Time-dependent Density-functional Theory: Summary S

I. What I learn about TDDFT II. My own calc: How to implement TDKS eq., i.e., how to calc v_{xc} → explicit expression and algorithm for calc v_{xc}. 1989.10.11

I. Fundamentals

(1) Invertibility Theorem

> The mapping $G: \{v(r,t)+c(t)\} \longmapsto n(r,t)$ 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.

①Proof1 [Runge & Gross, PRL 52, 997(1984)]

When $v(r,t)$ can be expanded into a Taylor series at $t=t_0$, RG proved that if $(\partial/\partial t)^k[v(r,t)-v'(r,t)]_{t=t_0} \neq c(t)$ for some k, then $(\partial/\partial t)^{k+2}[n(r,t)-n'(r,t)]_{t=t_0} \neq 0$. Therefore, G is one-to-one.

②Proof2 [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 $\int_{t_0}^{t} dt\,(t-t')[v(r,t')-v'(r,t')] \neq c(t)$ for some t, then $n(r,t)-n'(r,t) \neq 0$ at the time.

(2) Density Functional Theorem [Runge&Gross ('84)]

As a consequence of the invertibility theorem,

> The expectation value of an arbitrary operator is a functional of $n(r,t)$.

☺ The mapping,

$$n(r,t) \xrightarrow[G^{-1}]{} \{v(r,t)+C(t)\} \longmapsto \{\exp[-i\alpha(t)/\hbar]|\Psi(t)\rangle \,|\, \dot{\alpha}(t)=NC(t)\}$$

$$\longmapsto \langle\Psi(t)|\text{arbitrary operator}|\Psi(t)\rangle$$

specifies the expectation value uniquely, where N is the total number of electrons. //

(3) Action Principle [Runge & Gross ('84)]

The action integral

$$A_v[n(r,t)] = \int_{t_0}^{t_1} dt \langle\Psi(t)|i\hbar\partial/\partial t - T - U|\Psi(t)\rangle - \int_{t_0}^{t_1} dt \int d^3r\, n(r,t)\, v(r,t) \qquad (1)$$

is stationary at the exact density, i.e.,

$$\delta A_v / \delta n(r,t) = 0 \quad \text{at} \quad n(r,t) = G\cdot v(r,t) \qquad (2)$$

where T and U are the kinetic and Coulomb-interaction parts of the Hamiltonian.

(4) Time-dependent Kohn-Sham Scheme [Runge & Gross ('84)]

We define the exchange-correlation (XC) action as

$$A_{xc} = -\int_{t_0}^{t_1} dt \langle\Psi(t)|i\hbar\partial/\partial t - T - U|\Psi(t)\rangle + \int_{t_0}^{t_1} dt \langle\Psi(t)|i\hbar\partial/\partial t - T|\Psi(t)\rangle_{e^2=0}$$
$$- \frac{e^2}{2}\int_{t_0}^{t_1} dt \iint \frac{d^3r\, d^3r'}{|r-r'|}\, n(r_1,t)\, n(r_2,t) \qquad (3)$$

Then the Eular equation (2) for $n(r,t)$ is equivalent to calculating $n(r,t)$ as follows:

$$\begin{cases} [i\hbar\partial/\partial t + \hbar\nabla^2/2m - v(r,t) - \int d^3r' (e^2/|r-r'|)\, n(r',t) - v_{xc}(r,t)]\,\psi_i(r,t) = 0 & (4) \\ n(r,t) = \sum_{i=1}^{N} |\psi_i(r,t)|^2 & (5) \end{cases}$$

where the xc potential $v_{xc}(r,t)$ is given by

$$v_{xc}(r,t) = \delta A_{xc} / \delta n(r,t). \qquad (6)$$

Combination of KS eq. and noneq. GF theory → calc. of any physical quantity.

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) $G(1,1')$, the xc action A_{xc}, and the xc potential $v_{xc}(1)$, 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

$$G_0(1,1') = -i\left[\theta_p(t_1-t_1')\sum_i \psi_i(1)\psi_i^*(1')f_i - \theta_p(t_1'-t_1)\sum_i \psi_i(1)\psi_i^*(1')(1-f_i)\right] \qquad (7)$$

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 $G(1,1')$ and $v_{xc}(1)$. Because of causality, we can calculate $\psi_i(r,t)$, $G(1,1')$, and $v_{xc}(1)$ at each time step only with the knowledge of these functions in previous time steps.

