Time-dependent Density Functional Theory: Fundamentals

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§. System

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

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

where $\rho(r) = \sum_\sigma \psi_\sigma^\dagger(r)\psi_\sigma(r)$.

We define a map 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

$$[i\hbar\partial/\partial t - H(t)]|\psi(t)\rangle = 0, \quad |\psi(t_0)\rangle = |\psi_0\rangle \tag{6}$$

§. Invertibility Theorem

If $v(r,t) - v'(r,t) \neq C(t)$ and can be expanded into a Taylor series around t_0, then $n(r,t) \neq n'(r,t)$, i.e., the map $\{G \mid v(r,t) + C(t) \longmapsto n(r,t)\}$ is one-to-one and is invertible.

$$\boxed{\mathbf{j}(r) = \frac{1}{2}\sum_{\sigma}\left[\psi^{+}_{\sigma}(r)\frac{\hbar\nabla}{im}\psi_{\sigma}(r) - \left(\frac{\hbar\nabla}{im}\psi^{+}_{\sigma}(r)\right)\psi_{\sigma}(r)\right] \qquad (7)}$$

$$i\hbar\frac{\partial}{\partial t}[\underbrace{j(r,t)-j'(r,t)}_{\Delta j(r,t)}] = \langle\psi(t)|\,[\,j(r),\ \underbrace{H(t)-H'(t)}_{\int d^3x\,\rho(x)\,[\underbrace{v(x,t)-v'(x,t)}_{\Delta v(x,t)}]}\,]\,|\psi(t)\rangle$$

$$[j(r),\Delta H(t)] = \frac{\hbar}{2im}\sum_{\sigma\lambda}\int d^3x\,\Delta v(x,t)\,[\underbrace{\psi^{+}_{\sigma}(r)\nabla_r\psi_{\sigma}(r) - (\nabla_r\psi^{+}_{\sigma}(r))\psi_{\sigma}(r),\ \psi^{+}_{\lambda}(x)\psi_{\lambda}(x)}]$$

$$\psi^{+}_{\sigma}(r)[\underbrace{\nabla_r\delta_{\sigma\lambda}\delta(x-r)}_{-\nabla_x\delta_{\sigma\lambda}\delta(x-r)}]\psi_{\lambda}(x) - \psi^{+}_{\lambda}(x)\delta_{\sigma\lambda}\delta(x-r)\nabla_r\psi_{\sigma}(r)$$

$$-(\nabla_r\psi^{+}_{\sigma}(r))\delta_{\sigma\lambda}\delta(x-r)\psi_{\lambda}(x) + \psi^{+}_{\lambda}(x)[\underbrace{\nabla_r\delta_{\sigma\lambda}\delta(x-r)}_{-\nabla_x\delta_{\sigma\lambda}\delta(x-r)}]\psi_{\sigma}(r)$$

$$= \frac{\hbar}{2im}\sum_{\sigma}\Big\{-\psi^{+}_{\sigma}(r)\int d^3x\,[\nabla_x\delta(x-r)]\,\psi_{\lambda}(x)\Delta v(x,t)$$

$$-\psi^{+}_{\sigma}(r)[\nabla_r\psi_{\sigma}(r)]\,\Delta v(r,t)$$

$$-[\nabla_r\psi^{+}_{\sigma}(r)]\,\psi_{\sigma}(r)\,\Delta v(r,t)$$

$$-\int d^3x\,[\nabla_x\delta(x-r)]\,\psi^{+}_{\lambda}(x)\Delta v(x,t)\cdot\psi_{\sigma}(r)\Big\}$$

$$= \frac{\hbar}{2im}\sum_{\sigma}\Big\{\psi^{+}_{\sigma}(r)\,\nabla[\psi_{\sigma}(r)\Delta v(r,t)] - \psi^{+}_{\sigma}(r)[\nabla\psi_{\sigma}(r)]\Delta v(r,t)$$

$$-[\nabla\psi^{+}_{\sigma}(r)]\psi_{\sigma}(r)\Delta v(r,t) + \nabla[\psi^{+}_{\sigma}(r)\Delta v(r,t)]\psi_{\sigma}(r)\Big\}$$

