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Density-functional theory for two noninteracting spinless fermions

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A method is presented for relating a ground-state density distribution to the effective single-particle potential which has this density for its ground state for a noninteracting system of particles. The method is useful for systems consisting of a small number of spinless fermions and in the case of two particles a second-order, nonlinear differential equation relates the density and the effective potential. The question of v representability is addressed through examples of densities for one- and three-dimensional systems. It is found that densities of the form e^{-ar} for two-particle systems are not ground-state v representable. The added flexibility of three dimensions over one allows an effective potential which does not necessarily have the chosen density as its ground state, but as its lowest nondegenerate state.

Density-functional theory addresses the relationship between the ground-state density of a many-particle system and the ground-state energy and Hamiltonian of the system. Hohenberg and Kohn[1] showed that the external local potential acting on the system is a unique functional, apart from an additive constant, of the ground-state density assuming that the ground state is nondegenerate. Given the form of the interactions the system is equally well characterized by its ground-state density as by the external field. A further development of the theory was achieved by Kohn and Sham[2] through the introduction of an auxiliary system of noninteracting particles having the same ground-state density as the interacting system of interest and moving in some effective one-body potential V_{eff}. This effective potential must also be a unique functional of the ground-state density. There is therefore interest in the functional relationship between the one-body potential and the corresponding ground-state density for a noninteracting system because of the application to the interacting many-body problem through the auxiliary noninteracting system of particles introduced by Kohn and Sham. In this Rapid Communication we consider the relationship for systems consisting of a small number of fermions.

Consider N noninteracting fermions moving in a one-body potential V_{eff} and having a ground-state density distribution n. Neglecting spin we may write the ground-state density in terms of the N lowest single-particle energy eigenfunctions ψ_i,

$$n=\sum_{i=1}^{N}|\psi_i|^2 . \tag{1}$$

This establishes an implicit functional relationship for n in terms of V_{eff} since the ψ_i are solutions of the single-particle wave equation. We wish to address the inverse problem and investigate the functional relationship for V_{eff} in terms of n. Aside from its intrinsic interest a simple relationship would shed light on the class of functions which can be realized as ground-state densities of noninteracting particles in an external field. This is the so-called ground-state, noninteracting V-representability problem which we shall abbreviate to v representability in what follows.

For $N=1$ the solution of the inverse problem is given trivially by[3]

$$V_{\text{eff}}(\mathbf{r})=\frac{1}{2}\frac{1}{\sqrt{n}}\nabla^2\sqrt{n}+\varepsilon_0 , \tag{2}$$

but little progress has been reported for $N\geqq 2$. There have been attempts to deduce effective potentials from electron densities for atomic systems. Notable among these is the work of Talman and Shadwick[4] who use a variational method to minimize the total energy of an atom with a single Slater determinant as a trial wave function, but unlike the Hartree-Fock method the orbitals are restricted to be solutions of single-particle wave equations with a local effective field. Almbladh and Pedroza[5] have obtained effective potentials from Hartree-Fock and correlated electron densities for light atoms through a trial-and-error approach based on a potential with adjustable parameters. Although the latter method can, in principle, yield potentials to any desired accuracy it is in practice approximate by its nature and the functional form of the relationship between V_{eff} and n cannot readily be investigated. It also requires *a priori* knowledge of the form of the effective potential. Werden and Davidson[6] have reported a similar iterative approach based on linear response theory for the one-dimensional case.