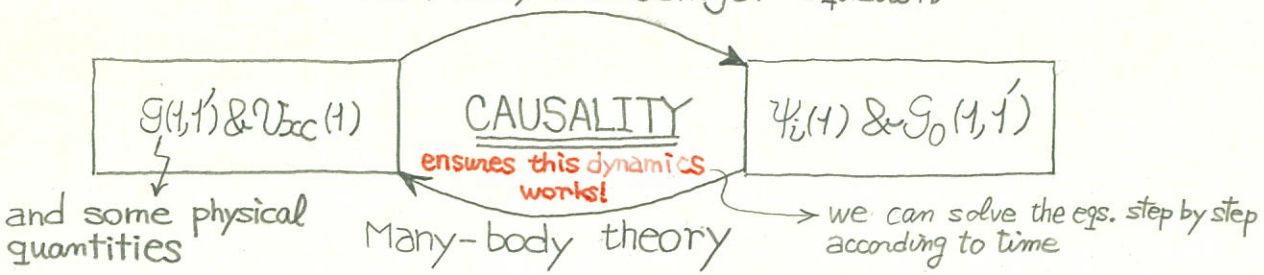
also some other physical quantities if necessary!

(ex) mobility: $j/\mathcal{E}n = e^2\tau/m$

$j(r,t) = \frac{i\hbar}{m}(\nabla_r - \nabla_{r'})G_{+-}(r't;rt)|_{r'=r}$

$G_{+-}(1,1') = \frac{i}{\Omega}\sum_\sigma \langle \psi_\sigma^+(1')\psi_\sigma(1)\rangle$

≪Density-functional Dynamics≫



(1) Self-Energy Formula for $v_{xc}(r;t)$

With the closed-time path expression for the action and the oridinary nonequilibrium GF theory, we can derive the following expression for $v_{xc}(1)$,

$$v_{xc}(1) = -2i\int_p d2\int_p d3\int_p d4\, \pi^{-1}(1,2)\, g_0(2,3)\Sigma_{xc}(3,4)g(4,2) \tag{8a}$$

$$= -2i\pi_r^{-1}[g_0^r\Sigma_{xc}^r g^c + g_0^r\Sigma_{xc}^c g^a + g_0^c\Sigma_{xc}^a g^a] \tag{8b}$$

where p denotes the integration over the closed time path,

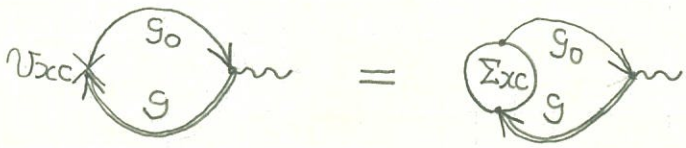
$$g_0^{r\atop a}(1,1') = \mp i\begin{Bmatrix}\theta(t_1-t_1')\\ \theta(t_1'-t_1)\end{Bmatrix}\sum_i \psi_i(1)\psi_i^*(1') \tag{9a}$$

$$g_0^c(1,1') = -i\sum_i \psi_i(1)\psi_i^*(1') \tag{9b}$$

$$\pi_r(1,2) = -2i\hbar^{-1}[g_0^r(1,2)g^c(2,1) + g_0^c(1,2)g^a(2,1)], \tag{10}$$

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

Equation (8b) crearly guarantee the causality; for the calculation of $v_{xc}(1)$, 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 [PRB32, 3876 (1985)]. The formulation of A_{xc} in terms of the Keldysh closed time path has been suggested by Peuckert [J. Phys. C11, 4945 (1978)].

