Generalized Kohn-Sham system in one-matrix functional theory

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A system of electrons in a local or nonlocal external potential can be described with one-matrix functional theory (1MFT), which is similar to density-functional theory (DFT) but takes the one-particle reduced density matrix (one-matrix) instead of the density as its basic variable. Within 1MFT, Gilbert derived [Phys. Rev. B **12**, 2111 (1975)] effective single-particle equations analogous to the Kohn-Sham (KS) equations in DFT. The self-consistent solution of these 1MFT-KS equations reproduces not only the density of the original electron system but also its one-matrix. While in DFT it is usually possible to reproduce the density using KS orbitals with integer (0 or 1) occupancy, in 1MFT reproducing the one-matrix requires in general fractional occupancies. The variational principle implies that the KS eigenvalues of all fractionally occupied orbitals must collapse at self-consistency to a single level. We show that as a consequence of the degeneracy, the iteration of the KS equations is intrinsically divergent. Fortunately, the level-shifting method, commonly introduced in Hartree-Fock calculations, is always able to force convergence. We introduce an alternative derivation of the 1MFT-KS equations that allows control of the eigenvalue collapse by constraining the occupancies. As an explicit example, we apply the 1MFT-KS scheme to calculate the ground state one-matrix of an exactly solvable two-site Hubbard model.

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I. INTRODUCTION

Density functional theory (DFT) benefits from operating with the electron density, which as a function of just three coordinates is much easier to work with than the full many-body wave function. According to the Hohenberg-Kohn (HK) theorem,[1] the density of an electron system in a local external potential $v(\vec{r})$ may be found by minimizing a universal energy functional $E_v[n]$, whose basic variable is the density. Remarkably, the density uniquely determines the ground state wave function (if it is nondegenerate), i.e., there can be only one ground state wave function yielding a given density, no matter what $v(\vec{r})$ is. However, if the external potential is nonlocal, then the density alone is generally not sufficient to uniquely determine the ground state (see Appendix for a simple example). Gilbert[2] extended the HK theorem to systems with nonlocal and spin dependent external potential $v(x,x')$, where $x=(\vec{r},\sigma)$. It was proved that (i) the ground state wave function is uniquely determined by the ground state one-matrix (one-particle reduced density matrix) and (ii) there is a universal energy functional $E_v[\gamma]$ of the one-matrix, which attains its minimum at the ground state one-matrix. The one-matrix is defined as

$$\gamma(x,x') = N\int dx_2 \ldots dx_N \rho(x,x_2,\ldots,x_N;x',x_2,\ldots,x_N), \quad (1)$$

where $\int dx = \Sigma_\sigma \int d^3r$ and $\hat{\rho}=\Sigma_i w_i |\Psi_i\rangle\langle\Psi_i|$ is the full N-electron density matrix with ensemble weights w_i such that $\Sigma_i w_i = 1$. An external potential may be nonlocal with respect to the space coordinates and/or the spin coordinates. For example, pseudopotentials are nonlocal in space, and Zeeman coupling $-(\hbar|e|/mc)\vec{B}\cdot\vec{\sigma}$, where $\vec{\sigma}$ is the vector of Pauli matrices, is nonlocal in spin space. The coupling $(|e|/2mc)(\vec{p}\cdot\vec{A}+\vec{A}\cdot\vec{p})$ of an external vector potential to the electron motion may also be treated as a nonlocal potential because $\vec{p}$ is a differential operator. It is rather intuitive that for such external potentials, which couple to the system in more complex ways than the local potential $v(\vec{r})$, it is necessary—in order to permit statements analogous to the HK theorem—to refine the basic variable accordingly. Hence, spin-DFT,[3,4] in which the basic variables are the density and the magnetization density, applies to systems with Zeeman coupling. Current-DFT,[5,6] in which the basic variables are the density and the paramagnetic current density, has the scope to treat systems in which the current is coupled to an external magnetic field. Generally, if one considers an external potential that is nonlocal in space and spin, the necessary basic variable is the one-matrix,[2] which contains all of the single-particle information of the system, including the density, magnetization density, and paramagnetic current density.

The DFT-type approach that takes the one-matrix as basic variable will be referred to here as one-matrix functional theory (1MFT). As in DFT, an exact and explicit energy functional is unknown in general. An important difference between 1MFT and DFT is that the kinetic energy is a simple linear functional of the one-matrix, while it is not a known functional of the density. Thus, in 1MFT the only part of the energy not known explicitly is the electron-electron interaction energy $W[\gamma]$. Several approximate one-matrix energy functionals have been proposed and tested recently (see Ref. 7 and references therein.) A functional based on an approximate construction of the two matrix in terms of the one-matrix has been shown to yield accurate molecular energies, dipole moments, and vertical ionization potentials.[8,9] The so-called BBCn approximations,[10] which are modifications of the Buijse-Baerends functional,[11] have given fairly

accurate results for the potential-energy curves of diatomic molecules[10] and the momentum distribution and correlation energy of the homogeneous electron gas.[7] In Ref. 7, an energy functional was defined by introducing a density dependent fitting parameter into the BBC1 functional and choosing the parameter such that the resulting functional yields the correct correlation energy of the homogeneous electron gas for all values of the density. There is also the prospect of using 1MFT to obtain accurate estimates for the band gaps of insulators.[12] Many of the approximate functionals that have been proposed are similar to an early approximation by Müller.[13] Recently, several special properties of the Müller functional were investigated in detail.[14]

Actual calculations in 1MFT are more difficult than in DFT. The energy functional $E_v[\gamma]$ must be minimized in a space of higher dimension because the one-matrix is a more complex quantity than the density. In the calculations cited above, the energy has been minimized directly by standard methods, e.g., the conjugate gradient method. In DFT the energy is generally not minimized by such direct methods. Instead, the Kohn-Sham (KS) scheme[15] provides an efficient way to find the ground state density. In this scheme, one introduces an auxiliary system of N noninteracting electrons, called the KS system, which experiences an effective local potential $v_s(\vec{r})$. This effective potential is a functional of the density such that the self-consistent ground state of the KS system reproduces the ground state density of the interacting system. It is interesting to ask whether there is also a KS scheme in 1MFT. The question may be stated as follows: does there exist a one-matrix dependent effective potential $v_s(x,x')$ such that, at self-consistency, a system of noninteracting electrons experiencing this potential reproduces the exact ground state one-matrix of the interacting system? Although Gilbert[2] derived such an effective potential, the implications were thought to be "paradoxical" because the KS system was found to have a high (probably infinite) degree of degeneracy. Evidently, the KS eigenvalues in 1MFT do not have the meaning of approximate single-particle energy levels, in contrast to DFT and other self-consistent-field theories, where the eigenvalues may often be interpreted as approximately the negatives of ionization energies, owing to Koopmans' theorem. The status of the KS scheme in 1MFT has remained unresolved,[16,17] and recently it has been argued that the KS scheme does not exist in 1MFT.[7,12,18,19] Gilbert[2] derived effective single-particle equations (generalized KS equations) from the stationary principle for the energy. The effective potential was found to be

$$v_s(x,x') = v(x,x') + \delta W/\delta\gamma(x',x). \tag{2}$$

In this paper, we propose an alternative derivation of the generalized KS equations (1MFT-KS equations), which, in our view, gives insight into the nature of the paradoxical degeneracy of the KS system.

Although the concept of the KS system can indeed be extended to 1MFT, it has in this setting some very unusual properties. In particular, the KS orbitals must be fractionally occupied, for otherwise the KS system could not reproduce the one-matrix of the interacting system, which always has noninteger eigenvalues (occupation numbers). This is different from the situation in DFT, where it is usually possible to reproduce the density using only integer (0 or 1) occupation numbers, or in any case, only a finite number of fractionally occupied states. Due to the necessity of fractional occupation numbers, the 1MFT-KS system cannot be described by a single Slater determinant. However, we find that it can be described by an ensemble of Slater determinants, i.e., a mixed state. In order that the variational principle is not violated, all the states that comprise the ensemble must be degenerate. This implies that the eigenvalues of all fractionally occupied orbitals collapse to a single level. The degeneracy has important consequences for the solution of the KS equations by iteration. We prove that the iteration of the KS equations is intrinsically divergent because the KS system has a divergent response function $\chi_s = \delta\gamma/\delta v_s$ at the ground state. Fortunately, convergence can always be obtained with the level-shifting method.[20] To illustrate explicitly the unique properties of the 1MFT-KS system, we apply it to a simple Hubbard model with two sites. The model describes approximately systems which have two localized orbitals with a strong on-site interaction, e.g., the hydrogen molecule with large internuclear separation.[21] The Schrödinger equation for this model is exactly solvable, and we find that the KS equations in 1MFT and in DFT can be derived analytically. It is interesting to compare 1MFT and DFT in this context. We demonstrate that divergent behavior will appear also in DFT when the operator $1-\chi_s\chi^{-1}$, where χ and χ_s are the density response functions of the interacting and KS systems, respectively, has any eigenvalue with modulus greater than 1. In this expression the null space of χ is assumed to be excluded.

This paper is organized as follows. In Sec. II, we derive the KS equations in 1MFT and discuss how to solve them self-consistently by iteration. In Sec. III, we compare three approaches to ground state quantum mechanics—direct solution of the Schrödinger equation, 1MFT, and DFT—by using them to solve the two-site Hubbard model.

II. KOHN-SHAM SYSTEM IN ONE-MATRIX FUNCTIONAL THEORY

It is not obvious that a KS-type scheme exists in 1MFT for the following reason. Recall that in DFT the KS system consists of N noninteracting particles and reproduces the density of the interacting system. The density of the KS system, if it is nondegenerate, is the sum of contributions of the N lowest energy occupied orbitals

$$n(\vec{r}) = \sum_{i}^{\text{occ}} |\phi_i(\vec{r})|^2. \tag{3}$$

On the other hand, in 1MFT the KS system should reproduce the one-matrix of the interacting system. The eigenfunctions of the one-matrix are the so-called natural orbitals, and the eigenvalues are the corresponding occupation numbers.[22] Occupying the N lowest energy orbitals in analogy to Eq. (3), one obtains

$$\gamma(x,x') = \sum_{i}^{\text{occ}} \phi_i(x)\phi_i^*(x'). \tag{4}$$

Such an expression, in which the orbitals have only integer (0 or 1) occupation numbers, cannot reproduce the one-matrix of an interacting system because the orbitals of an interacting system have generally fractional occupation (see the discussion in Sec. II A). The difference between the one-matrix in Eq. (4) and the one-matrix of an interacting system is clearly demonstrated by the so-called idempotency property. The one-matrix in Eq. (4) is idempotent, i.e., $\int dx' \gamma(x,x')\gamma(x',x'') = \gamma(x,x'')$, while the one-matrix of an interacting system is never idempotent. However, if the KS system is degenerate and its ground state is an ensemble state, the one-matrix becomes

$$\gamma(x,x') = \sum_{i} f_i \phi_i(x)\phi_i^*(x'), \tag{5}$$

with fractional occupation numbers f_i. The N-electron ground state density matrix of the KS system is $\hat{\rho}_s = \Sigma_i w_i |\Phi_i\rangle\langle\Phi_i|$, where the Φ_i are Slater determinants each formed from N degenerate KS orbitals. The occupation numbers f_i are related to the ensemble weights w_i by

$$f_i = \sum_{j} w_j \Theta_{ji}, \tag{6}$$

where Θ_{ji} equals 1 if ϕ_i is one of the orbitals in the determinant Φ_j and 0 otherwise.[23]

A. Derivation of the one-matrix functional theory Kohn-Sham equations

In this section, we discuss Gilbert's derivation[2] of the KS equations in 1MFT and propose an alternative derivation. We begin by reviewing the definition of the universal one-matrix energy functional $E_v[\gamma]$.