This article offers an exact solution to the problem which facilitates study of the functional form for a small number of particles. For convenience we consider the simplest nontrivial case of two noninteracting spinless fermions bound in one dimension. Let $n(x)$ be the given ground-state density and $V_{\text{eff}}(x)$ be the corresponding effective potential. Suppose ψ_0 and ψ_1 are the two lowest single-particle states corresponding to V_{eff} so that ψ_0 and ψ_1 satisfy the single-particle Schrödinger equations

$$-\frac{1}{2}\frac{d^2\psi_0}{dx^2}+V_{\text{eff}}\psi_0=\varepsilon_0\psi_0 , \tag{3}$$

$$-\frac{1}{2}\frac{d^2\psi_1}{dx^2}+V_{\text{eff}}\psi_1=\varepsilon_1\psi_1 , \tag{4}$$

with $\varepsilon_1>\varepsilon_0$, there being no degeneracy for bound states in one dimension. Furthermore,

$$n(x)=\psi_0^2+\psi_1^2 . \tag{5}$$

From (3) and (5) we have, respectively,

$$V_{\text{eff}}=\frac{1}{2}\frac{1}{\psi_0}\frac{d^2\psi_0}{dx^2}+\varepsilon_0\ , \tag{6}$$

$$\psi_0=\sqrt{n-\psi_1^2}\ . \tag{7}$$

Since ψ_0 is a single-particle ground state it has no nodes and can be chosen to be positive definite (except at the boundaries). Consequently, the substitution of (7) in (6) yields

$$V_{\text{eff}}=\frac{1}{2\sqrt{n-\psi_1^2}}\frac{d^2}{dx^2}\sqrt{n-\psi_1^2}+\varepsilon_0 \tag{8}$$

and

$$-\frac{1}{2}\frac{d^2\psi_1}{dx^2}+\frac{1}{2\sqrt{n-\psi_1^2}}\frac{d^2}{dx^2}\sqrt{n-\psi_1^2}\,\psi_1=(\varepsilon_1-\varepsilon_0)\psi_1 \tag{9}$$

results upon the substitution of (8) in (4). With Eq. (9) regarded as a second-order nonlinear differential equation in ψ_1 a relationship is established between n and ψ_1 and through (8) also with V_{eff}. The determination of ψ_1 and the constant $\varepsilon=\varepsilon_1-\varepsilon_0>0$ requires the application of boundary conditions. If $-L\leq x\leq L$ the boundary conditions are

$$\text{(i)}\ \psi_1(-L)=\psi_1(L)=0\ , \tag{10}$$

$$\text{(ii)}\ \int_{-L}^{+L}dx\,\psi_1^2=1\ , \tag{11}$$

$$\text{(iii)}\ \psi_1\ \text{must have only one node}\ . \tag{12}$$

One node ensures that ψ_1 is the first excited single-particle state.[7] These boundary conditions determine uniquely ψ_1 and ε in terms of n and hence also V_{eff} apart from an additive constant. To determine ε_1 and ε_0 separately, appeal must be made to the physical situation. One procedure for determining V_{eff} is to solve (8) for an arbitrary ε and then adjust ε so that (11) is satisfied.

The extension of this approach to the case $N>2$ is straightforward and yields a set of $(N-1)$ coupled differential equations.

For $N=2$ the transformation

$$\psi_0=\sqrt{n}\cos\theta\ ,$$

$$\psi_1=\sqrt{n}\sin\theta$$

in (8) leads to the following simplification:

$$\frac{d^2\theta}{dx^2}+\frac{1}{n}\frac{dn}{dx}\frac{d\theta}{dx}+\varepsilon\sin(2\theta)=0\ , \tag{13}$$

with $-\pi/2\leq\theta\leq\pi/2$. We note that the dependence of θ and hence V_{eff} on the density comes through the logarithmic derivative of n.

It is also interesting to note that the differential equation (9) and equivalently (13) can be deduced from a variational principle. For example (13) is the Euler-Lagrange equation obtained by minimization of the (kinetic energy) functional $T=\int dx\,n(d\theta/dx)^2$ subject to the normalization condition $\int dx\,n\sin^2\theta=1$. That is

$$\delta\left[\int dx\,n\left(\frac{d\theta}{dx}\right)^2-\varepsilon\int dx\,n\sin^2\theta\right]=0 \tag{14}$$

gives (13) with ε being a Lagrange undetermined multiplier.