$$= \frac{\hbar}{2im}\sum_{\sigma}\big(\cancel{\psi^{+}\nabla\psi\Delta v} + \psi^{+}\psi\,\nabla\Delta v - \cancel{\psi^{+}\nabla\psi\Delta v}$$

$$\underbrace{-\cancel{\nabla\psi^{+}\psi\Delta v} + \cancel{\nabla\psi^{+}\psi\Delta v} + \psi^{+}\psi\,\nabla\Delta v}_{2\psi^{+}_{\sigma}(r)\psi_{\sigma}(r)\,\nabla[\Delta v(r,t)]}\big)$$

$$= \frac{\hbar}{im}\,\rho(r)\,\nabla[\Delta v(r,t)]$$

$$\therefore \quad i\hbar\frac{\partial}{\partial t}\Delta j(r,t) = \langle\psi(t)|\,\frac{\hbar}{im}\rho(r)\nabla[\Delta U(r,t)]\,|\psi(t)\rangle \tag{8}$$

$$\left(i\hbar\frac{\partial}{\partial t}\right)^2\Delta j(r,t) = \langle\psi(t)|\,\frac{\hbar}{im}\underbrace{[\rho(r),\Delta H(t)]}_{=0\ (\because\ \Delta H(t)\text{ contains no momentum})}\nabla[\Delta U(r,t)] + \frac{\hbar}{im}\rho(r)\nabla\left[\Delta i\hbar\frac{\partial U}{\partial t}\right]|\psi(t)\rangle$$

$$= \frac{\hbar}{im}\langle\psi(t)|\rho(r)\nabla\left[\Delta i\hbar\frac{\partial U}{\partial t}\right]|\psi(t)\rangle$$

$$\boxed{\therefore \quad \left(i\hbar\frac{\partial}{\partial t}\right)^{k+1}\Delta j(r,t) = \frac{\hbar}{im}n(r,t)\nabla\left(i\hbar\frac{\partial}{\partial t}\right)^k\Delta U(r,t)} \tag{9}$$

$$i\hbar\frac{\partial}{\partial t}\rho(r) = [\rho(r), T] \quad (\because \text{The other terms do not contain momentum})$$

$$= \sum_{\sigma\lambda}\int d^3x\,\underbrace{[\psi^\dagger_\sigma(r)\psi_\sigma(r),\ \psi^\dagger_\lambda(x)\left(-\frac{\hbar^2}{2m}\nabla_x^2\right)\psi_\lambda(x)]}$$

$$\psi^\dagger_\sigma(r)\delta_{\sigma\lambda}\delta(r-x)\left(-\frac{\hbar^2}{2m}\nabla_x^2\right)\psi_\lambda(x) - \psi^\dagger_\lambda(x)\left(-\frac{\hbar^2}{2m}\nabla_x^2\right)\delta_{\sigma\lambda}\delta(x-r)\,\psi_\sigma(r)$$

$$= -\frac{\hbar^2}{2m}\sum_\sigma\left\{\underbrace{\psi^\dagger_\sigma(r)\nabla^2\psi_\sigma(r)} - [\nabla^2\psi^\dagger_\sigma(r)]\psi_\sigma(r)\right\}$$

$$\nabla[\psi^\dagger_\sigma(r)\nabla\psi_\sigma(r)] - \cancel{\nabla\psi^\dagger_\sigma(r)\nabla\psi_\sigma(r)}$$

$$- \nabla[(\nabla\psi^\dagger_\sigma(r))\psi_\sigma(r)] + \cancel{\nabla\psi^\dagger_\sigma(r)\nabla\psi_\sigma(r)}$$

$$\boxed{\begin{aligned}\therefore \quad \frac{\partial}{\partial t}\rho(r) &= -\frac{\hbar}{2im}\nabla\cdot\sum_\sigma[\psi^\dagger_\sigma(r)\nabla\psi_\sigma(r) - (\nabla\psi^\dagger_\sigma(r))\psi_\sigma(r)] \\ &= -\nabla\cdot j(r)\end{aligned}} \tag{10}$$