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

① Correlation-function Formula [Ng, PRB31, 9947 (1989), for the static case.]

$$v_{xc}(1) = -\frac{i\hbar}{2}\int_0^1 d\lambda \int d^3r_2 \int d3 \int d4 \frac{e^2}{|r_2 - r_3|} \chi_a^{(3)}(r_2, t_3; r_3, t_3; 4)_\lambda \chi_a^{-1}(4,1) \qquad (11)$$

② Linear Response Scheme [Gross & Kohn, PRL55, 2850 (1985)]

$$v_{xc}(r,\omega) = \int d^3r' f_{xc}^r(r,r';\omega)\, \delta n(r,\omega) \qquad (12)$$

$$\begin{cases} f_{xc}^r(r,r';\omega) = \chi_{or}^{-1}(r,r';\omega) - \chi_r^{-1}(r,r';\omega) - e^2/|r-r'| & (13) \\ \chi_{or}(r,r';\omega) = \sum_{ij} \dfrac{\psi_i^*(r)\psi_j(r)\psi_j^*(r')\psi_i(r')}{\omega - (\epsilon_j - \epsilon_i) + i0}(f_i - f_j) & (14) \end{cases}$$

(Local-density Approximation)

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

where f_{xc}^h 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 Σ_x =  to semiconductors and have solved it approximately. In the same level of approx, DFD will be also feasible.

Time-dependent Density-functional Theory: Fundamentals

1989.10.11

§. System

The Hamiltonian of the system is given by

$$H(t) = T + U + V(t) \tag{1}$$

$$\begin{cases} T = \sum_\sigma \int d^3r\, \psi_\sigma^\dagger(r)\,(-\hbar^2\nabla^2/2m)\,\psi_\sigma(r) & (2) \\ U = \frac{1}{2}\sum_{\sigma\sigma'} \int d^3r \int d^3r'\, \psi_\sigma^\dagger(r)\,\psi_{\sigma'}^\dagger(r')\,u(r-r')\,\psi_{\sigma'}(r')\,\psi_\sigma(r) & (3) \\ V(t) = \int d^3r\, \rho(r)\, v(r,t) & (4) \end{cases}$$

where $\psi_\sigma^\dagger(r)$ and $\psi_\sigma(r)$ are the creation and annihilation operators for an electron with spin σ, $\rho(r) = \sum_\sigma \psi_\sigma^\dagger(r)\psi_\sigma(r)$, $u(r) = e^2/r$, and $v(r,t)$ is an external field.

We define a mapping G such that

$$G:\ v(r,t) \longmapsto n(r,t) = \langle \Psi(t)|\rho(r)|\Psi(t)\rangle \tag{5}$$

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

$$[i\hbar\partial/\partial t - H(t)]\,|\Psi(t)\rangle = 0 \tag{6}$$

with a <u>fixed</u> initial condition,

$$|\Psi(t=t_0)\rangle = |\Psi_0\rangle. \tag{7}$$

§. Invertibility Theorem

The mapping

$$G:\{v(r,t) + c(t)\} \longmapsto n(r,t) \tag{8}$$

is one-to-one, and therefore is invertible. Here, $c(t)$ is a time dependent constant.

(1) Proof 1 [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 $n(r,t) - n'(r,t) \neq 0$.

☺ ① The following relation can be derived

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

☺ First, consider the equation of motion for the current

$$j(r,t) = \langle\Psi(t)|\hat{j}(r)|\Psi(t)\rangle \quad (10)$$

where

$$\hat{j}(r) = \frac{1}{2}\sum_\sigma\left\{\Psi^\dagger_\sigma(r)\frac{\hbar\nabla}{im}\Psi_\sigma(r) - \left[\frac{\hbar\nabla}{im}\Psi^\dagger_\sigma(r)\right]\Psi_\sigma(r)\right\}. \quad (11)$$

The equation for the difference in current is given by

$$\frac{\partial}{\partial t}[j(r,t_0)-j'(r,t_0)] = -\frac{i}{\hbar}\langle\Psi(t_0)|[\hat{j}(r), V(t_0)-V'(t_0)]|\Psi(t_0)\rangle$$

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

because $n(r,t_0) = \langle\Psi_0|\hat{\rho}(r)|\Psi_0\rangle$ is common by assumption. Higher order derivatives are derived as

$$\left(\frac{\partial}{\partial t}\right)^2[j(r,t_0)-j'(r,t_0)] = -\frac{i}{\hbar}\langle\Psi(t_0)|\underbrace{[\hat{\rho}(r), V(t_0)-V'(t_0)]}_{0}|\Psi(t_0)\rangle\frac{\hbar}{im}\nabla\frac{\partial}{\partial t}[v-v']$$

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

and so on. The result is

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

Combining Eq. (12) and the continuity equation,

$$\frac{\partial}{\partial t}n(r,t) = -\nabla\cdot j(r,t), \quad (13)$$

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 $(\partial/\partial t)^{k}[v(r,t)-v'(r,t)] \neq C(t)$.

