Supplementary Materials: Electron Correlations in Local Effective Potential Theory

Viraht Sahni, Xiao-Yin Pan and Tao Yang

1. Supplementary Material: Derivation of the General “Quantal Newtonian” Second Law

We provide here the derivation of the “Quantal Newtonian” second law of Equation (16) corresponding to the time-dependent Schrödinger equation of Equation (15). We rewrite the Hamiltonian as

\[ \hat{H}(t) = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{ij} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \left[ v(y_i) - \Phi(y_i) \right] + \sum_i \tilde{\omega} \left[ y_i; \mathbf{A}(y_i) \right], \]  

(S1)

where

\[ \tilde{\omega} \left[ y; \mathbf{A}(y) \right] = \frac{1}{2} A^2(y) - i\tilde{\Omega}(y), \]  

(S2)

\[ \tilde{\Omega}(y) = \frac{1}{2} \left[ \nabla \cdot \mathbf{A}(y) + 2\mathbf{A}(y) \cdot \nabla \right], \]  

(S3)

with \( y = r/t; y_i = r_i/t \). In general, the wave function may be written as \( \Psi(Xt) = \Psi^R(Xt) + i\Psi^I(Xt) \), where \( \Psi^R(Xt) \equiv \Psi^R(t) \) and \( \Psi^I(Xt) \equiv \Psi^I(t) \) are its real and imaginary parts. On substituting the wave function into the Schrödinger equation of Equation (15), we have

\[ \frac{i}{\hbar} \frac{\partial \Psi^R(t)}{\partial t} - \frac{\partial \Psi^I(t)}{\partial t} = \left\{ -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i \left[ v(y_i) - \Phi(y_i) \right] \right\} \Psi^R(t) + i\Psi^I(t). \]  

(S4)

Equating the real parts of Equation (S4) yields

\[ \sum_i \left[ v(y_i) - \Phi(y_i) \right] + \frac{1}{2} \sum_{ij} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_i A^2(y_i) \]

\[ + \frac{1}{\Psi^R(t)} \frac{\partial}{\partial t} \Psi^I(t) = \frac{1}{\Psi^R(t)} \left\{ \frac{1}{2} \sum_i \left[ \nabla_i^2 \Psi^R(t) - \tilde{\Omega} \Psi^I(t) \right] \right\}. \]  

(S5)

On differentiating Equation (S5) with respect to \( r_{1\alpha} \), where \( r_{1\alpha} \) is the \( \alpha \) coordinate of \( r_1 \), and then multiplying both sides by \( [\Psi^R(t)]^2 \), we obtain

\[ \frac{\partial}{\partial r_{1\alpha}} \left[ v(y_i) - \Phi(y_i) \right] + \frac{1}{2} \sum_{ij \neq 1} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} A^2(y_i) \]

\[ + \frac{1}{\Psi^R(t)} \frac{\partial}{\partial t} \Psi^I(t) [\Psi^R(t)]^2 \]

\[ = \frac{1}{2} \sum_i \sum_{\beta} \left[ \Psi^R(t) \frac{\partial^2 \Psi^R(t)}{\partial r_{1\alpha} \partial r_{1\beta}} - \frac{\partial \Psi^R(t)}{\partial r_{1\alpha}} \frac{\partial^2 \Psi^R(t)}{\partial r_{1\beta}} \right] \]

\[ - \sum_i \sum_{\beta} \left[ \Psi^R(t) \frac{\partial}{\partial r_{1\alpha}} (A_{\alpha\beta} \frac{\partial \Psi^I(t)}{\partial r_{1\beta}}) - A_{\alpha\beta} \frac{\partial \Psi^I(t)}{\partial r_{1\beta}} \frac{\partial \Psi^R(t)}{\partial r_{1\alpha}} \right] \]

\[ - \frac{1}{2} \sum_i \sum_{\beta} \left[ \Psi^R(t) \frac{\partial}{\partial r_{1\alpha}} (\Psi^I(t) \frac{\partial A_{\alpha\beta}}{\partial r_{1\beta}}) - \Psi^I(t) \frac{\partial A_{\alpha\beta}}{\partial r_{1\beta}} \frac{\partial \Psi^R(t)}{\partial r_{1\alpha}} \right]. \]  

(S6)
Now since

\[
\frac{1}{4} \frac{\partial^3 \Psi^R(t) \Psi^R(t)}{\partial r_{1\beta} \partial r_{1\beta} \partial r_{1\alpha}} \frac{1}{2} \frac{\partial^2 \Psi^R(t) \partial \Psi^R(t)}{\partial r_{1\alpha}^2} + \frac{\partial \Psi^R(t) \partial^2 \Psi^R(t)}{\partial r_{1\alpha}^2} + \frac{1}{2} \frac{\Psi^R(t) \partial^3 \Psi^R(t)}{\partial r_{1\beta} \partial r_{1\beta} \partial r_{1\alpha}}.
\]  