As an example, we have investigated particle densities for two spinless fermions moving in the simple harmonic potential $x^2/2$. Given a density, the numerical solution of (13) for θ and ε posed on difficulties, and the corresponding effective potential was easily obtained from (8). Two cases were considered. The density for the ground state of the system obtained by occupying the two lowest oscillator states gave back the original oscillator potential as required. For the second case we constructed n for an excited state of the system with the lowest and second excited single-particle oscillator states being occupied. The corresponding V_{eff} which has this n as its ground-state density was then deduced. The results for θ and V_{eff} for these two cases are shown in Figs. 1 and 2. The functions θ are

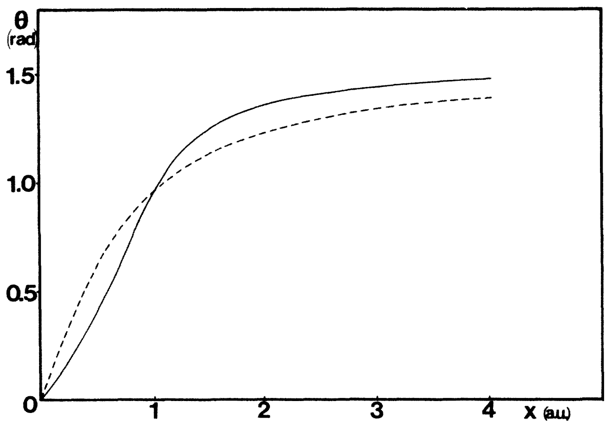

FIG. 1. The solutions of Eq. (13) with $n=\psi_0^2+\psi_1^2$ (dashed curve) and $n=\psi_0^2+\psi_2^2$ (full curve); ψ_n is an harmonic oscillator eigenfunction.

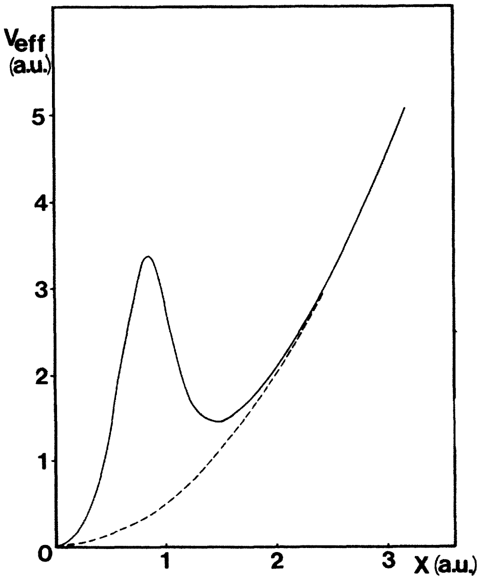

FIG. 2. The effective potentials deduced from densities $n=\psi_0^2+\psi_1^2$ (dashed curve $=\frac{1}{2}x^2$) and $n=\psi_0^2+\psi_2^2$ (full curve), where ψ_n is an harmonic oscillator eigenfunction.

featureless and are typical of our experience. The $V_{\rm eff}$ for the second case differs from that for the first, the original oscillator potential $x^2/2$, through the introduction of symmetric peaks which tend to raise the first excited state energy with respect to the single-particle ground and second excited states. Evidently, the density in the second case, although it comes from an excited two-particle state of the oscillator, is V representable.

We now extend the method to three dimensions in anticipation of application to atoms. By analogy with the development of (9) we have for the case of $N=2$,

$$-\tfrac{1}{2}\nabla^2\psi_1+\frac{1}{2\sqrt{n-\psi_1^2}}\nabla^2\sqrt{n-\psi_1^2}\,\psi_1=\varepsilon\psi_1 \ , \qquad (15)$$

where $\varepsilon=\varepsilon_1-\varepsilon_0$. The straightforward extension to $N>2$ gives again $N-1$ coupled equations. If the system is spherically symmetric, and with the assumption that the two lowest states are s states, we have the following compact form for (15) analogous to (13) for the one-dimensional case