One-matrix functional theory describes the ground state of a system of N electrons with the Hamiltonian $\hat{H} = \Sigma_{i=1}^{N}(\hat{t}_i + \hat{v}_i) + \hat{W}$, where $\hat{t} = -\nabla_r^2/2$ is the kinetic-energy operator, $\hat{v}$ is the local or nonlocal external potential operator, and $\hat{W} = \Sigma_{i<j}|\vec{r}_i - \vec{r}_j|^{-1}$ is the electron-electron interaction (in atomic units $\hbar = m = e = 1$). The ground state one-matrix and ground state energy can be found by minimizing the functional

$$E_v[\gamma] = \text{Tr}[(\hat{t} + \hat{v})\gamma] + W[\gamma], \tag{7}$$

where

$$W[\gamma] = \langle \Psi_0 | \hat{W} | \Psi_0 \rangle. \tag{8}$$

By extending the HK theorem, Gilbert[2] proved that a nondegenerate ground state wave function Ψ_0 is uniquely determined by the ground state one-matrix, i.e., Ψ_0 is a functional of γ. For this reason the interaction energy, as defined in Eq. (8), is a functional of γ. It is apparent that Eq. (8) defines $W[\gamma]$ only for γ that are the ground state one matrices of some system (with Hamiltonian $\hat{H}$). In this paper, a one-matrix is said to be v representable (VR) if it is the ground state one-matrix of some system with local or *nonlocal* external potential. Gilbert remarked [see the discussion between Eqs. (2.24) and (2.25) in Ref. 2] that, in principle, the domain of $W[\gamma]$ can be extended to the space of ensemble N-representable (ENR) one matrices. A one-matrix is said to be ENR if it can be constructed via Eq. (1) from some N-electron density matrix $\hat{\rho} = \Sigma_i w_i |\Psi_i\rangle\langle\Psi_i|$, which is not required to be a ground state ensemble. One possible extension to the ENR space is provided by the so-called constrained search functional[16,24]

$$W[\gamma] = \min_{\hat{\rho}\to\gamma} \text{Tr}(\hat{W}\hat{\rho}), \tag{9}$$

where the interaction energy $\text{Tr}(\hat{W}\hat{\rho})$ is minimized in the space of N-electron density matrices $\hat{\rho}$ that yield γ via Eq. (1). Definition (9) is a natural extension to the ENR space because when it is adopted Eq. (7) may be expressed as

$$E_v[\gamma] = \min_{\hat{\rho}\to\gamma} \text{Tr}(\hat{H}\hat{\rho}). \tag{10}$$

This is a variational functional which attains its minimum at the ground state one-matrix, as seen from

$$\min_{\gamma} E_v[\gamma] = \min_{\hat{\rho}} \text{Tr}(\hat{H}\hat{\rho}) = E_0, \tag{11}$$

where E_0 is the ground state energy. The extension to the ENR domain is significant, especially for applications of the variational principle, because the conditions a one-matrix must satisfy to be ENR are known and simple to impose on a trial one-matrix, while the conditions for v representability are unknown in general. The necessary and sufficient conditions[25] for a one-matrix γ to be ENR are (i) γ must be Hermitian, (ii) $\int dx \gamma(x,x) = N$, and (iii) all eigenvalues of γ (occupation numbers) must lie in the interval $[0,1]$. The third condition is a consequence of the Pauli exclusion principle.

The 1MFT-KS equations were derived[2] from the stationary conditions for the energy with respect to arbitrary independent variations of the natural orbitals ϕ_i and angle variables θ_i chosen to parametrize the occupation numbers according to $f_i = \cos^2\theta_i$ $(0 \le \theta_i \le \pi/2)$. For the purpose of describing a variation in the ENR space, this set of variables, namely, $\{\delta\phi_i, \delta\phi_i^*, \delta\theta_i\}$, is redundant. An arbitrary set of such variations may or may not correspond to an ENR variation, and when it does the variations will not be linearly independent. This causes no difficulty, of course, because it is always possible to formulate stationary conditions in a space whose dimension is higher than necessary, provided the appropriate constraints are enforced with Lagrange multipliers. Accordingly, the Lagrange multiplier terms $\Sigma_{ij}\lambda_{ij}(\langle\phi_i|\phi_j\rangle - \delta_{ij})$ which maintain the orthogonality of the orbitals and the term $\mu(\Sigma_i f_i - N)$ which maintains the total particle number were introduced. The KS equations were found to be

$$(\hat{t} + \hat{v}_s)|\phi_i\rangle = \epsilon_i|\phi_i\rangle, \tag{12}$$

where the kernel of the effective potential is $v_s(x,x') = v(x,x') + \delta W/\delta\gamma(x',x)$, if the functional derivative exists. The stationary conditions imply that all fractionally occupied KS orbitals have the same eigenvalue $\epsilon_i = \mu$. Gilbert[2] described this result as paradoxical because in interacting systems essentially all orbitals are fractionally occupied.

The above stationary conditions assume E_v to be stationary with respect to variations in the ENR space (except variations of occupation numbers equal to exactly 0 or 1 in the ground state, which are excluded by the parametrization). However, it is not known, in general, whether E_v is stationary in the ENR space; the minimum property [Eq. (11)] ensures only that it is variational. Recall that the ENR space consists of all γ that can be constructed from an ensemble, and the energy of an ensemble is not stationary with respect to variations of the many-body density matrix $\hat{\rho}$. Therefore, the stationary conditions applied in the ENR space may be too strong. On the other hand, the Rayleigh-Ritz variational principle guarantees that E_v is stationary with respect to variations in the VR space,[26] but it is not known how to determine whether a given γ is VR. Hence, it is not known how to constrain the variations of γ to the VR space. Nevertheless, it may be that, in some systems, the entire neighborhood of γ_{gs} in the ENR space is also VR. In such cases, E_v is stationary in the ENR space, and the stationary conditions applied in Ref. 2 are satisfied at the ground state.

We find it helpful to construct an alternative derivation of the KS equations. Consider the energy functional

$$\mathcal{G}_v[\gamma] = E_v[\gamma] - \sum_j \epsilon_j (f_j - q_j), \tag{13}$$

where $\epsilon_j = \epsilon_j(\{q_i\})$ are Lagrange multipliers that constrain the occupation numbers f_j of the natural orbitals to chosen values q_j, which satisfy $0 \leq q_j \leq 1$ and $\Sigma_j q_j = N$. These Lagrange multipliers allow us to investigate the degeneracy of the KS eigenvalues, which leads to the "paradox" described by Gilbert.[2] We have omitted the Lagrange multipliers λ_{ij} and μ used in Gilbert's derivation.[2] They are not necessary in our derivation because we formulate the stationary conditions with respect to variations of the one-matrix instead of the orbitals and occupation numbers. We adopt definition (9) for $W[\gamma]$, so the domain of $\mathcal{G}_v[\gamma]$ is the ENR space. Therefore, the f_j in Eq. (13) are not independent variables because they must satisfy $\Sigma_j f_j = N$; in fact, they are functionals of γ, namely, $f_j = \langle \phi_j[\gamma] | \hat{\gamma} | \phi_j[\gamma] \rangle$. A variation $\delta\gamma$ will be said to be admissible if $\gamma_{\mathrm{gs}} + \delta\gamma$ is ENR. For convenience we assume that the static response function $\chi = \delta\gamma / \delta v$ for the interacting system under consideration has no null vectors apart from the null vectors associated with (a) a constant shift of the potential (which is a null vector also in DFT) and (b) integer occupied orbitals, i.e., orbitals with occupation numbers exactly 0 or 1. If χ has additional null vectors, the following derivation must be modified; the necessary modifications are discussed below. Granting the above assumption, $\mathcal{G}_v$ is guaranteed to be stationary with respect to an arbitrary admissible variation of γ. The KS equations can be derived from the stationary condition $\delta\mathcal{G}_v = 0$. The first variation of $\mathcal{G}_v$ is

$$\begin{aligned}
\delta\mathcal{G}_v &= \mathrm{Tr}[(\hat{t} + \hat{v})\delta\hat{\gamma}] + \mathrm{Tr}(\hat{w}\delta\hat{\gamma}) - \sum_i \epsilon_i \delta f_i \\
&= \sum_{ij} \langle \phi_i | (\hat{t} + \hat{v} + \hat{w}) | \phi_j \rangle \langle \phi_j | \delta\hat{\gamma} | \phi_i \rangle \\
&\quad - \sum_{ij} \epsilon_i \langle \phi_i | \phi_j \rangle \langle \phi_j | \delta\hat{\gamma} | \phi_i \rangle \\
&= \sum_{ij} (h_{ij} - \epsilon_i \delta_{ij}) \delta\gamma_{ji},
\end{aligned} \tag{14}$$

where the variation of the one-matrix is expressed as $\delta\gamma_{ij} = \langle \phi_i | \delta\hat{\gamma} | \phi_j \rangle$ in the basis of natural orbitals that minimize $\mathcal{G}_v$ and $\delta W = \mathrm{Tr}(\hat{w}\delta\hat{\gamma})$ defines a single-particle operator $\hat{w}$. In Eq. (14), we used the relation $\delta f_i = \langle \phi_i | \delta\hat{\gamma} | \phi_i \rangle$, which follows from the Hellmann-Feynman theorem. We have also defined the single-particle Hermitian operator

$$\hat{h} = \frac{\delta E_v}{\delta\gamma} = \hat{t} + \hat{v} + \hat{w}, \tag{15}$$

which will be seen to be the KS Hamiltonian. If the last line of Eq. (14) is to be zero for an arbitrary admissible variation $\delta\gamma$, then we must have $h_{ij} - \epsilon_j \delta_{ij} = c\,\delta_{ij}$. An arbitrary constant c appears because the $\delta\gamma_{ii}$ are not linearly independent, in particular, $\Sigma_i \delta\gamma_{ii} = 0$. If we choose $c = 0$, we can identify the Lagrange multipliers ϵ_i with the KS eigenvalues. We assume this choice in all of the following. The matrix elements h_{ij} are functionals of the one-matrix, and the one-matrix that satisfies the stationary conditions $h_{ij} - \epsilon_j \delta_{ij} = 0$ can be found by solving self-consistently the single-particle equations

$$\hat{h} | \phi_i \rangle = \epsilon_i | \phi_i \rangle \tag{16}$$

together with Eq. (5) where $f_i = q_i$. These are the KS equations in 1MFT. If they are solved self-consistently with the occupation numbers fixed to the values q_i, they give the orbitals which minimize E_v subject to the constraints $f_i = q_i$. The KS potential is $\hat{v}_s = \hat{v} + \hat{w}$. The term $\hat{w}$ is the effective contribution of the electron-electron interaction to the KS potential. In coordinate space, its kernel is

$$w(x,x') = \langle x | \hat{w} | x' \rangle = \frac{\delta W}{\delta\gamma(x',x)}, \tag{17}$$

which recovers Gilbert's result.[2] The kernel of the KS Hamiltonian may be written in the familiar form,

$$\begin{aligned}
h(x,x') &= \delta(x - x') \left(-\frac{1}{2}\nabla_r^2 \right) + v(x,x') + \delta(x - x') v_H(x) \\
&\quad + v_{\mathrm{xc}}(x,x'),
\end{aligned} \tag{18}$$

where $v(x,x')$ is the external potential and $w(x,x')$ has been divided into the Hartree $v_H(x)$ and exchange-correlation $v_{\mathrm{xc}}(x,x')$ potentials. In 1MFT, the exchange-correlation potential is nonlocal.