$\nabla\cdot$ Eq. (9)

$$\left(\frac{\partial}{\partial t}\right)^{k+1} \underbrace{\nabla\cdot j(r,t)}_{-\frac{\partial}{\partial t}\Delta n(r,t)} = \frac{\hbar}{im}\nabla\cdot\left[n(r,t)\nabla\left(\frac{\partial}{\partial t}\right)^{k}\Delta v(r,t)\right]$$

$-\frac{\partial}{\partial t}\Delta n(r,t)$ ∵ continuity equation

$$\boxed{\therefore \left(\frac{\partial}{\partial t}\right)^{k+2}\Delta n(r,t) = \frac{i\hbar}{m}\nabla\cdot\left[n(r,t)\nabla\left(\frac{\partial}{\partial t}\right)^{k}\Delta v(r,t)\right] \qquad (11)}$$

Equation (11) tells that if $(\partial/\partial t)^k[v(r,t)-v'(r,t)] \neq C(t)$, then $(\partial/\partial t)^{k+2}[n(r,t)-n'(r,t)] \neq 0$.

∵ (reductio ad absurdum)

Assume $\nabla\cdot[n(r,t)\nabla u(r)] = 0$ with $u(r) \neq const$; then

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

$$= \oint df\cdot\cancel{(\underbrace{un\nabla u}_{\frac{1}{2}n\nabla u^2})} - \int d^3r\, n\,(\nabla u)^2 \longrightarrow \text{absurdum}$$

if the density falls off rapidly //

§. Action Functional

There exists a maping

$$n(r,t) \longmapsto v(r,t)+C(t) \mapsto e^{i\alpha(t)}|\Psi(t)\rangle \mapsto \langle\Psi(t)|{}^{\forall}\mathcal{O}|\Psi(t)\rangle;$$

thus the expectation value of an arbitrary operator $\mathcal{O}$ is a functional of $n(r,t)$.

∵ The class of potentials $v(r,t)+C(t)$ give the unique expectation value of $\langle\mathcal{O}\rangle$:

$$V'(t) = \int d^3r\,[v(r,t)+C(t)]\,\rho(r) = V(t) + \underbrace{NC(t)}_{C(t)}$$

then $|\Psi'(t)\rangle = e^{-i\alpha(t)/\hbar}|\Psi(t)\rangle$ where $\dot{\alpha}(t) = C(t)$.

$$\left(\begin{aligned} &∵\ i\hbar\,\partial/\partial t\{e^{-i\alpha(t)/\hbar}|\Psi(t)\rangle\} \\ &= [\dot{\alpha}(t)e^{-i\alpha/\hbar} + e^{-i\alpha/\hbar}(i\hbar\partial/\partial t)]|\Psi(t)\rangle \\ &= \underbrace{[H(t)+\dot{\alpha}(t)]}_{H'(t)}\,e^{-i\alpha t/\hbar}|\Psi(t)\rangle \qquad // \end{aligned}\right)$$

Consequently,

$$\langle\Psi'(t)|\mathcal{O}|\Psi'(t)\rangle = \langle\Psi(t)|\cancel{e^{i\alpha t/\hbar}}\mathcal{O}\cancel{e^{-i\alpha t/\hbar}}|\Psi(t)\rangle = \langle\Psi|\mathcal{O}|\Psi\rangle \qquad //$$

In particular,

the action integral

$$A_v[n] \equiv \int_{t_0}^{t_1} dt\,\langle\Psi(t)|i\hbar\partial/\partial t - T - U|\Psi(t)\rangle - \int_{t_0}^{t_1} dt\int d^3r\,n(r,t)\,v(r,t) \qquad (12)$$

is a functional of $n(r,t)$. $A_v[n]$ is stationary at the exact density $n(r,t) = G\,v(r,t)$

$$\frac{\delta A_v}{\delta n(r,t)} = 0 \qquad (13)$$

∵ First,

$$A_v[\psi(t)] = \int_{t_0}^{t_1} dt \, \langle \psi(t) | i\hbar\partial/\partial t - H_v(t) | \psi(t) \rangle \tag{14}$$

is stationary under variation of $|\psi(t)\rangle$ at the exact point.

