Nonuniqueness in spin-density-functional theory on lattices

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In electronic many-particle systems, the mapping between densities and spin magnetizations, \( \{n(r), \mathbf{m}(r)\} \), and potentials and magnetic fields, \( \{v(r), \mathbf{B}(r)\} \), is known to be nonunique, which has fundamental and practical implications for spin-density-functional theory (SDFT). This paper studies the nonuniqueness (NU) in SDFT on arbitrary lattices. Two new, non-trivial cases are discovered, here called local saturation and global noncollinear NU, and their properties are discussed and illustrated. In the continuum limit, only some well-known special cases of NU survive.

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Density-functional theory (DFT) is a widely used approach for calculating the electronic structure of atoms, molecules, and many types of materials. The fundamental theorem of Hohenberg and Kohn establishes that the ground-state density \( n(r) \) of a nonmagnetic, nondegenerate electronic system uniquely determines the scalar potential \( v(r) \), apart from an arbitrary additive constant \( C \). However, many applications of interest involve electronic ground states that have a spin magnetization, \( \mathbf{m}(r) \), and/or are exposed to external magnetic fields, \( \mathbf{B}(r) \). Such situations can be handled with spin-density-functional theory (SDFT), where the fundamental variable is the 4-density \( \{n(r), \mathbf{m}(r)\} \), which couples to the 4-potential \( \{v(r), \mathbf{B}(r)\} \).

Using the Rayleigh-Ritz variational principle, one can prove that a given physical 4-density uniquely determines the ground-state wave function \( \Psi_0 \) (apart from trivial phase factors). This guarantees that any property of the system expressible in terms of \( \Psi_0 \) is a functional of the 4-density. Following the Hohenberg-Kohn theorem of DFT, one might expect that there is also a unique map from ground-state wave functions to 4-potentials. However, it was recognized long ago by von Barth and Hedin, and more recently by Capelle and Vignale and Eschrig and Pickett that such a unique correspondence does not exist. These authors showed that the extent of nonuniqueness (NU) in SDFT is much greater than the addition of a mere constant \( C \) to \( v(r) \) for the nonmagnetic systems considered in DFT. As a consequence, some applications of SDFT such as the calculation of excitation energies or of one-electron spin gaps in half-metallic ferromagnets must be critically reexamined.

NU in SDFT means that an \( N \)-particle ground state \( \Psi_0 \) remains unchanged under addition of a 4-potential \( \{\Delta v(r), \Delta \mathbf{B}(r)\} \). This happens if and only if \( \Psi_0 \) is an eigenstate of the operator

\[
\Delta H = \sum_{j=1}^{N} [\Delta v(r_j) - \Delta \mathbf{B}(r_j) \cdot \mathbf{\sigma}_j],
\]

where \( \mathbf{\sigma}_j \) is the vector of Pauli matrices acting on the spin of the \( j \)th electron, and we use units where the Bohr magneton \( \mu_B = 1 \). The entire spectrum \( \{\Psi\} \) is invariant if \( \Delta H \) is related to a constant of motion (systematic NU); all other cases are called accidental NU. Similar conditions for NU can be given for other multi-component generalizations of DFT, e.g. for current-carrying or superconducting systems. Thus, NU appears to be a characteristic feature of generalized DFTs, and its fundamental and practical consequences need to be explored in detail. In the first place, it is important to know what types of NU can occur in practice. The following classes of examples have been identified in SDFT:

(a) \( \{\Delta v = C, \Delta \mathbf{B} = B\hat{e}_z\} \), with constant \( B \), for systems with an energy gap and a collinear spin arrangement along the \( z \)-axis, where the \( \{\Psi\} \) are eigenstates of \( \hat{S}_z \) (systematic NU). \( B \) should be sufficiently small to avoid level crossings in order for \( \Psi_0 \) to remain the ground state. As shown by Gidopoulos, the mapping in the collinear case is unique in the broader sense that spin-potentials \( \{v_\uparrow(r), v_\downarrow(r)\} \) which differ by more than a spin-dependent constant always have different ground states.

(b) In a fully spin polarized Kohn-Sham system with \( n_\uparrow(r) = n(r) \) and \( n_\downarrow = 0 \) and an energy gap, there is an infinite number of spin-down Kohn-Sham potentials that produce the same ground state (accidental NU).

(c) \( \{\Delta v = \lambda u(r), \Delta \mathbf{B} = \lambda u(r) \mathbf{m}(r)/m(r)\} \) for one-electron systems only, where \( u(r) \) is an arbitrary function and \( \lambda \) is sufficiently small (accidental NU).