(S7)

the first term of the right side in Equation (S6) can be written as

\[
\frac{1}{4} \frac{\partial^3 \Psi^R(t) \Psi^R(t)}{\partial r_{1\beta} \partial r_{1\beta} \partial r_{1\alpha}} \frac{1}{2} \frac{\partial^2 \Psi^R(t) \partial \Psi^R(t)}{\partial r_{1\alpha}^2} - \frac{1}{2} \frac{\partial \Psi^R(t) \partial^2 \Psi^R(t)}{\partial r_{1\alpha}^2}.
\]  

(S8)

Thus, Equation (S6) is

\[
\frac{\partial}{\partial r_{1\alpha}} \left[ \nu(y_1) - \Phi(y_1) + \frac{1}{2} A^2(y_1) + \frac{1}{2} \sum_{j=2} \frac{1}{\beta_1 - r_j} \right] \\
+ \frac{1}{\Psi^R(t) \partial t} \Psi^I(t) \]  

\[(\Psi^R(t))^2 = \sum_i \sum_{\beta} \left[ \frac{1}{4} \frac{\partial^3 \Psi^R(t) \Psi^R(t)}{\partial r_{1\alpha}^2} \frac{\partial^2 \Psi^R(t)}{\partial r_{1\alpha}^2} - \frac{\partial \Psi^R(t) \partial \Psi^R(t)}{\partial r_{1\alpha}^2} \right] \\
- \sum_i \sum_{\beta} \left[ \Psi^R(t) \frac{\partial}{\partial r_{1\alpha}} (\Psi^I(t) \frac{\partial \Psi^I(t)}{\partial r_{1\alpha}}) - \Psi^R(t) \frac{\partial \Psi^I(t)}{\partial r_{1\alpha}} \right] \\
- \frac{1}{2} \sum_i \sum_{\beta} \left[ \Psi^I(t) \frac{\partial}{\partial r_{1\alpha}} (\Psi^I(t) \frac{\partial \Psi^I(t)}{\partial r_{1\alpha}}) - \Psi^I(t) \frac{\partial \Psi^I(t)}{\partial r_{1\alpha}} \right].
\]  

(S9)

Similarly we have the following equation for the imaginary part of the wave function \(\Psi^I(t)\):

\[
\frac{\partial}{\partial r_{1\alpha}} \left[ \nu(y_1) - \Phi(y_1) + \frac{1}{2} A^2(y_1) + \frac{1}{2} \sum_{j=2} \frac{1}{\beta_1 - r_j} \right] \\
+ \frac{1}{\Psi^I(t) \partial t} \Psi^R(t) \]  

\[(\Psi^I(t))^2 = \sum_i \sum_{\beta} \left[ \frac{1}{4} \frac{\partial^3 \Psi^I(t) \Psi^I(t)}{\partial r_{1\alpha}^2} \frac{\partial^2 \Psi^I(t)}{\partial r_{1\alpha}^2} - \frac{\partial \Psi^I(t) \partial \Psi^I(t)}{\partial r_{1\alpha}^2} \right] \\
- \sum_i \sum_{\beta} \left[ \Psi^I(t) \frac{\partial}{\partial r_{1\alpha}} (\Psi^R(t) \frac{\partial \Psi^R(t)}{\partial r_{1\alpha}}) - \Psi^R(t) \frac{\partial \Psi^R(t)}{\partial r_{1\alpha}} \right] \\
- \frac{1}{2} \sum_i \sum_{\beta} \left[ \Psi^I(t) \frac{\partial}{\partial r_{1\alpha}} (\Psi^I(t) \frac{\partial \Psi^I(t)}{\partial r_{1\alpha}}) - \Psi^I(t) \frac{\partial \Psi^I(t)}{\partial r_{1\alpha}} \right].
\]  

(S10)

Using the fact that

\[
\frac{\partial}{\partial r_{1\alpha}} \left( \frac{1}{\Psi^R(t) \partial t} \Psi^I(t) \right) [\Psi^R(t)]^2 - \frac{\partial}{\partial r_{1\alpha}} \left( \frac{1}{\Psi^I(t) \partial t} \Psi^R(t) \right) [\Psi^I(t)]^2$

\[= \frac{\partial}{\partial t} \left( \Psi^R(t) \frac{\partial}{\partial r_{1\alpha}} \Psi^R(t) - \Psi^I(t) \frac{\partial}{\partial r_{1\alpha}} \Psi^R(t) \right),
\]  

