Functional relations for the density functional exchange and correlation functionals connecting functionals at three densities.

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(Dated: 21 September 2011)

It is shown that the DFT exchange and correlation functionals satisfy

\[ 0 = \gamma E_{\text{ex}} [\rho] + 2E_{\text{c}}^0 [\rho] - \gamma E_{\text{ex}} [\rho_{N-1}] - 2E_{\text{c}}^0 [\rho_{N-1}] + 2 \int d^3 r' (\rho_{N-1}'(r) - \rho_{N-1}'(r)) v^0 (|\rho_N| : r) + \int d^3 r' (\rho_{N-1}'(r) - \rho_{N-1}'(r)) r . \nabla v^0 (|\rho_N| : r) + \int d^3 r' \rho_{N-1}(r) r . \nabla \gamma (|\rho_N| : r) - \int d^3 r' \rho_{N-1}'(r) r . \nabla \gamma (|\rho_{N-1}| : r) - \int d^3 r' f^\gamma (r) r . \nabla \gamma_{\text{hxc}} (|\rho_N| : r) - 2 \int d^3 r' f^\gamma (r) \gamma_{\text{hxc}} (|\rho_N| : r) \]

In the derivation of this equation the adiabatic connection formulation is used where the ground state density of an N-electron system, \( \rho_N \), is kept constant independent of the electron-electron coupling strength \( \gamma \). Here \( E_{\text{ex}} [\rho] \) is the Hartree plus exchange energy, \( E_{\text{c}}^0 [\rho] \) is the correlation energy, \( \gamma_{\text{hxc}} [\rho] \) is the Hartree plus exchange-correlation potential, \( \rho_{N-1} \) is the correlation potential and \( v^0 [\rho] \) is the Kohn-Sham potential. The charge densities \( \rho_N \) and \( \rho_{N-1} \) are the N- and (N-1)-electron ground state densities of the same Hamiltonian at electron-electron coupling strength \( \gamma \). \( f^\gamma (r) = \rho_N (r) - \rho_{N-1} (r) \) is the Fukui function. This equation can be useful in testing the internal self-consistency of approximations to the exchange and correlation functionals.

PACS numbers: 31.15.E-,71.15.Mb

Keywords: density functional, Coulomb interaction energy, exchange-correlation

Density Functional Theory (DFT) is one of the most important tools for the calculation of electronic structure and structural properties of molecules and solids. In all practical applications of DFT, however, approximations to the exact functionals have to be used. Exact relations for density functionals and density functional derivatives can play an important role in the development of accurate approximations to the exact functionals. A successful approach to the design of improved approximate density functionals is by “constraint satisfaction”, where the approximate functionals are required to satisfy properties of the exact functionals. The accuracy of approximate functionals can be tested by comparing to accurate calculations or to experimental data. A useful additional test will be to determine the internal self-consistency of approximations. With this in mind, the following expression is derived:

\[ 0 = \gamma E_{\text{ex}} [\rho_N] + 2E_{\text{c}}^0 [\rho_N] - \gamma E_{\text{ex}} [\rho_{N-1}] - 2E_{\text{c}}^0 [\rho_{N-1}] + 2 \int d^3 r' (\rho_{N-1}'(r) - \rho_{N-1}'(r)) v^0 (|\rho_N| : r) + \int d^3 r' (\rho_{N-1}'(r) - \rho_{N-1}'(r)) r . \nabla v^0 (|\rho_N| : r) + \int d^3 r' \rho_{N-1}(r) r . \nabla \gamma (|\rho_N| : r) - \int d^3 r' \rho_{N-1}'(r) r . \nabla \gamma (|\rho_{N-1}| : r) - \int d^3 r' f^\gamma (r) r . \nabla \gamma_{\text{hxc}} (|\rho_N| : r) - 2 \int d^3 r' f^\gamma (r) \gamma_{\text{hxc}} (|\rho_N| : r) \] (1)

In the derivation of this expression the adiabatic connection formulation is used where the ground state density of an N-electron system, \( \rho_N \), is kept constant.

