Are the Unconventional Density Variations Really Unconventional?

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ABSTRACT: Based on numerical evidence and theoretical arguments, we demonstrate that the unconventional density variations are not really unconventional and should be included in the density variational domain of any ground-state density. As a result, Lieb’s Theorem 3.10 (Lieb, Int J Quantum Chem 1983, 24, 243) is reconfirmed. More specifically, the energy variation \( \delta E_v \) is of order higher than linear order of the density variation \( \delta n(r) \) about the ground-state density \( n_0(r) \) of a system with a fixed number of electrons in Hilbert space, whereas \( \delta E_v \) is of linear order of \( \delta n(r) \) about the ground-state density of a system with a varied number of electrons in Fock space. The unconventional density variations are not the cause for the linear-order behavior of \( \delta E_v \) in Fock space and the derivative discontinuity of the total energy. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 3199–3216, 2009

Key words: density variation; density functional theory; functional derivative; functional differentiability

1. Background

The unconventional density variation (UDV) was first introduced over 20 years ago [1, 2]. The functional differentiability theorems by Lieb and by Englische and Englische [3] allow such UDV’s from any ground-state (GS) densities in density-functional theory (DFT) [4–9]. (To avoid any interruption of the main text, we have put all technical details regarding the mathematical foundation of DFT in Appendices A–C.)

Normally, a family of density variations (DV’s) about a GS density \( n_0(r) \) of a system with a fixed number of electrons in Hilbert space can be defined as

\[
\delta n(r) = n(r) - n_0(r) = y f(r),
\]

where \( y \) is a small positive DV parameter \( (y \ll 1) \) and \( f(r) \) is continuous and differentiable with a null normalization \( \langle f(r) \rangle = 0 \). Without losing generality, \( y \) will only take very small numerical values \( (y \rightarrow 0^+) \) unless otherwise noted hereafter.

In the entire set of DV’s \( \{\delta n(r)\} \), the UDV’s \( \{\delta n_u(r)\} \) were defined as those DV’s violate the following condition [1]:

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where \( L^2 \) denotes the space of square-integrable functions, and \( M \) is a finite positive number. Hereafter, capital italic Roman characters, such as \( M, P, \) and \( Q \), will be used to denote arbitrary finite positive numbers unless otherwise noted.

It was further argued [1] that energy variations of \( \delta n(r) \) from the GS energy will be of order \( y \), not the conventional \( y^2 \) behavior,

\[
\delta E_v[n_\delta] \propto \delta n \propto \mathcal{O}(y). 
\]

A noninteracting two-electron Hydrogen anion was used as an illustration [1] to confirm the above conclusion and to justify the derivative discontinuity of the total energy [4, 5].

However, it is well known that for a GS density \( n_\delta(r) \), the energy variation of any \( \delta n(r) \) can be written as [3–7]

\[
\delta E_v[n_\delta, \delta n] = E_v[n_\delta + \delta n] - E_v[n_\delta] 
\]

\[
= \left( -\mu \frac{\delta E_v}{\delta n_0(r)} \right) \delta n(r) + \text{h.o.}, 
\]

where “h.o.” denotes higher order term in \( \delta n(r) \). Because of the variational principle in DFT, the functional derivative \( \frac{\delta E_v}{\delta n_0} \) is the chemical potential \( \mu \), a constant [4–7],

\[
\frac{\delta E_v}{\delta n_0(r)} = \mu. 
\]

From Eqs. (1) and (7), we can immediately conclude that on the right-hand side (RHS) of Eq. (6), the first term (linear in \( y \)) is zero and the residual “h.o.” term must be nonlinear (higher than linear) in \( y \):

\[
\delta E_v[n_\delta, \delta n] = y \mu (f(r)) + \text{h.o.} = \mathcal{O}(y^3), 
\]

where \( \mu \) is some positive constant greater than 1. Clearly, Eq. (8) invalidates Eq. (5). If Eq. (5) were correct, one would have instead claimed

\[
\frac{\delta E_v}{\delta n_0(r)} \neq \text{constant}, 
\]

which would have destroyed the variational principle in DFT.

In the following, we will utilize both numerical and theoretical arguments to further show that Eq. (5) is incorrect. For a direct comparison, we will adopt a very similar notational system to that of Ref. [1].

### 2. The Model System

For a noninteracting two-electron Hydrogen anion, its exact GS energy density functional is known to be a sum of the von Weizsäcker (vW) functional [6, 7] and the nuclear-electron attraction energy density functional:

\[
E_v[n(r)] = \int V_{ne}[n(r)] + V_{nu}[n(r)] - \frac{\nabla n(r)}{\nabla \delta n(r)} \right) - \frac{n(r)}{r}. 
\]

The Euler–Lagrange equation of the above explicit energy density functional is conveniently written as an eigenvalue equation [1, 7, 8]:

\[
\left( -\frac{1}{2} \nabla^2 - \frac{1}{r} \right) \psi(r) = \epsilon \psi(r). 
\]

In Ref. [1], Eq. (11) was equated to the Schrödinger equation for the Hydrogen atom:

\[
\left( -\frac{1}{2} \nabla^2 - \frac{1}{r} \right) \psi(r) = \epsilon \psi(r) 
\]

whose first two solutions,

\[
\psi_1(r) = \pi^{-1/2} r^{-1} e^{-r} 
\]

and

\[
\psi_2(r) = (8\pi)^{-1/2} \left( 1 - \frac{r}{2} \right) e^{-r/2} 
\]
were claimed to be identical to the first two solutions of Eq. (11). This association is obviously flawed [2]: \( \psi_{2s}(r) \) is not a solution of Eq. (11), because \( \sqrt{n(r)} \) has to be nonnegative everywhere, but \( \psi_{2s}(r) \) is not so. Wang and Carter [7] have discussed this issue related to the \( \sqrt{n(r)} \)-formulation of Eq. (11) and used the correct \( \phi(r) \)-formulation:

\[
\left( -\frac{1}{2} \nabla^2 - \frac{1}{r} \right) \phi(r) = \mu \phi(r), 
\]

(15)

where \( \phi^2(r) = n(r) \). More generally, one should use the complex-\( \phi(r) \)-formulation employed for inhomogeneous Bose-condensed fluids [10], in which \( |\phi(r)|^2 = n(r) \).

From the two solutions in Eq. (13), two different DV paths were then introduced [1]: the UDV path,

\[ n_s(r, y) = (1 - y)n_{1s}(r) + y n_{2s}(r), \]

(16)

and the conventional density variation (CDV) path,

\[ n_s(r, y) = (1 - y)A(1 - \alpha)^2n_{1s}(r) + \beta Be^{-\beta y}n_{2s}(r), \]

(17)

where \( \alpha = 0.5(y^2 - 1), \beta = (2y - 1)(y - 1) + 1, A = (1 - 3\alpha + 3\alpha^2)^{-1}, \beta = \beta^2/(\beta^2 - 3\beta + 3), n_{1s}(r) = 2|\psi_{1s}(r)|^2, \) and \( n_{2s}(r) = 2|\psi_{2s}(r)|^2, \) respectively.

In Figure 1 [11], we have used Mathematica [12] and reproduced the same Figure 1 of Ref. [1], but we have not observed the energy change behavior as stated in Eq. (5) for the UDV path [1]. The UDV energy curve of Figure 1 for very small values of \( y \) is zoomed in to very fine details in Figure 2 [11], which clearly illustrates that this UDV curve has a zero slope when \( y \) goes to zero, even though in Figure 1, on a larger scale, the same UDV curve appears to vary linearly with small values of \( y \). In fact, the exact energy curve can be accurately fitted with a nonlinear power function: \( E_{2}[n_s(r, y)] = -1 + 64.06y^{1.65} \), which immediately invalidates the general correctness of Eq. (5).