In Ref. \cite{1}, a general condition for NU in \( N \)-electron systems is given: If \( \Psi_0 \) is invariant under the addition of a 4-potential, then this 4-potential must have the form \( \{\Delta v(r) = C, \Delta \mathbf{B}(r) = B\hat{e}_z(r)\} \), i.e., \( \Delta \mathbf{B} \) may possibly be noncollinear but must be constant in magnitude. However, Argaman and Makov have raised doubts whether such noncollinear 4-potentials can really be found.

It thus appears that NU for \( N > 1 \) electrons, while interesting and of potential practical relevance, is limited to rather simple situations of collinear spin arrangement or full, ferromagnetic spin polarization. The purpose of this paper is to examine NU in SDFT for arbitrary lattice systems. This has technical advantages over dealing with continuum systems since one can use linear algebra methods in finite vector spaces. We discover two new,
non-trivial classes of NU for N-electron systems with noncollinear spins, both of the “accidental” type. These examples require the ground state 4-density to satisfy certain constraints on the lattice. In the continuum limit, we show that only some well-known special cases survive, and we discuss consequences for practical applications.

We consider a noninteracting N-electron system on a finite-size lattice with P lattice points whose specific geometry is not important for the following. We assume that the kinetic-energy operator $\hat{T}$ has been suitably discretized on this lattice, for example using a finite-difference approach. The single-particle wave functions $\psi_j$ obey the following Schrödinger equation:

$$[\hat{T} + \hat{V} - \mathbf{B} \cdot \mathbf{\sigma}] \psi_j = E_j \psi_j, \quad j = 1, \ldots, 2P.$$  

(2)

For the spatial part of the wave functions we use a localized basis, $\varphi_{ik} = \delta_{ik}$, $i, k = 1, \ldots, P$. The jth eigenstate on lattice site k can then be written as

$$\psi_{jk} = \sum_{i=1}^{P} \varphi_{ik} (c_{jk} \alpha + d_{jk} \beta) = c_{jk} \alpha + d_{jk} \beta,$$

(3)

where $\alpha, \beta$ are the usual two-component spinors. The coefficients $c_{jk}, d_{jk}$ follow from diagonalizing the Hamiltonian matrix associated with the lattice-specific $\hat{T}$ and the given 4-potential $\{v, \mathbf{B}\}$. The resulting 4-density on lattice site k is

$$\begin{pmatrix} n_k \\ m_k^2 \\ m_k^z \\ m_k^\pm \end{pmatrix} = \sum_{j=1}^{N} \begin{pmatrix} |c_{jk}|^2 + |d_{jk}|^2 \\ ic_{jk}d_{jk}^* - ic_{jk}^*d_{jk} \\ |c_{jk}|^2 - |d_{jk}|^2 \end{pmatrix}.$$  

(4)

A trivial case of NU arises when the lattice holds the maximum number of electrons allowed by the Pauli principle, $N = 2P$, for then $n = 2$ and $m = 0$ for all external 4-potentials. We now formulate the first new nontrivial example for NU on lattice systems, which we call local saturation NU.

**Theorem I:** A noninteracting N-electron ground state on a P-point lattice is invariant under a perturbation with 4-potential $\{v' = 0, \mathbf{B}' = \lambda \mathbf{m}/m\}$, $|\lambda| = $ const., if the ground state satisfies $\text{sign}(\lambda)(n_1 - n_2)/m = $ const.

Here, $\bar{n}_1$ and $\bar{n}_2$ denote the two occupied orbital densities, with $\bar{n}_{jk} = |c_{jk}|^2 + |d_{jk}|^2$, $j = 1, 2$. To prove Theorem I, one needs to show that the magnetic field $\mathbf{B}' = \lambda \mathbf{m}/m$ causes at most an orthogonal rotation within the space spanned by the two lowest single-particle eigenstates, $\psi_1$ and $\psi_2$, which leaves the associated 2-particle Slater determinant invariant. Thus,

$$\left( H_0 - \frac{\mathbf{m} \cdot \mathbf{\sigma}}{m} \right) (\gamma_{11} \psi_1 + \gamma_{21} \psi_2) = \varepsilon_i (\gamma_{11} \psi_1 + \gamma_{21} \psi_2),$$