The 1MFT-KS scheme optimizes the orbitals for a chosen set of occupation numbers, but it does not itself provide a rule for choosing the occupation numbers. On this point, it is different from the DFT-KS scheme, where the occupation numbers are uniquely determined by the Aufbau principle ($T = 0$ Fermi statistics).[27] In 1MFT, the KS equations have a self-consistent solution for any $\{q_i\}$ that satisfy $0 \leq q_i \leq 1$ and $\Sigma_i q_i = N$. The Lagrange multipliers ϵ_i, which are seen to be the KS eigenvalues, adopt values such that the minimum of $\mathcal{G}_v$ occurs for a one-matrix γ_{min} whose occupation numbers are precisely the set $\{q_i\}$. Therefore, the unconstrained minimum of $\mathcal{G}_v$ coincides with the minimum of E_v subject to the constraints $f_i = q_i$. To find the ground state occupation num-

bers, $\{q_i^{\rm gs}\}$, one can search for the minimum of the function $G_v(\{q_i\})=\min_\gamma \mathcal{G}_v[\gamma]$, where the minimization of $\mathcal{G}_v[\gamma]$ can be performed by the KS scheme.

What can be said about the KS eigenvalues ϵ_j? As we have assumed that E_v is stationary with respect to all admissible variations except variations of occupation numbers equal to 0 or 1, we have

$$\epsilon_j(\{q_i^{\rm gs}\}) = \langle \phi_j|\hat{h}[\gamma_{\rm gs}]|\phi_j\rangle = \langle \phi_j| \frac{\delta E_v}{\delta \gamma}\bigg|_{\gamma_{\rm gs}} |\phi_j\rangle = 0 \quad (19)$$

for all j such that $0<q_j^{\rm gs}<1$. Thus, we find that the KS eigenvalues of all orbitals that are fractionally occupied in the ground state collapse to a single level when the chosen set of occupation numbers approaches their ground state values, i.e., as $q_i \to q_i^{\rm gs}$. In Gilbert's derivation[2] of the 1MFT-KS equations, arbitrary variations of the occupation numbers were allowed, and the condition $\Sigma_i f_i = N$ was enforced by the Lagrange multiplier μ, the chemical potential. In such an approach, $c=\mu$ and ϵ_i collapse to μ instead of 0. Equation (19) does not apply to orbitals with occupation numbers exactly 0 or 1 because these values lie on the boundary of the allowed interval [0,1] specified by ENR condition (iii). All that can be concluded from the fact that E_v has a minimum in the ENR space are $\epsilon_j \geq 0$ for orbitals with $f_j=0$ and $\epsilon_j \leq 0$ for orbitals with $f_j=1$. States with occupation numbers exactly 0 or 1 have been called "pinned states."[7,12] Instances of such states in real systems have been reported,[28] though their occurrence is generally considered to be exceptional.[7,12]

At the ground state, the eigenvalues collapse and the KS Hamiltonian becomes the null operator

$$\hat{h}[\gamma_{\rm gs}] = \hat{0} \quad (20)$$

in the subspace of fractionally occupied orbitals. Gilbert[2] described a similar result (with $\mu\hat{I}$ replacing $\hat{0}$) as paradoxical, which is a view that has been repeated.[16,17] The problem with Eq. (20) is that while we expect the KS Hamiltonian to define the natural orbitals, *any* state is an eigenstate of the null operator. However, the KS Hamiltonian is a functional of the one-matrix, and when the occupation numbers are perturbed from their ground state values, the degeneracy is lifted and the KS Hamiltonian does define unique orbitals. In the KS scheme outlined above, this corresponds to the optimization of the orbitals for occupation numbers fixed to values q_i, perturbed from the ground state values. In the limit that the occupation numbers approach their ground state values, the optimal orbitals approach the ground state natural orbitals. The natural orbitals which belong to a degenerate occupation number are only defined modulo unitary rotation in the degenerate subspace. The KS eigenvalues generally split linearly with respect to the perturbation from the ground state. In particular,

$$\frac{\partial \epsilon_i}{\partial q_j} = \int dy dy' \langle \phi_i| \frac{\delta \hat{h}}{\delta \gamma(y,y')} \frac{\partial \gamma(y,y')}{\partial q_j} |\phi_i\rangle$$

$$= -\int dx dx' dy dy' \phi_i^*(x)\phi_i(x') \times \chi^{-1}(xx',yy')\phi_j(y)\phi_j^*(y'). \quad (21)$$

Here, χ is the static response function defined as

$$\chi(x,x';y,y') = \frac{\delta \gamma(x,x')}{\delta v(y,y')}. \quad (22)$$

The relation $\delta h/\delta\gamma = -\chi^{-1}$ used in Eq. (21) is derived in Sec. II B. If χ has a null space, its inverse is defined only on a restricted space. For example, Eq. (21) does not apply to pinned states as there is a null vector associated with each pinned state (see below).

Our derivation of the 1MFT-KS equations, in fact, assumes that the static response function χ of the interacting system has no null vectors except for those associated with pinned states and a constant shift of the potential. We now show that this guarantees $\mathcal{G}_v$ to be stationary. If the interacting system has any other null vectors, we can no longer be certain that $\mathcal{G}_v$ is stationary and the derivation should be modified as described below. We have remarked already (see Ref. 26) that $\mathcal{G}_v$ is stationary in the VR space, i.e., it satisfies the stationary condition $\delta\mathcal{G}_v=0$ with respect to an arbitrary variation of the one-matrix in the VR space. However, our derivation of the KS equations requires $\mathcal{G}_v$ to be stationary in the ENR space. As the VR space is a subspace of the ENR space, this is a stronger condition. The assumption that χ has no null vectors (apart from those associated with pinned states) is equivalent to assuming that any ENR variation (apart from variations of the pinned occupation numbers) is also a VR variation. For if χ has no null vectors, then it is invertible and any ENR variation $\delta\hat{\gamma}$ can be induced by the perturbation $\delta\hat{v}=\chi^{-1}\delta\hat{\gamma}$.[29] Hence, with the above assumption, $\mathcal{G}_v$ is guaranteed to be stationary with respect to any ENR variation. The above arguments do not apply to variations of pinned occupation numbers because there are null vectors associated with such variations; nevertheless, $\mathcal{G}_v$ is stationary with respect to such variations as this is maintained by the Lagrange multipliers ϵ_i. It is now clear how to modify the derivation of the KS equations when χ has additional null vectors. By introducing Lagrange multipliers, the additional null vectors can be treated in analogy with the pinned states. For example, suppose χ has one additional null vector $\hat{u}=\Sigma_{ij}u_{ij}|\phi_i\rangle\langle\phi_j|$, where $\hat{u}$ is Hermitian and $\mathrm{Tr}(\hat{u}\hat{u})=1$. The energy functional $\mathcal{G}_v'[\gamma]=\mathcal{G}_v[\gamma]-\kappa(\gamma_u-p_u)$ will be stationary with respect to an arbitrary variation in the ENR space. Here, the Lagrange multiplier κ enforces the constraint $\gamma_u=p_u$, where $\gamma_u=\mathrm{Tr}(\hat{\gamma}\hat{u})$ is the component of $\hat{\gamma}$ corresponding to $\hat{u}$. The stationary condition $\delta\mathcal{G}_v'=0$ leads to the set of equations $h_{ij}-\epsilon_j\delta_{ij}-\kappa u_{ij}=0$ in the basis of natural orbitals. The one-matrix that satisfies these equations can be found by solving self-consistently the eigenvalue equation $\hat{h}|\xi_i\rangle=\omega_i|\xi_i\rangle$ together with $\gamma(x,x')=\Sigma_{ijk}q_i S_{ji}S_{ki}^*\xi_j(x)\xi_k^*(x')$, where S is the unitary matrix that diagonalizes the matrix u in the basis of natural orbitals, i.e., $SuS^\dagger$ is diagonal. The energy of the self-consistent solution defines a function $G_v'(\{q_i\},p_u)$, for which the minimum with respect to $\{q_i\}$ and p_u is the ground state energy. It may not be known in advance whether the response function of a given interacting system will have null vectors. Therefore, it is helpful to understand how null vectors occur.

Null vectors of χ are connected with the so-called nonuniqueness problem[3,30,31] in various extensions of DFT. A system with the ground state Ψ_0 is said to have a nonuniqueness problem if there is more than one external potential for which Ψ_0 is the ground state. The Schrödinger equation defines a unique map from the external potential to the ground state wave function (if it is nondegenerate), but when there is more than one external potential yielding the same ground state wave function, the map cannot be inverted uniquely. In 1MFT the generality of the external potential (nonlocal in space and spin coordinates) allows greater scope for nonuniqueness than in the other extensions of DFT. Of course, every degree of nonuniqueness is a null vector of χ because if $\delta\hat{v}$ does not change the ground state wave function, it does not change the one-matrix either, and hence it is a null vector. In fact, every null vector of χ can be attributed to nonuniqueness; the existence of a null vector $\delta\hat{v}$ that induced a nonzero $\delta\Psi_0$ would contradict the one-to-one relationship $\gamma \leftrightarrow \Psi_0$ proved by the extension of the HK theorem to 1MFT.[2] It was mentioned above that there are null vectors associated with the pinned states. Suppose ϕ_k is a natural orbital with occupation number $f_k=0$ in the ground state. The perturbation of the external potential $\delta\hat{v}=\lambda|\phi_k\rangle\langle\phi_k|$ does not change the ground state if the system has an energy gap between the ground state and excited states and λ is small enough because $\delta\hat{V}|\Psi_0\rangle=0$, where $\delta\hat{V}=\int dxdx'\,\hat{\psi}^\dagger(x)\delta v(x,x')\hat{\psi}(x')$ and $\hat{\psi}$ and $\hat{\psi}^\dagger$ are field operators. If $f_k=1$, $\delta\hat{V}|\Psi_0\rangle=\lambda|\Psi_0\rangle$ and the ground state is again unchanged by the perturbation. The "vector" $|\phi_k\rangle\langle\phi_k|$ is therefore a null vector of χ if ϕ_k is a pinned state. Another type of nonuniqueness, which has been called systematic nonuniqueness,[31] is related to constants of the motion. Suppose $\hat{A}=\int dxdx'\,\hat{\psi}^\dagger(x)a(x,x')\hat{\psi}(x')$ is a constant of the motion. The ground state, if it is nondegenerate, is an eigenstate of $\hat{A}$ as constants of the motion commute with the Hamiltonian. If the system has an energy gap between the ground state and the first-excited state, then a perturbation $\delta\hat{V}=\lambda\hat{A}$ will not change the ground state wave function if λ is small enough. Thus, $\hat{A}$ is a null vector of χ.

