the last two terms in Eq. (50) seem unimportant; the most important term for \( \nu_{xc}(1) \) is then, by differentiating Eq. (50) w.r.t. \( \eta(1) \),

\[
\nu_{xc}(1) = \frac{\hbar}{2} \int_0^1 d\lambda \ U(\lambda, 3, 3) \chi^{(3)}(1, 3, 4) \chi^{-1}(4, 1)  \\
\]

(51)

or, by physical representation,

\[
\nu_{xc}(1) = \frac{\hbar}{2} \int_0^1 d\lambda \ U(\lambda, 3, 3) \chi^{(3)}(\lambda, 3, 4) \chi^{-1}(4, 1)  \\
\]

(52)

Equation (52) is an extension of the similar expression by Ng [PRB32, 9947 (1989)] to time-dependent DFT.