3. Numerical Tests in Hilbert Space

To further examine the validity of the UDV condition in Eqs. (2)–(4), we test the following family of DV's:

\[ n_{1s}(r, y, Z) = (1 - y)n_{1s}(r) + y n_{1s}(r, Z), \]

(18)

where \( n_{1s}(r, Z) = 2|\psi_{1s}(r, Z)|^2 \) is the GS density of a noninteracting two-electron Hydrogen-like atom with nuclear charge \( Z \) (\( Z > 0 \)) and GS wave function,

\[ \psi_{1s}(r, Z) = (Z^3/\pi)^{1/2} e^{-Zr}. \]

(19)
Figures 3–5 [11] exhibit the energy functional curves as functions of $Z$ for very small values of $y$. It is clear that for all cases, the energy density functional does not vary linearly with respect to $y$: 

$$ E_y[n_{1s}(r, y, Z)] = -1 + ay^b, $$

where the exponent $b$ is greater than 1.

On the other hand, it is intriguing to study the consequences if $Z = 0$, even though it is formally not allowed for number-conserving densities. Nonetheless, it can be thought to be a general case in Fock space [5]. It is then straightforward to derive either an UDV or a CDV in Eq. (18).

For example, one can obtain the following expressions from Eqs. (1), (13), (14), and (18):

$$ \delta n_{1s}(r, y, Z) = n_{1s}(r, y, Z) - n_{1s}(r) = y(n_{1s}(r, Z) - n_{1s}(r)) = y f_1(r, Z), $$

(i) When $Z > 1$, $n_{1s}(r, Z)$ decays faster than $n_{1s}(r)$ and $\sqrt{n_{1s}(r)}$. This DV path is conventional:

$$ \lim_{r \to \infty} \frac{|f_1(r, Z)|}{\sqrt{n_{1s}(r)}} = 0, \lim_{r \to \infty} \frac{\delta n_{1s}(r, y, Z)}{n_{1s}(r)} = -y. $$

Similarly, (ii) when $1 > Z > 0.5$, one again has a CDV path:

$$ \lim_{r \to \infty} \frac{|f_1(r, Z)|}{\sqrt{n_{1s}(r)}} = 0, \lim_{r \to \infty} \frac{\delta n_{1s}(r, y, Z)}{n_{1s}(r)} = -y. $$

(iii) When $Z = 0.5$, one instead has an UDV path:

$$ \lim_{r \to \infty} \frac{|f_1(r, Z)|}{\sqrt{n_{1s}(r)}} = \sqrt{2/\pi Z^3}, \lim_{r \to \infty} \frac{\delta n_{1s}(r, y, Z)}{n_{1s}(r)} \to \infty. $$

(iv) When $0.5 > Z > 0$, one again has an UDV path:

$$ \lim_{r \to \infty} \frac{|f_1(r, Z)|}{\sqrt{n_{1s}(r)}} \to +\infty, \lim_{r \to \infty} \frac{\delta n_{1s}(r, y, Z)}{n_{1s}(r)} \to \infty. $$

Through controlling the value of $Z$, we can introduce either an UDV or a CDV in Eq. (18).
duce the following expressions for $Z = 0$ from Eqs. (18) to (22):

$$n_{1z}(r, y, Z = 0) = (1 - y)n_{1z}(r), \quad (28)$$
$$n_{1z}(r, Z = 0) = 0, \quad (29)$$

$$E_Y[n_{1z}(r, y, Z)] = -1 + ay^b.$$  

4. Theoretical Analysis

After careful reading of the argument as presented in Section IV on Page 6,268 of Ref. [1], we learned that Eq. (33) of Ref. [1] is incomplete. To show the analysis, let us reason along the lines of Ref. [1] as follows.

For a given GS density $n_0(r)$, there is a GS wave function $\Psi_0(r_1\sigma_1, \ldots, r_N\sigma_N)$ with spatial and spin coordinates $[r_i\sigma_i]$ uniquely mapped to it:

$$n_0(r) = \left\langle \Psi_0 \sum_{j=1}^N \delta(r - r_j) \right\rangle \Psi_0^* = N(|\Psi_0|^2)_{N-1}, \quad (36)$$

where the subscript “$N-1$” indicates the integration of $|\Psi_0|^2$ to be carried out only for $(N-1)$ spatial coordinates and for all $N$ spin coordinates. The constrained search will associate a normalized, antisymmetric wave function variation $y\chi(r_1\sigma_1, \ldots, r_N\sigma_N)$ with $\delta n(r) = yf(r)$, such that

$$f(r) = N(\langle \Psi_0^* \chi + \chi^* \Psi_0 \rangle_{N-1} + yN(|\chi|^2)_{N-1})$$
$$= N(\langle \Psi_0^* \chi + \chi^* \Psi_0 \rangle_{N-1} + yn_s(r)), \quad (37)$$

where $n_s(r)$ is the density of wave function $\chi(r_1\sigma_1, \ldots, r_N\sigma_N)$. It should be emphasized that the second term on the RHS of Eq. (37) must not be ignored, because $y\chi(r_1\sigma_1, \ldots, r_N\sigma_N)$ might be bigger in magnitude than $\Psi_0(r_1\sigma_1, \ldots, r_N\sigma_N)$ for some regions in space. With Eq. (37) in place of Eq. (33) of Ref. [1], one will attain the full version of Eq. (39) of Ref. [1]:

$$\delta n_{1z}(r, y, Z = 0) = n_{1z}(r, y, Z = 0) - n_{1z}(r)$$
$$= -yn_{1z}(r) = yf_{1z}(r, Z = 0), \quad (30)$$

$$\frac{|f_{1z}(r, Z = 0)|}{\sqrt{n_{1z}(r)}} = \sqrt{n_{1z}(r)} = \sqrt{2/\pi e^{-r}}, \quad (31)$$

and

$$\frac{\delta n_{1z}(r, y, Z = 0)}{n_{1z}(r)} = -yn_{1z}(r) = -y. \quad (32)$$

Obviously, when $Z = 0$, we score a CDV path:

$$\lim_{r \to \infty} \frac{|f_{1z}(r, Z = 0)|}{\sqrt{n_{1z}(r)}} = \frac{0}{0}; \quad \frac{\delta n_{1z}(r, y, Z = 0)}{n_{1z}(r)} = y < +\infty,$$

on which the energy density functional varies linearly with respect to $y$:

$$E_Y[n_{1z}(r, y, Z = 0)] = -1 + y. \quad (34)$$

Figures 3–5 and the earlier analysis indicate that the energy density functional has different power-law dependence on $y$ as $Z$ passes through the UDV region to the CDV region:
whose second term on the RHS can be unbound for UDV’s in the asymptotic region in space for a finite nonzero $y$:

$$\lim_{r \to \infty} y n_{n_0}(r) \to +\infty. \quad (39)$$

Consequently, there should be no condition like Eqs. (2)–(4) imposed on any DV, and UDV’s are not abnormal. Of course, if one sets $y = 0$ in Eqs. (37) and (38), one might claim to recover the original truncated Eqs. (33) and (39) of Ref. [1], but there is no density variation when $y = 0$.

We can also rigorously prove our argument based on the analysis of the Gâteaux functional derivative [3]. Formally speaking, the variation of a density functional $H[n(r)]$ at a GS density $n_0(r)$ due to a DV $\delta n(r)$ can be expressed as

$$\delta H[n_0, \delta n] = H[n_0 + \delta n] - H[n_0] = \langle h[(n_0); r] \delta n(r) \rangle + \xi_{\vW}[n_0, \delta n], \quad (40)$$

where $h[(n_0); r]$ is the Gâteaux functional derivative [3] of $H[n(r)]$ at the GS density $n_0(r)$:

$$\frac{\delta H[n(r)]}{\delta n(r)} \bigg|_{n_0} = h[(n_0); r], \quad (41)$$

if $h[(n_0); r]$ is a single-valued bounded function without any dependence on $\delta n(r)$ and the residual satisfies

$$\lim_{y \to 0} \frac{\xi_{\vW}(n_0, y \delta n)}{y} = 0. \quad (42)$$

Applying this formalism to the energy density functional of Eq. (10), we get

$$\delta E_{\vW}[n_0, \delta n] = E_{\vW}[n_0 + \delta n] - E_{\vW}[n_0] = \langle e_{\vW}[(n_0); r] \delta n(r) \rangle + \xi_{\vW}[n_0, \delta n], \quad (43)$$

where the Gâteaux functional derivative of $E_{\vW}[n(r)]$ at $n_0(r)$ and the residual of the vW functional are

$$e_{\vW}[(n_0); r] = \frac{\delta E_{\vW}[n(r)]}{\delta n(r)} \bigg|_{n_0} = -\frac{1}{r} + t_{\vW}[(n_0); r], \quad (44)$$

and

$$\xi_{\vW}[n_0, y \delta n] = \frac{y^2}{2} \left[ \frac{\delta n(r)}{n(r)} - \frac{\delta \delta n(r)}{n(r)} \right]^2, \quad (46)$$

respectively, for arbitrary $\delta n(r)$ with $n_0(r) + y \delta n(r) = n(r,y)$. Eqs. (44) and (45) evidently indicate that $e_{\vW}[(n_0); r]$ is independent of $\delta n(r)$.