☺ (reductio ad absurdum)

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

$$0 = \int d^3r\, U(r)\, \nabla\cdot[n(r,t)\nabla U(r)]$$

$$= \frac{1}{2}\oint df\cdot n(r,t)\nabla U^2(r) - \int d^3r\, n(r,t)\,[\nabla U(r)]^2$$

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

③ If $v(r,t)-v'(r,t) \neq C(t)$, there is some k where $(\partial/\partial t)^{k}[v(r,t_0)-v'(r,t_0)] \neq C(t)$. 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 2 [Ng & Singwi, PRL 59, 2627 (1987)]

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,

$$\delta n(r,t) = \int d^3r' \int_{t_0}^{t} dt'\, \chi(r,t;r',t')\, v(r',t') \qquad (14)$$

where

$$\chi(r,t;r',t') = -i\hbar^{-1}\langle[\rho(r,t),\rho(r',t')]\rangle. \qquad (15)$$

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

$$\chi(r,t;r',t') = \sum_{n=1}^{\infty} \frac{(t-t')^n}{n!}\left(-\frac{i}{\hbar}\right)^{n+1}\langle[[\cdots[\rho(r),H],\cdots;H],\rho(r')]\rangle_t \qquad (16)$$

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

$$\chi(r,t;r',t') = \frac{i}{\hbar}(t-t')\nabla_r \cdot \langle [j(r), \rho(r')] \rangle_{t'}$$

$$= -\frac{t-t'}{2m}\nabla_r \cdot \langle \rho(r)\delta(r'-r) + \sum_\sigma [\psi_\sigma^\dagger(r)\psi_\sigma(r') + \psi_\sigma^\dagger(r')\psi_\sigma(r)]\nabla_{r'}\delta(r'-r) \rangle_{t'} \quad (17)$$

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

$$n(r,t) - n'(r,t) = \frac{1}{m}\nabla \cdot \{ n(r) \nabla \int_{t_0}^{t} dt'(t-t')[v(r,t') - v'(r,t')] \} \quad (18)$$

Therefore, unless $\int_{t_0}^{t} dt'(t-t')[v(r,t') - v'(r,t')] = C(t)$ for all small t where this expansion is valid, $n(r,t) - n'(r,t) \neq 0$ for some t. (See, (1) ② for the proof.) $\nabla U(r,t) = \nabla \int_{t_0}^{t} dt'(t-t')[v(r,t') - v'(r,t')]$ cannot be zero at all time t and all space point r. Because if we assume it identically zero, then $\nabla \frac{\partial^2}{\partial t^2} U(r,t) = \nabla[v(r,t) - v'(r,t)] = 0$ for all space-time point; this contradicts the assumption $\nabla[v(r,t) - v'(r,t)] \neq 0$ at some time t.

§. Density Functional

As a consequence of the invertibility,

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

☺ $n(r,t) \xrightarrow[G^{-1}]{} \{v(r,t) + C(t)\}$ 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.,

$$\{v(r,t) + C(t)\} \longmapsto \{\exp[-i\alpha(t)/\hbar]|\Psi(t)\rangle \mid \dot{\alpha}(t) = NC(t)\} \quad (19)$$

This phase factor does not enter the expectation value of any quantity; thus, $n(r,t)$ specifies any expectation value uniquely. //

§. Action Principle

The action integral

$$A_v[n] = \int_{t_0}^{t_1} dt \langle \Psi(t) | i\hbar\partial/\partial t - T - U | \Psi(t) \rangle - \int_{t_0}^{t_1} dt \int d^3r\, n(r,t)\, v(r,t) \tag{20}$$

is stationary at the exact density, i.e.,

$$\frac{\delta A_v}{\delta n(r,t)} = 0 \quad \text{for} \quad n(r,t) = G \cdot v(r,t) \tag{21}$$

