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Fractional occupation numbers in density-functional theory

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Density-functional theory for ensembles defined by fixed weights and fractional occupation numbers is derived using a Lagrange-multiplier version of the constrained-search procedure. This is related to an adiabatic connection between a generalized Kohn-Sham ensemble for noninteracting electrons and a minimum-energy ensemble including the electronic Coulomb interaction. Using this formalism, it is shown that discontinuous changes of the chemical potential of a finite electronic system result from constraints on density variations imposed by Fermi statistics. Such discontinuities do not exclude the possibility of defining an exchange-correlation energy functional that is free of derivative discontinuities for unconstrained density variations. [S1050-2947(97)08409-6]

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I. INTRODUCTION

Perdew *et al.* [1] showed some time ago that the chemical potential of any isolated open system with a discrete energy gap, in particular of any atom, is described by a step function that has a finite step for each integral number of electrons. This was attributed to derivative discontinuities in the exchange-correlation density functional evaluated for varying numbers of electrons [2]. Although a formula for the derivative discontinuity derived by Sham and Schlüter [3] was later shown to vanish [4], Gunnarsson and Schönhammer [5,4] derived such a discontinuity from an exactly solvable model of a finite linear chain of atoms with two nondegenerate energy levels.

In apparent contrast to these developments in density-functional theory, the Fermi-liquid theory of Landau [6,7] postulates an energy functional for interacting electrons that is a smooth function of occupation numbers for Fermion quasiparticles [8]. Slater and Wood [9] showed that one-electron energies computed as eigenvalues of an effective one-electron Hamiltonian in a statistical theory of interacting electrons are partial derivatives of the total energy with respect to variations of fractional occupation numbers, as in Landau theory. Slater [10,11] pointed out that Fermi statistics, appropriate to Landau quasiparticles, is a consequence of a statistical theory of weakly interacting identical atoms forming a superlattice or equivalent crystal, and also that the derivative formula for one-electron energies is valid for any statistical density theory. This was confirmed by Janak [12] for density-functional theory.

The present paper is concerned with reconciling these two different approaches to the statistical theory of interacting electrons. The goal is to justify the use of Landau theory, using fractional occupation numbers, for finite or localized electronic systems. An important distinction made here is that discontinuities in the chemical potential appropriate to such systems may arise either from explicit derivative discontinuities in the appropriate energy functionals of electron density or from constraints due to the Fermi statistics of the relevant electron quasiparticles. It will be shown that the step-function character of the chemical potential for atoms considered by Perdew *et al.* [1] is a direct consequence of Fermi statistics and does not in itself imply derivative discontinuities in the energy functionals for unconstrained variations of the electron density.

In order to discuss these issues, a derivation of statistical density-functional theory is given here, in Sec. II, in which the effective external potential appears explicitly as a Lagrange-multiplier field in a constrained-search formalism [13]. This approach builds in a mutually determining reciprocal relationship between the statistical electron density and the external potential, both taken here to be spin-indexed scalar fields defined in $\mathfrak{R}^3$. When the electronic Coulomb interaction is scaled by a coupling constant λ, this formalism provides a generalized adiabatic connection for intermediate values $0 \leqslant \lambda \leqslant 1$ [14,15]. The result is to unify the adiabatic-connection formalism with the use of fractional occupation numbers.

Section III defines the chemical potential and one-electron energies in terms of the ensemble theory. In Sec. IV this theory is applied to consider the charge state of an atom in statistical equilibrium with a reservoir of electrons at chemical potential μ. It is shown that the chemical potential of the atom is indeed described by a step function, in agreement with Perdew *et al.* [1], as a result of constraints on occupation numbers due to Fermi statistics. But the present derivation makes it clear that this result is consistent with an independent postulate of smooth variation of the density functional with respect to unconstrained variations of the electron density. Conclusions are summarized in Sec. V.