B. Iteration of the Kohn-Sham equations

In this section we prove that the "straightforward" procedure for iterating the KS equations [Eqs. (5) and (16)] is intrinsically divergent. The KS equations are nonlinear because the KS Hamiltonian itself depends on the one-matrix. In favorable cases such nonlinear equations can be solved by iteration. Given a good initial guess for the one-matrix, iteration may lead to the self-consistent solution corresponding to the ground state. In order to iterate Eq. (16), one needs an algorithm to define the one-matrix of iteration step $n+1$ from the one-matrix of step n, i.e., one needs to "close" the KS equations. In Sec. II A, we saw that in the 1MFT-KS scheme the occupation numbers f_i are held fixed during the optimization of the natural orbitals. The following is a straightforward algorithm that optimizes the natural orbitals: (i) the KS Hamiltonian for step $n+1$ is defined by

$$\hat{h}^{(n+1)}=\hat{h}[\gamma^{(n)}], \tag{23}$$

where $\hat{h}$ is given by Eq. (15) and $\gamma^{(n)}$ is the one-matrix of iteration step n; (ii) the eigenstates of $\hat{h}^{(n+1)}$ are taken as the natural orbitals of step $n+1$; (iii) the one-matrix of step $n+1$ is constructed from the natural orbitals of step $n+1$ by the expression

$$\gamma^{(n+1)}(x,x')=\sum_i f_i\phi_i^{(n+1)}(x)\phi_i^{*(n+1)}(x'). \tag{24}$$

Operation (ii) requires further comment. Let u_i be the eigenstates of the KS Hamiltonian $\hat{h}^{(n+1)}$. The natural orbitals $\phi_i^{(n+1)}$ are chosen from among the u_i such that the $\phi_i^{(n+1)}$ have maximum overlap with the $\phi_i^{(n)}$, i.e., $\mathrm{Tr}[(\hat{\gamma}^{(n+1)}-\hat{\gamma}^{(n)})^2]$ is the minimum possible. If the above procedure converges to the stationary one-matrix $\gamma_{\min}$ giving the lowest energy possible for the fixed set of occupation numbers, then it defines the function $G_v(\{f_i\})$, introduced in Sec. II A, for which the ground state energy is the absolute minimum. However, as we will show, for any set of occupation numbers $\{f_i\}$ sufficiently close to the ground state occupation numbers, this procedure never converges to $\gamma_{\min}$. In other words, the straightforward algorithm defines an iteration map for which the ground state γ_{gs} is an unstable fixed point.

The divergence of the iteration map can be revealed by a linear analysis of the fixed point. Suppose the occupation numbers are fixed to values perturbed from their ground state values by δf_i. Let us consider an iteration step n and ask whether the next iteration takes us closer to the stationary point $\gamma_{\min}$ that gives the minimum energy for the fixed occupation numbers. The linearization of the iteration map at the stationary point gives

$$\begin{aligned}\delta\hat{\gamma}^{(n+1)}&=\hat{\gamma}^{(n+1)}-\hat{\gamma}_{\min}\approx\hat{\chi}_s[\gamma_{\min}](\hat{v}_s^{(n+1)}-\hat{v}_s^{\min})\\&=\hat{\chi}_s[\gamma_{\min}](\hat{h}^{(n+1)}-\hat{h}^{\min})\approx-\hat{\chi}_s[\gamma_{\min}]\hat{\chi}^{-1}\delta\hat{\gamma}^{(n)},\end{aligned} \tag{25}$$

where $\hat{v}_s=\hat{v}+\hat{v}_H+\hat{v}_{\mathrm{xc}}$ is the KS potential. The response function χ was defined in Eq. (22). The KS response function is

$$\begin{aligned}\chi_s(x,x';y,y')&=\frac{\delta\gamma(x,x')}{\delta v_s(y,y')}\\&=\sum_i\sum_{j\neq i}\frac{f_i-f_j}{\epsilon_i-\epsilon_j}\phi_j(x)\phi_i^*(x')\phi_j^*(y)\phi_i(y').\end{aligned} \tag{26}$$

In the last line of Eq. (25), we have used

$$\hat{h}^{(n+1)}-\hat{h}^{\min}\approx-\hat{\chi}^{-1}\delta\hat{\gamma}^{(n)}, \tag{27}$$

which can be established by the following arguments. First consider

$$\hat{h}^{(n+1)}-\hat{h}^{\min}\approx\left.\frac{\delta\hat{h}[\gamma]}{\delta\gamma}\right|_{\gamma_{\min}}\delta\hat{\gamma}^{(n)}, \tag{28}$$

which follows from Eq. (23). The KS Hamiltonian is an implicit functional of the one-matrix, and Eq. (28) defines the

first-order change in the KS Hamiltonian with respect to a perturbation of that implicit dependence. Since the occupation numbers are close to their ground state values, we may make the replacement

$$\left.\frac{\delta\hat{h}}{\delta\gamma}\right|_{\gamma_{\min}} \rightarrow \left.\frac{\delta\hat{h}}{\delta\gamma}\right|_{\gamma_{\rm gs}}, \tag{29}$$

which is valid to $\mathcal{O}[\max(|\delta f_i|)]$. Thus, to establish Eq. (27) it is sufficient to show $\delta\hat{h}/\delta\gamma=-\hat{\chi}^{-1}$ at the ground state. The KS Hamiltonian $\hat{h}$ is associated with the original many-body Hamiltonian $\hat{H}$, which has external potential $v(x,x')$. According to Eq. (20),[32] $\hat{h}[\gamma_{\rm gs}]=\hat{0}$. Consider now a Hamiltonian $\hat{H}'$ with a slightly different external potential $v'(x,x')=v(x,x')+\delta v(x,x')$ such that its ground state one-matrix is $\gamma'_{\rm gs}=\gamma_{\rm gs}+\delta\gamma$. The associated KS Hamiltonian is $\hat{h}'=\hat{h}+\hat{v}'-\hat{v}$. At the new ground state, $\hat{h}'[\gamma'_{\rm gs}]=\hat{0}$. This allows us to relate $\delta\hat{h}$ to $\delta\hat{v}$ as

$$\delta\hat{h}=\hat{h}[\gamma'_{\rm gs}]-\hat{h}[\gamma_{\rm gs}]=\hat{h}[\gamma'_{\rm gs}]+\delta\hat{v}-\delta\hat{v}=-\delta\hat{v}. \tag{30}$$

Finally, using $\delta\hat{v}=\hat{\chi}^{-1}\delta\hat{\gamma}$ we obtain $\delta\hat{h}/\delta\gamma=-\hat{\chi}^{-1}$, which verifies Eq. (27).

Returning to the question of convergence, we see that Eq. (25) implies that the next iteration takes us farther away from the stationary point $\gamma_{\min}$. The deviation $\delta\hat{\gamma}^{(n+1)}$ is related to the deviation $\delta\hat{\gamma}^{(n)}$ by the operator $-\hat{\chi}_s[\gamma_{\min}]\hat{\chi}^{-1}$. For occupation numbers sufficiently close to the ground state values, generally all eigenvalues of this operator have modulus greater than 1 (the null space of χ is assumed to be excluded). Therefore, any perturbation $\delta\hat{\gamma}$ from the ground state is amplified by iteration. According to Eqs. (21) and (26) the KS response diverges as $\gamma\rightarrow\gamma_{\rm gs}$ because $\epsilon_i-\epsilon_j\sim\mathcal{O}[\max(|\delta f_k|)]$. The ground state is said to be an unstable fixed point of the iteration map. A fixed point is stable if and only if all eigenvalues of the linearized iteration map have modulus of less than 1.

C. Level-shifting method

In Sec. II B, we showed that the straightforward iteration of the KS equations is intrinsically divergent. To obtain a practical KS scheme, the iteration map must be modified. It is well known that divergence can be encountered also in the Hartree-Fock approximation. In order to achieve convergence, various modifications of the iteration procedure have been introduced, for example, Hartree damping (also called configuration mixing) and level shifting.[20] It has been suggested[33] that the level-shifting method could also be used in 1MFT. The level-shifting method is particularly attractive in 1MFT because it manifestly prevents the collapse of eigenvalues that is the origin of divergent behavior. In this section we obtain a necessary and sufficient condition for convergence from a linear analysis of the iteration map with level shifting.

In the straightforward iteration procedure, the change in the orbitals, to first order, from iteration step n to iteration step $n+1$ is

$$\phi_i^{(n+1)}(x)-\phi_i^{(n)}(x)=\sum_{j\neq i}\frac{\langle\phi_j|\hat{h}^{(n+1)}-\hat{h}^{(n)}|\phi_i\rangle}{\epsilon_i-\epsilon_j}\phi_j(x), \tag{31}$$

where $\hat{h}^{(n)}$ is the KS Hamiltonian for iteration step n and on the right hand side the orbitals and eigenvalues are from iteration step n. In the level-shifting method, the first-order change in the orbitals given by Eq. (31) is altered by applying the shifts $\epsilon_i\rightarrow\epsilon_i+\zeta_i$ to the eigenvalues in the denominator. To first order, this modification is equivalent to adding the term $\hat{\Delta}=\Sigma_i\zeta_i|\phi_i^{(n)}\rangle\langle\phi_i^{(n)}|$ to the KS Hamiltonian for step $n+1$. Let $\hat{h}_\zeta=\hat{h}+\hat{\Delta}$ define the level shifted Hamiltonian. Repeating the linear analysis of Sec. II B, we find

$$\begin{aligned}\delta\hat{\gamma}^{(n+1)}&\approx\hat{\chi}_s[\gamma_{\min}](\hat{v}_s^{(n+1)}-\hat{v}_s^{\min})=\hat{\chi}_s[\gamma_{\min}](\hat{h}_\zeta^{(n+1)}-\hat{h}_\zeta^{\min})\\&\approx(-\hat{\chi}_s[\gamma_{\min}]\hat{\chi}^{-1}+\hat{\Omega})\delta\hat{\gamma}^{(n)},\end{aligned} \tag{32}$$

where we have defined the operator $\hat{\Omega}$ with the kernel,

$$\begin{aligned}\Omega(xx',yy')&=\int dzdz'\chi_s(xx',zz')\frac{\delta\Delta(zz')}{\delta\gamma(yy')}\\&=\sum_i\sum_{j\neq i}\phi_j(x)\phi_i^*(x')\phi_j^*(y)\phi_i(y').\end{aligned} \tag{33}$$

From Eq. (32), we obtain a necessary and sufficient condition for the convergence of the iteration map. All of the eigenvalues of the operator

$$\hat{\mathcal{A}}=-\hat{\chi}_s[\gamma_{\min}]\hat{\chi}^{-1}+\hat{\Omega} \tag{34}$$

must have modulus of less than 1. The dependence on the level shift parameters ζ_i enters only through the shifted eigenvalues in the denominator of χ_s. The level-shifting method is effective because it prevents the divergence of χ_s at the ground state and there is a cancellation between the two terms in Eq. (34). Unfortunately, the convergence criterion depends on χ, which is unknown at the outset of a calculation. In Sec. III B, the level-shifting method is applied in an explicit example.

D. Properties of the Kohn-Sham system

The distinguishing feature of the KS system in 1MFT is the degeneracy of the eigenvalues. This has surprising consequences. We showed in Sec. II A that the KS eigenvalues split linearly as we move away from the ground state one-matrix. Therefore, the total KS energy changes linearly with respect to the displacement, i.e., $E_s[\gamma_{\rm gs}+\delta\gamma]-E_s[\gamma_{\rm gs}]\propto\delta\gamma$, where $E_s[\gamma]=\mathrm{Tr}(\hat{h}[\gamma]\gamma)$ (for a specific example see Fig. 4 in Sec. III B). This is surprising because such linear changes do not occur for the energy functional E_v (in the VR space). The immediate implication is that $E_s[\gamma]$ is not stationary at the ground state. While this causes no difficultly in principle—we need only the functional E_v to be stationary—it is intimately connected with the divergence of the iteration map. Precisely at the ground state, $E_s[\gamma_{\rm gs}]=\Sigma_i'\epsilon_i$, where the prime indicates that only the pinned states with $f_i=1$ contribute to the sum. Away from the ground state, the KS eigenvalue spectrum splits, and $E_s[\gamma]$ is a multival-

ued functional due to the choice implied in occupying the KS levels. This is the same choice encountered in the iteration of the KS equations (see Sec. II B), where the natural orbitals $\phi_i^{(n+1)}$ were selected from among the eigenstates of the KS Hamiltonian. Near the self-consistent solution, there will be one such choice for which the resulting $\gamma^{(n+1)}$ is very close to $\gamma^{(n)}$.