(8)

for $i = 1, 2$, where the $\gamma_{ij}$ form an orthogonal $2 \times 2$ matrix, and $H_0$ is the unperturbed single-particle Hamiltonian whose first two eigenstates and energies are $\psi_{1,2}$ and $E_{1,2}$, see Eq. (2). Now consider a lattice site k. After some straightforward algebra, using $m^\pm = m^z \pm im^y$, one arrives at the following expression:

$$\begin{pmatrix} c_{1k} E_1 - \frac{\lambda_k}{m_k} (c_{1k} m_k^z + d_{1k} m_k^-) \\ d_{1k} E_1 - \frac{\lambda_k}{m_k} (c_{1k} m_k^+ - d_{1k} m_k^z) \end{pmatrix} \begin{pmatrix} c_{2k} E_2 - \frac{\lambda_k}{m_k} (c_{2k} m_k^- + d_{2k} m_k^z) \\ d_{2k} E_2 - \frac{\lambda_k}{m_k} (c_{2k} m_k^+ - d_{2k} m_k^z) \end{pmatrix} = \begin{pmatrix} \gamma_{11} \\ \gamma_{21} \end{pmatrix},$$

(9)

which has the form of a generalized $2 \times 2$ eigenvalue problem. Eq. (9) can be easily transformed into a standard eigenvalue problem by multiplying with the inverse of the right-hand coefficient matrix. Using relations (4), one finds
which leads to a characteristic second-degree polynomial with solution
\[ \varepsilon_{1,2} = \frac{E_1 + E_2}{2} \pm \sqrt{\left(\frac{\Delta E}{2}\right)^2 + \lambda_k^2 \Delta E \frac{n_1 - n_2}{m_k}}, \]
where \( \Delta E = E_1 - E_2 \). We see immediately that for \( \lambda = 0 \) this reduces to \( \varepsilon_{1,2} = E_{1,2} \).

So far, the derivation was for a specific lattice site \( k \). To ensure that the solution \( \varepsilon_{1,2} \) and the associated orthogonal eigenvectors \( \gamma_j \) are the same for all \( P \) lattice sites, we need to impose the constraints
\[ \text{sign}(\lambda_1) \frac{n_1 - n_2}{m_1} = \ldots = \text{sign}(\lambda_P) \frac{n_1P - n_2P}{m_P}, \]
which completes the proof of Theorem II, and determines \( \text{sign}(\lambda_k) \). Global noncollinear NU thus requires two-electron ground states whose orbital densities and total magnetization are related according to Eq. \( 12 \). An explicit example for this will be given below.

Furthermore, from the normalization of the orbital densities, \( \sum_{P} (\bar{n}_1 - \bar{n}_{21}) = 0 \), one finds that global noncollinear NU requires a total magnetization of the form
\[ \text{sign}(\lambda_1)m_1 = -\text{sign}(\lambda_2)m_2 - \text{sign}(\lambda_3)m_3 - \ldots - \text{sign}(\lambda_P)m_P. \]
Some additional remarks are in order:

**One-electron case.** For a single electron, \( 9 \) reduces to
\[ \varepsilon = E_1 - \lambda k n_1/m_k. \]
Again, we require this to be the same on all lattice sites. But, of course, \( n = m \) everywhere for a single electron, so that we end up with the condition \( \lambda = \text{const.}, \) i.e. \( \varepsilon = E_1 - \lambda \). This leads to the statement that any one-electron ground state is unchanged under the influence of a magnetic field \( B' = \lambda m/m \) (provided \( \lambda \) is sufficiently small such that the order of the lowest levels is not changed). This is a special case already contained in the one-electron limit of Theorem I.

**N-electron case.** Global noncollinear NU cannot occur for systems with more than two electrons, which can be seen as follows. The 2-electron derivation is easily generalized up to the point where one arrives at a generalized eigenvalue problem similar to Eq. \( 9 \), but of the type
\[ R^T \varepsilon S^T \gamma = \gamma^T \varepsilon S^T \gamma \] where \( R, S \) are \( 2 \times N \) rectangular matrices, and \( \gamma \) is an \( N \)-component column vector. Such underdetermined problems are singular, that is, one can find at most two eigenvalues, all remaining \( N - 2 \) eigenvalues are undefined \( 11 \). Often one finds no eigenvalues at all. This means that, except for trivial situations or by accident, there is no noncollinear field \( B' \) that results only in a rotation within the single-particle ground-eigenspace. The \( N \)-particle ground-state Slater determinant is thus not invariant for \( N > 2 \).

**2-point lattices.** For the special case \( P = 2 \) one can show that all well-behaved 4-potentials produce two-electron ground states whose magnetization has *same* magnitude on the two lattice sites, \( m_1 = m_2 \). This result is independent of electron interactions. Global noncollinear NU is thus *always* present on 2-point lattices.

