Non-existence of a Hohenberg-Kohn Variational Principle in Total Current Density Functional Theory

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Abstract

For a many-electron system, whether the particle density $\rho(r)$ and the total current density $j(r)$ are sufficient to determine the one-body potential $V(r)$ and vector potential $A(r)$, is still an open question. For the one-electron case, a Hohenberg-Kohn theorem exists formulated with the total current density. Here we show that the generalized Hohenberg-Kohn energy functional $E_{V_0,A_0}(\rho,j) = \langle \psi(\rho,j), H(V_0,A_0)\psi(\rho,j) \rangle$ can be minimal for densities that are not the ground-state densities of the fixed potentials $V_0$ and $A_0$. Furthermore, for an arbitrary number of electrons and under the assumption that a Hohenberg-Kohn theorem exists formulated with $\rho$ and $j$, we show that a variational principle for Total Current Density Functional Theory as that of Hohenberg-Kohn for Density Functional Theory does not exist. The reason is that the assumed map from densities to the vector potential, written $(\rho,j) \mapsto A(\rho,j;r)$, enters explicitly in $E_{V_0,A_0}(\rho,j)$. 
I. INTRODUCTION

A cornerstone of modern density functional theory is the Hohenberg-Kohn theorem, which states that knowledge of the one-body density of a quantum-mechanical system determines the one-body potential \( V \) of the same system [1] (see also [2] for a complete proof). It has been argued [3, 4] that one can extend this theorem to a statement that knowledge of the one-body particle density plus knowledge of the one-body total current density suffices to determine the one-body potential and the magnetic vector potential for a many electron system (up to a gauge transformation). Since the proofs in [3] and [4] have been shown to contain errors (cf. [5, 6]), the existence of such a theorem remains an open question except for the one-electron case. For a system with only one electron, however, it can be shown that the particle density and the total current density determine the potentials up to a gauge transformation [3, 4]. Moreover, it is well-known that the same statement made with the paramagnetic current density in place of the total current density is not true. For instance, Vignale and Capelle [7] have constructed a counterexample that shows that different Hamiltonians can share a common ground-state for systems with magnetic fields.

In the classical Hohenberg-Kohn theory, one studies a system of \( N \) interacting electrons subjected to an electric field. Define the system’s Hamiltonians to be (in suitable units)

\[
H(V) = \sum_{j=1}^{N} \left( -\Delta_j + V(r_j) \right) + \sum_{j<k} |r_j - r_k|^{-1}.
\]

The Hohenberg-Kohn theorem then states that the particle density \( \rho(r) \) determines the potential \( V(r) \) up to a constant, and thereby the ground-state of \( H(V) \). Let \( \mathcal{A}'_N \) be the set of particle densities having the following property: there exists a \( V(r) \) such that \( H(V)\psi = e\psi \), \( \psi = \psi(\rho) \) is the unique ground-state of \( H(V) \) and \( \rho(r) = N \int |\psi|^2 dr_2 \cdots dr_N \).

Now, fix \( V_0(r) \) such that \( H(V_0)\psi_0 = e_0\psi_0 \), where \( \psi_0 \) is the unique ground-state and \( \rho_0(r) \) the ground-state particle density. On \( \mathcal{A}'_N \), we can define

\[
\mathcal{E}'_{V_0}(\rho) = \langle \psi(\rho), H(V_0)\psi(\rho) \rangle = \langle \psi(\rho), H(0)\psi(\rho) \rangle + \int \rho(r)V_0(r)
= F'_{HK}(\rho) + \int \rho(r)V_0(r),
\]

where the last equality defines the Hohenberg-Kohn functional \( F'_{HK} \). The Hohenberg-Kohn
variational principle for Density Functional Theory then states that

\[ e_0 = \mathcal{E}'_{V_0}(\rho_0) = \min_{A_0'} \{ \mathcal{E}'_{V_0}(\rho) \}. \]

The map \( \rho(\mathbf{r}) \mapsto V(\mathbf{r}) \), guaranteed to exist by the Hohenberg-Kohn theorem, does not enter explicitly in the functional to be minimized. Also note that \( \rho_0 \) is the unique minimizer of \( F'_{HK}(\rho) + \int \rho V_0. \) (To see this, assume that \( \rho' \in A_0' \) is another minimizer. Then there is a \( V'(\mathbf{r}) \neq V_0(\mathbf{r}) + \text{constant} \), such that \( H(V') \) has a ground-state \( \psi' \) with particle density \( \rho' \). Since \( V'(\mathbf{r}) \neq V_0(\mathbf{r}) + \text{constant} \), we can conclude that \( \psi' \) is not the ground-state of \( H(V_0) \). But then, \( e_0 < \langle \psi', H(V_0) \psi' \rangle = \mathcal{E}'_{V_0}(\rho') = e_0, \) which is a contradiction.)

