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Effective potentials in density-functional theory

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The problem of deducing the effective single-particle potential of density-functional theory is addressed. A systematic approach is introduced based on the reduction of the system of N one-body Schrödinger equations to a system of $N-1$ nonlinear differential equations which involve the given density directly. The approach is useful for systems consisting of a small number of particles and applications are made to Be and Ne atoms for which exchange and exchange-correlation potentials are found, and to one-dimensional systems. Densities corresponding to two and three spinless fermions in one dimension are considered and all the examples treated are found to be ground-state v-representable. It is shown that any density for two spinless fermions in one dimension is v-representable and we speculate that the same is likely to be true for any number of particles in one dimension. In contrast densities in three dimensions are given which are not v-representable. However, all these are of the class of ensemble ground-state densities introduced by Levy and Lieb. It remains to be seen if all densities are either ground-state or ensemble–ground-state v-representable.

I. INTRODUCTION

Density-functional theory[1,2] has become one of the most important tools in treating electronic systems. An important feature of the theory is the adoption of the ground-state density as the basic variable. The density depends only on three coordinate variables at most, independent of the size of the system in contrast to the many-body wave function which depends on $3N$ coordinate variables and evidently becomes very complicated as the number of particles, N, increases. The utility of density-functional theory rests on the fact that the interacting many-body Schrödinger equation may be reduced to a set of single-particle Schrödinger equations which are numerically much more tractable. Unlike other reductions of the many-body problem to a single-particle theory such as Hartree-Fock or the $X\alpha$ method, density-functional theory is in principle exact and general.

Density-functional theory is based on the theorem of Hohenberg and Kohn[1] which showed that for an electronic system, or any system of identical particles, knowledge of the ground-state density $n(\mathbf{r})$ is sufficient to fully characterize the system. In other words, the ground-state density uniquely determines the external potential $V_{\text{ext}}(\mathbf{r})$ acting on the system up to an arbitrary constant. Since V_{ext} determines the electronic properties of the system, including excited-state properties, so does $n(\mathbf{r})$. This means that all electronic properties are functionals of the ground-state density.

Of all electronic properties, the total energy has special importance in density-functional theory for, as also shown by Hohenberg and Kohn,[1] there exists a ground-state energy functional $E[n]$, which yields the true ground-state energy $E_{\text{g.s.}}$ upon substitution of the ground-state density $n_{\text{g.s.}}$, and which is subject to a variational principle $E[n]\geq E_{\text{g.s.}}$ for other densities n. Following Levy's prescription,[3] $E[n]$ may be defined as follows:

$$E[n]=\min_{\Psi\in n}\{\langle\Psi\mid(T+V_{ee})\mid\Psi\rangle\}+\int d\mathbf{r}\,V_{\text{ext}}n\ , \quad (1)$$

where T is the kinetic-energy operator and

$$V_{ee}=\tfrac{1}{2}\sum_{\substack{i,j\\ i\neq j}} r_{ij}^{-1}\ .$$

For a given n, the first term searches over all the antisymmetric wave functions that yield n and delivers the minimum. The variational property of $E[n]$ follows trivially from the definition in (1).

An important step in developing a computational scheme for calculating the ground-state energies was made by Kohn and Sham[2] who introduced an auxiliary system of noninteracting electrons moving in some common local effective potential and having the same density as that of the original interacting system. The energy functional can be written

$$E[n]=T_0[n]+U_{\text{Coul}}[n]+\int d\mathbf{r}\,V_{\text{ext}}n+E_{\text{xc}}[n]\ . \quad (2)$$