∵

$$\delta A = \int dt \quad \delta\langle\psi(t)| \underbrace{i\hbar\partial/\partial t - H(t)|\psi(t)\rangle}_{0} + \underbrace{\langle\psi(t)| i\hbar\partial/\partial t - H(t) | \delta\psi(t)\rangle}_{\{-i\hbar\partial/\partial t \underbrace{\langle\psi(t)| - \langle\psi(t)|H(t)}_{\{[i\hbar\partial/\partial t - H(t)]|\psi(t)\rangle\}^{\dagger} = 0} \} |\delta\psi(t)\rangle}$$

$$= 0 \quad //$$

$A_v[n+\delta n]$ corresponding to $A_v[\psi+\delta\psi]$ is thus stationary. //

§. Time-dependent Kohn-Sham Scheme

We define $A_{xc}[n]$ through

$$A[n] \equiv \langle \Psi(t) | i\hbar\partial/\partial t - H(t) | \Psi(t) \rangle \tag{14}$$

$$= T_s[n] - \int d^3r\, n(r,t) v(r,t) - \frac{1}{2}\int d^3r \int d^3r'\, U(r-r') n(r,t) n(r',t) - A_{xc}[n] \tag{15}$$

where

$$T_s[n] = \langle \Psi(t) | i\hbar\partial/\partial t - T | \Psi(t) \rangle \text{ in a system } U=0 \tag{16}$$

and

$v(r,t)$ in Eq. (15) is $G^{-1} n(r,t)$ not independent of $n(r,t)$ (17)

Then,

$$A_v[n] = T_s[n] - \int d^3r\, n(r,t) v(r,t) - \frac{1}{2}\int d^3r \int d^3r'\, U(r-r') n(r,t) n(r',t) - A_{xc}[n] \tag{18}$$

$v(r,t)$ here is independent of $v(r,t)$.

Thus, the Eular equation

$$\frac{\delta A_v}{\delta n} = \frac{\delta T_s}{\delta n} - v(r,t) - \int d^3r'\, U(r-r') n(r',t) - \frac{\delta A_{xc}}{\delta n(r,t)} \tag{19}$$

states that the true density is obtained by solving the free Fermion problem in the effective potential $\delta A_{xc}/\delta n(r,t)$.

Suppose that the initial state is given by

$$|\Psi_0\rangle = \prod_{i=1}^{N} a_i^\dagger |vac\rangle \tag{20}$$

then we can obtain the true $n(r,t)$ under $v(r,t)$ by solving

$$\begin{cases} [i\hbar\partial/\partial t + \hbar^2\nabla^2/2m - v_{eff}(r,t)]\,\psi_i(r,t) = 0 & (21) \\ n(r,t) = \sum_{i=1}^{N} |\psi_i(r,t)|^2 & (22) \end{cases}$$

where

$$v_{eff}(r,t) = v(r,t) + \int dr'\, u(r-r')\, n(r',t) + v_{xc}(r,t) \tag{23}$$

$$v_{xc}(r,t) = \delta A_{xc} / \delta n(r,t) \tag{24}$$

Invertibility of $G: \{v(r,t) + C(t)\} \mapsto n(r,t)$: Ng & Singwi Version

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We start at time t_0 with the initial state $|\Psi_0\rangle$. For small time $t-t_0$, the induced density $n(r,t)$ is small, thus can be treated in the linear response scheme.

$$n(r,t) = \int d^3r' \int_{t_0}^{t} dt' \, \chi(r,t;r',t') \, v(r',t') \tag{1}$$

where

$$\chi(r,t;r',t') = -i\hbar^{-1} \langle [\rho(r,t), \rho(r',t')] \rangle \tag{2}$$

(Short-time Expansion)

For small time, we can use the short-time expansion of χ,

$$\chi(r,t;r',t') = -i\hbar^{-1} \sum_{n=1}^{\infty} \frac{(t-t')^n}{n!} \langle [\rho^{(n)}(r,t'), \rho(r',t')] \rangle \tag{3a}$$

$$= \sum_{n=1}^{\infty} \frac{(t-t')^n}{n!} \left(-\frac{i}{\hbar}\right)^{n+1} \langle [[\cdots[\rho(r), H], \cdots H], \rho(r')] \rangle_{t'} \tag{3b}$$