$$\frac{d^2\theta}{dr^2}+\frac{1}{\rho}\frac{d\rho}{dr}\frac{d\theta}{dr}+\varepsilon\sin(2\theta)=0 \ , \qquad (16)$$

where the radial wave functions are given by

$$R_{1s}=\sqrt{\rho}\cos\theta \ , \qquad R_{2s}=\sqrt{\rho}\sin\theta \ , \qquad (17)$$

with $\rho=r^2n$ and $-\pi/2\leqq\theta\leqq\pi/2$. The effective potential is given by

$$V_{\rm eff}=\frac{1}{2}\frac{1}{R_{1s}}\frac{d^2}{dr^2}R_{1s}+\varepsilon_0 \ , \qquad (18)$$

where n is the particle density. The boundary conditions on (17) are with $R_{2s}\to\sqrt{\rho}$ as $r\to\infty$: (i) $\theta\to-\pi/2$, $r\to\infty$, (ii) $\int_0^\infty dr\,\rho\cos^2\theta=1$, and (iii) θ must have only one node.

We have made application to the Be atom. This falls within the domain of the method if we account for electron spin by doubly occupying the two lowest effective single-particle states. Using the Hartree-Fock density[8] for n gave an effective potential V_x which is defined as the difference between the total effective potential and the Hartree potential. We also took the configuration-interaction (CI) electron density from the work of Bunge[9] and this gave an effective potential $V_{\rm xc}$ which includes both exchange and correlation effects. To find absolute potentials it is necessary to know either ε_{1s} or ε_{2s}. In principle, ε_{2s} can be obtained from the asymptotic form of the density but the asymptotic form (Hartree-Fock or CI) is not sufficiently accurate for our purposes and we have used the fact that ε_{2s} equals the ionization energy.[5,10] The effective potentials for these cases are illustrated in Fig. 3. The exchange-correlation potential is in agreement with that obtained by Almbladh and Pedroza[5] as is also the energy difference $\varepsilon_{2s}-\varepsilon_{1s}$. Calculation of the single-particle energy eigenvalues for the two effective potentials confirm that the $1s$ and $2s$ states lie lowest, the nearest other state being the $2p$ which was found to be 0.13 a.u. above the $2s$ for the CI case. Both densities are therefore v representable.

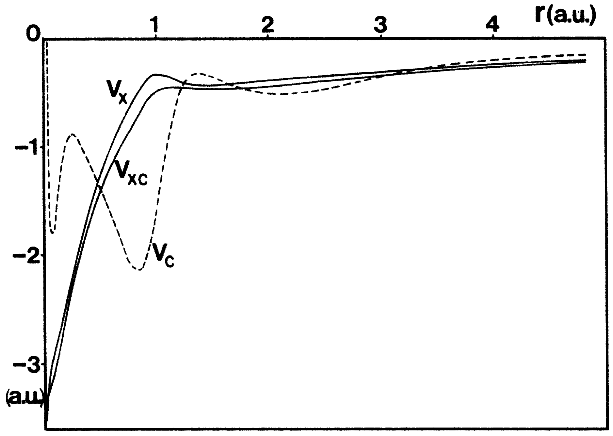

FIG. 3. The effective exchange and exchange-correlation potential of Be deduced from Hartree-Fock and CI density, respectively (full curves). The dashed curve is the effective correlation potential, $v_c=v_{\rm xc}-v_x$, magnified ten times.

Finally, we consider two cases for which the density is not v representable. Both are spherically symmetric densities and no difficulties were encountered in solving (16) for θ and using (17) and (18) to deduce $V_{\rm eff}$. The first example is due to Levy[11] and to Lieb[12] and is presented by them as illustrations of their general arguments on v representability. The density is constructed from a linear combination of degenerate ground-state densities as follows:

$$\rho(r)=|R_{1s}|^2+\alpha|R_{2s}|^2+\beta|R_{2p}|^2 \ , \qquad (19)$$

where R_{nl} is the radial hydrogenic function for $Z=2$ and where $\alpha+\beta=1$. The effective potential was found for a number of vaues of α between 0 and 1. However, the density (19) does not correspond to the ground state of these potentials but rather to the lowest nondegenerate $1s2s$ state as the $2p$ state lies lower in energy than the $2s$ state. The difference between ε_{2s} and ε_{2p} approaches zero as $\alpha\to1$.