(☺ Action integral is stationary at the state satisfies Eq. (6), so that is stationary at the corresponding $n(r,t)$. //)

§. Time-dependent Kohn-Sham Scheme

We define the exchange-correlation (xc) action through the relation,

$$\int_{t_0}^{t_1} dt \langle \Psi(t) | i\hbar\partial/\partial t - T - U | \Psi(t) \rangle = \int_{t_0}^{t_1} dt \langle \Psi(t) | i\hbar\partial/\partial t - T | \Psi(t) \rangle_{e^2=0} - \frac{1}{2} \int_{t_0}^{t_1} dt \int d^3r \int d^3r' u(r-r') n(r,t) n(r',t) - A_{xc} \tag{22}$$

Then, the Eular equation (21) becomes

$$\frac{\delta}{\delta n(r,t)} \int_{t_0}^{t_1} dt \langle \Psi(t) | i\hbar\partial/\partial t - T | \Psi(t) \rangle_{e^2=0} - v_{eff}(r,t) = 0 \tag{23}$$

where

$$v_{eff}(r,t) = v(r,t) + \int d^3r' u(r-r') n(r',t) + v_{xc}(r,t) \tag{24}$$

and the xc potential $v_{xc}(r,t)$ is defined by

$$v_{xc}(r,t) = \delta A_{xc} / \delta n(r,t) \tag{25}$$

Equation (23) is the same equation for determing $n(r,t)$ of a non-interacting system in a field $v_{eff}(r,t)$. Therefore, $n(r,t)$ is given by solving the following equations, supposing that $|\Psi_0\rangle = \prod_{i=1}^{N} a_i^{+} |\text{vacuum}\rangle$:

$$\begin{cases} [i\hbar\partial/\partial t + \hbar^2\nabla^2/2m - v_{eff}(r,t)]\,\psi_i(r,t) = 0 & (26) \\ n(r,t) = \sum_{i=1}^{N} |\psi_i(r,t)|^2 & (27) \end{cases}$$

Exchange-correlation Potential in the Time-dependent Density-functional Theory

1989.10.10

§. Definitions

The Hamiltonian of the system is given by

$$H(t) = T + U + V(t) \tag{1}$$

$$\begin{cases} T = \sum_\sigma \int d^3r\, \psi_\sigma^\dagger(r)\,(-\hbar^2\nabla^2/2m)\,\psi_\sigma(r) & (2) \\ U = \frac{1}{2}\sum_{\sigma\sigma'} \int d^3r \int d^3r'\, \psi_\sigma^\dagger(r)\psi_{\sigma'}^\dagger(r')\,u(r-r')\,\psi_{\sigma'}(r')\psi_\sigma(r) & (3) \\ V(t) = \int d^3r\, \rho(r)\, v(r,t) & (4) \end{cases}$$

where $\psi_\sigma^\dagger(r)$ and $\psi_\sigma(r)$ are the creation and annihilation operators of an electron with spin σ, $\rho(r) = \sum_\sigma \psi_\sigma^\dagger(r)\psi_\sigma(r)$, $u(r) = e^2/r$, and $v(r,t)$ is an external field.

We split the Hamiltonian (1) into two parts,

$$H(t) = [\,T + V_{eff}(t)\,] + [\,U + V(t) - V_{eff}(t)\,] \tag{5a}$$

$$= H_0(t) + H_1(t) \tag{5b}$$

Here,

$$\begin{cases} V_{eff}(t) = \int d^3r\, \rho(r)\, v_{eff}(r,t) & (6) \\ v_{eff}(r,t) = v(r,t) + \int d^3r' u(r',t) n(r',t) + v_{xc}(r,t) & (7) \end{cases}$$

where the exchange-correlation (XC) potential $v_{xc}(r,t)$ is given by

$$v_{xc}(r,t) = \delta A_{xc} / \delta n(r,t) \tag{8}$$

with the XC action A_{xc} defined through the relation

$$A = \int_{t_i}^{t_f} dt \langle \psi(t) | i\hbar\partial/\partial t - H(t) | \psi(t) \rangle \tag{9a}$$

$$= \int_{t_i}^{t_f} dt \langle \psi(t) | i\hbar\partial/\partial t - T | \psi(t) \rangle_{e^2=0} - \int_{t_i}^{t_f} dt \int d^3r\, n(r,t) v(r,t)$$

$$- \frac{1}{2}\int_{t_i}^{t_f} dt \int d^3r_1 \int d^3r_2\, u(r_1-r_2) n(r_1,t) n(r_2,t) - A_{xc}. \tag{9b}$$

$n(r,t) = \langle\psi(t)|\rho(r)|\psi(t)\rangle$ is the density expectation value.