T_0 is the kinetic energy of the auxiliary system, $T_0[n]=\min_{\Psi_0\in n}\{\langle\Psi_0\mid T\mid\Psi_0\rangle\}$, where Ψ_0 is a single Slater determinant, U_{Coul} is the classical Coulomb energy of the electrons

$$U_{\text{Coul}}[n]=\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ ,$$

and E_{xc} is the exchange-correlation energy which is defined by Eq. (2). Kohn and Sham then used the variational property of the energy functional $E[n]$. By varying $E[n]$ with respect to n subject to the conservation of particle number

$$\frac{\delta}{\delta n}\left[E[n]-\mu\int d\mathbf{r}\,n\right]=0\ ,$$

and noting that T_0 is the kinetic energy of the noninteracting system, they arrived at the set of single-particle Schrödinger equations,

$$-\tfrac{1}{2}\nabla^2\phi_i+V_{\text{eff}}\phi_i=\varepsilon_i\phi_i,\quad i=1,2,\ldots,N \tag{3}$$

where

$$V_{\text{eff}}(\mathbf{r})=V_{\text{ext}}(\mathbf{r})+\int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+V_{\text{xc}}(\mathbf{r})$$

and (4)

$$V_{\text{xc}}(\mathbf{r})=\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}\ .$$

The set of equations (3) is to be solved self-consistently such that

$$n(\mathbf{r})=\sum_{i=1}^{N}|\phi_i|^2\ . \tag{5}$$

The ground-state energy can then be written

$$E_{\text{g.s.}}=\sum_{i=1}^{N}\varepsilon_i-\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-\int d\mathbf{r}\,V_{\text{xc}}n+E_{\text{xc}}[n]\ . \tag{6}$$

The above scheme for calculating ground-state energies is so far exact but there are two fundamental problems. The first is our incomplete knowledge of E_{xc} and consequently V_{xc}. Fortunately, E_{xc} is usually small compared to the total energy and a simple local-density approximation[4] gives good results in many cases. This is the main reason for the success of the Kohn-Sham scheme and its broad application in atomic, molecular, and condensed-matter physics. The second problem is known as the *v*-representability problem which may not be crucially important in applications of the scheme because it rarely arises in practice but nevertheless it is an interesting and fundamental problem. Kohn and Sham assumed in deriving Eq. (3) that an interacting ground-state density is also a ground-state density of a noninteracting system, but as has been shown by Levy[5] and Lieb,[6] this assumption is not necessarily valid. They have shown that there are densities which are not ground-state densities of any local effective potentials. These densities are constructed from linear combinations of degenerate ground-state densities and look physically reasonable but there may be others in this class. Densities which are ground-state densities of local effective potentials are called *v*-representable.

The rearrangement of the energy functional (2) leading to the introduction of the E_{xc} also involves $T_0[n]$, the kinetic-energy functional for a system of noninteracting particles. This is treated exactly in the Kohn-Sham scheme by introducing the single-particle orbitals ϕ_i and by writing

$$T_0[n]=\tfrac{1}{2}\sum_{i=1}^{N}\int d\mathbf{r}\,|\nabla\phi_i|^2\ . \tag{7}$$

If T_0 was known as a functional of the density, then density-functional theory would be truly powerful because no matter how large and complicated the system is, we would have but a single Euler-Lagrange equation for the density. This would allow applications of density-functional theory to complex systems such as large molecules which at present remain largely unexplored.

The objective of this work is to facilitate a means of studying the exchange-correlation potentials, the *v*-representability problem, and the kinetic-energy functional for noninteracting systems. We approach these aspects of density-functional theory by studying the functional relationship between the effective or Kohn-Sham potential and the ground-state density.

Such a functional relationship between V_{eff} and n is implicit in the single-particle Schrödinger equations (3) which in principle relate ϕ_i's to V_{eff} and through (5) relate n to V_{eff}. But this route amounts to a functional expression of n in terms of V_{eff} which would not help us accomplish our objective. We wish instead to find the inverse relationship $V_{\text{eff}}[n]$ and for this reason we consider the following inverse problem: given an arbitrary density $n(\mathbf{r})$ we wish to find the effective potential $V_{\text{eff}}(\mathbf{r})$ for which $n(\mathbf{r})$ is the ground-state density.