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independent of the electron-electron coupling strength \( \gamma \). In Eq. (1), \( v_{\text{exc}}^{\gamma} [\rho] \) is the Hartree plus exchange-correlation potential, \( v_{\text{c}} [\rho] \) is the correlation potential and \( v^{0} [\rho] \) is the Kohn-Sham potential. \( E_{\text{ee}}^{\gamma} [\rho] \) is the correlation energy while \( E_{\text{ee}} [\rho] \) is the Hartree plus exchange energy. The charge densities \( \rho_N \) and \( \rho_{N-1}^{\gamma} \) are the \( N \)- and \( (N-1) \)-electron ground state densities of the same Hamiltonian at electron-electron coupling strength \( \gamma \) as discussed below. \( f^{\gamma} (r) = \rho_N (r) - \rho_{N-1}^{\gamma} (r) \) is the Fukui function.

Equation (1) couples functionals and functional derivatives evaluated at three different densities and two particle numbers. This equation can be used as a stringent test to check the internal self-consistency of approximations to the exchange and correlation functionals. If exact exchange is used it can serve as a check on approximations to the correlation energy functional.

Evaluation of (1) requires two independent self-consistent Kohn-Sham calculations, one for the \( N \)-electron system to determine \( \rho_N \) and \( \rho_{N-1}^{\gamma} \), and one for the \( (N-1) \)-electron system to determine \( \rho_{N-1}^{\gamma} \). Once the densities are found, the functionals and functional derivatives can be used in Eq. (1) as a test of how well the approximations work.

I. PROOF OF EQUATION (1)

According to the Hohenberg-Kohn theorem1 and its generalization to degenerate states12 the ground state energy \( E^{\gamma} [\rho] \) of a system of interacting electrons is a functional of \( \rho \), the ground state density13,14:

\[
E^{\gamma} [\rho] = T^{\gamma} [\rho] + \gamma V_{\text{ee}}^{\gamma} [\rho] + \int d^3 \rho (r) \nu^{\gamma} ([\rho]; r) \tag{2}
\]

where \( T^{\gamma} [\rho] \) is the kinetic energy and \( \gamma V_{\text{ee}}^{\gamma} [\rho] \) the mutual Coulomb interaction energy at density \( \rho \). In order to derive Eq. (1) the adiabatic connection approach will be used13,14 in which the external potential \( v_{\text{ext}}^{\gamma} ([\rho]; r) \) is constructed to keep the ground state density independent of the electron-electron interaction strength, scaled by \( \gamma \), and has the form15,16:

\[
\nu^{\gamma} ([\rho]; r) = (1 - \gamma) v_{\text{ee}} (|\rho|; r) + v_{\text{c}}^{1} ([\rho]; r) - v_{\text{c}}^{2} ([\rho]; r) + v_{\text{ext}} (r). \tag{3}
\]

\( v^{1} ([\rho]; r) = v_{\text{ext}} (r) \) is the external potential at full coupling strength, \( \gamma = 1 \), and \( v^{0} ([\rho]; r) \) is non-interacting Kohn-Sham potential. The exchange plus Hartree potential13,14,16 \( v_{\text{exc}} (|\rho|; r) \), is independent of \( \gamma \), while the correlation potential \( v_{\text{c}}^{\gamma} ([\rho]; r) \) depends in the scaling parameter \( \gamma \). The adiabatically scaled \( N \)-electron Hamiltonian \( \hat{H}^{\gamma} \) has the form13,14:

\[
\hat{H}^{\gamma} = \hat{T} + \gamma \hat{V}_{\text{ee}} + \nu^{\gamma} [\rho]. \tag{4}
\]

Atomic units, \( \hbar = e = m = 1 \) are used throughout. \( \hat{T} \) is the kinetic energy operator,

\[
\hat{T} = \frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^2, \tag{5}
\]

and \( \gamma \hat{V}_{\text{ee}} \) is a scaled electron-electron interaction,

\[
\gamma \hat{V}_{\text{ee}} = \gamma \sum_{i<j} \frac{1}{r_{i} - r_{j}}. \tag{6}
\]