In this paper, we will discuss the corresponding variational principle for Current Density Functional Theory formulated with the total current density, i.e., a variational principle for an energy functional \( \mathcal{E}_{V_0,A_0} \) given by

\[ \mathcal{E}_{V_0,A_0}(\rho, j) = \langle \psi(\rho, j), H(V_0, A_0) \psi(\rho, j) \rangle, \]

where \( V_0 \) and \( A_0 \) are the fixed scalar and vector potential, respectively. We will note the following:

- For the energy functional suggested in \[8\],

\[ \mathcal{E}_{V_0,A_0}(\rho, j) = F_{HK}(\rho, j) + 2 \int j(\mathbf{r}) \cdot A_0(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r})(V_0(\mathbf{r}) - |A_0(\mathbf{r})|^2) d\mathbf{r} \]

\[ \neq \mathcal{E}_{V_0,A_0}(\rho, j), \]

the counterexample in \[7\] shows that the densities \( \rho(\mathbf{r}) \) and \( j(\mathbf{r}) \) cannot satisfy a variational principle \[8\]. We shall here give a mathematical proof of this claim.

- For \( N = 1 \) and fixed potentials \( V_0 \) and \( A_0 \), the energy functional \( \mathcal{E}_{V_0,A_0}(\rho, j) \) is well-defined since \( \rho(\mathbf{r}) \) and \( j(\mathbf{r}) \) determine \( V_0(\mathbf{r}) \) and \( A_0(\mathbf{r}) \) up to a gauge transformation \[5, 6\]. However, \( \mathcal{E}_{V_0,A_0}(\rho, j) \) can be minimized by other densities then the ground-state densities of \( H(V_0, A_0) \).

- For any \( N \) and under the assumption that a Hohenberg-Kohn theorem exists formulated with \( \rho(\mathbf{r}) \) and \( j(\mathbf{r}) \), we show that no variational principle as that of Hohenberg-Kohn for Density Functional Theory exists for Current Density Functional Theory formulated with the total current density. This is due to the fact that the map
\((\rho, j) \mapsto A(\rho, j; r)\) enters explicitly in \(E_{V_0, A_0}(\rho, j)\). Furthermore, this implies that \(E_{V_0, A_0}(\rho, j)\) cannot be extended to \(N\)-representable density pairs \((\rho, j)\) by a Levy-Lieb approach (see Section III B below).

II. NON-EXISTENCE OF A VARIATIONAL PRINCIPLE FOR \(\tilde{E}_{V, A}\)

Let \(N = 1\) and consider the Schrödinger operator \(H(V, A) = (-i\nabla + A)^2 + V(r)\). For simplicity, we will assume that the ground-state is non-degenerate. Let \(H_0\) denote the Schrödinger operator, when the potentials are set to zero, i.e., \(H_0 = -\Delta\). For the non-degenerate ground-state \(\psi_0\), we compute the ground-state particle density and paramagnetic current density from \(\rho(r) = |\psi(r)|^2\) and \(j_p(r) = \text{Im} (\psi^*(r) \nabla \psi(r))\), respectively. The total current density is then given by the sum \(j(r) = j_p(r) + \rho(r) A(r)\).

For \(N = 1\), a Hohenberg-Kohn theorem exists formulated with the total current density \([5, 6]\), i.e., \(\rho(r)\) and \(j(r)\) determine \(V(r)\) and \(A(r)\) up to a gauge transformation. In particular, \(A(r) = a(\rho, j; r) - \nabla \chi(r)\) for some function \(\chi(r)\). Denote by \(A_1\) the set of density pairs \((\rho, j)\) such that a ground-state \(\psi_0 = \psi(\rho, j) e^{i\chi(r)}\) exists and fulfills

\[
\begin{align*}
\text{(i)} & \quad |\psi_0|^2 = \rho(r), \\
\text{(ii)} & \quad \text{Im}(\psi_0^* \nabla \psi_0) + |\psi_0|^2 A(r) = \text{Im}(\psi^*(\rho, j) \nabla \psi(\rho, j)) + |\psi(\rho, j)|^2 a(r) = j(r), \\
\text{(iii)} & \quad H(V, A) \psi_0 = \epsilon_0 \psi_0.
\end{align*}
\]