The solution for $N=1$ is readily given by inverting the Schrödinger equation

$$V_{\text{eff}}=\frac{1}{2\phi_0}\nabla^2\phi_0+E_0=\frac{1}{2\sqrt{n}}\nabla^2\sqrt{n}+E_0\ , \tag{8}$$

but little progress has been reported in obtaining solutions for $N\geq 2$. Methods for obtaining a numerical solution for V_{eff} have been presented by Almbladh and Pedroza,[7] and Werden and Davidson.[8] The former authors use a parametrized potential to calculate the density and vary the parameters until the calculated density agrees with the given one. This method is capable of yielding accurate potentials with a sufficiently large number of parameters but it requires *a priori* knowledge of the form of the potential and does not provide us with any relationship between V_{eff} and n. Werden and Davidson[8] employed a similar method but used linear-response theory in their iterative procedure. This technique was applied to one-dimensional problems containing a few particles.

A related work is the optimized potential method for atoms of Talman and Shadwick.[9] It is essentially a Hartree-Fock method but the orbitals are restricted to be solutions of single-particle Schrödinger equations with some local potential V_{TS}. By minimizing the energy with respect to the orbitals or V_{TS}, they arrived at an integral equation for V_{TS}. The effective potential V_{TS} obtained by this method turns out to be very close to the one deduced from the Hartree-Fock density.

All the methods described above are either approximate in nature or iterative yielding no transparent functional relationship $V_{\text{eff}}[n]$. A systematic solution to the inverse problem has been presented by us in an earlier paper[10] and the method is reviewed in the next section. This paper supplements the earlier one. In addition we will discuss through examples how the *v*-representability problem arises and propose a proof for the *v*-

representability of any two-fermion density in one dimension satisfying certain criteria.

The paper is organized as follows. In Sec. I a solution to the inverse problem for an arbitrary number of particles is presented. In Sec. II, the method of deducing the effective potential from a given density is applied to a number of examples in one and three dimensions including Be and Ne atoms. In Sec. III, the v-representability problem is discussed and a proof for the v-representability of any two-fermion density in one dimension is proposed. Section IV is reserved for conclusions.

II. THEORY

We consider N noninteracting, spinless fermions moving in an effective local potential V_{eff} and let $\psi_0, \psi_1, \ldots, \psi_{N-1}$ be the N lowest-energy eigenfunctions of the system satisfying the single-particle Schrödinger equations

$$-\tfrac{1}{2}\nabla^2\psi_k + V_{\text{eff}}\psi_k = E_k\psi_k\,, \quad k=0,1,\ldots,N-1\;. \tag{9}$$

If $n(\mathbf{r})$ is the given density assumed to be a ground-state density then, with the eigenfunctions chosen to be real,

$$n=\sum_{k=0}^{N-1}\psi_k^2\;, \tag{10}$$

with ψ_0 the single-particle ground state we may write

$$V_{\text{eff}}=\frac{1}{2\psi_0}\nabla^2\psi_0+E_0\;, \tag{11}$$

and from (10) we can write ψ_0 as

$$\psi_0=\left[n-\sum_{k=1}^{N-1}\psi_k^2\right]^{1/2} \tag{12}$$

The division in (11) and the choice of sign in (12) pose no difficulties because ψ_0, being the ground state, has no nodes and may be taken to be positive everywhere. This allows us to express V_{eff} in terms of the density as follows:

$$V_{\text{eff}}-E_0=\frac{1}{2\left[n-\sum_{k=1}^{N-1}\psi_k^2\right]^{1/2}}\nabla^2\left[n-\sum_{k=1}^{N-1}\psi_k^2\right]^{1/2} \tag{13}$$