In Appendix C, Theorem 6 shows the detailed derivation for Eqs. (45) and (46), and Theorem 7 proves that Eq. (46) is $O(y^2)$, where $b > 1$. Consequently, Eq. (42) is satisfied, and the energy variation manifests an $O(y^2)$ behavior (with $b > 1$),

$$\delta E_{\vW}[n_0, \delta n] = \langle e_{\vW}[(n_0); r] \delta n(r) \rangle + \xi_{\vW}[n_0, \delta n] = \xi_{\vW}[n_0, \delta n] \in O(y^2), \quad (47)$$

where the term involving the Gâteaux functional derivative is zero due to the Euler–Lagrange equation at the GS density $n_0(r)$,

$$e_{\vW}[(n_0); r] = \frac{\delta E_{\vW}[n(r)]}{\delta n(r)} \bigg|_{n_0} = \mu_r, \quad (48)$$

and the null normalization $\langle \delta n(r) \rangle = 0$. Furthermore, in Eq. (47), $b = 2$ if $|\delta n(r)|/n_0(r)$ is bounded everywhere; otherwise, $b > 1$.

To this end, had Eq. (5) been correct, the Euler-Lagrange equation at the GS density $n_0(r)$, Eq. (48), would have been invalid in order to produce an $O(y^2)$ behavior in Eq. (47) and the entire edifice of DFT [3–9] would have been in danger as a result. Fortunately, it is not so as we just proved!

5. More Numerical Evidence

We continue to verify our theory through the following family of DV’s:

$$n_{2s}(r, y, Z) = (1 - y)n_{1s}(r) + yn_{2s}(r, Z), \quad (49)$$

where $n_{2s}(r, Z) = 2|\psi_{2s}(r, Z)|^2$ is the total 2s-orbital density of a noninteracting two-electron Hydrogen-
The fine detail of the energy density functional does not vary linearly with respect to $y$, if $Z > 0$. More amusingly, when $Z = 0$, the energy density functional varies linearly with respect to $y$ for a CDV path.

Accordingly, we readily establish the four DV regions, according to the values of $Z$:

\[
\begin{align*}
\text{CDV: } Z &> 2, \quad \lim_{r \to 0} \frac{f_{2s}(r, Z)}{\sqrt{n_{1s}(r)}} = 0, \quad \lim_{r \to 0} \frac{\delta n_{2s}(r, y, Z)}{n_{1s}(r)} = 0; \\
\text{CDV: } 2 \geq Z > 1, \quad \lim_{r \to 0} \frac{f_{2s}(r, Z)}{\sqrt{n_{1s}(r)}} = 0, \quad \lim_{r \to 0} \frac{\delta n_{2s}(r, y, Z)}{n_{1s}(r)} \to \infty; \\
\text{UDV: } 1 \geq Z > 0, \quad \lim_{r \to r_c} \frac{f_{2s}(r, Z)}{\sqrt{n_{1s}(r)}} \to +\infty, \quad \lim_{r \to 0} \frac{\delta n_{2s}(r, y, Z)}{n_{1s}(r)} \to \infty; \\
\text{CDV: } Z = 0, \quad \lim_{r \to r_c} \frac{f_{2s}(r, Z)}{\sqrt{n_{1s}(r)}} = 0, \quad \lim_{r \to 0} \frac{\delta n_{2s}(r, y, Z)}{n_{1s}(r)} = y < M < +\infty.
\end{align*}
\]

We can achieve either an UDV or a CDV in Eq. (49) by controlling the value of $Z$. For example, one can straightforwardly write the following expressions from Eqs. (1), (13), (14), and (49):

\[
\delta n_{2s}(r, y, Z) = n_{2s}(r, y, Z) - n_{1s}(r) = y[n_{2s}(r, Z) - n_{1s}(r)] = y f_{2s}(r, Z), \quad (51)
\]

\[
\left| f_{2s}(r, Z) \right| = \left| n_{2s}(r, Z) - n_{1s}(r) \right| = \sqrt{2/\pi} e^{-r^2/2} \left| 32(Z^2 - 2Zr)^2 e^{-(2Zr - 1)} - 1 \right|, \quad (52)
\]

and

\[
\frac{\delta n_{2s}(r, y, Z)}{n_{1s}(r)} = y \left| \frac{n_{2s}(r, Z) - 1}{n_{1s}(r)} \right| = y \left| \frac{Z^2}{32}(2Zr)^2 e^{-(2Zr - 1)} \right|. \quad (53)
\]

6. Density Variations in Fock Space

Until now our discussions are mainly restricted in Hilbert space, where the density variations do not change the normalization of the total electron density. However, in Fock space, we can straightforwardly write the following expressions:

\[
E_a[n_{2s}(r, y, Z)] = -1 + cy^d \quad \left\{ \begin{array}{ll}
\text{CDV: } d = 1, & \text{if } Z = 0; \\
\text{UDV: } d \to 1+, & \text{if } Z \to 0+; \\
\text{UDV: } d > 2 > 1, & \text{if } 1 \geq Z > 0; \\
\text{CDV: } d = 2, & \text{if } Z > 1.
\end{array} \right.
\]
density. It is interesting to extend our study to Fock space, in which the number of the electrons is not fixed. We want to study the following family of model densities:

\[ n_{2y}(r, y, Z) = 0.5(1 - y)n_{1y}(r) + yn_{2y}(r, Z), \]

with normalization \( \langle n_{2y}(r, y, Z) \rangle = 1 + y \).

Figures 8 and 9 display the curves of the energy functional for small values of \( y \). When \( Z = 2.0 \), one has a CDV path, whereas \( Z = 0.67 \) represents an UDV path. In both cases, the energy behaves nonlinearly, lying above the straight line \( E_v = -0.5y \), which is the exact GS energy curve for the fixed external potential of the model system in Fock space [4]. Such a nonlinear behavior is very different from that of a typical sublinear function (the dashed curve in Fig. 9), which goes below the true GS straight-line segment for very small values of \( y \). This fact confirms our conclusion that the order of the nonlinear energy curve should be higher than one. Moreover, the insets of Figures 8 and 9 unveil that the energy behaves almost linearly for very small values of \( y \), and the slope of the energy curve converges to the chemical potential of the model system, which is \( -0.5 \), as \( y \to 0 \). These two numerical tests lend further support to the thermodynamical interpretation of the functional derivative of the energy density functional in Fock space [4, 5].

To further understand the behavior of the energy density functional variation in Fock space, we consider the following general scenario, using the similar notational system of Ref. [1].