II. CONSTRAINED SEARCH USING LAGRANGE MULTIPLIERS

The derivation presented here is intended to generalize and encompass earlier derivations of density-functional theory for statistical ensembles. The theory of Hohenberg and Kohn (HK), for N-electron ground states [16], was extended to the grand canonical ensemble at nonzero temperatures by Mermin [17]. A statistical postulate was introduced by Janak [12] in order to define continuous variations of occupation numbers in an extended Kohn-Sham [18] theory. Using the constrained search logic of Levy [13], Perdew *et al.* [1] considered statistical ensembles of states with dif-

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ferent electron numbers N. Gross, Oliveira, and Kohn [19] considered ensembles of fractionally occupied states with the same number of electrons, thus generalizing the theory to excitation energies.

To establish a suitable notation, an ensemble of wave functions $\{\Psi_\gamma\}$ defines the statistical mean value $\langle X\rangle$ of any observable X as the sum $\Sigma_\gamma w_\gamma \langle X\rangle_\gamma$ with fixed weight coefficients $w_\gamma \geqslant 0$ that sum to unity. Each correlated wave function Ψ_γ is defined for an integral number of electrons N_γ and determines an electronic density function ρ_γ, such that the statistical ensemble density function is $\rho=\langle\rho\rangle=\Sigma_\gamma w_\gamma \rho_\gamma$. Following the ansatz of Kohn and Sham (KS) [18], a reference state Φ_γ that is a wave function for noninteracting electrons is defined for each wave function Ψ_γ such that the density function ρ_γ is the same for both states. An alternative ansatz, requiring Φ to have maximum projection on Ψ for each index γ, used in the recently developed reference-state density-functional theory (RDFT) [20], will be considered in a separate publication.

An ensemble of variational trial functions is denoted here by $\{\Psi\}_t$, where each trial function $\Psi_{\gamma t}$ satisfies a defining condition that characterizes the index γ, for example, the value of N_γ or the integral occupation numbers that characterize the reference states $\Phi_{\gamma t}$. A functional of $\rho(\mathbf{r})$ is defined by

$$F_v[\rho]=\min_{\{\Psi\}_t}\left(\langle(\Psi|T+U|\Psi)/(\Psi|\Psi)\rangle_t+\int v(\rho_t-\rho)d^3\mathbf{r}\right)$$

$$=E[v]-\int v\rho d^3\mathbf{r}. \tag{1}$$

The external potential function $v(\mathbf{r})$, common to all members of the ensemble, acts as a Lagrange-multiplier field. $E[v]$ here is the minimum ensemble energy consistent with the defining constraints that characterize index γ. The minimizing ensemble determines electron density ρ_v. Generalized Hohenberg-Kohn theorems follow immediately from this definition. If $v=v_\rho$, such that $\rho_v=\rho$, the minimizing ensemble $\{\Psi\}_\rho$ defines a universal functional such that

$$F[\rho]=\langle(\Psi|T+U|\Psi)/(\Psi|\Psi)\rangle_\rho$$

$$=F_v[\rho_v]=E[v]-\int v\rho_v d^3\mathbf{r}, \tag{2}$$

the appropriate generalization of the second HK theorem. Suppose that $F[\rho]$ is determined by an ensemble $\{\Psi\}_\rho$ for which $v_\rho \neq v$. Then

$$E_v[\rho]=F[\rho]+\int v\rho d^3\mathbf{r}=\langle(\Psi|T+V+U|\Psi)/(\Psi/\Psi)\rangle_\rho$$

$$\geqslant E[v], \tag{3}$$

which generalizes the first HK theorem.

In analogy to Kohn-Sham theory, an ensemble of reference states $\{\Phi\}$ is defined by applying Eq. (1) to the kinetic energy operator only. The Lagrange-multiplier field in this case is v_{KS}. Because all trial ensemble density functions ρ_t integrate to the same constant total number of electrons $\langle N\rangle$, the integral of $\rho_t-\rho$ must vanish, and v_{KS} is determined only up to an additive constant potential. It will be assumed here that this constant is chosen so that v_{KS} vanishes for an electron far outside the charge distribution. The universal functional for this reference-state ensemble defines the kinetic energy functional $T[\rho]$. An ensemble exchange-correlation functional is defined by subtraction,

$$E_{\mathrm{xc}}[\rho]=F[\rho]-T[\rho]-U[\rho], \tag{4}$$

where $U[\rho]$ is the classical Coulomb energy.