Finally, substitution of V_{eff} in (9) yields $(N-1)$ coupled differential equations:

$$-\tfrac{1}{2}\nabla^2\psi_k+\left[\frac{1}{2\left[n-\sum_{k=1}^{N-1}\psi_k^2\right]^{1/2}}\nabla^2\left[n-\sum_{k=1}^{N-1}\psi_k^2\right]^{1/2}\right]\psi_k=\varepsilon_k\psi_k\,,\quad k=1,2,\ldots,N-1 \tag{14}$$

where $\varepsilon_k=E_k-E_0$ with $\varepsilon_{k+1}\geq\varepsilon_k$. The energy eigenvalues with respect to the ground-state energy E_0 are determined by the boundary conditions which are problem dependent. When degeneracy exists, the number of differential equations may be reduced considerably as illustrated later by examples. Electron spin may be accommodated in the theory by double occupancy when there is no spin polarization. If the system is spin polarized two separate effective potentials may be introduced for spin-up and spin-down electrons but if these are to be determined additional information in the form of the spin polarization is required.

By elimination of the potential the N single-particle Schrödinger equations have been reduced to a set of $(N-1)$ coupled nonlinear second-order differential equations in which the single-particle wave functions are determined by the density instead of the potential. The set relates the wave functions to the density and through (11) offers the possibility of expressing the potential in terms of the density. This is in contrast to the Schrödinger equations which relate the wave functions to the potential and in turn provides the possibility of expressing the density in terms of the potential.

Before embarking on applications to physical systems in the next section, we illustrate the approach by considering some simple, model, one-dimensional systems. We start with the simplest nontrivial one-dimensional case of $N=2$ for which the set of equations (14) reduces to the single differential equation

$$-\frac{1}{2}\frac{d^2\psi_1}{dx^2}+\left[\frac{1}{2(n-\psi_1^2)^{1/2}}\frac{d^2}{dx^2}(n-\psi_1^2)^{1/2}\right]\psi_1=\varepsilon_1\psi_1\;, \tag{15}$$

where $\varepsilon_1=E_1-E_0>0$ is the difference between the ground and first excited single-particle energies, E_0 and E_1, respectively. For $0\leq x\leq L$ the appropriate boundary conditions are

$$\psi_1(0)=\psi_1(L)=0\;, \tag{16a}$$

$$\psi_1 \text{ must have one node only}\;, \tag{16b}$$

$$\int_0^L dx\,\psi_1^2=1\;. \tag{16c}$$

One node ensures that ψ_1 is the first excited state.[11] Equation (15) together with the boundary conditions is sufficient to determine ψ_1 uniquely. It is then a simple matter to construct the V_{eff} corresponding to the selected n by using ψ_1 in conjunction with (11) and (12).

Equation (15) can be simplified by the following transformation:

$$\psi_0=\sqrt{n}\,\cos\theta\;, \tag{17}$$

$$\psi_1=\sqrt{n}\,\sin\theta\;, \tag{18}$$

where $-\pi/2\leq\theta\leq\pi/2$. This transformation automatically satisfies (10) and the range of θ ensures that the ground state ψ_0 has no node. Substitution of (18) into (15) yields[12]

$$\frac{d^2\theta}{dx^2}+\left[\frac{1}{n}\frac{dn}{dx}\right]\frac{d\theta}{dx}+\varepsilon_1\sin(2\theta)=0 \tag{19}$$

with boundary conditions

$$\theta \text{ must have one node only }, \tag{20a}$$

$$\int_0^L dx\, n \sin^2\theta = \int_0^L dx\, n \cos^2\theta = 1 \; . \tag{20b}$$

These are equivalent, respectively, to (16b) and (16c). An examination of (19) reveals $d\theta/dx=0$ at $x=0,L$ and it transpires that θ is a monotonically decreasing function if $\theta(0)$ is chosen to be positive. We shall return to a discussion of general features of $\theta(x)$ in a later section.

Equation (19) which is equivalent to the equation of motion for a pendulum with a varying "resistance" coefficient equal to $(1/n)(dn/dx)$ looks deceptively simple. However, the only analytic solution that we know of is when $n=\text{const}$ which is not physically realizable. An iterative technique has been used to obtain a solution when $(1/n)(dn/dx)=\text{const}$ but only for small θ.[13] In our application θ is not necessarily small as is evident from (20b). Furthermore, the corresponding density, which is an exponential, is nonphysical for a one-dimensional system. Finding a general solution to (19) is clearly not a simple task. However, it is straightforward to obtain numerical solutions for specific situations.