An interesting implication of this is that magnetizations with \( m_1 \neq m_2 \) can arise on a 2-point lattice only as ensemble 4-densities of degenerate ground states. Similar consequences of NU are expected for lattices with more than 2 points, i.e., certain classes of 4-densities can only come from ensembles of degenerate ground states. For the case of non-magnetic DFT, the topology of the \( v \)- and \( n \)-spaces on lattices was recently clarified \( 12 \), with the result that pure- and ensemble- \( v \)-representable densities have the same mathematical measure. In SDFT, this general statement no longer holds due to the much richer NU, as is evident from the 2-point lattice example.

Fig. 4 illustrates an example for global noncollinear NU on a linear 3-point lattice with lattice constant \( a \) and sites 1.2.3, using a finite-difference \( \hat{T} \). To discover this and many other examples, the 4-potential parameter space was numerically searched with a multidimensional simplex algorithm \( 12 \) until a two-electron ground state was found to satisfy Eq. \( 12 \), with \( m_1 = m_2 + m_3 \), to within an accuracy of \( 10^{-14} \) (similar numerical techniques yield examples for local saturation NU). Measuring energies in units of \( \hbar^2 / 2ma^2 \), we give the 4-potential and resulting 4-density in Table 1. All magnetic fields \( B' = B \pm \lambda m/m \) (on site 1, \(-\) on sites 2,3) produce the *same* two-electron ground state 4-density (keeping \( v \) fixed), for \(-1.7 < \lambda < 0.7 \). Values of \( \lambda \) outside that range result in level crossings and thus different ground states.

We now turn to the continuum limits of our lattice examples.

**1. Local saturation NU.** It is possible that the local condition \( n(r) = m(r) \) is satisfied in lower-dimensional subspaces (e.g., points or lines) for a continuum system.
are satisfied, with lattice 4-density is dimensionless. Constraints (12) and (13) completely polarized, ferromagnetic case. In the continuum limit, namely, the 1-electron and the well-known special cases of local saturation NU survive. Thus, only the potentials that are confined to the same local subspaces and vanish everywhere else are highly pathological. But 4-potentials that are confined to the same local subspaces and vanish everywhere else are highly pathological (involving delta- or step functions). Thus, only the 1-electron special case survives. (setting $\mu_B = 1$). The lattice 4-density is dimensionless. Constraints (12) and (13) are satisfied, with $|n_1 - n_2|/m = 0.99756$ on each lattice site.

![FIG. 1: Global noncollinear NU for a linear 3-point lattice with $m_1 = m_2 + m_3$. All magnetic fields shown here, where $B_1^z = B_1 + \lambda m_1/m_1$ and $B_{2,3}^z = B_{2,3} - \lambda m_{2,3}/m_{2,3}$ (see Table I), produce the same 4-density (keeping $v$ fixed).](image)

| TABLE I: The 4-potential and 4-density used in Fig. 1 on lattice sites 1, 2, and 3. Potentials and magnetic fields are measured in units of $\hbar^2/2ma^2$ (setting $\mu_B = 1$). The lattice 4-density is dimensionless. Constraints (12) and (13) are satisfied, with $|n_1 - n_2|/m = 0.99756$ on each lattice site. |
|---|---|---|
| $v$ | 1.62192 | 1.55381 | 1.0 |
| $B_1^z$ | 0.87156 | -0.14000 | -0.50808 |
| $B_1^y$ | 0.15523 | 0.23990 | 0.69702 |
| $B_1^x$ | 0.08899 | 0.05986 | -0.54760 |
| $n_1, n_2$ | 0.96869, 0.07157 | 0.02926, 0.20498 | 0.00205, 0.72345 |
| $m_1^z$ | 0.40883 | -0.10282 | -0.46681 |
| $m_2^y$ | 0.08899 | -0.05086 | -0.54760 |
| $m_3^z$ | 0.79605 | -0.12989 | -0.07209 |
| $m$ | 0.89931 | 0.17614 | 0.72317 |

These findings are reassuring for the practical application of SDFT to electronic structure calculations in atoms, molecules and solids. In the collinear case, all that is required in a spin-dependent Kohn-Sham calculation is to fix two constants in the spin-up and spin-down channel, for example through the asymptotic behavior of the potentials. In the noncollinear case, a single constant appears to be sufficient. In situations with full spin polarization, such as in half-metallic ferromagnets, the NU in SDFT is likely to result in the occurrence of discontinuities in the exchange-correlation potential, which will require further study.

On the other hand, spin systems on small lattices are of great interest in the field of spintronics and quantum computation. From a basic point of view, for example, a quantum dot molecule constitutes a two-point lattice. The results presented in this paper will be relevant for the manipulation of electronic charges and spins on such small lattice systems, for instance in performing qubit operations using external magnetic fields.

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