The static response function of the KS system is a functional of γ which diverges at the ground state. Thus, even an infinitesimal perturbation $\delta\hat{v}_s$ may induce a finite change in γ. At the ground state, all of the natural orbitals, except those which have an occupation number that is degenerate, are uniquely defined. When a perturbation $\delta\hat{v}$ is introduced, the natural orbitals change discontinuously to the eigenstates of the perturbed KS Hamiltonian $\hat{h}=\delta\hat{v}$. These eigenstates may be any functions in the degenerate Hilbert space because $\delta\hat{v}$ is arbitrary.

III. TWO-SITE HUBBARD MODEL

The 1MFT-KS system has some unusual features such as the collapse of the KS eigenvalues at the ground state, so it is desirable to derive explicitly the KS equations for a simple model. The Hubbard model on two sites provides a convenient example because it is exactly solvable and especially easy to interpret. Also, analytic expressions for the one-matrix energy functional and KS Hamiltonian can be obtained. In Secs. III A and III C, for the purpose of comparison, we find the ground state of the two-site Hubbard model by three methods—direct solution of the Schrödinger equation, 1MFT, and DFT.

A. Direct solution

The Hamiltonian of the two-site Hubbard model is $\hat{H}=\hat{T}+\hat{U}+\hat{V}$ with

$$\hat{T}=-\sum_{\sigma}(t_{12}c_{1\sigma}^{\dagger}c_{2\sigma}+t_{21}c_{2\sigma}^{\dagger}c_{1\sigma}),$$

$$\hat{U}=U(\hat{n}_{1\uparrow}\hat{n}_{1\downarrow}+\hat{n}_{2\uparrow}\hat{n}_{2\downarrow}),$$

$$\hat{V}=V\frac{1}{2}(\hat{n}_1-\hat{n}_2), \tag{35}$$

where $t_{12}=t_{21}=t$, $c_{i\sigma}^{\dagger}$ and $c_{i\sigma}$ are the creation and annihilation operators of an electron at site i with spin σ, and $\hat{n}_i=\Sigma_{\sigma}c_{i\sigma}^{\dagger}c_{i\sigma}$. We consider only the sector of states with $N=2$ and $S_z=0$, i.e., a spin unpolarized system. In this sector, the eigenstates of $\hat{T}+\hat{U}$ are

$$\Phi_0=\frac{1}{\sqrt{2}}(y,x,x,y),\quad \Phi_1=\frac{1}{\sqrt{2}}(0,1,-1,0),$$

$$\Phi_2=\frac{1}{\sqrt{2}}(1,0,0,-1),\quad \Phi_3=\frac{1}{\sqrt{2}}(x,-y,-y,x) \tag{36}$$

in the site basis $\{c_{1\uparrow}^{\dagger}c_{1\downarrow}^{\dagger}|0\rangle, c_{1\uparrow}^{\dagger}c_{2\downarrow}^{\dagger}|0\rangle, c_{2\uparrow}^{\dagger}c_{1\downarrow}^{\dagger}|0\rangle, c_{2\uparrow}^{\dagger}c_{2\downarrow}^{\dagger}|0\rangle\}$. The following variables have been introduced $x=\cos(\pi/4-\alpha_0/2)$, $y=\sin(\pi/4-\alpha_0/2)$, and $\tan\alpha_0=U/4t$ with $0\leq\alpha_0\leq\pi/2$. The eigenvalues of $\hat{T}+\hat{U}$ for the states Φ_i are

$$\lambda_0=-By^2,\quad \lambda_1=0,$$

$$\lambda_2=B(x^2-y^2),\quad \lambda_3=Bx^2,$$

where $B=\sqrt{U^2+T^2}$ and $T=4t$. Φ_0, Φ_2, and Φ_3 are spin singlet states ($S=0$) and Φ_1 is the triplet state with $S=1$ and $S_z=0$. We will omit Φ_1 from consideration as is not coupled to the other states by the spin-independent external potential chosen in Eq. (35). The Hamiltonian can be written as $\hat{H}=\lambda_0\hat{I}+B\hat{K}$, where

$$K=\begin{pmatrix}0 & \nu y & 0\\ \nu y & x^2 & \nu x\\ 0 & \nu x & 1\end{pmatrix} \tag{37}$$

in the basis $\{\Phi_0,\Phi_2,\Phi_3\}$. We have defined the dimensionless variable $\nu=V/B$. The secular equation $|\hat{K}-\kappa_i\hat{I}|=0$ is

$$\kappa_i^3-(x^2+1)\kappa_i^2+(x^2-\nu^2)\kappa_i+\nu^2y^2=0. \tag{38}$$

The normalized eigenvectors of $\hat{H}$ are

$$\Psi_i=\frac{1}{\eta_i}\begin{pmatrix}\nu^2xy\\ \nu x\kappa_i\\ \beta_i\end{pmatrix} \tag{39}$$

and have energies $E_i=\lambda_0+B\kappa_i$ for $i=0,2,3$, where κ_i is a root of the secular [Eq. (38)]. We have also defined

$$\beta_i=\kappa_i(\kappa_i-x^2)-\nu^2y^2 \tag{40}$$

and

$$\eta_i=\{\kappa_i^2[\nu^2(3x^2-1)+y^2]+\kappa_i[x^2y^2(2\nu^2-1)]+\nu^2y^2(\nu^2-y^2)\}^{1/2}. \tag{41}$$

The system has two dimensionless energy scales—the interaction strength U/T and the bias V/T. The behavior with respect to these energy scales is illustrated in Fig. 1. The quantity $m=(n_1-n_2)/2$, where n_i is the average ground state occupancy of site i, is plotted with respect to the external potential V for various values of the interaction strength U. For the ground state,

$$m=\langle\Psi_0|\hat{m}|\Psi_0\rangle=\frac{2\nu\kappa_0^2x^2}{\eta_0^2}(\kappa_0-x^2), \tag{42}$$

where $\hat{m}=(\hat{n}_1-\hat{n}_2)/2$. A weakly interacting system [e.g., the solid (blue) curve in Fig. 1] responds strongly to the external potential. In contrast, a strongly interacting system [e.g., the dashed (red) curve] responds weakly up to a threshold $V/B\sim 1$ (for a strongly interacting system $B\approx U$.) This behavior has a simple interpretation: in order for the external bias to induce charge transfer, it must overcome the on-site Hubbard interaction. In the limit $U\rightarrow\infty$, the curve develops steplike behavior near $V/B\sim\pm 1$.

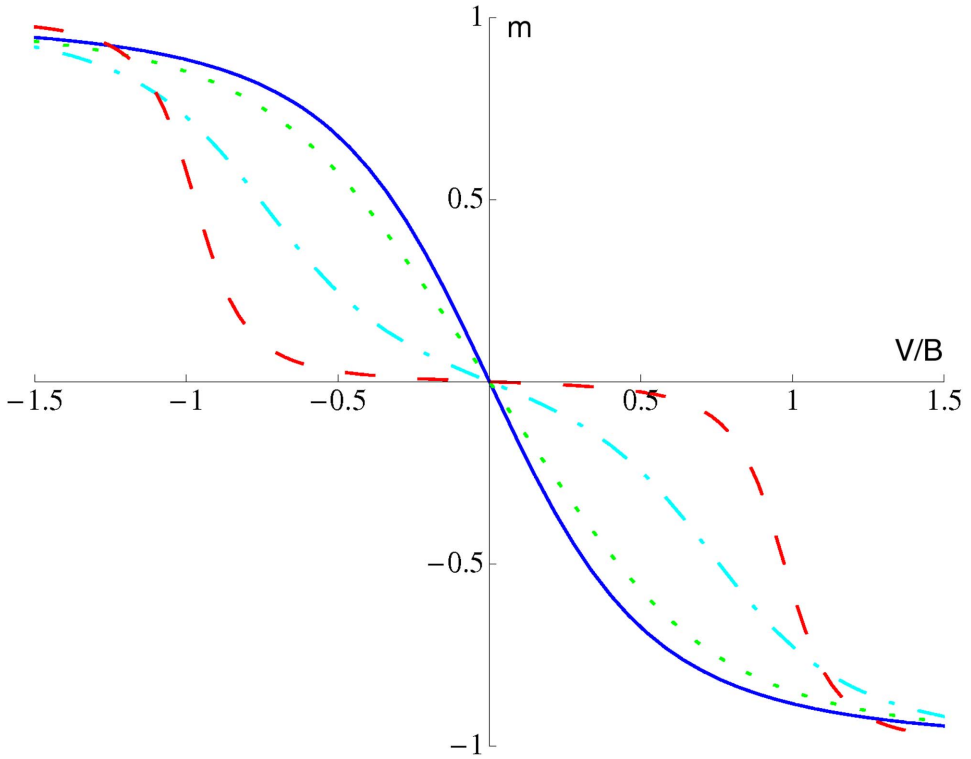

FIG. 1. (Color online) The density variable $m=(n_1-n_2)/2$ is shown with respect to the dimensionless external potential $\nu=V/B$ $(B=\sqrt{T^2+U^2})$. The curves for $U/T=(1/16,1/4,1,4)$ are shown as solid (blue), dotted (green), dash-dotted (light blue), and dashed (red) curves, respectively.

B. Solution from one-matrix functional theory

In the first part of this section, we derive the 1MFT energy functional and KS Hamiltonian. In the second part, we demonstrate the divergence of the straightforward iteration of the KS equations. In the third part, we use the level-shifting method[20] to obtain a convergent KS scheme.

1. Energy functional and Kohn-Sham Hamiltonian

For lattice models such as the Hubbard model, the one-matrix is defined as

$$\gamma(i\sigma,j\tau)=\langle\Psi|c_{i\sigma}^{\dagger}c_{j\tau}|\Psi\rangle. \tag{43}$$

One may ask whether the HK theorem (or Gilbert's extension[2] in 1MFT) applies when the density (or one-matrix) is defined over a discrete set of points, i.e., when the continuous density function $n(r)$ is replaced by the site-occupation numbers n_i. This has been investigated,[34,35] and it was found that HK-like theorems remain valid. We consider here only spin unpolarized states $(S_z=0)$. Accordingly, we define the *spatial* one-matrix

$$\gamma(ij)=\sum_{\sigma}\gamma(i\sigma,j\sigma), \tag{44}$$

which may be expressed as [cf. Eq. (5)],

$$\gamma(ij)=\sum_{\alpha}f_{\alpha}\phi_{\alpha}(i)\phi_{\alpha}^{*}(j), \tag{45}$$

where ϕ_α are the spatial natural orbitals. As our system is spin unpolarized, the spin-up- and spin-down-spin orbitals have the same spatial factors. Therefore, in Eq. (45) each spatial orbital ϕ_α may be occupied twice (once by a spin-up electron and once by a spin-down electron), i.e., $0\le f_\alpha\le 2$. It is convenient to parametrize the natural orbitals as

$$\phi_a=\begin{pmatrix}\cos(\theta/2)\\ \sin(\theta/2)\end{pmatrix}\quad\text{and}\quad\phi_b=\begin{pmatrix}\sin(\theta/2)\\ -\cos(\theta/2)\end{pmatrix}. \tag{46}$$

In terms of this parametrization, the one-matrix in the site basis is

$$\gamma=I+A(\cos\,\theta\sigma_z+\sin\,\theta\sigma_x)=I+\vec{\gamma}\cdot\vec{\sigma},\quad\vec{\gamma}=(\gamma_x,\gamma_z), \tag{47}$$

where σ_i are the Pauli matrices and $A=(f_a-f_b)/2=\cos\,\alpha$.