Accordingly, $H_1(t)$ is given by

$$\begin{cases} H_1(t) = U - \int d^3r\, \rho(r)\, w(r,t) & (10) \\ w(r,t) = \int d^3r\, u(r-r')\, n(r',t) + v_{xc}(r,t) & (11) \end{cases}$$

§. Action Integral

To analyze the structure of action, it is convenient to extend the time region $(t_i \to t_f)$ to the Keldysh closed time path $(t_i \to t_f \to t_i)$. [For the closed time path formalism, see for example, Chou et al. Phys. Rep. 118, 1 (1985).] Accordingly, the extended action is given by

$$A = \int_p dt\, \langle\psi(t)|i\hbar\partial/\partial t - H(t)|\psi(t)\rangle \qquad (12)$$

where p denotes the integration over the closed time path.

We here introduce a dimensionless coupling constant λ such that

$$H(t) = H_0(t) + \lambda H_1(t), \qquad (13)$$

then we can show that [Peuckert, J. Phys. C11, 4945 (1978)]

$$A - A_{\lambda=0} = -\int_0^1 d\lambda \int_p dt\, \langle\psi(t)|H_1(t)|\psi(t)\rangle \qquad (14)$$

(Generating Functional)

To proceed further, we introduce the generating functional W as [see for example, Chou et al. ('85)],

$$W = -(\hbar/2)\, \ln Z \qquad (15)$$

$$Z = \mathrm{tr}(S\hat{\rho}) \tag{16}$$

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

$$S = T_P \exp\left[-\frac{i}{\hbar}\sum_\sigma \int_P d1 \int_P d1' \, \psi^\dagger_{H\sigma}(1)\,\phi(1,1')\,\psi_{H\sigma}(1')\right] \tag{17}$$

where $1 = (\vec{r}_1, t_1)$, 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,

$$W - W_{\lambda=0} = \frac{i}{2}\int_0^1 d\lambda \int_P dt \, \langle H_1(t)\rangle_\lambda \tag{18}$$

where the expectation value here is given by

$$\langle \theta(t)\rangle = Z^{-1}\,\mathrm{tr}\{T_P[\theta_H(t) S]\,\hat{\rho}\}, \tag{19}$$

thus coincides the physical expectation value when $\phi(1,1') = 0$.

Comparing Eqs. (14) and (18),

$$A - A_{\lambda=0} = 2i\,(W - W_{\lambda=0}) \tag{20}$$

§. Analysis of the Generating Functional

The single-particle Green's function (GF),

$$G(1,1') = -(i/2)\sum_\sigma \langle T_P[\psi_\sigma(1)\psi^\dagger_\sigma(1')]\rangle \tag{21}$$

is generated from W by the functional derivative,

$$\frac{\delta W}{\delta\phi(1',1)} = G(1,1') \tag{22}$$

The vertex functional Γ is then defined as

$$\Gamma[G] = W[\phi] - \int_P d1 \int_P d1' \, G(1,1')\,\phi(1',1) \tag{23}$$

Then, using Eq. (22),

$$\frac{\delta\Gamma}{\delta G(1,1')} = -\Phi(1',1) \tag{24}$$

(Functional Representation for W)