For an open system with its number of electrons \( N \) between two adjacent integers \((J - 1)\) and \( J \), the density \( n(N; r) \), the GS density \( n_0(N; r) \), the energy \( E_0[n(N; r)] \), and the GS energy \( E_0[n_0(N; r)] \) are linear interpolations of the two adjacent corresponding entities with integer numbers of electrons [1, 4–6]:

\[
n(N; r) = (N - J + 1) n(J; r) + (J - N) n(J - 1; r),
\]

\[
n_0(N; r) = (N - J + 1) n_0(J; r) + (J - N) n_0(J - 1; r),
\]

\[
E_v[n(N; r)] = (N - J + 1) E_v[n(J; r)] + (J - N) E_v[n(J - 1; r)],
\]

and

\[
E_v[n_0(N; r)] = (N - J + 1) E_v[n_0(J; r)] + (J - N) E_v[n_0(J - 1; r)],
\]

respectively.
FIGURE 9. The energy density functional curve of Eq. (56) for \( Z = 0.67 \) and the density variation parameter \( y \) (from 0 to \( 4.0 \times 10^{-3} \)). The solid line is the exact energy curve (shifted upward by 0.5 Hartrees for a better view). The dotted straight line is the true ground-state energy curve, which has a slope of \(-0.5\) (the theoretical chemical potential of the model system). The dashed line shows a typical square root curve lying below the straight line for very small values of \( y \). The prefactor of the square root function is chosen to make a reasonable comparison with the other two curves. The inset shows the convergence of the solid and dotted curves for very small values of \( y \). Both the \( x \) and \( y \) coordinates of the inset should be multiplied by \( 10^{-11} \).

### 6.1. ELECTRON-DEFICIENT CASE

If \( y = (J-N) \rightarrow 0+ \), the DV of Eq. (57) is measured from the GS density \( n_0(\mathbf{r}; \mathbf{r}) \):

\[
\delta n_0(\mathbf{r}; \mathbf{r}) = n(\mathbf{r}; \mathbf{r}) - n_0(\mathbf{r}; \mathbf{r}) = y f(\mathbf{r})
\]

\[
= \{ n(\mathbf{r}; \mathbf{r}) - n_0(\mathbf{r}; \mathbf{r}) \} + \{ n_0(\mathbf{r}; \mathbf{r}) - n_0(\mathbf{r}; \mathbf{r}) \}
\]

\[
= \delta n_0(\mathbf{r}; \mathbf{r}) + y(\delta n_0 - 1; \mathbf{r}) - n_0(\mathbf{r}; \mathbf{r})
\]

(61)

where \( n_0(\mathbf{r}; \mathbf{r}) \) is introduced as a reference density. The first term of the last expression in Eq. (61) is the DV from the reference density when the number of electrons is fixed to \( N \),

\[
\delta n_0(\mathbf{r}; \mathbf{r}) = n(\mathbf{r}; \mathbf{r}) - n_0(\mathbf{r}; \mathbf{r})
\]

\[
= (1 - y)\{ n(\mathbf{r}; \mathbf{r}) - n_0(\mathbf{r}; \mathbf{r}) \}
\]

\[
\quad + y(\delta n_0 - 1; \mathbf{r}) - n_0(\mathbf{r}; \mathbf{r})
\]

\[
= (1 - y)\delta n_0(\mathbf{r}; \mathbf{r}) + y(\delta n_0 - 1; \mathbf{r})
\]

(62)

which is obviously linear in \( y \) according to Eq. (61),

\[
\delta n_0(\mathbf{r}; \mathbf{r}) = y\{ f(\mathbf{r}) + n_0(\mathbf{r}; \mathbf{r}) - n_0(\mathbf{r}; \mathbf{r}) \}
\]

(63)

Consequently, the energy variation of Eq. (59) is also measured from the GS density \( n_0(\mathbf{r}; \mathbf{r}) \):

\[
\delta E_r[n_0(\mathbf{r}; \mathbf{r}), y] = E_r[n(\mathbf{r}; \mathbf{r})] - E_r[n_0(\mathbf{r}; \mathbf{r})]
\]

\[
= \{ E_r[n(\mathbf{r}; \mathbf{r})] - E_r[n_0(\mathbf{r}; \mathbf{r})] \}
\]

\[
+ \{ E_r[n_0(\mathbf{r}; \mathbf{r})] - E_r[n_0(\mathbf{r}; \mathbf{r})] \}
\]

\[
= \delta E_r[n_0(\mathbf{r}; \mathbf{r})] + y\{ E_r[n_0(\mathbf{r}; \mathbf{r})] - E_r[n_0(\mathbf{r}; \mathbf{r})] \}
\]

\[
= \delta E_r[n_0(\mathbf{r}; \mathbf{r})] + n_0(\mathbf{r}; \mathbf{r})
\]

(64)

where \( I_r \) is the first ionization potential of the \( J \)-electron GS state. The first term of the last expression in Eq. (64) reveals the energy variation with the fixed number of electrons,

\[
\delta E_r[n_0(\mathbf{r}; \mathbf{r})] = E_r[n(\mathbf{r}; \mathbf{r})] - E_r[n_0(\mathbf{r}; \mathbf{r})]
\]

\[
= (1 - y)\{ E_r[n(\mathbf{r}; \mathbf{r})] - E_r[n_0(\mathbf{r}; \mathbf{r})] \}
\]

\[
+ y\{ E_r[n(\mathbf{r}; \mathbf{r})] - E_r[n_0(\mathbf{r}; \mathbf{r})] \}
\]

\[
= (1 - y)\delta E_r[n_0(\mathbf{r}; \mathbf{r})] + y\delta E_r[n_0(\mathbf{r}; \mathbf{r})]
\]

(65)

which must be nonlinear in \( y \),

\[
\delta E_r[n_0(\mathbf{r}; \mathbf{r})] \approx O(y^b), b > 1,
\]

(66)

as being guaranteed by Eqs. (8) and (63) for small enough \( y \). Thus, as \( y \rightarrow 0 \), Eq. (64) will become linear in \( y \),

\[
\delta E_r[n_0(\mathbf{r}; \mathbf{r}), y] = y I_r
\]

(67)

fully consistent to Figures 8 and 9.

Equation (67) might come as a surprise, because it is true for all DV’s, conventional and unconventional. In the traditional approach, only DV’s along the GS ridge, Eqs. (58) and (60), were considered [1, 4–6]. In this case, Eq. (61) results the following expressions:

\[
\frac{|\delta n_0(\mathbf{r}; \mathbf{r})|}{n_0(\mathbf{r}; \mathbf{r})} = y \left| \frac{n_0\mathbf{(J-1); r}}{n_0(\mathbf{r}; \mathbf{r})} - 1 \right| < M < +\infty
\]

(68)

and

\[
\frac{|f(\mathbf{r}; \mathbf{r})|}{\sqrt{n_0(\mathbf{r}; \mathbf{r})}} = \left| \frac{n_0\mathbf{(J-1); r}}{\sqrt{n_0(\mathbf{r}; \mathbf{r})}} - \sqrt{n_0(\mathbf{r}; \mathbf{r})} \right| < P < +\infty
\]

(69)
because the GS densities \( n_0(f - 1; r) \) and \( n_0(f; r) \) are everywhere positive \([3, 5, 13]\) and have the exponential asymptotic limits \([5, 6, 9]\):

\[
\lim_{r \to \infty} n_0(f; r) \sim e^{-2r/\sqrt{2r}},
\]

(70)

and

\[
\lim_{r \to \infty} n_0(J - 1; r) \sim e^{-2r/\sqrt{2r}1},
\]

(71)

governed by their ionization potentials \( I_j \) and \( I_{j-1} \) with \( I_{j-1} \geq I_j \geq 0 \). In other words, if the DV is on the electron-deficient side of \( J \) along the GS segment, the DV will be a CDV, which covers only half of the scenarios.