The subsequent derivation of one-electron equations follows as in KS theory. Expressed in terms of E_{xc}, the effective Hamiltonian takes the form

$$\mathcal{H}=\mathcal{H}_{\mathrm{Hartree}}+v_{\mathrm{xc}}, \tag{5}$$

where $v_{\mathrm{xc}}=(\delta/\delta\rho)E_{\mathrm{xc}}[\rho]$. This derivation implies that the Lagrange-multiplier field v_{KS} in the noninteracting case must be identical to the KS potential function except for a possible additive constant. To show this in detail, the absolute minimum property of Eqs. (2) and (3) implies that the ensemble energy functional $E_v[\rho]$ is stationary for variations of ρ about ρ_v that conserve $\langle N\rangle$. This is consistent with

$$\int d^3\mathbf{r}\left(\frac{\delta}{\delta\rho}F[\rho]+v(\mathbf{r})-\mu\right)\delta\rho(\mathbf{r})=0, \tag{6}$$

for unconstrained variations, where the chemical potential μ is determined by fixing a specific value of $\langle N\rangle$. Similarly, for the ensemble describing noninteracting electrons,

$$\int d^3\mathbf{r}\left(\frac{\delta}{\delta\rho}T[\rho]+v_{\mathrm{KS}}(\mathbf{r})-\mu\right)\delta\rho(\mathbf{r})=0. \tag{7}$$

These two equations determine the same density ρ if the two chemical potentials are equal and if $v_{\mathrm{KS}}=v+v_{\mathrm{cl}}+v_{\mathrm{xc}}$, where

$$v_{\mathrm{cl}}=\frac{\delta U[\rho]}{\delta\rho}, \quad v_{\mathrm{xc}}=\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho}. \tag{8}$$

Since the field v_{KS} is the same for all states in the ensemble, a single orthonormal set of noninteracting one-electron eigenfunctions suffices to construct all of the relevant reference states. This fact justifies, in retrospect, the definition of states in the ensemble by different values of index γ according to occupation numbers for these orbital functions. Different KS orbital functions are occupied in each restricted set of trial reference functions $\Phi_{\gamma t}$. Each trial density $\rho_{\gamma t}$ must be compatible with this occupation pattern.

An adiabatic connection [14,15] can be established by defining an intermediate Hamiltonian, for each integral number of electrons in the ensemble,

$$H_\lambda=T+V_\lambda+\lambda U. \tag{9}$$

With ρ fixed, the potential $v_\lambda(\mathbf{r})$ is determined for all values of λ by the constrained-search procedure. This ensures that $v_1=v$ if $\{\Psi\}$ is the minimizing ensemble for $\lambda=1$ and that $v_0=v_{\mathrm{KS}}$ if $\{\Phi\}$ is the minimizing ensemble for noninteracting electrons. It can be shown [21] that the Hellmann-Feynman theorem is valid for ensembles as defined here. Then for each λ

$$\frac{\partial}{\partial\lambda}E_\lambda=\left\langle U+\frac{\partial}{\partial\lambda}V_\lambda\right\rangle_\lambda, \tag{10}$$

where E_λ is the minimal mean energy of the ensemble. On integrating over λ this gives

$$E_1=E_0+\int_0^1 d\lambda\left\langle U+\frac{\partial}{\partial\lambda}V_\lambda\right\rangle_\lambda=\langle H_1\rangle=E[v]. \tag{11}$$

This determines the exchange-correlation energy functional for the defined ensemble,

$$E_{\mathrm{xc}}[\rho]=\int_0^1 d\lambda(\langle U\rangle_\lambda-U[\rho]), \tag{12}$$

where $U[\rho]$ is the classical Coulomb energy.