Using the equation of motion for G, we can derive the Dyson equation,

$$G^{-1}(1,1') = G_0^{-1}(1,1') - \hbar^{-1}\Phi(1,1') - \Sigma(1,1') \tag{25}$$

Here,

$$G_0^{-1}(1,1') = [i\partial/\partial t_1 + \hbar\nabla_1^2/2m - \hbar^{-1}v_{eff}(1)]\,\delta_p(1,1') \tag{26}$$

$$\Sigma(1,1') = \Sigma_{xc}(1,1') - \hbar^{-1}[w(1) - u(1,\bar{2})n(\bar{2})]\,\delta_p(1,1') \tag{27}$$

$$\Sigma_{xc}(1,1') = -2^{-1}u(1,\bar{2})\chi^{(2)}(\bar{3},1;\bar{2}^+,\bar{2})G^{-1}(\bar{3},1') \tag{28}$$

where $\delta_p(1,1') = \delta(r_1 - r_2)\delta_p(t_1 - t_2)$ is the delta function on the closed time path, $u(1,2) = u(r_1 - r_2)\delta_p(t_1 - t_2)$,

$$\chi^{(\nu)}(1,1';\ldots;\nu,\nu') = \frac{\delta^{\nu-1}}{\delta\phi(\nu,\nu')\cdots\delta\phi(2,2')}\sum_\sigma \langle T[\psi_\sigma^+(1)\psi_\sigma(1')]\rangle, \tag{29}$$

and the bars indicate the integration over the indices.

Comparing Eqs. (24) and (25), we get

$$\Gamma = \hbar\,\mathrm{tr}[\ln G - G_0^{-1}G + 1] + \hbar\Xi \tag{30}$$

where $\mathrm{tr}\,a = a(\bar{1},\bar{1}^+)$ and

$$\delta\Xi/\delta G(1',1) = \Sigma(1,1') \tag{31}$$

Using Eqs. (23) and (30),

$$W = \hbar\,\mathrm{tr}[\ln G - \Sigma G] + \hbar\Xi \tag{32}$$

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 $\Phi(1,1') = 0$,

$$W - W_{\lambda=0} = \hbar\,\mathrm{tr}[\ln(G/G_0) - G_0^{-1}G + 1] - \tfrac{1}{2}w(\bar{1})n(\bar{1}) + \tfrac{1}{4}u(\bar{1},\bar{2})n(\bar{1})n(\bar{2}) + \Xi_{xc} \qquad (33)$$

where

$$\delta\Xi_{xc}/\delta G(1',1) = \Sigma_{xc}(1,1'). \qquad (34)$$

8. The Exchange Correlation Action

The xc action

$$A_{xc} = -A + \int_p dt \langle\Psi(t)|i\hbar\partial/\partial t - T|\Psi(t)\rangle_{e^2=0} - n(\bar{1})v(\bar{1}) - \tfrac{1}{2}u(\bar{1},\bar{2})n(\bar{1})n(\bar{2}) \qquad (35)$$

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

$$A_{\lambda=0} = \int_p dt \langle\Psi(t)|i\hbar\partial/\partial t - T|\Psi(t)\rangle_{e^2=0} - n(\bar{1})v_{eff}(\bar{1}) \qquad (36)$$

as

$$A_{xc} = -2i\,\mathrm{tr}[\ln(G/G_0) - G_0^{-1}G + 1] - 2i\Xi_{xc} \qquad (37)$$

Diagrammatically, Ξ_{xc} corresponds to all the closed, connected, skelton graphs, excluding the w-field and Hartree terms, i.e.,

This expression is a generalization of that for E_{xc} in the static case by Sham [PRB 32, 3876 (1985)].

§. The Exchange Correlation Potential

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

$$\frac{\delta}{\delta G(1,1')}\left[W - W_{\lambda=0}\right] = 0 \tag{38}$$

from Eqs. (33), (25), and (27), for the system $\Phi(1,1') = 0$. Then, consider the change $\delta v_{eff}(1)$; $W - W_{\lambda=0}$ changes only through the explicit dependence of $G_0(1,1')$ on $v_{eff}(1)$ (see Eq. (26)), because of the variational principle (38), i.e.,

$$\delta A_{xc} = -2i\left[G(\bar{1},\bar{1}^+) - G_0(\bar{1},\bar{1}^+)\right]\delta v_{eff}(\bar{1}) \tag{39a}$$

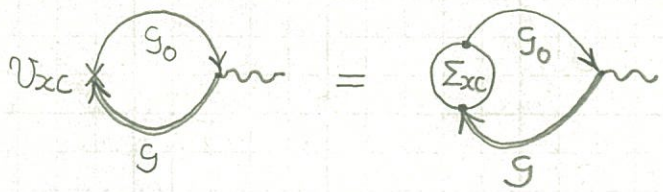
$$= \left[n(\bar{1}) - n_0(\bar{1})\right]\delta v_{eff}(\bar{1}) \tag{39b}$$