### 6.2. ELECTRON-ABUNDANT CASE

If \( y = (N - J + 1) \to 0^+ \), the DV of Eq. (57) and the energy variation of Eq. (59) are measured from the GS density \( n_0(J - 1; r) \):

\[
\delta n_0(J - 1; r, y) = n(N; r) - n_0(J - 1; r) = yf(J - 1; r)
\]

(72)

and

\[
\delta E_{\Sigma}[n_0(J - 1; r, y) = E_{\Sigma}[n(N; r)] - E_{\Sigma}[n_0(J - 1; r)]
\]

\[
= \{E_{\Sigma}[n(N; r)] - E_{\Sigma}[n_0(N; r)]\}
\]

\[
+ \{E_{\Sigma}[n_0(N; r)] - E_{\Sigma}[n_0(J - 1; r)]\}
\]

\[
= \delta E_{\Sigma}[n_0(N; r)] + y\delta E_{\Sigma}[n_0(J; r) - n_0(J - 1; r)]
\]

(73)

where

\[
\delta n_0(N; r) = yf(J - 1; r) + n_0(J - 1; r) - n_0(J; r),
\]

(74)

and

\[
\delta E_{\Sigma}[n_0(N; r)] \propto C(y^b), b > 1.
\]

(75)

As a result, as \( y \to 0 \), Eq. (73) is also linear in \( y \),

\[
\delta E_{\Sigma}[n_0(J - 1; r, y)] = - y\lambda_j
\]

(76)

for any allowed CDV’s and UDV’s.

Again, in the existing literature, only DV’s along the GS valley, Eqs. (58) and (60), were considered \([1, 4–6]\). In this case, Eq. (72) results the following expressions as \( r \to \infty \):

\[
\frac{\delta n_0(J - 1; r, y)}{n_0(J - 1; r)} = y\left[\frac{n_0(J; r)}{n_0(J - 1; r)} - 1\right]
\]

\[
\sim e^{\sqrt{\delta E_{\Sigma}/\sqrt{2r}1}},
\]

(77)

and

\[
\frac{\delta f(J - 1; r)}{\sqrt{n_0(J - 1; r)}} = \left|\frac{n_0(J; r)}{\sqrt{n_0(J - 1; r)}} - \sqrt{n_0(J - 1; r)}\right|
\]

\[
\sim e^{-\sqrt{\delta E_{\Sigma}/\sqrt{2r}1}},
\]

(78)

where the asymptotic limit of Eq. (78) depends on the sign of \((4I_j - I_{j-1})\). If \(4I_j > I_{j-1}\), Eq. (78) will be square-integrable. Table I collects the values of \((4I_j - I_{j-1})\) for the ground states of atomic ions with 2 to 18 electrons, based on the highly accurate theoretical ionization potential data of Davidson and coworkers \([14]\). (Table I and the ionization potential data of Davidson and coworkers \([14]\) can be downloaded from the web: http://www.chem.ubc.ca/faculty/wang/groupsite/papers/IPdiff.htm.) Apparently, most of the values of \((4I_j - I_{j-1})\) are positive and Eq. (78) is thus square-integrable. However, there are many negative values of \((4I_j - I_{j-1})\), for which Eq. (78) is no longer square-integrable. In fact, regardless of the square-integrability of Eq. (78), the energy variation is always \( C(y) \) for the DV’s on the electron-abundant side of \((J - 1)\) because of Eq. (76).

Summarizing both cases, we can safely say that the linear-order behavior of the energy variation for open systems in Fock space has nothing to do with the square-integrability of \(|f(r)|/\sqrt{n_0(r)}\), regardless of whether the DV is an UDV or a CDV. Therefore, UDV’s cannot give rise to the derivative discontinuity of the total energy \([4]\).

### 7. Conclusions

Numerical evidence and theoretical arguments suggest that all density variations, unconventional and conventional, are properly included in the allowed density variation domain of any ground-state density. In Hilbert space where the number of electrons of a system is fixed, the energy variation is...
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of nonlinear order higher than linear order of the density variation about the ground-state density. In Fock space where the number of electrons of a system is flexible, the energy variation behaves linearly with respect to the density variation about the ground-state density.

**Appendix A**

Throughout the text, our analysis is built upon the mathematical foundation constructed by Lieb and by Englisch and Englisch [3]. All densities with fixed integral normalization belong to the convex set of $N$-representable densities, $J_N$:

$$J_N = \{ n(r) | n(r) \geq 0, \langle n(r) \rangle = N, \sqrt{n(r)} \in \mathcal{H}(\mathbb{R}^3) \},$$

(A1)

which is a subset of the Banach space $Y$,

$$J_N \subset Y = \mathcal{L}^1 \cap \mathcal{L}^3.$$  

(A2)

Here, $\mathbb{R}^3$ denotes the three-dimensional coordinate real space; $\mathcal{H}(\mathbb{R}^3)$ is a Sobolev space:

$$\mathcal{H}(\mathbb{R}^3) = \{ g | g \in \mathcal{L}^2(\mathbb{R}^3), \nabla g \in \mathcal{L}^2(\mathbb{R}^3) \};$$

(A3)

and $\mathcal{L}^b(\mathbb{R}^3)$ is a Banach space with a norm

$$\| f \|_b = \langle |f(r)|^b \rangle^{1/b} < +\infty, 0 < b < +\infty.$$  

(A4)

The direct sum of $J_N$ defines the convex set for all $N$-representable densities with varied normalizations,

$$J = \{ n(r) | n(r) \in J_N, N \in \mathbb{R}^+ \}$$

$$= \{ n(r) | n(r) \geq 0, n(r) \in \mathcal{L}^3, \sqrt{|n(r)|} \in \mathcal{L}^3 \} \subset Y,$$

(A5)

where $\mathbb{R}^+$ denotes the space of positive real numbers. It was further showed by Lieb [3] that the external potentials $\{ v(r) \}$, corresponding to the ground-state densities

$$\{ n_0(r) \} \subset J_N \subset J \subset Y,$$

(A6)

belong to the dual space of $Y$, which again is a Banach space,

$$Y^* = \mathcal{L}^{3/2} \cap \mathcal{L}^\infty = \{ v(r) | v(r) = v_{3/2}(r) + v_\infty(r), v_{3/2}(r) \in \mathcal{L}^{3/2}, v_\infty(r) \in \mathcal{L}^\infty \}.$$  

(A7)

$\mathcal{L}^\infty$ is the Banach space of bounded functions, with the norm $\| f \|_\infty = \text{ess sup } |f(r)| < \infty$, where the essential supremum is the smallest upper bound of $|f(r)|$ almost everywhere [15]. In particular, the ground-state densities of some external potentials in $Y^*$ are everywhere positive,

$$n_0(r) > 0,$$

(A8)

due to the Unique Continuation Theorem [3, 13].

Hereafter, we will state a few theorems based on the above mathematical definitions.

**Theorem 1.** For any density $n(r) \in J$, the following limits at infinity are true:

$$\lim_{r \to \infty} n(r) = 0,$$

(A9)

$$\lim_{r \to \infty} \sqrt{n(r)} = 0,$$

(A10)

$$\lim_{r \to \infty} \nabla \sqrt{n(r)} = 0.$$  

(A11)

**Proof.** This theorem is obviously true because $n(r) \in \mathcal{L}^1$, $\sqrt{n(r)} \in \mathcal{L}^2$, and $\nabla \sqrt{n(r)} \in \mathcal{L}^2$. $\blacksquare$

**Theorem 2.** For any density $n(r) \in J$, the following integral identities are true:

$$\langle | \nabla \sqrt{n(r)} |^2 \rangle = - \langle \sqrt{n(r)} \nabla \sqrt{n(r)} \rangle,$$  

(A12)

$$\langle \nabla^2 n(r) \rangle = 0.$$  

(A13)

**Proof.** Utilizing Green’s theorem [16], we can rewrite the left-hand side (LHS) of Eq. (A12) as

$$\langle | \nabla \sqrt{n(r)} |^2 \rangle = \oint_{\mathcal{S}} \nabla \sqrt{n(r)} \cdot dS - \langle \sqrt{n(r)} \nabla \sqrt{n(r)} \rangle,$$

(A14)

where the first term on the RHS is a surface integral at infinity. Because of Eqs. (A10) and (A11) of Theorem 1, the surface integral must be zero,

$$\oint_{\mathcal{S}} \nabla \sqrt{n(r)} \cdot dS = 0.$$  

(A15)

Thus, Eq. (A12) is true.