Gilbert's extension[2] of the HK theorem proves that the many-body ground state is a functional of γ. For the two-site Hubbard model, we find explicitly $\Psi_0=\cos(\alpha/2)\Phi_{aa}-\sin(\alpha/2)\Phi_{bb}$, where Φ_{ii} is the Slater determinant composed of the natural spin orbitals $\phi_{i\uparrow}$ and $\phi_{i\downarrow}$ $(i=a,b)$. The terms of the energy functional $E[\gamma]=T[\gamma]+U[\gamma]+V[\gamma]$ are found to be

$$T[\gamma]=\langle\Psi_0|\hat{T}|\Psi_0\rangle=-2tA\,\sin\,\theta,$$

$$U[\gamma]=\langle\Psi_0|\hat{U}|\Psi_0\rangle=U-\frac{U}{2}(1+\sqrt{1-A^2})\sin^2\,\theta,$$

$$V[\gamma]=\langle\Psi_0|\hat{V}|\Psi_0\rangle=VA\,\cos\,\theta. \tag{48}$$

The electron-electron interaction energy functional $U[\gamma]$ agrees with the general exact result for two-electron closed-shell systems.[36,37] We may partition $U[\gamma]$ into the Hartree energy

$$E_H[\gamma] = \frac{1}{2}\sum_{ij} n_i n_j U \delta_{ij} = U(1 + A^2 \cos^2 \theta) \tag{49}$$

and the exchange-correlation energy

$$E_{\rm xc}[\gamma] = U[\gamma] - E_H[\gamma] = -UA^2 \cos^2 \theta - \frac{U}{2}(1 + \sqrt{1 - A^2})\sin^2 \theta. \tag{50}$$

In Sec. II A the KS Hamiltonian was derived from the stationary principle for the energy. For the present model the KS Hamiltonian is a real 2×2 matrix. In the site basis its elements are $h(ij) = \langle 0|c_i \hat{h} c_j^\dagger|0\rangle$. This matrix may be expressed as $h = \vec{h}\cdot\vec{\sigma}$ with

$$h_x = -\frac{B}{4}\left(\cos\alpha_0 - \frac{\sin\alpha_0}{\sin\alpha}\cos\alpha\sin\theta\right) - \frac{B}{4}\frac{\sin\alpha_0(1+\sin\alpha)^2}{\sin\alpha\cos\alpha}\sin\theta\cos^2\theta,$$

$$h_y = 0,$$

$$h_z = \frac{B}{4}\frac{\sin\alpha_0(1+\sin\alpha)^2}{\sin\alpha\cos\alpha}\sin^2\theta\cos\theta + \frac{V}{2}. \tag{51}$$

In these expressions the variable α represents the dependence on the occupation numbers through the definition $\alpha = \cos^{-1} A = \cos^{-1}[(f_a - f_b)/2]$, $\alpha_0 = \tan^{-1}(U/4t)$ is the ground state value of α when $V=0$, and θ represents the dependence on the natural orbitals [cf. Eq. (46)]. Let us verify Eq. (20) for the uniform case $V=0$, for which the ground state one-matrix has $\theta = \pi/2$ and $\alpha = \alpha_0$. At these values $h_x = h_y = h_z = 0$, which verifies the eigenvalue collapse in this case.

2. Iteration of the Kohn-Sham equations

We now demonstrate the iteration of the KS equations following the straightforward algorithm described in Sec. II B. During the optimization of the orbitals, the occupation numbers (i.e., α) are held fixed. Let us examine each operation in the algorithm. In operation (i), the KS Hamiltonian for step $n+1$ is found by evaluating Eq. (51) at the one-matrix $\gamma^{(n)}$, i.e., at $\theta = \theta_n$. In operation (ii), we find the eigenstates u_i of $\hat{h}^{(n+1)}$. These eigenstates are taken as the natural orbitals $\phi_i^{(n+1)}$ for step $n+1$, which we parametrize in form (46) with $\theta = \theta_{n+1}$. This means that each of the $\phi_i^{(n+1)}$ is set equal to a distinct eigenstate u_i. In the present case, the natural orbitals are chosen such that θ_{n+1} is as close as possible to θ_n. In operation (iii), $\gamma^{(n+1)}$ is constructed from the $\phi_i^{(n+1)}$ by Eq. (45). We may now condense these three operations into a discrete iteration map on θ, i.e., a map $\theta_n \to \theta_{n+1}$. It is defined by

$$\cos\theta_{n+1} = \mathrm{sgn}(A - A_{\rm gs}) \left.\frac{h_z}{\sqrt{h_x^2 + h_z^2}}\right|_{\theta=\theta_n} \tag{52}$$

for $0 < \theta_n < \pi$ and $A > 0$ $(0 < \alpha < \pi/2)$. In Eq. (52), $A_{\rm gs}$ is the ground state value of A. An example of the iteration map for $t=1$, $U=1$, $V=0$, and $A = A_{\rm gs} - 0.02$ is shown in Fig. 2. The solid (black) and dashed (red) curves are the left- and right-hand sides of Eq. (52). Generally, any intersection of the two curves is a fixed point of the iteration map which corresponds to a self-consistent solution of the KS equations. For the present example, the fixed point at $\theta = \pi/2$ corresponds to the ground state. A sequence of iterations can be represented graphically by alternately drawing vertical lines from the solid curve to the dashed curve and horizontal lines from the dashed curve to the solid curve. The dotted (blue) curve shows an example of the first two iterations beginning from an initial guess θ_0. The next iterations θ_1 and θ_2 move farther away from the ground state, and the map does not converge to the ground state fixed point $\theta = \pi/2$.

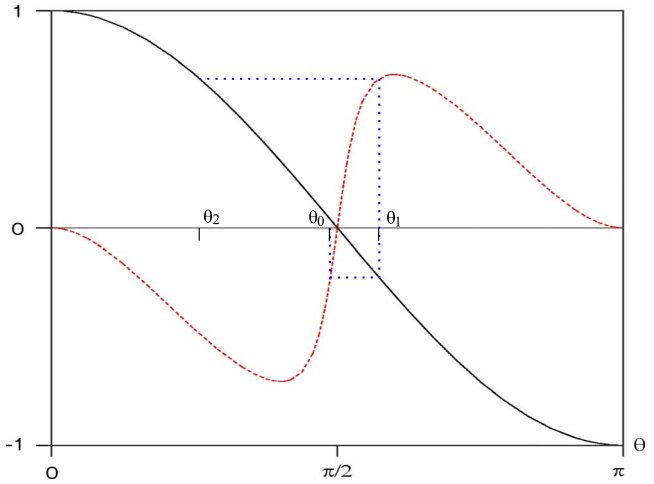

FIG. 2. (Color online) The iteration map [Eq. (52)] is shown for $t=1$, $U=1$, $V=0$, and $A = A_{\rm gs} - 0.02$. The solid (black) curve is the left-hand side of Eq. (52). The dashed (red) curve is the right-hand side. The dotted (blue) curve demonstrates the first two iterations. The iteration map does not converge to the ground state fixed point $\theta = \pi/2$.

The iteration map is nonlinear and may exhibit quite complex behavior. The linearization of the map at a fixed point tells us whether the fixed point is stable or unstable. As an example, let us consider the uniform case $V=0$, for which the ground state fixed point is $\theta = \pi/2$. Linearization of Eq. (52) in terms of the variable $m = (n_1 - n_2)/2 = A\cos\theta$ gives

$$m_{n+1} \approx \mathrm{sgn}(A - A_{\rm gs})\frac{h_z}{|h_x|} \approx -\xi m_n, \tag{53}$$

where

$$\xi = \frac{(1+\sin\alpha)^2}{(\cot\alpha_0 - \cot\alpha)\sin\alpha\cos\alpha}. \tag{54}$$

Suppose the occupation numbers are close to their ground state values, i.e., $A = A_{\rm gs} + \delta A$, where δA is a small displacement. The leading approximation for ξ gives

$$\xi \approx -\frac{U^2(U+B)^2}{TB^3}\frac{1}{\delta A}. \tag{55}$$

For any nonzero values of t and U, there is a threshold $d>0$ such that for $|\delta A|<d$, $|\xi|>1$. Therefore, the ground state is an unstable fixed point. In Sec. II B, the divergence of the iteration map was connected to the divergence of the static KS response function. Let us verify Eq. (25) explicitly for the present case. As seen in Eq. (53), the linearized iteration map affects only the diagonal elements of the one-matrix, i.e., the density, which is described by the variable m. Therefore, the relevant response functions are the density-density response for the KS system,

$$\chi_s = \sum_i \sum_{j\neq i} \frac{f_i - f_j}{\epsilon_i - \epsilon_j}\langle\phi_i|\hat{m}|\phi_j\rangle\langle\phi_i|\hat{m}|\phi_j\rangle \approx 2\frac{TU^2}{B^4}\frac{1}{\delta A}, \tag{56}$$

and the density-density response for the interacting system,

$$\chi = \sum_{k\neq 0} \frac{\langle\Psi_0|\hat{m}|\Psi_k\rangle\langle\Psi_k|\hat{m}|\Psi_0\rangle}{E_0 - E_k} + \text{c.c.} = 2\frac{U-B}{B(B+U)}. \tag{57}$$

For the two-site Hubbard model, these response functions are just constants. The KS response has a functional dependence on the one-matrix. It diverges as the ground state is approached, i.e., in the limit $\delta A \to 0$. The linearized iteration map [Eq. (25)] is simply multiplication by the constant

$$-\chi_s\chi^{-1} = \frac{U^2(U+B)^2}{TB^3}\frac{1}{\delta A} = -\xi, \tag{58}$$

which agrees with the direct calculation [Eq. (55)].

3. Iteration with level shifting

In actual calculations it is necessary to have a convergent iteration scheme. One possibility for obtaining convergence is the level-shifting method,[20] whose application in 1MFT was discussed in Sec. II C. In this method, one introduces artificial shifts of the KS eigenvalues in order to improve convergence. A shift of the KS eigenvalue ϵ_i by an amount ζ_i is equivalent to adding a term $\zeta_i|\phi_i\rangle\langle\phi_i|$ to the KS Hamiltonian, where ϕ_i is the orbital with eigenvalue ϵ_i. The KS system for the two-site Hubbard model has two orbitals. As the divergence of the iteration map is due to the degeneracy of the KS eigenvalues at the ground state, it seems sensible to prevent degeneracy by introducing a separation 2ζ between the levels. Thus, we add the following term to the KS Hamiltonian at iteration step n:

$$-\zeta|\phi_a\rangle\langle\phi_a| + \zeta|\phi_b\rangle\langle\phi_b| = -\zeta(\sin\theta_n\sigma_x + \cos\theta_n\sigma_z), \tag{59}$$

where ϕ_a and ϕ_b are evaluated at $\theta=\theta_n$. An example of the effect of level shifting is shown in Fig. 3. Convergence is achieved when ζ exceeds a threshold, which may be calculated from convergence criterion (34). The dashed (red) curve in Fig. 3 shows the iteration map with a level shift value greater than the threshold. For the two-site Hubbard model, the criterion for convergence can be visualized graphically as the condition that the magnitude of the slope of the level shifted curve be less than the slope of the solid (black) curve at the fixed point.