Define the energy functional13,14:

\[
F^{\gamma} [\rho] = T^{\gamma} [\rho] + \gamma V_{\text{ee}}^{\gamma} [\rho] = T^{0} [\rho] + \gamma E_{\text{ee}} [\rho] + E_{\text{c}}^{\gamma} [\rho] \tag{8}
\]

where \( E_{\text{ee}} [\rho] \) is the Hartree plus exchange energy, and \( E_{\text{c}}^{\gamma} [\rho] \) is the correlation energy. Note that \( E_{\text{ee}} [\rho] \) is independent of \( \gamma \). As shown in appendix A

\[
\mu = \nu^{\gamma} (r) + \frac{1}{2} \nabla \nu^{\gamma} (r) + \frac{1}{2} (v_{\text{exc}}^{\gamma} (r) - t_{c}^{\gamma} (r)) - \frac{1}{2} \int d^3 r' \rho (r') \nabla' \frac{\delta^2 F^{\gamma} [\rho]}{\delta \rho (r') \delta \rho (r)}, \tag{9}
\]

where \( t_{c}^{\gamma} ([\rho]; r) = \frac{\delta T^{\gamma} [\rho]}{\delta \rho (r)} \) with \( T^{\gamma} [\rho] \) the correlation part of the kinetic energy and \( v_{\text{exc}}^{\gamma} (r) = \gamma v_{\text{ee}} (r) + v_{\text{c}}^{\gamma} (r) \). For notational convenience the functional dependence on \( \rho \) has been suppressed. The chemical potential \( \mu \) depends on the asymptotic decay of the charge density17,18, and hence, since the charge density \( \rho \) is independent of \( \gamma \) by construction, \( \mu \) is independent of \( \gamma \).

The Fukui function19,20:

\[
f^{\gamma} (r) = \frac{\delta \mu}{\delta \nu^{\gamma} (r)} \bigg|_{N} = \frac{\delta \mu (r)}{\delta N} \bigg|_{v^{\gamma}}. \tag{10}
\]

satisfies

\[
\int d^3 r' \frac{\delta^2 F^{\gamma} [\rho]}{\delta \rho (r') \delta \rho (r')} f^{\gamma} (r') = \frac{\delta \mu}{\delta N} \bigg|_{v^{\gamma}} \tag{11}
\]

and

\[
\int d^3 r' f^{\gamma} (r') = 1. \tag{12}
\]

Since

\[
\int d^3 r' (3 \rho (r') + r'' \cdot \nabla \rho (r')) = 0, \tag{13}
\]

it follows from (9), (11) and (12) that

\[
\mu = \int d^3 r' f^{\gamma} (r) \nu^{\gamma} (r) + \frac{1}{2} \int d^3 r' f^{\gamma} (r) r . \nabla \nu^{\gamma} (r) + \frac{1}{2} \int d^3 r' f^{\gamma} (r) (v_{\text{exc}}^{\gamma} (r) - t_{c}^{\gamma} (r)). \tag{14}
\]
Using (3), this equation can be reduced to
\[
\int d^3r' f^\gamma (r) \left[ 2v^0 (r) + r \cdot \nabla v^0 (r) \right] - 2\mu
\]
\[
= \int d^3r' f^\gamma (r) \, r \cdot \nabla \rho_{hxc} (r)
\]
\[
+ \int d^3r' f^\gamma (r) \left[ v_{hxc}^\gamma (r) + t_c^\gamma (r) \right].
\] (15)
From the virial theorem for the Kohn-Sham independent particle wavefunctions\textsuperscript{21}
\[
\int d^3r' \left[ \rho_N (r) - \rho_{N-1}^\gamma (r) \right] \left[ 2v^0 (r) + r \cdot \nabla v^0 (r) \right]
\]
\[
= 2 \left( E^0 [\rho] - E^0 [\rho_{N-1}^\gamma] \right),
\] (16)
where \( E^0 [\rho] \) and \( E^0 [\rho_{N-1}^\gamma] \) are the Kohn-Sham ground state energies of the independent \( N \)- and \((N-1)\)-particle systems of the same Kohn-Sham Hamiltonian with potential \( v^0 \). By definition, since \( \mu \) is independent of \( \gamma \),
\[
\mu = E^\gamma [\rho_N] - E^\gamma [\rho_{N-1}^\gamma]
\] (17)
where \( E^\gamma [\rho_N] \) and \( E^\gamma [\rho_{N-1}^\gamma] \) are the ground state energies of the \( N \)- and \((N-1)\)-particle systems of the same Hamiltonian \( H^\gamma \). Eq. (11), with \( \rho_N \) and \( \rho_{N-1}^\gamma \) the corresponding ground state densities. By construction \( \rho_{N-1}^\gamma = \rho_N \) is independent of \( \gamma \) but \( \rho_{N-1}^\gamma \) is expected to be a function of \( \gamma \).