Employing Gauss’s theorem [16], we can rewrite the LHS of Eq. (A13) also as a surface integral at infinity,

$$\langle \nabla^2 n(r) \rangle = \oint_{\mathcal{S}} \nabla n(r) \cdot dS.$$  

(A16)
Because of Eq. (A15) and the following identity,
\[ \nabla n(r) = 2\sqrt{n(r)}\nabla \sqrt{n(r)}, \] (A17)
the surface integral in Eq. (A16) is zero,
\[ \oint S \nabla n(r) \cdot dS = 2\oint S \sqrt{n(r)}\nabla \sqrt{n(r)} \cdot dS = 0. \] (A18)

Hence, Eq. (A13) is true. \( \square \)

Theorem 3. For a ground-state \( n_\alpha(r) \in J \), the following limit at infinity is true:
\[ \lim_{r \to \infty} \left| \frac{\nabla n_\alpha(r)}{n_\alpha(r)} \right| = \text{constant} < +\infty. \] (A19)

Proof. For a potential \( v(r) \in \gamma_* = \gamma^{3/2} + L^\infty \), its ground-state density must approach an exponential function at infinity \[9\],
\[ n_\alpha(r) = f(r)e^{-r}, \] at \( r \to \infty \), (A20)
where the exponent \( \alpha \) is a positive constant and the (positive) prefactor \( f(r) \) behaves weaker than an exponential function,
\[ |\ln f(r)| \leq r^c, \quad c < 1. \] (A21)

From Eqs. (A20) and (A21), we can infer that at infinity,
\[ \lim_{r \to \infty} \left| \frac{\nabla n_\alpha(r)}{n_\alpha(r)} \right| = \lim_{r \to \infty} |\nabla \ln f(r) - \alpha | = \alpha < +\infty. \] (A22)

Theorem 4. For a ground-state \( n_\alpha(r) \in J \) and any function \( g(r) \) with
\[ \lim_{r \to \infty} g(r) = 0, \] (A23)
the following integral identity is true:
\[ \left\langle \frac{\nabla n_\alpha(r)}{n_\alpha(r)} \cdot \frac{\nabla g(r)}{n_\alpha(r)} \right\rangle = - \left\langle g(r) \nabla \left( \frac{n_\alpha(r)}{n_\alpha(r)} \right) \right\rangle. \] (A24)

Proof. Employing Green’s theorem \[16\], we have
\[ \oint g(r) \frac{\nabla n_\alpha(r)}{n_\alpha(r)} \cdot dS = \left\langle g(r) \nabla \left( \frac{n_\alpha(r)}{n_\alpha(r)} \right) \right\rangle = \left\langle \nabla n_\alpha(r) \cdot \nabla g(r) \right\rangle, \] (A25)
where the first term on the LHS is a surface integral at infinity. With the help of Theorem 3 and Eq. (A23), we immediately conclude that the surface integral must be identically zero,
\[ \oint g(r) \frac{\nabla n_\alpha(r)}{n_\alpha(r)} \cdot dS = 0. \] (A26)

Therefore, Eq. (A24) is true. \( \square \)

Appendix B

Theorem 5. For a ground-state density \( n_\alpha(r) \in J \) of some potential \( v(r) \in \gamma_* = \gamma^{3/2} + L^\infty \),
\[ \frac{\nabla^2 n_\alpha(r)}{n_\alpha(r)} \in \gamma^*, \] (B1)
\[ \frac{|\nabla n_\alpha(r)|^2}{n_\alpha(r)} \in \gamma^*, \] (B2)
\[ \frac{\nabla^2 n_\alpha(r)}{n_\alpha(r)} \in \gamma^*. \] (B3)

Proof. It has been well established that any ground-state density satisfies the following eigenvalue equation \[7\,8\],
\[ \left[ -\frac{1}{2} \nabla^2 + v_{\alpha}(r) \right] \sqrt{n_\alpha(r)} = \mu \sqrt{n_\alpha(r)}, \] (B4)
where \( \mu \) is the chemical potential (a constant)[4] and \( v_{\alpha}(r) \) is some effective local potential. In other words, \( \sqrt{n_\alpha(r)} \) can be regarded as an unnormalized one-electron ground-state wave function of the Hamiltonian defined in Eq. (B4). Multiplying \( \sqrt{n_\alpha(r)} \) to the left of Eq. (B4) and integrating over the entire space, we get
\[ T_{\alpha}[n_\alpha(r)] = \langle (\mu - v_{\alpha}) n_\alpha(r) \rangle, \] (B5)
which immediately suggests that \( v_{\alpha}(r) \in \gamma^* \) after applying Lieb’s arguments [3]. We then divide Eq. (B4) by \( \sqrt{n_\alpha(r)} \) and obtain Eq. (B1):
\[ \frac{\nabla^2 n_\alpha(r)}{n_\alpha(r)} = 2(\mu - v_{\alpha}) \in \gamma^*. \] (B6)

On the other hand, we have the following identity through vector analysis,
In Eq. (B7), if either term on the RHS has a singularity not in $L^{3/2}$, this strong must be exactly canceled between the two terms on the RHS; Otherwise, the LHS will not belong to $\gamma^*$. The equality between the two terms on the RHS of Eq. (B7) produces a simple differential equation,

$$\nabla^2 n_0(r) = 0. \quad (B8)$$

The general solution of Eq. (B8) is

$$n_0(r) = \sum_{i,j,k} a_{ijk} r^i y^j z^k > 0, \quad (B9)$$

where $i, j, k$ are either 0 or 1, $a_{ijk}$ is some constant coefficient, and the summation is over all possible combinations of $[i, j, k]$. Clearly, Eq. (B9) will not produce any singularity for the two terms on the RHS of Eq. (B7); Thus, both terms must belong to $\gamma^*$. In addition, for all other regions in space where the two terms on the RHS of Eq. (B7) are not equal, both terms must belong to $\gamma^*$ automatically. Therefore, Eqs. (B2) and (B3) are both true. \[\square\]

**Appendix C**

Consider the von Weizsäcker (vW) functional [6, 7],

$$T_{vW}[n(r)] = \frac{1}{2} \left( \frac{\nabla n(r)}{n(r)} \right)^2$$

where $n(r)$ is an $N$-representable density $n(r) \in J$. The equivalence between the different expressions of the vW functional in Eq. (C1) is established by Eq. (A12) of Theorem 2 in Appendix A.

Theorem 6. At a ground-state density $n_0(r) \in J$ of some potential $\nu(r) \in \gamma^* = L^{3/2} + L^\infty$, for arbitrary density variation $\delta n(r)$ with $n_0(r) + \delta n(r) = n(r) \in J$, the variation of the vW functional,

$$\delta T_{vW}[n_0, \delta n] = T_{vW}[n_0 + \delta n] - T_{vW}[n_0], \quad (C2)$$

can be exactly written as a sum of two terms,

$$\delta T_{vW}[n_0, \delta n] = \langle t_{vW}(n_0) ; \delta n(r) \rangle + \xi_{vW}[n_0, \delta n], \quad (C3)$$

where

$$t_{vW}(n_0) ; r) = \frac{1}{8} \left( \frac{\nabla n_0(r)}{n_0(r)} \right)^2 - \frac{1}{2} \frac{\nabla^2 n_0(r)}{n_0(r)}, \quad (C4)$$

and

$$\xi_{vW}[n_0, \delta n] = \frac{1}{8} \left( \frac{\nabla n_0(r)}{n_0(r)} \right) \cdot \delta n(r) \cdot \left( \frac{\nabla n_0(r)}{n_0(r)} \right)^2. \quad (C5)$$