III. FERMI STATISTICS AND THE CHEMICAL POTENTIAL

Defining $E[\rho]=F[\rho]+\int v\rho d^3\mathbf{r}$ for fixed v, Eq. (6) implies for variations of the electron density ρ

$$\int d^3\mathbf{r}\left(\frac{\delta}{\delta\rho}E[\rho]-\mu\right)\delta\rho(\mathbf{r})=0, \tag{13}$$

or $\delta E-\mu\delta N=0$. Hence $\mu=\partial E/\partial N$ [22]. If the density function can be varied freely at each point in $\mathfrak{R}^3$, for fixed v, this equation also implies

$$\frac{\delta F}{\delta\rho}+v(\mathbf{r})=\mu, \tag{14}$$

a classical equation to be solved for ρ. When the kinetic energy functional is simplified and the exchange-correlation functional omitted this becomes the basic equation of the Thomas-Fermi method [23]. For variations that conserve N, $\delta\rho$ integrates to zero, and the term in μ drops out of Eq. (13). This implies that μ can only be determined by variations that do not conserve N [22]. The status of Eq. (14) in an ensemble theory, in which all information comes from wave functions defined only for integral values of N, is unclear.

The derivation of Janak's theorem [12]

$$\epsilon_i=\frac{\partial E[\rho]}{\partial n_i} \tag{15}$$

also assumes that the energy functional can be varied freely without conserving N. In the context of Kohn-Sham theory, an implicit assumption is made that the rules of Fermi statistics apply to occupation numbers associated with the KS orbital eigenfunctions. At zero temperature,

$$n_i=1,\ \epsilon_i<\mu,\quad 0\leq n_i\leq 1,\ \epsilon_i=\mu,\quad n_i=0,\ \epsilon_i>\mu. \tag{16}$$

In a theory based on N-electron wave functions, variations of ρ must be consistent with these limits on the range of occupation numbers. It will be argued below that this is a genuine constraint, implying that the Thomas-Fermi equation is not strictly valid in quantum theory, even if augmented by an exchange-correlation functional and modified to incorporate the kinetic energy functional of Kohn and Sham.

IV. CONSTRAINT ON VARIATIONS DUE TO FERMI STATISTICS

Consider an atom in equilibrium with a reservoir of electrons. The chemical potential of the reservoir is fixed. In thermochemical equilibrium, the chemical potential of the atom must adjust to equal the reservoir value, thus determining the charge state of the atom. Perdew *et al.* [1] consider an ensemble of charge states with $N=Z-1$, $N=Z$, and $N=Z+1$. Postulating that the energy of the ensemble is minimized and that $E(N)$ is defined for integral N but interpolated by a function that is concave upwards, the assumption of nonnegative weights confines nonzero weights to the two adjacent integral values of N that enclose a given nonintegral mean value. This implies that the mean energy must vary linearly between each two successive states of integral N. The derivative function $\mu=\partial E/\partial N$ is a step function [1]

$$\mu=-I,\ Z-1<N<Z,\quad \mu=-A,\ Z<N<Z+1, \tag{17}$$

where I is the ionization potential and A is the electron affinity. This is discontinuous for the neutral atom, $N=Z$. The average of the two limiting values at $N=Z$ is $-\frac{1}{2}(I+A)$, or minus the Mulliken electronegativity. Comparing Kohn-Sham theory, this discontinuous behavior may arise from a discontinuity in the functional derivative $\delta E_{\mathrm{xc}}/\delta\rho$, or be explicitly due to a discontinuous change of the undetermined constant in the potential field v_{KS} [2].

The weight coefficients for three adjacent charge states can be expressed in terms of occupation numbers n_I, for the highest occupied level of the state $N=Z$, and n_A, for the highest occupied level of the state $N=Z+1$. In the range $Z-1\leq N\leq Z+1$, these occupation numbers are related to the weight functions by

$$n_I=w_Z+w_{Z+1},\quad n_A=w_{Z+1}, \tag{18}$$

such that $n_I+n_A=N-Z+1$. Equivalently, the weight functions are given by

$$w_{Z-1}=1-n_I,\quad w_Z=n_I-n_A,\quad w_{Z+1}=n_A, \tag{19}$$

such that $w_{Z-1}+w_Z+w_{Z+1}=1$. Fermi statistics requires $0\leq n_A$, and forces $n_A=0$ in the range $Z-1\leq N\leq Z$, so that $n_I+n_A=N-Z+1$ implies $n_I=N-Z+1$ in this range. Fermi statistics requires $n_I\leq 1$ and forces $n_I=1$ for $Z\leq N\leq Z+1$, so that $n_I+n_A=N-Z+1$ implies $n_A=N-Z$ in this range. The derivatives dn/dN and dw/dN are discontinuous at $N=Z$ because of these restrictions on the occupation numbers. These constraints are equivalent to the condition that the weight coefficients should be positive, and the implied weight constants agree with those deduced by Perdew *et al.* [1], giving the same step function for $\mu(N)$. However, the present argument shows that this discontinuity is a direct consequence of Fermi statistics, and gives no information about a possible derivative discontinuity of the energy functional if defined for all possible density functions ρ.