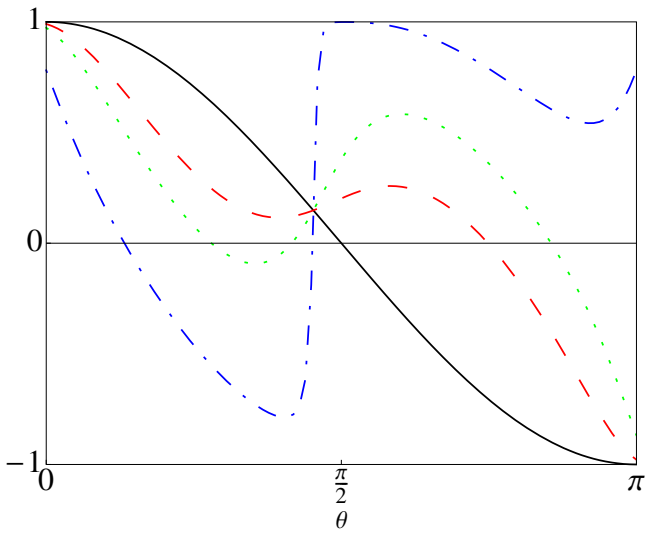

FIG. 3. (Color online) The iteration map for $t=1$, $U=5$, $V=-2.5$, and $A=A_{gs}-0.1$. The solid (black) curve is the left-hand side of Eq. (52). The dash-dotted (blue), dotted (green), and dashed (red) curves are the right-hand side with level shift $\zeta=(0,3,6)$. The threshold level shift for convergence is $\zeta_c\approx 4.07$, which may be calculated with Eq. (34).

At each iteration step the KS system has an "instantaneous" energy $E_s[\gamma]=\mathrm{Tr}(\hat{h}[\gamma]\gamma)$, which has, of course, no physical meaning when the KS system is not self-consistent. This "KS energy" is shown in Fig. 4 as a function of the deviation $\delta\vec{\gamma}=(\delta\gamma_x,\delta\gamma_z)$ of one-matrix (47) from the ground

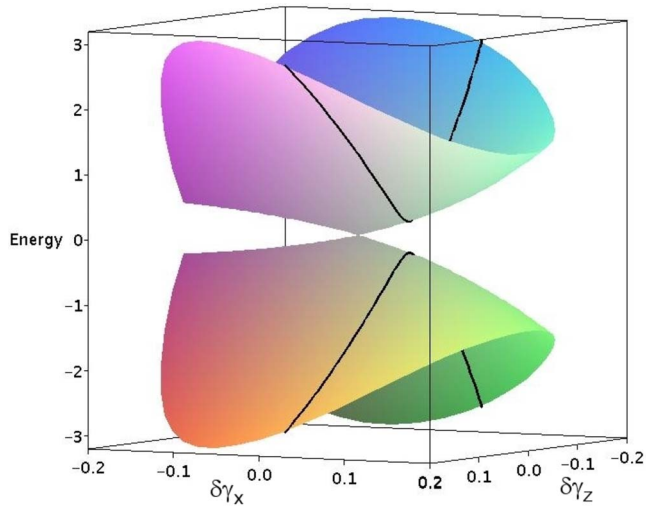

FIG. 4. (Color online) The "KS energy" for $t=1$, $U=3.5$, and $V=0$ is shown as a function of the deviation $(\delta\gamma_x,\delta\gamma_z)$ from the ground state. The two surfaces represent the two branches of the KS energy. The space curves show the energy as a function of θ for fixed occupation numbers. Optimization of the orbitals corresponds to moving along one of these curves to the stationary point. The ground state is the point of conic intersection at the origin.

state one-matrix. It is immediately seen that the KS energy is not stationary at the ground state one-matrix, which is a cusp point where the energy E_s changes linearly with respect to $\delta\gamma$. The KS energy is multivalued due to the choice implied in occupying the KS levels when the system is not self-consistent (see Sec. II D). The space curve in Fig. 4 shows the energy as a function of θ for fixed occupation numbers, i.e., for fixed A. The KS response is proportional to the inverse separation between the two branches of the space curve. The separation necessarily vanishes as the curve approaches the conic point, which is the origin of divergent KS response.

C. Solution from density functional theory

The two-site Hubbard model with the local external potential chosen in Eq. (35) may be described also with DFT. It is interesting to compare the 1MFT-KS scheme with the DFT-KS scheme, especially with regard to their convergence behavior. The variational energy functional and KS Hamiltonian may be constructed explicitly. An interesting result of the investigation is that the straightforward iteration map is divergent when $U>1.307t$ (for $V=0$). We derive a general condition for the convergence of the DFT-KS equations.

1. Energy functional

The HK energy functional for a lattice is

$$E_v[n] = \sum_i v(i)n_i + F[n], \tag{60}$$

where $v(i)$ is the external potential at site i and $F[n]$ is a universal functional of the density (here, site occupancy) defined as

$$F[n] = \langle \Psi_0[n] | \hat{T} + \hat{U} | \Psi_0[n] \rangle, \tag{61}$$

where $\hat{T}$ is the kinetic energy operator and $\hat{U}$ is the electron-electron interaction. In the following treatment of the two-site Hubbard model, we depart from standard practice by enforcing the normalization condition $n_1+n_2=N$ explicitly (i.e., through the parametrization), rather than with a Lagrange multiplier. Thus, we take as basic variable the single parameter $m=(n_1-n_2)/2$ that uniquely specifies the density. Similarly, the external potential is specified by the single parameter $V=v(1)-v(2)$. The functional $F[n]$ is then just a function $F(m)$. Also, the HK energy $E_V(m)=Vm+F(m)$ is a function of m.

2. Kohn-Sham Hamiltonian

Following standard practice, the KS Hamiltonian takes over, unchanged, the kinetic energy operator from the many-body Hamiltonian. Thus, we consider the KS Hamiltonian

$$\hat{h} = \hat{t} + \hat{v}_s, \tag{62}$$

where $\hat{t}=-t(c_1^\dagger c_2 + c_2^\dagger c_1)$ is the kinetic energy operator and $v_s(i)$ is the KS potential at site i defined by

$$v_s(i) = \frac{\partial Q}{\partial n_i}, \tag{63}$$

where $Q[n]=E_v[n]-T_s[n]$ contains the Hartree and exchange-correlation energy as well as the external potential energy and $T_s[n]$ is the kinetic energy of the KS system. We do not separate these contributions explicitly. The KS potential is determined only to within an arbitrary additive constant, which we choose such that $v_s(1)+v_s(2)=0$. In the site basis, the KS Hamiltonian is a 2×2 matrix which may be expressed as $h=-t\sigma_x+(V_s/2)\sigma_z$, where $V_s=v_s(1)-v_s(2)$. The kinetic energy of the KS system is evaluated as

$$T_s = \sum_i^{\text{occ}} f_i \langle \phi_i | \hat{t} | \phi_i \rangle = 2\langle \phi_a | \hat{t} | \phi_a \rangle = -2t \sin\theta, \tag{64}$$

where ϕ_a is the lowest energy eigenstate of Eq. (62) and is twice occupied (once by a spin-up electron and once by a spin-down electron). It is parametrized as in Eq. (46) with $\tan\theta=-2t/V_s$. The density of the KS system is

$$m_s = \sum_i^{\text{occ}} f_i \langle \phi_i | \hat{m} | \phi_i \rangle = \cos\theta. \tag{65}$$

Thus, from Eqs. (64) and (65) the kinetic energy T_s is a known function of m_s. From Eqs. (60), (63), and (64), the KS potential is

$$V_s = \left.\frac{\partial Q}{\partial m}\right|_{m=m_s} = \left.\frac{\partial}{\partial m}[E_V(m) - T_s(m)]\right|_{m=m_s}$$
$$= V + f(m_s) - \left.\frac{\partial T_s}{\partial m}\right|_{m=m_s}, \tag{66}$$

where $V=v(1)-v(2)$ is the given external potential and

$$f(m_s) = \left.\frac{\partial F}{\partial m}\right|_{m=m_s}. \tag{67}$$

Equation (66) is simply the familiar expression $v_s(r)=v(r)+v_H(r)+v_{\text{xc}}(r)$ with a different partitioning of the terms. It is seen that the terms $f-\partial T_s/\partial m$ together correspond to the Hartree and exchange-correlation potentials.

3. Iteration of the Kohn-Sham equations

Let us investigate the iteration of the KS equations in the present context. The conventional iteration map consists of the following steps: (i) the KS potential for step $n+1$ is determined from the density of step n using Eq. (66), i.e., $V_s^{(n+1)}=V_s(m_s^{(n)})$, (ii) the eigenstates of $\hat{h}^{(n+1)}$ are found, and (iii) the density of step $n+1$ is calculated with Eq. (65).

Consider step (i) in more detail. The KS potential is obtained from Eq. (66),

$$V_s^{(n+1)} = V + f(m_s^{(n)}) - \left.\frac{\partial T_s}{\partial m}\right|_{m=m_s^{(n)}}. \tag{68}$$

The right-hand side may be expressed differently by using the stationary conditions for the energy function $E_V(m)$ and the KS energy $E_s=T_s+\Sigma_i v_s(i)n_i$. The stationary condition

$\partial E_V/\partial m=0$ gives $f=-V(m)$, where $V(m)$ is the external potential such that the interacting system has ground state density m. Similarly, the stationary condition applied to E_s gives $\partial T_s/\partial m=-V_s$. Substituting these relations in Eq. (68) yields

$$V_s^{(n+1)} = V - V(m_s^{(n)}) + V_s(m_s^{(n)}). \tag{69}$$

At self-consistency the V_s terms cancel, and we obtain the expected result $V=V(m_{\rm gs})$, where $m_{\rm gs}$ is the ground state density. For the present model, the ground state density could be found by solving $V=V(m)$ because $V(m)$ is known exactly from Eq. (42). However, in general the ground state must be found by iteration. Equation (69) implies an iteration map for the density, i.e., a map $m_s^{(n)} \to m_s^{(n+1)}$, because $V_s^{(n+1)}$ determines $m_s^{(n+1)}$. From Eq. (65) and the definition $\tan\theta = -2t/V_s$, we find the relationship

$$V_s = -2t\frac{m_s}{\sqrt{1-m_s^2}}. \tag{70}$$

The density may be iterated until self-consistency is reached. However, we encounter a technical difficulty for the present model. In order to express explicitly the term $V(m_s^{(n)})$ in Eq. (69), we must invert Eq. (42), which involves solving a cubic equation. As the solutions are rather unwieldy, we take here a different approach: We iterate the external potential. It is unusual to iterate the external potential, which is given in the statement of the problem. Nevertheless, the iteration map for V provides an "image" of the iteration map for m_s by virtue of the HK theorem. Such an approach allows us to investigate certain features of the iteration map, in particular its convergence behavior. In order to express Eq. (69) as an iteration map for V, we need to express V_s as a function of V. In other words, we find the value of V_s such that the KS system has density $m_s=m$, where m is the density of the interacting system with V. The composition of Eqs. (70) and (42) yields the desired function

$$\tilde{V}_s(V) = V_s[m(V)]. \tag{71}$$

Using Eq. (71) in Eq. (69), we obtain the iteration map for the external potential

$$\tilde{V}_s(V^{(n+1)}) = V - V^{(n)} + \tilde{V}_s(V^{(n)}), \tag{72}$$

which is expressed in implicit form.