Moreover, the vW functional can be written as

$$T_{vW}[n(r)] = \langle t_{vW}(n_0) ; n(r) \rangle. \quad (C6)$$

Proof. It is straightforward to show the following identity through vector analysis,

$$t_{vW}(n_0) ; r] = \frac{1}{8} \left( \frac{\nabla n_0(r)}{n_0(r)} \right)^2 - \frac{1}{2} \frac{\nabla^2 n_0(r)}{n_0(r)}, \quad (C7)$$

which immediately validates Eq. (C4) for $n_0(r)$. Multiplying $n(r)$ to Eq. (C7) and integrating over the entire space, we have

$$\langle t_{vW}(n_0) ; n(r) \rangle = \frac{1}{8} \left( \frac{\nabla n(r)}{n(r)} \right)^2 - \frac{1}{4} \frac{\nabla^2 n(r)}{n(r)}, \quad (C8)$$

where the last term is zero because of Theorem 2 in Appendix A. Comparing Eqs. (C1) and (C8), we find Eq. (C6) is true. Next, substituting Eq. (C4) into the first term on the RHS of Eq. (C3), we get

$$\frac{1}{8} \delta n(r) \cdot \left( \frac{\nabla n_0(r)}{n_0(r)} \right)^2 = \langle t_{vW}(n_0) ; r) \delta n(r) \rangle. \quad (C9)$$

Additionally, for $n_0(r) \in J, n(r) \in J$, and $\delta n(r) = n(r) - n_0(r)$, we know
\[
\lim_{r \to r_0} \delta n(r) = 0, \quad (C10)
\]

from Theorem 1 in Appendix A. Then, employing Theorem 4 in Appendix A, we have

\[
\left\langle \frac{\nabla n_0(r) \cdot \nabla \delta n(r)}{n_0(r)} \right\rangle = - \left\langle \delta n(r) \nabla \left( \frac{n_0(r)}{n_0(r)} \right) \right\rangle. \quad (C11)
\]

Taking the advantage of the following identity,

\[
\nabla \left( \frac{n_0(r)}{n_0(r)} \right) = \nabla^2 \frac{n_0(r)}{n_0(r)} - 2 \left( \frac{n_0(r)}{n_0(r)} \right)^2, \quad (C12)
\]

we can rewrite Eq. (C11) as

\[
\delta T_{vw}[n_0, \delta n] = T_{vw}[n_0 + \delta n] - T_{vw}[n_0]
= \frac{1}{8} \left\langle \frac{\nabla n_0(r) \cdot \nabla \delta n(r)}{n(r)} - \frac{\nabla n_0(r)}{n_0(r)} \right\rangle
= \frac{1}{8} \left\langle \frac{\nabla \delta n(r)}{n(r)} + 2 \nabla n_0(r) \cdot \nabla \delta n(r) \right\rangle
= \frac{1}{8} \left\langle \frac{\nabla \delta n(r)}{n(r)} - 2 \frac{n_0(r)}{n_0(r)} \nabla \delta n(r) \right\rangle.
\]

Eliminating the last terms on the LHS’s of Eqs. (C9) and (C13), we obtain

\[
\left\langle \frac{\nabla n_0(r) \cdot \nabla \delta n(r)}{n_0(r)} - \delta n(r) \left( \frac{\nabla n_0(r)}{n_0(r)} \right)^2 \right\rangle
= \left\langle t_{vw}([n_0]; r) \delta n(r) \right\rangle. \quad (C14)
\]

Now, we work out the detailed expression for Eq. (C2):

\[
\xi_{vw}[n_0, \delta n] = \delta T_{vw}[n_0, \delta n] - \left\langle t_{vw}([n_0]; r) \delta n(r) \right\rangle
= \frac{1}{8} \left\langle \frac{\nabla \delta n(r)}{n(r)} + 2 \nabla n_0(r) \cdot \nabla \delta n(r) \right\rangle
= \frac{1}{8} \left\langle \frac{\nabla \delta n(r)}{n(r)} - 2 \frac{n_0(r)}{n_0(r)} \nabla \delta n(r) \right\rangle.
\]
The last expression of Eq. (C16) is identical to Eq. (C5).

**Theorem 7.** At a ground-state density \( n_0(r) \in \mathcal{J} \), for any arbitrary \( \delta n(r) \) such that \( n_0(r) + y \delta n(r) = n(r, y) \in \mathcal{J} \),

\[
\xi_{\text{vol}}[n_0, y \delta n] = \frac{y^2}{8} \left( \frac{\nabla n_0(r)}{n_0(r)} - \nabla \delta n(r) \right)^2 \propto \mathcal{O}(y^2),
\]

(C17)

where \( y \) is a small positive number and the exponent \( b > 1 \).

**Proof.** First, substituting \( n(r, y) \) for \( n(r) \) in Eq. (C5), we immediately obtain the expression for \( \xi_{\text{vol}}[n_0, y \delta n] \) shown in Eq. (C17). It yet remains to be proven that \( \xi_{\text{vol}}[n_0, y \delta n] \propto \mathcal{O}(y^2) \), where \( b > 1 \).

Because of the general inequality for two complex or vector entities \( p \) and \( q \),

\[
|p - q|^2 \leq 2(|p|^2 + |q|^2),
\]

(C18)

\( \xi_{\text{vol}}[n_0, y \delta n] \) obeys the following inequality,

\[
\xi_{\text{vol}}[n_0, y \delta n] \leq \frac{y_2}{4} \left( \frac{\omega(r) \delta n(r)}{n(r, y)} \right) + \frac{y^2}{4} \left( \nabla \delta n(r) \right)^2,
\]

(C19)

where

\[
\omega(r) = \delta n(r) \frac{\nabla n_0(r)}{n_0(r)}.
\]

(C20)

Because of the fact that \( n_0(r) \) is a GS density, one can use Theorem 5 in Appendix B and immediately infer the following condition:

\[
\left| \nabla n_0(r) \right|^2 = u(r) = u_3/2(r) + u_4(r) \in \gamma^*.
\]

(C21)

Utilizing the famous Hölder inequality in functional analysis [3, 13, 15]:

\[
\|fg\| \leq \|f\| \cdot \|g\|_{L^d}
\]

(C22)

for \( 1/c + 1/d = 1, f \in L^c, \) and \( g \in L^d, \) we can then straightforwardly conclude that for arbitrary \( \delta n(r) \) with \( n_0(r) + y \delta n(r) = n(r, y) \in \mathcal{J}, \) the integral of \( |\omega(r)| \) in Eq. (C20) is also finite,

\[
\left\| \omega(r) \right\| = \left\langle \omega(r) \right\rangle = \left\langle \delta n(r) \cdot \left| \nabla n_0(r) \right| / n_0(r) \right\rangle = \left\| \delta n(r) u(r) \right\|_1 \\
\leq \left\| \delta n(r) u_3(r) \right\|_1 + \left\| \delta n(r) u_4/2(r) \right\|_1 \\
\leq \left\| \delta n(r) \right\|_1 \cdot \left\| u_3(r) \right\|_1 + \left\| \delta n(r) \right\|_1 \cdot \left\| u_4/2(r) \right\|_1/2 \\
< R < +\infty.
\]

(C23)

Here, we have used the facts that \( \delta n(r) \in \gamma = L^3 \cap L^4 \) and \( u(r) \in \gamma^* \).

Now, let us consider the following inequality,

\[
\left| \left\langle \frac{y \omega(r) \delta n(r)}{n(r, y)} \right\rangle \right| = \left| \left\langle s(r, y) \omega(r) \right\rangle \right| \\
\leq \left| \left\langle s(r, y) \right\rangle \right| < S(y)R,
\]

(C24)

where the function \( s(r, y) \) is defined as

\[
s(r, y) = \frac{y \delta n(r)}{n(r, y)},
\]

(C25)

and \( S(y) \), a function of \( y \), is the upper bound of \( s(r, y) \) for all space of \( r \),

\[
|s(r, y)| \leq S(y) < +\infty.
\]

(C26)

If \( |\delta n(r)| / n_0(r) \) is bounded everywhere by a finite constant \( W \), we easily ascertain that \( S(y) \in \mathcal{O}(y) \),

\[
|s(r, y)| \leq S(y) = \frac{yW}{1 - yW} \propto \mathcal{O}(y) < +\infty,
\]

(C27)

for \( y \) less than \( W^{-1} \).