From the definition of $v_{eff}(1)$, $n(1) = n_0(1)$, so that $\delta A_{xc} = 0$. Using the Dyson equation, $G = G_0 + G_0 \Sigma G$ (see Eq. (25)), this stationality is rewritten in the form

$$G_0(1,\bar{2})\Sigma(\bar{2},\bar{3})G(\bar{3},1) = 0 \tag{40}$$

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

$$v_{xc}(\bar{2})G_0(1,\bar{2})G(\bar{2},1) = \hbar\, G_0(1,\bar{2})\Sigma_{xc}(\bar{2},\bar{3})G(\bar{3},1) \tag{41}$$



(Physical Representation of $v_{xc}(1)$)

We now define the physical GF's,

$$\begin{cases} G_r(1,1') = -(i/2)\,\theta(t_1-t_{1'})\sum_\sigma \langle\{\psi_\sigma(1),\psi^\dagger_\sigma(1')\}\rangle & (42)\\ G_a(1,1') = (i/2)\,\theta(t_{1'}-t_1)\sum_\sigma \langle\{\psi_\sigma(1),\psi^\dagger_\sigma(1')\}\rangle & (43)\\ G_c(1,1') = -(i/2)\sum_\sigma \langle[\psi_\sigma(1),\psi^\dagger_\sigma(1')]\rangle & (44)\end{cases}$$

In particular, the zeroth order GF's are expressed in terms of the Kohn-Sham states $\varphi_i(r,t)$, as

$$\begin{cases} G_{or}(1,1') = -i\,\theta(t_1-t_{1'})\sum_i \varphi_i(1)\,\varphi_i^*(1') & (45)\\ G_{oa}(1,1') = i\,\theta(t_{1'}-t_1)\sum_i \varphi_i(1)\,\varphi_i^*(1') & (46)\\ G_{oc}(1,1') = -i\sum_i \varphi_i(1)\,\varphi_i^*(1')\,(1-2f_i) & (47)\end{cases}$$

where f_i is the occupation number of ith state.

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

$$v_{xc}(1) = -2i\,\pi_r^{-1}(1,\bar{2})\,[\,G_0^r(\bar{2},\bar{3})\Sigma_{xc}^r(\bar{3},\bar{4})G^c(\bar{4},\bar{2}) + G_0^r\Sigma_{xc}^c G^a + G_0^c\Sigma_{xc}^a G^a\,] \quad (48)$$

where

$$\pi_r(1,2) = -2i\hbar^{-1}\,[\,G_0^r(1,2)G^c(2,1) + G_0^c G^a\,] \quad (49)$$

Note that the causality is automatically guaranteed; i.e., to calculate $v_{xc}(1)$, we have only to know the KS states $\varphi_i(r,t)$ with $t < t_1$.

§. Correlation-function Representations

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

$$A_{xc} = \frac{i\hbar}{2}\int_0^1 d\lambda\, u(\bar{1},\bar{2})\,\chi(\bar{1},\bar{2})_\lambda$$
$$- \frac{1}{2}\int_0^1 d\lambda\, u(\bar{1},\bar{2})\,[n(\bar{1})n(\bar{2}) - n_\lambda(\bar{1})n_\lambda(\bar{2})]$$
$$- \int_0^1 d\lambda\, w(\bar{1})\,[n_\lambda(\bar{1}) - n(\bar{1})] \qquad (50)$$

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

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

$$v_{xc}(1) = \frac{i\hbar}{2}\int_0^1 d\lambda\, u(\bar{2},\bar{3})\,\chi^{(3)}(\bar{2},\bar{3},\bar{4})_\lambda\,\chi^{-1}(\bar{4},1) \qquad (51)$$

or, by physical representation,

$$v_{xc}(1) = \frac{i\hbar}{2}\int_0^1 d\lambda\, u(\bar{r}_2-\bar{r}_3)\,\chi_a^{(3)}(\bar{r}_2,\bar{t}_2;\bar{r}_3,\bar{t}_2;\bar{4})_\lambda\,\chi_a^{-1}(\bar{4},1) \qquad (52)$$

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