Since the Fukui function\textsuperscript{22,23}
\[
f^\gamma (r) = \left. \frac{\delta \rho (r)}{\delta N} \right|_{\gamma^0}
\]
\[
= \rho_N (r) - \rho_{N-1}^\gamma (r)
\] (18)
is the difference between the ground state densities of the \( N \)-particle and \((N-1)\)-particle systems, it follows from \textsuperscript{13,14,25} that
\[
2 \int d^3r' \left( \rho_{N-1}^\gamma (r) - \rho_{N-1}^\gamma (r) \right) v^0 (r) +
\]
\[
+ \int d^3r' \left( \rho_{N-1}^\gamma (r) - \rho_{N-1}^\gamma (r) \right) r \cdot \nabla v^0 (r)
\]
\[
= \int d^3r' f^\gamma (r) \, r \cdot \nabla \rho_{hxc} (r)
\]
\[
+ \int d^3r' f^\gamma (r) \left[ v_{hxc}^\gamma (r) + t_c^\gamma (r) \right].
\] (19)
The reference to the correlation part of the kinetic energy can be eliminated as follows. Since\textsuperscript{15}
\[
\gamma V_{ee}^\gamma [\rho] = \gamma E_{hxc} [\rho] + E_c^\gamma [\rho] - T_c^\gamma [\rho],
\] (20)
the last line in (19) can be written as
\[
\int d^3r' f^\gamma (r) \left[ v_{hxc}^\gamma (r) + t_c^\gamma (r) \right]
\]
\[
= -\gamma \int d^3r' f^\gamma (r) \left. \frac{\delta V_{ee}^\gamma [\rho]}{\delta \rho (r)} \right|_{\gamma^0}
\]
\[
+ 2 \int d^3r' f^\gamma (r) \, v_{hxc}^\gamma (r)
\] (21)
As shown in appendix\textsuperscript{24,25}
\[
\int d^3r' f^\gamma (r) \left. \delta V_{ee}^\gamma [\rho_N] \right|_{\gamma^0} = V_{ee}^\gamma [\rho_N] - V_{ee}^\gamma [\rho_{N-1}^\gamma].
\] (22)
Since\textsuperscript{15}
\[
E_c^\gamma [\rho] + T_c^\gamma [\rho] = - \int d^3r' \rho (r) \cdot \nabla \left[ v_c^\gamma ([\rho] ; r) \right],
\] (23)
it follows from (20), (21), (22) and (23) that
\[
\int d^3r' f^\gamma (r) \left[ v_{hxc}^\gamma (r) + t_c^\gamma (r) \right]
\]
\[
+ \int d^3r' \rho_N (r) \, r \cdot \nabla v_c^\gamma ([\rho_N] ; r)
\]
\[
- \int d^3r' \rho_{N-1}^\gamma (r) \, r \cdot \nabla v_c^\gamma ([\rho_{N-1}^\gamma] ; r)
\]
\[
= \gamma E_{hxc} [\rho_{N-1}^\gamma] + 2 E_c^\gamma [\rho_{N-1}^\gamma]
\]
\[
- \gamma E_{hxc} [\rho_N] - 2 E_c^\gamma [\rho_N]
\]
\[
+ 2 \int d^3r' f^\gamma (r) \, v_{hxc}^\gamma (r).
\] (24)
Combining (19) and (24) leads to Equation (1).

This equation is now entirely in terms of the exchange and correlation energy and potentials and other known density dependent quantities.

II. DISCUSSION AND SUMMARY

Equation (1) is valid for pure state DFT\textsuperscript{13,14} since equations (10) and (22) have been shown to be correct for pure states. Throughout it was assumed that the functionals derivatives are well defined\textsuperscript{13,14,25}.

Note that \( \rho_{N-1}^\gamma \neq \rho_{N-1}^0 \). In order to determine \( \rho_{N-1}^\gamma \) a Kohn-Sham calculation with\textsuperscript{26}
\[
v^0 [\rho_{N-1}^\gamma] = v^\gamma [\rho_N] + \gamma v_{hxc} [\rho_{N-1}^\gamma] + v_c^\gamma [\rho_{N-1}^\gamma]
\]
has to be performed. Note that \( v^\gamma [\rho_{N-1}^\gamma] = v^\gamma [\rho_N] \).