(S11)
Then on summing Equations (S9) and (S10) and operating by $N \sum_{\alpha} f(X^{N-1})$ on the resulting equation, we have that

$$N \sum_{\alpha} \int dX^{N-1} \left[ \frac{\partial}{\partial r_{1\alpha}} (v(y_1) - \Phi(y_1)) + \frac{1}{2} A^2(y_1) + \sum_{i=2}^{N} \frac{1}{|r_1 - r_i|} \right] |\Psi(t)|^2$$

$$+ N \sum_{\alpha} \int dX^{N-1} \partial_t \left( \Psi^R(t) \frac{\partial}{\partial r_{1\alpha}} \Psi^I(t) - \Psi^I(t) \frac{\partial}{\partial r_{1\alpha}} \Psi^R(t) \right)$$

$$+ N \sum_{\alpha} \int dX^{N-1} \partial_t \left( \Psi^R(t) \frac{\partial}{\partial r_{1\alpha}} \Psi^I(t) - \Psi^I(t) \frac{\partial}{\partial r_{1\alpha}} \Psi^R(t) \right)$$

$$= N \sum_{\alpha} \int dX^{N-1} \left[ \frac{1}{4} \frac{\partial^3 |\Psi(t)|^2}{\partial r_{1\alpha}^3} \right] + \frac{1}{2} \frac{\partial}{\partial r_{1\alpha}} \left( \frac{\partial \Psi^R(t)}{\partial r_{1\beta}} \frac{\partial \Psi^I(t)}{\partial r_{1\alpha}} + \frac{\partial \Psi^I(t)}{\partial r_{1\alpha}} \frac{\partial \Psi^R(t)}{\partial r_{1\beta}} \right)$$

$$+ \Psi^I(t) \frac{\partial}{\partial r_{1\alpha}} \left( A_{1\beta} \frac{\partial \Psi^R(t)}{\partial r_{1\alpha}} \right) - A_{1\beta} \frac{\partial \Psi^I(t)}{\partial r_{1\alpha}} \frac{\partial \Psi^R(t)}{\partial r_{1\beta}}$$

As the wave function and its derivative vanish at infinity, the last term of Equation (S12) vanishes on integration over $dr_{1\beta}$. The second and third terms of Equation (S12) may be rewritten as

$$\sum_{\beta} \left[ - \Psi^R(t) \frac{\partial}{\partial r_{1\alpha}} (A_{1\beta} \frac{\partial \Psi^I(t)}{\partial r_{1\beta}}) + \Psi^I(t) \frac{\partial}{\partial r_{1\alpha}} (A_{1\beta} \frac{\partial \Psi^R(t)}{\partial r_{1\beta}}) \right]$$

$$+ A_{1\beta} \left( \frac{\partial \Psi^R(t)}{\partial r_{1\alpha}} \frac{\partial \Psi^I(t)}{\partial r_{1\beta}} - \frac{\partial \Psi^I(t)}{\partial r_{1\alpha}} \frac{\partial \Psi^R(t)}{\partial r_{1\beta}} \right)$$

Then Equation (S13) can be expressed in terms of the paramagnetic current density $j_y(y)$ as

$$k_y(y, A) = \sum_{\beta} \left[ \{ \nabla_y A_{\beta}(y) \} j_{\beta}(y) + \nabla_\beta \{ A_{\beta}(y) j_y(y) \} \right]$$

(S14)
where
\[
j_p(y) = -\frac{i}{2} \left[ \nabla_{r'} - \nabla_{r''} \right] \gamma(r + r'; r + r'', t) \bigg|_{r' = r'' = 0}, \tag{S15}
\]
and \(\gamma(r'r')\) is the single-particle density matrix.

Finally, to address the first term of Equation (S12), we note that the kinetic "force" \(z(y)\) is defined by its component as
\[
z_a(y) = 2 \sum \frac{\partial}{\partial r_b} t_{a\beta}(y), \tag{S16}
\]
where \(t_{a\beta}(y)\) is the kinetic energy density tensor defined in terms of the single-particle density matrix \(\gamma(r'r')\) as
\[
t_{a\beta}(y) = \frac{1}{4} \left[ \frac{\partial^2}{\partial r_{\alpha}' \partial r_{\beta}''} + \frac{\partial^2}{\partial r_{\beta}' \partial r_{\alpha}''} \right] \gamma(r'r'r'r) \bigg|_{r' = r'' = r}. \tag{S17}
\]