Examples of the iteration map for a uniform system ($V=0$) are shown in Figs. 5 and 6, where the left- and right-hand sides of Eq. (72) are plotted. Suppose an initial value $V^{(0)} \neq 0$ is chosen. For a system with $V=0$, the ground state has uniform density ($m=0$), but the initial density $m_s^{(0)}$ associated with $V^{(0)}$ is not uniform. Upon iteration, we expect the KS system to relax to a uniform density, i.e., we expect the KS potential to be such as to push the system closer to uniform occupancy in the next iteration. The solid curves in Figs. 5 and 6 represent the left-hand side of Eq. (72), while the dashed curves represent the right-hand side. The iteration map can be demonstrated graphically by alternately drawing vertical lines from the solid curve to the dashed curve and horizontal lines from the dashed curve to the solid curve. The map displays "charge oscillation." The ground state is a stable fixed point if the magnitude of the slope of the dashed curve at the origin is less than the slope of the solid curve at the origin. For weakly interacting systems, the iteration map is convergent, while for strongly interacting systems, it is not convergent. The threshold for convergence is $U \approx 1.307t$.

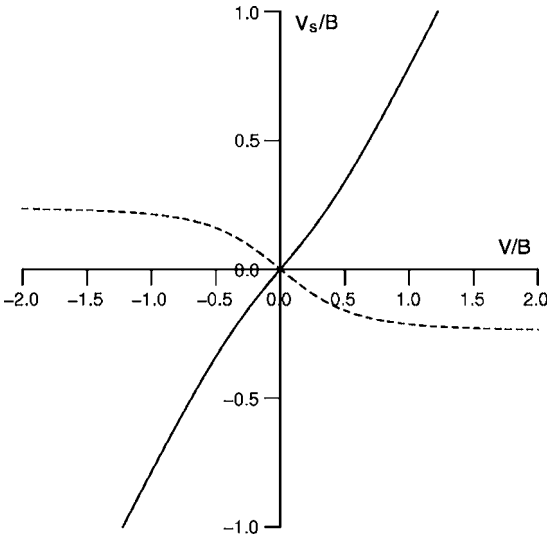

FIG. 5. The iteration map for the external potential V is shown for a weakly interacting system with $U=t$. The left- and right-hand sides of Eq. (72) are shown as solid and dashed curves, respectively.

4. Linearization of the Kohn-Sham equations

The nature of the fixed point and the origin of diverent behavior are revealed by linearization of the iteration map. We linearize the map by expanding both sides of Eq. (69) with respect to $\delta m_s = m_s - m_{\rm gs}$, where $m_{\rm gs}$ is the ground state density. We find

$$\chi_s^{-1}\delta m_s^{(n+1)} \approx \chi_s^{-1}\delta m_s^{(n)} - \chi^{-1}\delta m_s^{(n)},$$

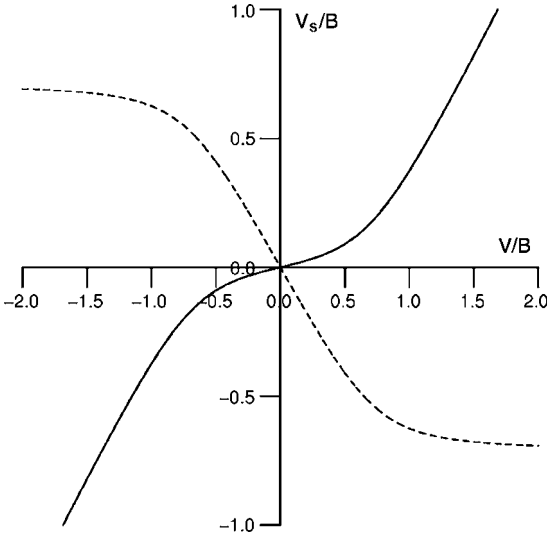

FIG. 6. The iteration map for the external potential V is shown for a strongly interacting system with $U=4t$. The left- and right-hand sides of Eq. (72) are shown as solid and dashed curves, respectively.

$$\delta m_s^{(n+1)} \approx \chi_s(\chi_s^{-1} - \chi^{-1})\,\delta m_s^{(n)}, \tag{73}$$

where χ_s and χ are the density-density response functions defined in Eqs. (56) and (57). The criterion for convergent behavior is

$$|1 - \chi_s \chi^{-1}| \leq 1, \tag{74}$$

or equivalently, $\chi_s\chi^{-1} \leq 2$. Note the change from 1 for 1MFT to 2 for DFT on the right-hand side [cf. Eq. (25)]. Consider the case $V=0$, which has uniform density in the ground state ($m_{\mathrm{gs}}=0$). Using the Eqs. (56) and (57) in Eq. (74) gives the threshold condition

$$\cos(\pi/4 - \alpha_0/2) = 4[\sin(\pi/4 - \alpha_0/2)]^3, \tag{75}$$

which corresponds to $U \approx 1.307t$. Let us consider the limit $U \to \infty$. The leading behavior of the KS response is independent of U,

$$\chi_s \sim \frac{1}{T}, \tag{76}$$

while the response of the interacting system vanishes as

$$\chi \sim \frac{1}{4}\frac{T^2}{U^3}. \tag{77}$$

For sufficiently large U, threshold (74) is crossed and divergent behavior results. In DFT, as also in 1MFT, the source of divergent behavior is a KS response that is too large in relation to the exact response. In 1MFT the imbalance results from a divergent KS response, whereas in DFT the KS response generally remains finite but the response of the interacting system becomes too small as U increases.

In standard DFT [with continuous $n(r)$], the analog of the linearized iteration map [Eq. (73)] can be written as

$$n^{(n+1)}(r) \approx \int dr'\,dr''\chi_s(r,r')[v_c(r',r'') + f_{\mathrm{xc}}(r',r'')]n^{(n)}(r''), \tag{78}$$

where $n^{(n)}(r)$ is the density of iteration step n, v_c is the kernel of the Coulomb interaction, and $f_{\mathrm{xc}} = \delta v_{\mathrm{xc}}/\delta n$ is the exchange-correlation kernel. The necessary and sufficient condition for convergence of the KS equations is that all eigenvalues of the operator

$$\hat{\chi}_s(\hat{v}_c + \hat{f}_{\mathrm{xc}}) \tag{79}$$

have modulus of less than 1.

IV. CONCLUSIONS

The status of the generalized KS scheme in 1MFT has been uncertain. Although Gilbert[2] derived effective single-particle equations from the stationary conditions for the energy functional, the degeneracy of essentially all of the resulting orbitals was thought to be paradoxical.[2,16,17] We have presented an alternative derivation in which the degeneracy is lifted by constraining the occupation numbers. Such a KS scheme is well behaved in the neighborhood of the ground state occupation numbers. Therefore, the correct natural orbitals are obtained in the limit that the ground state is approached. We have constructed explicitly the 1MFT-KS system for a simple two-site Hubbard model. While we find no paradoxical results, the KS system has many striking features, in particular the collapse of eigenvalues at the ground state. Although the KS eigenvalues in 1MFT do not have a physical interpretation[38] as in DFT, the orbitals, which are called natural orbitals, play an important role in the context of configuration interaction, i.e., the expansion of the full wave function as a sum of Slater determinants.[22] This may be important in the search for approximate energy functionals.

Beyond the question of the existence of the KS system in 1MFT, there is the issue of its utility. The KS system has been extremely useful in DFT calculations. The ground state density can be efficiently found by iterating the KS equations to self-consistency. In 1MFT, on the other hand, the straightforward iteration of the KS equations never converges to the self-consistent solution representing the ground state. We have shown that the level-shifting method can be used to obtain a convergent iteration scheme. The iteration of the KS equations can be viewed as a discrete map. We have proved that the straightforward iteration procedure is intrinsically divergent because the ground state is an unstable fixed point. The source of the instability is the divergence of the KS static response function at the ground state, which in turn is due to the degeneracy of the KS spectrum. Degeneracy-driven instability is reminiscent of the Jahn-Teller effect, and the connection is strengthened if we regard the implicit one-matrix dependence of the KS Hamiltonian as analogous to the parametric dependence of the Born-Oppenheimer Hamiltonian on nuclear coordinates. In both cases, the energy spectrum splits linearly with respect to displacement from the degeneracy point. Thus, the energy may always be lowered by displacement. For the 1MFT-KS system, this means that the KS energy $E_s[\gamma] = \mathrm{Tr}(\hat{h}\hat{\gamma})$ can always be lowered by displacement from the ground state, leading to an instability of the iteration procedure. However, this is a fictitious energy and, of course, the HK-like energy functional $E_v[\gamma]$ always achieves its minimum at the ground state.

ACKNOWLEDGMENTS

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APPENDIX: GROUND STATE NOT DETERMINED BY THE DENSITY

We give here a simple example which shows that the density alone does not always uniquely determine the ground state wave function if the external potential is nonlocal. Our example is the two-site Hubbard model, which was solved for the case of a local external potential in Sec. III A. The Hamiltonian $\hat{H} = \hat{T} + \hat{V} + \hat{U}$ is given in Eq. (35). In such a lattice model, the hopping parameters t_{jk} are real numbers that represent the kinetic energy. A "magnetic field" can be introduced by giving t_{jk} a phase, i.e., by the transformation t_{jk}

$\rightarrow t_{jk} \exp[i\Sigma_{n=j}^{k} A(n)]$, where $A(n)$ is the "vector potential" at site n and the sum runs over a string of sites from site j to site k. For the two-site model this is just the transformation $t_{12} \rightarrow t_{12} e^{i\tau}$. We see that this magnetic field appears in the Hamiltonian in exactly the same manner as a nonlocal external potential, such as $v_{12} c_1^\dagger c_2 + \text{H.c.}$ because it modifies the nonlocal hopping terms. We can generate the above phase transformation by the $U(1)$ rotations $c_1 \rightarrow c_1 e^{i\pi/2}$ and $c_2 \rightarrow c_2 e^{-i\pi/2}$. The eigenstates of the transformed Hamiltonian are readily generated from the eigenstates of the original Hamiltonian by applying the same transformation. For example, without the magnetic field, the ground state to first order in small V is

$$\Psi_0 = \Phi_0 + \frac{\langle \Phi_2 | \hat{V} | \Phi_0 \rangle}{E_0 - E_2} \Phi_2, \tag{A1}$$

where Φ_i are given in Eq. (36). When the magnetic field is turned on, the Φ_i change, e.g.,

$$\Phi_0 \rightarrow \frac{1}{\sqrt{2}} \begin{pmatrix} y e^{-i\tau} \\ x \\ x \\ y e^{i\tau} \end{pmatrix} \tag{A2}$$

in the site basis $\{c_{1\uparrow}^\dagger c_{1\downarrow}^\dagger |0\rangle, c_{1\uparrow}^\dagger c_{2\downarrow}^\dagger |0\rangle, c_{2\uparrow}^\dagger c_{1\downarrow}^\dagger |0\rangle, c_{2\uparrow}^\dagger c_{2\downarrow}^\dagger |0\rangle\}$. Accordingly, the ground state acquires a nontrivial dependence on the magnetic field (τ dependence). At the same time, the ground state one-matrix is transformed to

$$\gamma = I + A_0 \begin{pmatrix} \cos\theta_0 & \sin\theta_0 e^{-i\tau} \\ \sin\theta_0 e^{i\tau} & -\cos\theta_0 \end{pmatrix}, \tag{A3}$$

where A_0 and θ_0 are the ground state values (for $\tau = 0$) of the variables defined in Eqs. (46) and (47). The density is given by the diagonal elements, which are unaffected by the transformation. Only the off-diagonal (nonlocal) elements are sensitive to the magnetic field. Therefore, the one-matrix rather than the density is required to uniquely specify the ground state.[2]

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