v-Representability and Density Functional Theory

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It is shown that if $n(r)$ is the discrete density on a lattice (enclosed in a finite box) associated with a nondegenerate ground state in an external potential $v(r)$ (i.e., is "v-representable"), then the density $n(r)+\mu m(r)$, with $m(r)$ arbitrary (apart from trivial constraints) and μ small enough, is also associated with a nondegenerate ground state in an external potential $v'(r)$ near $v(r)$; i.e., $n(r)+\mu m(r)$ is also v-representable. Implications for the Hohenberg-Kohn variational principle and the Kohn-Sham equations are discussed.

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I consider a system of N nonrelativistic interacting (or noninteracting) electrons in a nondegenerate ground state associated with a static external potential, $v(r)$. I denote the electron density in this state by $n(r)$ and call such a density v-representable (VR). Clearly, through the Schrödinger equation, $v(r)$ determines $n(r)$. An important issue, especially for density functional theory,[1] the so-called v-representability question, is the following converse question: given some function $n(r)$, is it v-representable, i.e., can it be reproduced as the nondegenerate ground-state density associated with some external potential $v(r)$? This Letter offers a partial, but useful, answer to this question.

The prior status of this question may be summarized as follows. First of all, it is obvious that not all functions $n(r)$ are VR. The following trivial classes are not: $n(r)<0$ for some r; $n(r)$ discontinuous; $n(r)$ such that $\int n(r)dr \neq$ integer. Recently Levy[2] and Lieb[3] have constructed some nontrivial, smooth density distributions which are not VR. It has also been clear that the class of functions $n(r)$ which *is* VR is not "negligible." Thus consider a one-electron system. Given a sufficiently smooth positive $n(r)$ integrating to unity, we can construct the ground-state wave function $\psi(r)=n^{1/2}(r)$ and from it the potential by the use of the Schrödinger equation,

$$v(r)-E=\frac{\frac{1}{2}\nabla^2\psi(r)}{\psi(r)}=\frac{\frac{1}{2}\nabla^2[n^{1/2}(r)]}{n^{1/2}(r)}. \qquad (1)$$

Next consider an infinite, nearly uniform system with prescribed density[1]

$$n(r)=n_0+\lambda n_1(r), \qquad (2)$$

where λ is infinitesimal and $n_1(r)$ is an *arbitrary*, sufficiently smooth function. Let v_0 be the potential associated with n_0. To first order in λ we now look for the perturbing potential, v_1, associated with n_1,

$$v(r)=v_0+\lambda v_1(r). \qquad (3)$$

Let us assume that both $n_1(r)$ and $v_1(r)$ can be represented as Fourier integrals and write

$$n_1(r)=(2\pi)^{-3/2}\int \exp(iq\cdot r)n_1(q)dq;$$
$$v_1(r)=(2\pi)^{-3/2}\int \exp(iq\cdot r)v_1(q)dq. \qquad (4)$$

In terms of the static linear response function of the uniform gas, defined by

$$\chi(q)\equiv n_1(q)/v_1(q), \qquad (5)$$

$v_1(r)$ is then given

$$v_1(r)=(2\pi)^{-3/2}\int \exp(iq\cdot r)[n_1(q)/\chi(q)]dq, \qquad (6)$$

provided only that the right-hand side exists.

In the present paper I shall demonstrate rigorously the v-representability of a broad and very important class of densities, $n(r)$, for a Schrödinger problem defined on a *lattice*, r, and enclosed in a box. I impose vanishing boundary conditions on lattice points *on* the surface of the box and assume that the density $n(r)>0$,[4] except on the boundary points.

I shall then prove the following:

Theorem.—If $n(r)$ is a VR density, then so is $n'(r)\equiv n(r)+\mu m(r)$, where $m(r)$ is arbitrary [except for the trivial conditions $\sum m(r)=0$, $m(r)=0$ on the boundary], provided that μ is small enough.