We next consider two-particle densities of the form e^{-ar} where $a=$const. With densities of this form (16) can be scaled by substituting $x=ar$ to yield

$$\frac{d^2\tilde\theta}{dx^2}+\left(\frac{2}{x}-1\right)\frac{d\tilde\theta}{dx}+\left(\frac{\varepsilon}{a^2}\right)\sin(2\tilde\theta)=0 \ . \qquad (20)$$

The normalization condition becomes

$$\int_0^\infty dx\,x^2e^{-x}\sin^2\theta=1 \qquad (21)$$

and the effective potential can also be scaled

$$V_{\rm eff}(r)=a^2\tilde V_{\rm eff}(x) \ . \qquad (22)$$

It was therefore necessary for us to perform calculations of the effective potential (22) for only one value of a. The radial Schrödinger equations can be similarly scaled and numerical solution for the single-particle eigenvalues reveals that for all $a>0$, $\varepsilon_{1s}<\varepsilon_{2p}<\varepsilon_{3d}<\varepsilon_{2s}$. As in the previous example the assumed $1s2s$ two-particle state is not the ground state for the effective potentials. Furthermore, any other assumed ground state, e.g., $1s2p$, cannot give a spherically symmetric density. We conclude that in both of these cases the densities are not ground-state v representable at least for $N=2$. The result for the former case verifies the arguments of Levy[11] and Lieb.[12] The case of the exponential density is a new and surprising result since the exponential form is frequently a first choice for a trial function in any variational calculation on a bound system. The class of functions which are acceptable as densities for noninteracting systems in that they are ground-state v representable may be more restricted than had previously been imagined.

In the cases of spherically symmetric densities we have only considered the possibility of spherically symmetric effective potentials. It is not inconceivable that anisotropic effective potentials exist with (19) or the exponential form as their ground state densities but the possibility seems remote. Nevertheless, the consequences of allowing anisotropy are worthy of study.

We have presented a method to deduce the effective potential of density-functional theory from the ground-state density. For the case of two noninteracting fermions the method reduces to the solution of a single second-order nonlinear differential equation. For N noninteracting fermions we have $(N-1)$ coupled differential equations. This provides a more direct functional relationship between the density and the effective potential than has been reported previously except for the trivial case of $N=1$, and questions of v representability may be more readily addressed through this method. The $N=2$ cases investigated show no exceptions to v representability for one dimension. This contrasts with three dimensions where, for example, densities of the form e^{-ar} are not noninteracting, ground-state v representable, at least for $N=2$. Clearly the existence of a solution to (16) for the three-dimensional case for a given density is a necessary but not sufficient condition for the density to be noninteracting, ground-state v representable.

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

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

[3] Units are such that $\hbar=m=1$.

[4] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[5] C. O. Almbladh and A. C. Pedroza, Phys. Rev. A **29**, 2322 (1984).

[6] S. H. Werden and E. R. Davidson, in *Local Density Approximations in Quantum Chemistry and Solid State Physics*, edited by J. P. Dahl and J. Avery (Plenum, New York, 1982), p. 33.

[7] When the states are ordered by energy starting with ψ_0 as the ground state, ψ_n must have n nodes for bound states in one dimension: P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Pt. I, Chap. 6.

[8] C. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[9] C. Bunge, At. Data Nucl. Data Tables **18**, 2893 (1976).

[10] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).

[11] M. Levy, Phys. Rev. A **28**, 1200 (1982).

[12] E. H. Lieb, in *Physics as a Natural Philosophy*, edited by A. Shimony and H. Feshback (MIT Press, Cambridge, MA, 1982).