Noting that

$$\frac{\partial}{\partial t} \rho(r) = -\nabla \cdot j(r) \tag{4}$$

with

$$j(r) = \frac{1}{2} \sum_{\sigma} \left[\psi_\sigma^\dagger(r) \frac{\hbar\nabla}{im} \psi_\sigma(r) - \left(\frac{\hbar\nabla}{im} \psi_\sigma^\dagger(r)\right) \psi_\sigma(r) \right], \tag{5}$$

the first term of the expansion is given by

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

$$[j(r),\rho(r')] = \frac{\hbar}{2im}\underbrace{\sum_{\sigma\lambda}[\psi_\sigma^+(r)\nabla_r\psi_\sigma(r) - (\nabla_r\psi_\sigma^+(r))\psi_\sigma(r), \psi_\lambda^+(r')\psi_\lambda(r')]}$$

$$- \psi_\sigma^+(r')\delta(r'-r)\nabla_r\psi_\sigma(r) + \psi_\sigma^+(r)[\underbrace{\nabla_r\delta(r'-r)}_{-\nabla_{r'}\delta(r'-r)}]\psi_\sigma(r')$$

$$+ \psi_\sigma^+(r')[\underbrace{\nabla_r\delta(r'-r)}_{-\nabla_{r'}\delta(r'-r)}]\psi_\sigma(r) - (\nabla_r\psi_\sigma^+(r))\delta(r'-r)\psi_\sigma(r')$$

$$\therefore \chi(r,t;r',t') = -\frac{t-t'}{2m}\nabla_r\cdot\sum_\sigma\Big\langle\Big\{[\psi_\sigma^+(r)\nabla_r\psi_\sigma(r) + (\nabla_r\psi_\sigma^+(r))\psi_\sigma(r)]\delta(r'-r)$$
$$+ [\psi_\sigma^+(r)\psi_\sigma(r') + \psi_\sigma^+(r')\psi_\sigma(r)]\nabla_{r'}\delta(r'-r)\Big\}\Big\rangle_{t'} \quad (6)$$

Substituting Eq. (6) in Eq. (1),

$$n(r,t) = -\frac{1}{2m}\nabla_r\cdot\int_{t_0}^{t}dt'(t-t')\Big\{[\nabla_r n(r,t')]v(r,t')$$

$$+ \underbrace{\sum_\sigma\int d^3r'\langle\psi_\sigma^+(r)\psi_\sigma(r')v(r',t') + \psi_\sigma^+(r')\psi_\sigma(r)v(r',t')\rangle_{t'}\nabla_{r'}\delta(r'-r)}$$

$$- \sum_\sigma\langle\psi_\sigma^+(r)\nabla_r\psi_\sigma(r)v(r,t')\rangle_{t'} - \sum_\sigma\langle[\nabla_r\psi_\sigma^+(r)v(r,t')]\psi_\sigma(r)\rangle_{t'}$$

$$= -\frac{1}{2m}\nabla_r\cdot\int_{t_0}^{t}dt'(t-t')\sum_\sigma\langle \cancel{\psi^+\nabla\psi v} + \cancel{\nabla\psi^+\psi v} - \cancel{\psi^+\nabla\psi v} - \psi^+\psi\nabla v$$
$$- \cancel{\nabla\psi^+\psi v} - \psi^+\psi\nabla v\rangle$$

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

eq. val.

$$\boxed{\therefore\ n(r,t) - n'(r,t) = \frac{1}{m}\nabla\cdot\Big\{n(r)\nabla\int_{t_0}^{t}dt'(t-t')[v(r,t') - v'(r,t')]\Big\} \quad (7)}$$

If

$$\int_{t_0}^{t} dt'(t-t')\,[v(r,t')-v'(r,t')] \neq C(t) \tag{8}$$

for some t, then $n(r,t)-n'(r,t) \neq 0$

☺ (reductio ad absurdum)

Assume $0 = \nabla\cdot[n(r)\nabla u(r,t)]$, then

$$0 = \int d^3r\, u(r,t)\,\underbrace{\nabla\cdot[n(r)\nabla u(r,t)]}_{\nabla\cdot[n(r)u(r,t)\nabla u(r,t)] - n(r)|\nabla u(r,t)|^2}$$

$$= \underbrace{\frac{1}{2}\oint df\cdot n(r)\nabla u^2(r,t)}_{\to 0} - \int d^3r\, n(r)\,|\nabla u(r,t)|^2 \to \text{nonsence} \; //$$

Addendum for I

In the proof by Ng and Singwi, after Eq. (8) of P.3, we need to prove another statement:

> If $v(r,t') - v'(r,t') \neq C(t')$ at <u>some</u> time $t' < t$, then
>
> $$\nabla U(r,t') = \int_{t_0}^{t'} dt''(t'-t'')\, \nabla[v(r,t'') - v'(r,t'')] \qquad \text{(A1)}$$
>
> cannot be idencitally zero at <u>all</u> times t' and <u>all</u> space point r.