On \(A_1\), we can define the generalized Hohenberg-Kohn functional

\[
F_{HK}(\rho, j) = \langle \psi(\rho, j), H_0 \psi(\rho, j) \rangle.
\]

Furthermore, for fixed \(V_0(r)\) and \(A_0(r)\), we define on \(A_1\), as in \([3]\), the energy functional

\[
\tilde{E}_{V_0, A_0}(\rho, j) = F_{HK}(\rho, j) + 2 \int j(r) \cdot A_0(r) dr + \int \rho(r)(V_0(r) - |A_0(r)|^2) dr.
\]

Note that \(\tilde{E}_{V_0, A_0}(\rho, j) \neq \langle \psi(\rho, j), H(V_0, A_0) \psi(\rho, j) \rangle\) on \(A_1\). Consequently, no variational principle for the density pair \((\rho, j)\) is immediately inherited from the variational principle for the wavefunction.

The following facts follow from Theorem 4 in \([6]\):
• For \( B < 0 \) small enough and \( 0 < |\tilde{B}| < |B| \), there exists a wavefunction \( \psi_0 \) that is the ground-state of both \( H(V, A) \) and \( H(\tilde{V}, \tilde{A}) \), where \( A(r) = (B/2) \hat{e}_z \times r \) and \( \tilde{A}(r) = (\tilde{B}/2) \hat{e}_z \times r \).

• With \( \varepsilon = (\tilde{B} - B)/2 > 0 \) and \( j_\varepsilon(r) = j_0(r) + \varepsilon(\rho_0 \hat{e}_z \times r) \), where \( \rho_0 \) and \( j_0 \) are the ground-state densities computed from \( \psi_0 \), it follows that \( F_{HK}(\rho_0, j_0) = F_{HK}(\rho_0, j_\varepsilon) \) for \( \varepsilon > 0 \) sufficiently small.

• The density pair \((\rho_0, j_\varepsilon)\) belongs to \( A_1 \) for \( \varepsilon > 0 \) sufficiently small.

We now note that

\[
\tilde{E}_{V,A}(\rho_0, j_\varepsilon) = F_{HK}(\rho_0, j_\varepsilon) + 2 \int j_\varepsilon(r) \cdot A_0(r) dr + \int \rho_0(r)(V(r) - |A_0(r)|^2) dr
\]

\[
= \tilde{E}_{V,A}(\rho_0, j_0) + \varepsilon B \int \rho_0(r)(\hat{e}_z \times r)^2 dr,
\]

by the above facts. Consequently,

\[
\tilde{E}_{V,A}(\rho_0, j_\varepsilon) - \varepsilon B \int \rho_0(r)(x^2 + y^2) dr = \tilde{E}_{V,A}(\rho_0, j_0),
\]

which implies \( \tilde{E}_{V,A}(\rho_0, j_\varepsilon) < \tilde{E}_{V,A}(\rho_0, j_0) \). Thus \( \tilde{E}_{V,A} \) does not satisfy a variational principle.

III. NON-EXISTENCE OF A HOHENBERG-KOHN VARIATIONAL PRINCIPLE FOR TOTAL CURRENT DENSITY

A. The one-electron case

Fix \( V_0(r) \) and \( A_0(r) \) such that \( H(V_0, A_0)\psi_0 = e_0 \psi_0 \), and let \( \rho_0(r) \) and \( j_0(r) \) denote the ground-state densities. On \( A_1 \), we define the energy functional

\[
\varepsilon_{V_0A_0}(\rho, j) = F_{HK}(\rho, j) + 2 \int j(r) \cdot A_0(r) dr + \int \rho(r)(V_0(r) - |A_0(r)|^2) dr
\]

\[
- 2 \int \rho(r) A_0(r) \cdot [a(\rho, j; r) - A_0(r)] dr,
\]

where \( [a - A] = 0 \) if \( a - A = \nabla \chi \) for some \( \chi \), and \( [a - A] = a - A \) otherwise. From (ii), (2) and the definition of \( F_{HK}(\rho, j) \), it follows that

\[
\varepsilon_{V,A}(\rho, j) = \langle \psi(\rho, j), H(V, A)\psi(\rho, j) \rangle,
\]

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for \((\rho, j) \in \mathcal{A}_1\). Furthermore, note that the map \((\rho, j) \mapsto \mathbf{a}(\rho, j; \mathbf{r})\) enters explicitly in the expression for the functional \(\mathcal{E}_{V, \mathcal{A}}(\rho, j)\).