The derivation given here, which covers the charge-state ensemble as a particular case, makes it very difficult to see where a derivative discontinuity might arise in the functional $E_{\mathrm{xc}}[\rho]$ if ρ is allowed to vary freely. This functional is universal for all external potentials and selects an appropriate potential as a Lagrange multiplier field. The arbitrary constant in the external potential function is determined by experimental conditions, and is ordinarily fixed in theoretical calculations by the condition that the potential should vanish in the limit of large separation of one electron from an N-electron system.

In order to separate the question of smooth variation of the universal functional $E_{\mathrm{xc}}[\rho]$ for free variations of ρ from constraints due to Fermi statistics, consider ground state values of $E(N)$ for an atom in three successive charge states such that $E(Z-1)=E(Z)+1$ and $E(Z+1)=E(Z)-A$. This is interpolated smoothly by a quadratic function

$$E(N)=E(Z)-\tfrac{1}{2}(I+A)(N-Z)+\tfrac{1}{2}(I-A)(N-Z)^2. \tag{20}$$

This formula gives the correct center $-\frac{1}{2}(I+A)$ and width $I-A$ of a band gap [24] for solids as well as for atoms or molecules. The implied chemical potential is a continuous linear function

$$\mu=-\tfrac{1}{2}(I+A)+(I-A)(N-Z). \tag{21}$$

If one adopts the point of view of Landau [6,7] and of Slater [10,11], the energy functional of a system of electrons should be considered to vary smoothly as a function of density or of unconstrained occupation numbers. The actual physical state of the system, however, is determined by Fermi-Dirac statistics through a distribution function that depends on one-electron energies, defined as partial derivatives with respect to freely variable occupation numbers. Values of the occupation numbers are determined that are subject to the restriction $0\leqslant n_i\leqslant 1$. Physically realizable variations of the electron density are constrained by this restriction, so that the full variability of the postulated energy functional cannot be explored. It is relevant to remark that in practical applications of DFT, exchange-correlation functionals are ordinarily used that necessarily have continuous derivatives, because they are derived from the local density or local density gradient, with no consideration of the total electron number [25,26].

V. CONCLUSIONS

The ensemble theory leads to a very strong constraint on variations of electron density ρ for nonintegral N. Mean values of all observables are determined by interpolation between their values for the two integral-N ground states that bound each interval of nonintegral N. Since only the two end values are specified and the weight coefficients are linear in N, ρ and all observables are interpolated as linear functions of N. At this point, the ensemble theory appears to be in contradiction with approximations to the kinetic energy, Coulomb, and exchange density functionals that indicate that these are nonlinear functions of density [25]. If ρ varies linearly with nonintegral N, this cannot also be true for the various components of the energy functional other than $V[\rho]$.

For any system with an energy gap, the ensemble theory implies a derivative discontinuity in the mean value of any observable at the integral value of electron number N just below the gap. The resulting chemical potential for any atom or molecule is a step function with a finite increment at each integral value of N. This discontinuity is inherent in Fermi statistics for electrons or electron quasiparticles. If a smoothly varying energy functional exists that gives correct values for integral N, this theory cannot exploit it.

Following the logical principle of Occam's razor, it might be more practical to interpolate this functional smoothly between values defined for integral numbers of electrons than to build derivative discontinuities into it. Such an interpolation is achieved with the superlattice model [10,20], in which fractional occupation numbers arise as in energy-band theory as the probability of locating an electron in a Bloch wave at a particular atomic site. The interaction energy terms are inherently nonlinear in electron number, and energy differences must be obtained by integrating over continuously varying occupation numbers [9]. The practical problem with this approach is that accurate solution of the interacting-electron problem is required on an extended space lattice in order to define numerical values of the implied universal functional.

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