In summary, an equation that couples exchange and correlation functionals and functional derivatives evaluated at three different densities and for two particle numbers has been derived. This equation can be used as a stringent test to check the internal self-consistency of approximations to the exchange and correlation functionals.

ACKNOWLEDGEMENTS

The author acknowledges support from the National Research Foundation (NRF).
Let \( \rho_\lambda (r) = \lambda^3 \rho (\lambda r) \), the uniformly scaled density. Then (see for example Eq.(A.33) in Appendix A of reference\(^{12}\))

\[
\frac{d}{d\lambda} \frac{\delta F^\gamma }{\delta \rho_\lambda (r)} \bigg|_{\rho_\lambda, \lambda=1} = \int d^3 r' \left( 3 \rho (r') + r' \cdot \nabla \rho (r') \right) \frac{\delta^2 F^\gamma }{\delta \rho (r') \delta \rho (r)}
\]

\[
= - \int d^3 r' r' \cdot \nabla \frac{\delta^2 F^\gamma }{\delta \rho (r') \delta \rho (r)}.
\]

(A1)

The last line is valid if \( \rho (r') \) vanishes when \( r \rightarrow \infty \) as would be the case for a finite system. Now consider the Schrödinger equation

\[
\left[ -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \gamma \sum_{i<j}^N \frac{1}{r_i-r_j} + \sum_{i=1}^N \lambda^2 v^\gamma_r (|\rho|; r_i) \right] \Psi^\gamma_r (\{r_i\}) = E^\gamma_r \left( v^\gamma_r (|\rho|) \right) \Psi^\gamma_r (\{r_i\})
\]

(A2)

from which it follows that

\[
\left[ -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \gamma \sum_{i<j}^N \frac{1}{r_i-r_j} + \sum_{i=1}^N \lambda^2 v^\gamma_r (|\rho|; r_i) \right] \Psi^\gamma_r (\{\lambda r_i\})
\]

\[
= \lambda^2 E^\gamma_r \left( v^\gamma_r (|\rho|) \right) \Psi^\gamma_r (\{\lambda r_i\})
\]

(A3)

If normalised \( \Psi^\gamma_r (\{r_i\}) \) yields \( \rho (r) \) then normalised \( \Psi^\gamma_r (\{\lambda r_i\}) \) yields \( \lambda^3 \rho (\lambda r) \). The Levy constrained minimization approach\(^{12}\) implies that normalised \( \Psi^\gamma_r (\{r_i\}) \) yields \( \lambda^3 \rho (\lambda r) \) and minimizes \( \left\langle \Psi^\gamma | \hat{T} + \gamma \hat{V}_{ee} \right| \Psi^\gamma \rangle \) \( \rightarrow \lambda^3 \rho (\lambda r) \). Therefore\(^{13,15,27}\)

\[
\frac{\delta E^\gamma_r (|\rho|)}{\delta \rho_\lambda (r)} + \lambda^2 v^\gamma_r (|\rho|; \lambda r) = \mu^\gamma_r
\]

(A4)

and

\[
\frac{d}{d\lambda} v^\gamma_r (|\rho|; r) \bigg|_{\lambda=1} = 2 v^\gamma_r (|\rho|; r) + r \cdot \nabla v^\gamma_r (|\rho|; r)
\]

(A5)

For an \( N \)-electron system,

\[
\mu^\gamma_r (|\rho|) = E^\gamma_r \left( \lambda^2 v^\gamma_r (|\rho|) \right) - E^\gamma_{N-1} \left( \lambda^2 v^\gamma_r (|\rho|) \right)
\]

(A6)

with \( E^\gamma_N \left( \lambda^2 v^\gamma_r (|\rho_N|) \right) \) and \( E^\gamma_{N-1} \left( \lambda^2 v^\gamma_r (|\rho_{N-1}|) \right) \) the groundstate energies of the \( N \)- and \( (N-1) \)-electron systems with the same external potential \( \lambda^2 v^\gamma_r (|\rho|) \). From Eq. (A3) it follows that

\[
\mu^\gamma_r (|\rho|) = E^\gamma_r \left( \lambda^2 v^\gamma_r (|\rho|) \right) - E^\gamma_{N-1} \left( \lambda^2 v^\gamma_r (|\rho|) \right)
\]

\[
= \lambda^2 \left( E^\gamma_N \left( v^\gamma_r (|\rho|) \right) - E^\gamma_{N-1} \left( v^\gamma_r (|\rho|) \right) \right)
\]

(A7)

where the last step follows from the definition of the chemical potential of the \( N \)-electron system. Note that the chemical potential \( \mu \) is independent of \( \gamma \).