If \( |\delta n(r)| / n_0(r) \) is unbounded asymptotically, we can partition the space into two regions: Region I where \( |\delta n(r)| / n_0(r) \) is bounded by \( X(y) \) and Region II otherwise. As \( y \) approaches zero, we can choose \( X(y) \), such that \( y \) is less than \( X^{-1}(y) \) and

\[
\lim_{y \to 0} X(y) = 0,
\]

(C28)

and Region II is completely outside of a sphere of radius \( r_s(y) \),

\[
\left| \frac{\delta n(r)}{n_0(r)} \right|_{\text{Reg. II}} > X(y) \geq \left| \frac{\delta n(r)}{n_0(r)} \right|_{r \leq r_s(y)}.
\]

(C29)

(Of course, part of Region I might be outside of this sphere, but Region II is exclusively outside of this sphere.)
From Eq. (C29), it is clear that as \( y \) goes to zero, both \( X(y) \) and \( r_s(y) \), as functions of \( y \), will diverge,

\[
\lim_{y \to 0} \frac{1}{X(y)} = \lim_{y \to 0} \frac{1}{r_s(y)} = 0. 
\]

We then can split the integral of Eq. (C24) into two pieces, according to the space partition:

\[
\langle s(r, y) w(r) \rangle = \langle s(r, y) w(r) \rangle_{\text{Reg}_1} + \langle s(r, y) w(r) \rangle_{\text{Reg}_2} \\
\leq \langle s(r, y) w(r) \rangle_{\text{Reg}_1} + \langle s(r, y) w(r) \rangle_{\text{Reg}_2} \\
\leq \frac{yRX(y)}{1 - yX(y)} + \langle s(r, y) w(r) \rangle_{r > r_f(y) / r} 
\]

where the subscripts outside of the integrals signify the integration domains of the integrals. At \( y \to 0 \), the limit of the second term of the last expression of Eq. (C31) is zero due to the upper bound shown in Eq. (C24) and the vanishing integration volume,

\[
\lim_{y \to 0} \langle s(r, y) w(r) \rangle_{r > r_f(y) / r} = \lim_{y \to 0} \langle s(r, y) w(r) \rangle_{r > r_f(y) / r} = 0.
\]

We thus conclude that if \( \delta n(r) / n_{01}(r) \) is bounded everywhere, \( \langle s(r, y) w(r) \rangle \) is \( \mathcal{O}(y) \) according to Eqs. (C24) and (C27); otherwise, \( \langle s(r, y) w(r) \rangle \) is \( \mathcal{O}(y^p) \) with \( k > 0 \) according to Eqs. (C24), (C28), (C30) to (C32). In other words, we have

\[
\lim_{y \to 0} \langle s(r, y) w(r) \rangle = 0.
\]

Hence, the first term on the RHS of Eq. (C19) is finite and \( \mathcal{O}(y^p) \) with \( b > 1 \) as \( y \to 0 \),

\[
\frac{y^4}{4 n(r, y)} \left( \frac{\langle s(r, y) w(r) \rangle}{4} \right) \propto \mathcal{O}(y^4) < +\infty.
\]

Moreover, for an arbitrary \( \delta n(r) \) with \( n_{01}(r, 1) = n_{01}(r) + \delta n(r) = n(r) \in \mathcal{J} \), one can derive the following inequality based on Eq. (C18),

\[
|\nabla \delta n(r)|^2 = |\nabla n(r) - \nabla n_{01}(r)|^2 \leq 2|\nabla n(r)|^2 + |\nabla n_{01}(r)|^2.
\]

Employing Eq. (C35) for the second term on the RHS of Eq. (C19), one gets

\[
\frac{y^2}{4} \left( \frac{|\nabla n_{01}(r)|^2}{n(r, y)} \right) \leq \frac{y^2}{2} \left( \frac{|\nabla n(r)|^2}{n(r, y)} \right) + \frac{y^2}{2} \left( \frac{|\nabla n_{01}(r)|^2}{n(r, y)} \right). 
\]

The first term on the RHS of Eq. (C36) obviously satisfies the following inequality,

\[
\frac{y^2}{2} \left( \frac{|\nabla n(r)|^2}{n(r, y)} \right) = \frac{y^2}{2} \left( \frac{|\nabla n(r)|^2}{n(r, y)} \right) \leq \frac{yM(y)}{2} \left( \frac{|\nabla n(r)|^2}{n(r)} \right) \\
< \frac{yM(y)}{2} \frac{P}{y} < +\infty,
\]

where the finite upper bound \( P \) is from the integral involving \( n(r) \) simply because \( n(r) \in \mathcal{J} \) and the upper bound \( M(y) \) is a function of \( y \),

\[
\frac{yM(y)}{2} \frac{P}{y} < +\infty.
\]

Following the same arguments presented from Eq. (C24) to Eq. (C33), we can readily conclude that if \( n(r) / n_{01}(r, y) \) is bounded everywhere, \( \langle y|\nabla n(r)|^2 / n_{01}(r, y) \rangle \) is \( \mathcal{O}(y) \); otherwise, \( \langle y|\nabla n(r)|^2 / n_{01}(r, y) \rangle \) is \( \mathcal{O}(y^p) \) with \( k > 0 \) as \( y \to 0 \). In general, we have

\[
\lim_{y \to 0} \left( \frac{yM(y)}{2} \frac{P}{y} \right) = 0.
\]

Thus, the first term on the RHS of Eq. (C36) is finite and \( \mathcal{O}(y^p) \) with \( b > 1 \) as \( y \to 0 \),

\[
\frac{y^2}{2} \left( \frac{|\nabla n(r)|^2}{n(r, y)} \right) \propto \mathcal{O}(y^4) < +\infty.
\]

Similarly, one can work with the second term on the RHS of Eq. (C36) and get another inequality,

\[
\frac{y^2}{2} \left( \frac{|\nabla n_{01}(r)|^2}{n(r, y)} \right) = \frac{y^2}{2} \left( \frac{|\nabla n_{01}(r)|^2}{n(r, y)} \right) \leq \frac{yN(y)}{2} \left( \frac{|\nabla n_{01}(r)|^2}{n_{01}(r)} \right) \\
< \frac{yN(y)}{2} Q < +\infty,
\]

where the finite upper bound \( Q \) is from the integral involving \( n_{01}(r) \) because \( n_{01}(r) \in \mathcal{J} \) and the upper bound \( N(y) \) is a function of \( y \).
Following the same arguments presented from Eq. (C24) to Eq. (C33), we can also conclude that if $\{n_0(r)/n(r,y)\}$ is bounded everywhere, $(\nabla n_0(r))^2/n(r,y) \in \mathcal{C}(y)$; otherwise, $(\nabla n_0(r))^2/n(r,y)) \in \mathcal{C}(y')$ with $k > 0$ as $y \to 0$. In general, we have
\[
\lim_{y \to 0} \left( \frac{y^2}{2} \frac{\nabla n_0(r)}{n(r,y)} \right) \propto \mathcal{O}(y') < +\infty.
\] (C44)

Combining Eqs. (C36), (C40), and (C44), we gather that the second term on the RHS of Eq. (C19) is finite and $\mathcal{O}(y')$ with $b > 1$ as $y \to 0$,
\[
0 < \frac{y^2}{4} \frac{\nabla \delta n(r)}{n(r,y)} \propto \mathcal{O}(y') < +\infty.
\] (C45)

for arbitrary $\delta n(r)$ with $n_0(r) + y\delta n(r) = n(r,y) \in j$.

Consequently, with the aid of Eqs. (C19), (C34), and (C45), Eq. (C17) is satisfied. Moreover, in Eq. (C17), $b = 2$ if $|\delta n(r)|/n_0(r)$ is bounded everywhere; otherwise, $b > 1$. ■

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References

11. Zahariev, F. E. (private communication). Dr. Federico E. Zahariev generated Figures 1–7 initially and Y.A.Z. independently replotted the same figures later with higher accuracy and better algorithm.