Proof.—Consider a system of N particles. The ground-state wave function, $\Psi(r^1,\ldots,r^N)$, is defined on the points of a finite cubic lattice, of lattice parameter a, and is required to vanish on the boundary points. The external potential, defined on the lattice points, is denoted by $v(r)$. The discrete Schrödinger equation satisfied by Ψ

is then

$$\left\{\sum_j\left[-\tfrac{1}{2}(\nabla^j)^2+v(r^j)\right]+\tfrac{1}{2}\sum_{j\neq k}\frac{1}{|r^j-r^k|}-E_0\right\}\times\Psi(r^1,\ldots,r^N)=0, \qquad (7)$$

where all r^j run over the lattice points r and ∇^2 is the discrete Laplacian, $\nabla^2 f(r)\equiv a^{-2}[\sum_\delta f(r+\delta)-6f(r)]$, where the six vectors δ describe the displacements to the six nearest neighbors. Let us denote by M the number of interior lattice points. The Schrödinger "equation" is a set of M^N linear equations for the M^N unknowns $\Psi(r^1,\ldots,r^N)$. The wave function is antisymmetric and normalized,

$$\sum_{r^1,\ldots,r^N}|\Psi(r^1,\ldots,r^N)|^2=1. \qquad (8)$$

The density is defined by

$$n(r)\equiv N\sum_{r^2,\ldots,r^N}|\Psi(r,r^2,\ldots,r^N)|^2, \qquad (9)$$

and, in view of (8), satisfies the equation

$$\sum n(r)=N. \qquad (10)$$

I shall now, as a preliminary, prove a lemma for this discrete model, following the reasoning of Ref. 1. Let

$$v'(r)\equiv v(r)+w(r), \qquad (11)$$

where $w(r)$ is arbitrary except that it is small enough so that the ground state, Ψ' corresponding to $v'(r)$ is also nondegenerate. Without loss of generality we can assume that $\sum w(r)=0$, since a constant $w(r)$ is trivial. Then, following Ref. 1, one can show immediately that if we write the new density $n'(r)$ associated with $v'(r)$ as

$$n'(r)\equiv n(r)+m(r;w), \qquad (12)$$

then $m(r;w)$ is nonvanishing on at least some interior points.[5]

Furthermore, if w is of first order in a small parameter λ ($w\to\lambda w$), m is also of first order in λ, as I shall now show. Denote the Hamiltonians corresponding to v and v' by H and H', respectively, and the corresponding ground-state energies by E_0 and E_0'. Then, for small λ, if follows from the Rayleigh-Ritz principle that

$$E_0=(\Psi,H\Psi)=(\Psi,H'\Psi)+[\Psi,(H-H')\Psi]$$
$$=[E_0'+\lambda^2\gamma+O(\lambda^3)]-\lambda\sum w(r)n(r). \qquad (13)$$

The coefficient γ is positive definite. To see this, expand Ψ in the orthonormal eigenstates of H',

$$\Psi=\sum\nolimits_0 c_n\Psi_n', \quad \sum|c_n|^2=1. \qquad (14)$$

Then

$$(\Psi,H'\Psi)=\sum\nolimits_0|c_n|^2E_n'$$
$$=E_0'+\sum\nolimits_1|c_n|^2(E_n'-E_0'). \qquad (15)$$

Since by first-order perturbation theory the coefficients c_n ($n>0$) are not all zero to first order in λ, comparison of Eq. (15) and Eq. (13) shows that $\gamma>0$. Similarly

$$E'=[E+\lambda^2\gamma'+O(\lambda^3)]+\lambda\sum w(r)n'(r), \qquad (16)$$

where $\gamma'>0$. Adding Eqs. (13) and (16) gives

$$(E+E')=(E+E')+\lambda^2(\gamma+\gamma')$$
$$-\lambda\sum w(r)[n(r)-n'(r)]+O(\lambda^3). \qquad (17)$$

This establishes the lemma,

$$n'(r)-n(r)=O(\lambda). \qquad (18)$$

Before proceeding further I want to automatically insure the condition $\sum m(r)=0$ and $\sum w(r)=0$. To this end I introduce the complete M-dimensional orthonormal basis

$$u_1(r)=M^{-1/2};\quad u_l(r),\quad l=2,3,\ldots,M. \qquad (19)$$

Because of the orthogonality to u_1, one has

$$\sum\nolimits_r u_l(r)=0,\quad l=2,3,\ldots,M, \qquad (20)$$

so that we now write,

$$w(r)=\sum_{l=2}^{M}A_l u_l(r), \qquad (21)$$

$$m(r)=\sum_{l=2}^{M}B_l u_l(r). \qquad (22)$$

Because of the nondegeneracy of the ground state Ψ, the Schrödinger equation provides a continuously differentiable mapping of the $(M-1)$-dimensional space of A_l on the space B_l ($l=2,\ldots,M$),

$$B_l=F_l(A_2,\ldots,A_M);$$
$$l=2,\ldots,M,\quad |A_l|<A_l^0, \qquad (23)$$

where the A_l^0 are finite positive numbers.