The correlation energy \( E^\gamma_c |\rho| \) is defined as\(^{13,15}\)

\[
E^\gamma_c |\rho| = \left\langle \Psi^\gamma_r \left| \hat{T} + \gamma \hat{V}_{ee} \right| \Psi^\gamma_r \right\rangle - \left\langle \Psi^0_r \left| \hat{T} \right| \Psi^0_r \right\rangle,
\]

(A8)

where \( \Psi^\gamma_r \) is the ground state wavefunction of \( H^\gamma \) that yields \( \rho \) and \( \Psi^0_r \) the Kohn-Sham independent \( N \)-electron groundstate wavefunction that yields the same density. The correlation part of the kinetic energy is given by

\[
T^\gamma_c |\rho| = \left\langle \Psi^\gamma_r \left| \hat{T} \right| \Psi^\gamma_r \right\rangle - \left\langle \Psi^0_r \left| \hat{T} \right| \Psi^0_r \right\rangle,
\]

(A9)

and \( \gamma V^\gamma_{ee} |\rho| \)\(^{13,15}\) can be written as

\[
\gamma V^\gamma_{ee} |\rho| = \gamma E_{hh} |\rho| + E^\gamma_c |\rho| - T^\gamma_c |\rho|,
\]

(A10)

where \( E_{hh} |\rho| \) is the sum of the Hartree and exchange energies. Note that \( E_{hh} |\rho| \) is independent of \( \gamma \). It follows from (A8) and (A9) that

\[
t^\gamma_c (r) + \gamma \frac{d}{d\gamma} v^\gamma_c (r) = 0,
\]

(A11)

where \( t^\gamma_c (|\rho|; r) \) and \( v^\gamma_c (|\rho|; r) = \frac{d T^\gamma_c (|\rho|; r)}{d\gamma} \) and \( \gamma \). Combining (9), (A11), (A3), (A5), (A7) and (A11) yields Eq. (9).

Appendix B: Derivation of Eq. (22)

Multiply Eq. (9) by the Fukui function and integrate over \( r \). Use Eq. (11), the fact that

\[
\int d^3 r' \left( 3 \rho (r') + r' \cdot \nabla \rho (r') \right) = 0
\]

(B1)

and Eq. (A11) to arrive at

\[
\int d^3 r' \left[ 2 v^\gamma (|\rho|; r') + r' \cdot \nabla v^\gamma (|\rho|; r') \right] f^\gamma (r') +
\]

\[
\int d^3 r' \left[ \gamma v_{hh} (|\rho|; r') + v^\gamma_c (|\rho|; r') - t^\gamma_c (|\rho|; r') \right] f^\gamma (r')
\]

\[
= 2 \mu.
\]

(B2)
From the definition of $E_c^\gamma [\rho]$ and $E_c^\gamma [\rho]$, Eqs. (A8) and (A9) and the fact that $E_{hx}[\rho] = \langle \Psi_0 | \hat{v}_{ee} | \Psi_0 \rangle$, it follows that

$$E_{hx}[\rho] = \langle \Psi_0 | \hat{v}_{ee} | \Psi_0 \rangle,$$

(B3)

it follows that

$$\gamma \frac{\delta V_{ee}^\gamma [\rho]}{\delta \rho (\mathbf{r})} = \gamma v_{hx} ([\rho] ; \mathbf{r}) + v_{c}^\gamma ([\rho] ; \mathbf{r}) - \xi_c^\gamma ([\rho] ; \mathbf{r}).$$

(B4)

Using the virial theorem15 and $\mu = E^\gamma [\rho_N] - E^\gamma [\rho_{N-1}^\gamma]$, we have

$$\int d^3r' [2v^\gamma ([\rho] ; \mathbf{r}') + \mathbf{r} \cdot \nabla v^\gamma ([\rho] ; \mathbf{r})] f^\gamma (\mathbf{r})$$

$$= 2\mu - \gamma V_{ee}^\gamma [\rho_N] + \gamma V_{ee}^\gamma [\rho_{N-1}^\gamma].$$

(B5)

Combining Eq. (B2), (B4) and (B5) yields Eq. (22). For a detailed discussion see references24.

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