On substituting the complex form of the wave function into the expression for \(\gamma(r'r')\), the tensor may be written as
\[
t_{a\beta}(y) = N^2 \sum \sigma \int dX \frac{1}{N-1} \left[ \frac{\partial}{\partial r_{\alpha}} \Psi^R(r', X^{N-1}t) \frac{\partial}{\partial r_{\beta}} \Psi^R(r', X^{N-1}t) \right.
\]
\[
+ \left. \frac{\partial}{\partial r_{\alpha}} \Psi^I(r', X^{N-1}t) \frac{\partial}{\partial r_{\beta}} \Psi^I(r', X^{N-1}t) \right]. \tag{S18}
\]

Employing Equations (S14)–(S16), we obtain Equation (S12) in terms of the various "forces" to be
\[
\rho(y) \nabla \left[ v(y) + \frac{1}{2} A^2(y) - \Phi(y) \right] - e_{ee}(y) + z(y) + d(y)
+ k(y) \rho A(y) + \frac{\partial}{\partial t} j_p(y) = 0, \tag{S19}
\]
where the "forces" \(e_{ee}(y), d(y)\) are defined in the text.

In terms of the physical current density \(j(y)\) which is
\[
\dot{j}(y) = j_p(y) + \rho(y) A(y), \tag{S20}
\]
the terms \(k_a(y)j_p A\) may be written as
\[
k_a(y)j_p A = k_a(y) j A - \sum_{\beta} \left[ \rho(y) A_{\beta} \nabla_{\alpha} A_{\beta} + A_{\beta} \nabla_{\beta} (\rho(y) A_{\alpha}) \right.
\]
\[
+ \left. \rho(y) A_{\alpha} \nabla_{\beta} A_{\beta} \right]. \tag{S21}
\]

Additionally, since the continuity equation is
\[
\nabla \cdot j(y) + \frac{\partial \rho(y)}{\partial t} = 0, \tag{S22}
\]
we have
\[
\frac{\partial}{\partial t} j_p(y) = \frac{\partial}{\partial t} \left[ j(y) - \rho(y) A(y) \right]
= \frac{\partial}{\partial t} j(y) + A(y) \nabla \cdot j(y) - \rho(y) \frac{\partial A(y)}{\partial t}. \tag{S23}
\]
Employing Equations (S21) and (S23), Equation (S19) is
\[
\rho(y) \left[ \nabla v(y) + E(y) \right] - e_{ee}(y) + z(y) + d(y) + A(y) \nabla \cdot j(y) + k(yA) - \sum_\beta \nabla_\beta \left[ \rho(y)A(\beta)(y)A_\beta(y) \right] = 0, \tag{S24}
\]
with \( E(y) = -\nabla \Phi(y) - \frac{\partial A(y)}{\partial t} \).

The last three terms of Equation (S24) contain the vector potential \( A(r) \) and can be afforded a physical interpretation as the sum of the external Lorentz “force” \( \ell(y) \) and a contribution \( i(y) \) to the internal “force”. The Lorentz “force” is
\[
\ell(y) = j(y) \times B(y), \tag{S25}
\]
so that with \( B(y) = \nabla \times A(y) \), we have
\[
\ell_\alpha(r) = \sum_\beta \left[ j_\beta(y) \nabla_\alpha A_\beta - j_\beta \nabla_\alpha A_\beta \right]. \tag{S26}
\]

The contribution of the magnetic field to the internal “force” \( i(y) \) is defined by its components as
\[
i_\alpha(y) = \sum_\beta \nabla_\beta I_{\alpha\beta}(y), \tag{S27}
\]
where
\[
I_{\alpha\beta}(y) = [j_\alpha(y)A_\beta(y) + j_\beta(y)A_\alpha(y)] - \rho(y)A_\alpha(y)A_\beta(y). \tag{S28}
\]

Hence, the sum
\[
\ell_\alpha(y) + i_\alpha(y) = k_\alpha(yjA) - \sum_\beta \nabla_\beta \left[ \rho(y)A_\alpha(y)A_\beta(y) \right] + \sum_\beta A_\alpha(y) \nabla_\beta j_\beta(y). \tag{S29}
\]

Thus, Equation (S24) may be written as the “Quantal Newtonian” second law of Equations (16)–(19).

For the model noninteracting fermion system in the same external field \( \mathcal{F}^\text{ext}(y) \) and possessing the same basic variables \( \{ \rho(y), j(y) \} \), a similar proof obtained by writing the orbitals as \( \phi_i(y) = \phi_i^R(y) + i\phi_i^I(y) \) then leads to the corresponding ‘Quantal Newtonian’ second law of Equations (22) and (23).