☺ (reductio ad absurdum)

$$\begin{cases} \dfrac{\partial}{\partial t'}\nabla U(r,t') = \cancel{t'\nabla[v(r,t') - v'(r,t')]} + \displaystyle\int_{t_0}^{t'} dt'' \nabla[v(r,t'') - v'(r,t'')] - \cancel{t'\nabla[v(r,t') - v'(r,t')]} \\[2ex] \dfrac{\partial^2}{\partial t'^2}\nabla U(r,t') = \nabla[v(r,t') - v'(r,t')] \end{cases}$$

Suppose $\nabla U(r,t') = 0$ at all times t' and all space point r, then $(\partial/\partial t')^2 \nabla U(r,t') = 0$, too. It contradicsts the assumption that $\nabla[v(r,t') - v'(r,t')] \neq 0$ at some time $t' < t$. //

8. Current Operator

$[a, bc]$
$= abc + bac - bac - bca$
$= \{a, b\}c - b\{a, c\}$

$$i\hbar \frac{\partial \rho}{\partial t} = [\rho, T + \cancel{V}]$$

$$= \sum_{\sigma\lambda} \int d^3x \, \underbrace{[\psi_\sigma^+(r)\psi_\sigma(r), \psi_\lambda^+(x)\left(-\frac{\hbar^2}{2m}\nabla_x^2\right)\psi_\lambda(x)]}$$

$$[\psi_\sigma^+(r), \psi_\lambda^+(x)\left(-\frac{\hbar^2}{2m}\nabla_x^2\right)\psi_\lambda(x)]\psi_\sigma(r) + \psi_\sigma^+(r)[\psi_\sigma(r), \psi_\lambda^+(x)\left(-\frac{\hbar^2}{2m}\nabla_x^2\right)\psi_\lambda(x)]$$

$$= -\psi_\lambda^+(x)\left(-\frac{\hbar^2}{2m}\nabla_x^2\right)\delta_{\sigma\lambda}\delta(x-r)\psi_\sigma(r) + \psi_\sigma^+(r)\delta_{\sigma\lambda}\delta(x-r)\left(-\frac{\hbar^2}{2m}\nabla_x^2\right)\psi_\lambda(x)$$

$$= \left\{\psi_\sigma^+(r)\left(-\frac{\hbar^2}{2m}\nabla_x^2\psi_\lambda(x)\right) - \left(-\frac{\hbar^2}{2m}\nabla_x^2\psi_\lambda^+(x)\right)\psi_\sigma(r)\right\}\delta_{\sigma\lambda}\delta(x-r)$$

$$= -\frac{\hbar^2}{2m}\underbrace{[\psi_\sigma^+(r)\nabla^2\psi_\sigma(r) - (\nabla^2\psi_\sigma^+(r))\psi_\sigma(r)]}_{\nabla\cdot(\psi^+\nabla\psi) - \cancel{\nabla\psi^+\cdot\nabla\psi} - \nabla\cdot(\nabla\psi^+\psi) + \cancel{\nabla\psi^+\cdot\nabla\psi}}$$

$$= -\frac{\hbar^2}{2m}\nabla\cdot[\psi^+\nabla\psi - (\nabla\psi^+)\psi]$$

$$\boxed{\begin{aligned} \frac{\partial \rho}{\partial t} &= -\nabla\cdot j(r) && (a1) \\ j(r) &= \frac{\hbar}{2mi}\left\{\psi_\sigma^+(r)\nabla\psi_\sigma(r) - [\nabla\psi_\sigma^+(r)]\psi_\sigma(r)\right\} && (a2) \end{aligned}}$$