By the variational principle for the wavefunction, with \(\rho(\mathbf{r})\) and \(j(\mathbf{r})\) in \(\mathcal{A}_1\), we have

\[
\mathcal{E}_{V_0, \mathcal{A}_0}(\rho, j) = \langle \psi(\rho, j), H(V_0, \mathcal{A}_0)\psi(\rho, j) \rangle 
\geq \langle \psi(\rho_0, j_0), H(V_0, \mathcal{A}_0)\psi(\rho_0, j_0) \rangle = \mathcal{E}_{V_0, \mathcal{A}_0}(\rho_0, j_0) = e_0.
\]

Thus \(e_0 = \mathcal{E}_{V_0, \mathcal{A}_0}(\rho_0, j_0) = \min_{\mathcal{A}_1} \{\mathcal{E}_{V_0, \mathcal{A}_0}(\rho, j)\}\). However, from the facts in Section II, it follows that the minimum of \(\mathcal{E}_{V_0, \mathcal{A}_0}(\rho, j)\) is not only achieved by the ground-state densities \(\rho_0(\mathbf{r})\) and \(j_0(\mathbf{r})\), but also achieved by infinitely many density pairs \((\rho_0, j_\epsilon)\),

\[
e_0 = \mathcal{E}_{V_0, \mathcal{A}_0}(\rho_0, j_\epsilon) = \min_{\mathcal{A}_1} \{\mathcal{E}_{V_0, \mathcal{A}_0}(\rho, j)\}. \tag{3}
\]

Thus, although a variational principle exists for \(\mathcal{E}_{V_0, \mathcal{A}_0}(\rho, j)\), there is no way of knowing whether a minimizer \((\rho, j)\) also is the ground-state densities of \(H(V_0, \mathcal{A}_0)\).

## B. Arbitrary number of electrons

Now, let \(H(V, \mathcal{A})\) be the Hamiltonian of a system of \(N\) electrons and where \(N\) is arbitrary, i.e.,

\[
H(V, \mathcal{A}) = \sum_{j=1}^{N} \left[(-i \nabla_j + A(r_j))^2 + V(r_j)\right] + \sum_{j<k} |r_j - r_k|^{-1}.
\]

Under the assumption that a Hohenberg-Kohn theorem could be proven formulated with \(\rho\) and \(j\), \(\mathcal{E}_{V, \mathcal{A}}(\rho, j)\) can be defined as in (2) for densities in \(\mathcal{A}_N\). Now \(F_{HK}(\rho, j)\) takes the form

\[
F_{HK}(\rho, j) = \langle \psi(\rho, j), (T + W)\psi(\rho, j) \rangle,
\]

\[
T + W = -\sum_{j=1}^{N} \Delta_j + \sum_{j<k} |r_j - r_k|^{-1},
\]

which agrees with (1) if \(N = 1\). Here \(\mathcal{A}_N\) is the obvious generalization of \(\mathcal{A}_1\). As in the case \(N = 1\), for \((\rho, j) \in \mathcal{A}_N\), we have

\[
\mathcal{E}_{V, \mathcal{A}}(\rho, j) = \langle \psi(\rho, j), H(V, \mathcal{A})\psi(\rho, j) \rangle.
\]

Also, recall that the map \((\rho, j) \mapsto \mathbf{a}(\rho, j; \mathbf{r})\), which by assumption exists for any \(N\), enters explicitly in the expression for \(\mathcal{E}_{V, \mathcal{A}}(\rho, j)\), while in the classical Hohenberg-Kohn theory, the
The corresponding map $\rho \mapsto V$ does not appear in the functional $\mathcal{E}_V'(\rho)$ (see Section I). The presence of $a(\rho,j;r)$ adds an additional layer of complexity to the generalized Hohenberg-Kohn energy functional $\mathcal{E}_{V,A}$. Furthermore, in the work of Lieb [2], $F_{HK}(\rho)$ is extended to the so called Levy-Lieb functional $F_{LL}(\rho) = \inf_\psi \{ \langle \psi, H(0) \psi \rangle : \psi \mapsto \rho \}$, which is defined on the set of $N$-representable particle densities, denoted $I_N$ (see [2]). This extension allows the functional $F_{LL}(\rho) + \int \rho V$ to be minimized freely on the known set $I_N$ instead of the unknown set $A'_N$. However, even if $F_{HK}(\rho,j)$ could be extended to a Levy-Lieb-type functional defined for $N$-representable density pairs $(\rho,j)$, no such extension is possible for $\mathcal{E}_{V,A}(\rho,j)$ because of the term $\int \rho A \cdot (a(\rho,j;r) - A)$, which is by definition only meaningful for $(\rho,j) \in A_N$.

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