I now show that the Jacobian of this mapping at the origin of the A space is nonvanishing and finite. For near $A_l=0$, the B_l can be calculated by a convergent power series (recall that we are expanding around a nondegenerate ground state),

$$B_l=\sum M_{lk}A_k+\sum M_{lkk'}A_kA_{k'}+\ldots$$
$$(l,k,k'=2,\ldots,M). \qquad (24)$$

At $A_l=0$, the Jacobian of this transformation is

$$\partial(B_2,B_3,\ldots,B_M)/\partial(A_2,A_3,\ldots,A_M)$$
$$=\mathrm{Det}|M_{lk}|. \qquad (25)$$

If this determinant were zero, there would exist a set of nonvanishing coefficients, $\bar{A}_k$, such that

$$M_{lk}\bar{A}_k = 0, \tag{26}$$

so that the corresponding B_l would vanish to first order in the $\bar{A}_k$. The associated potential perturbation, $\lambda\bar{w}(r) = \lambda\sum_2^M \bar{A}_k u_k(r)$, would thus lead to a density change vanishing to first order in λ, in conflict with the lemma, Eq. (18).

Under these circumstances we can apply a theorem on inverse transformations[6] which states that there is a finite neighborhood enclosing the origin in B space, $|B_l| < B_l^0$, such that every point inside this neighborhood is mapped in a continously differentiable way on a unique point in A space,

$$A_l = G_l(B_2, \ldots, B_M); \quad l = 2, \ldots, M, \quad |B_l| < B_l^0. \tag{27}$$

This completes the proof of the theorem.

We can express this theorem in the following geometric language. Every density, $n(r)$, of an N-particle system can be represented by an M-dimensional point, $\vec{n}$, with coordinates $(n(r_1), \ldots, n(r_M))$, lying on the plane, S, defined by $\sum n(r) = N$. The theorem states that if $n(r)$ is VR, the corresponding point, $\vec{n}$, is in the *interior* of an $(M-1)$-dimensional VR manifold located on the plane S.

An important question often asked in the context of density functional theory is this: Given a density distribution $n(r)$, how can we know whether it is VR? For a lattice we have proved that it is VR, provided it is sufficiently near a density distribution known to be VR. While in this note nothing is mathematically proved about the continuum problem, it is virtually certain that, subject to appropriate conditions of regularity and asymptotic behavior, similar theorems will apply. In physical applications of density functional theory one is aiming at the physical, and hence VR, density $n(r)$. Consequently, if one has some reasonable notion of what the physical $n(r)$ is, one will work with trial $n(r)$'s "near" it. Their v-representability is thus not a matter of exceptional accident but guaranteed if, in an appropriate sense, they are sufficiently "near" to the physical $n(r)$.

I conclude with two remarks about the Kohn-Sham (KS) equations.[7] These equations presuppose that a physical $n(r)$, which is necessarily VR for the *interacting* Schrödinger equation (VR-I), is also VR for the *noninteracting* Schrödinger equation (VR-N). If this is the case, the considerations of this paper also provide support for the use of the KS equations, which presuppose the existence of $T_s[n]$, the noninteracting kinetic energy functional, for densities in a neighborhood enclosing the physical $n(r)$.

However, obviously the physical density $n(r)$ need not *necessarily* be VR-N. Clearly, the density $n_{KS}(r)$ obtained from the Kohn-Sham equations with some single-particle—necessarily approximate—$v_{eff}(r)$ is VR-N. If n_{KS} is sufficiently near the physical $n(r)$ (which may be difficult to know), then, *a posteriori*, the considerations of this paper imply that the physical $n(r)$ is both VR-I and VR-N.

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[1]P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[2]M. Levy, Phys. Rev. A 26, 1200 (1982).

[3]E. Lieb, in *Physics as Natural Philosophy: Essays in Honor of Laszlo Tisza on His 75th Birthday,* edited by A. Shimony and H. Feshbach (MIT Press, Cambridge, Massachusetts, 1982), p. 111.

[4]It is possible that this condition is necessarily satisfied in the ground state but I am not aware of a proof. For noninteracting particles it is automatic. For interacting particles, if $n(r_1)$ is to be zero, all natural orbitals must vanish at r_1.

[5]The condition $n(r) \neq 0$ is needed here since, it $n(r_1) = 0$, the perturbing potential $w(r) = \text{const} \times \delta_{rr_1}$ would not change Ψ, thus blocking the proof of Eq. (12).

[6]A. E. Taylor and W. R. Mann, *Advanced Calculus* (Xerox College Publishing, Lexington, Massachusetts, 1972), Chap. 9.

[7]W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).