The case of particle densities for two spinless fermions moving in the simple harmonic potential $x^2/2$ was investigated in the earlier paper.[10] Two cases were considered, the ground-state and first excited-state densities: $n_1=\phi_0^2+\phi_1^2$ and $n_2=\phi_0^2+\phi_2^2$ where ϕ_n is the nth harmonic oscillator eigenfunction. Given the density, the solution of Eq. (19) posed no difficulties, and the corresponding V_{eff} was easily obtained. The density n_1 gave back the original oscillator potential $x^2/2$ as required since it is the two-particle ground-state density for this potential. The second density n_2 was then used to find the corresponding V_{eff} which has n_2 as its ground-state density. The V_{eff} differs substantially from $x^2/2$ through the appearance of two symmetric peaks which tend to raise the first excited-state energy with respect to the single-particle ground and second excited states. Even though n_2 is by construction an excited-state density for the harmonic potential, it is also a ground-state density of the other potential obtained from the solution of Eq. (19). By construction, n_1 is v-representable; the illustration shows that n_2 is equally well v-representable.

We have also considered one-dimensional systems consisting of three particles. This as we shall see is relevant to the treatment of the neon atom. Furthermore, it provides additional verification of v-representability for one-dimensional systems; a matter to which we shall return. For $N=3$, the set of $(N-1)$ coupled equations (14) reduces to the following pair:

$$-\frac{1}{2}\frac{d^2\psi_1}{dx^2}+\left[\frac{1}{2(n-\psi_1^2-\psi_2^2)^{1/2}}\times\frac{d^2}{dx^2}(n-\psi_1^2-\psi_2^2)^{1/2}\right]\psi_1=\varepsilon_1\psi_1 \; , \tag{21}$$

$$-\frac{1}{2}\frac{d^2\psi_2}{dx^2}+\left[\frac{1}{2(n-\psi_1^2-\psi_2^2)^{1/2}}\times\frac{d^2}{dx^2}(n-\psi_1^2-\psi_2^2)^{1/2}\right]\psi_2=\varepsilon_2\psi_2 \; , \tag{22}$$

with $\varepsilon_1=E_1-E_0$ and $\varepsilon_2=E_2-E_0$.

We chose two densities constructed from single-particle eigenfunctions of a square-well potential of width unity: $n_1=\phi_0^2+\phi_1^2+\phi_2^2$ and $n_2=\phi_0^2+\phi_1^2+\phi_3^2$ where $\phi_k=\sqrt{2}\sin[(k+1)\pi x]$. The first density n_1 which is the three-particle ground-state density of the square-well potential yielded the square-well potential as V_{eff} and provided a check on our numerical procedure. As in the two-particle case, it is of interest to discover whether an excited-state density of a square-well potential can be a ground-state density of some potential which, if it exists, will necessarily be different from a square well. For this purpose we considered n_2 which is the first excited-state density of three fermions in a square well, shown in Fig. 1. No difficulties were encountered in solving the pair of equations (21) and (22) and obtaining the corresponding V_{eff} and there were no indications of alternative solutions. The solutions ψ_0, ψ_1, and ψ_2 and the corresponding potential are shown in Figs. 2 and 3, respectively. The density n_2 is the ground-state density for this potential. This shows that whereas n_2 is by construction an excited-state density of the square-well potential, it is also the ground-state density of the different potential shown in Fig. 3. From this example and the results for the two-particle system, it seems likely that for an arbitrary density in one dimension we can always construct a potential such that the given density is its ground-state density. We shall return to the study of the existence of such a potential in Sec. IV.

III. APPLICATIONS

The examples presented in the previous section were intended for illustrative and pedagogical purposes. We

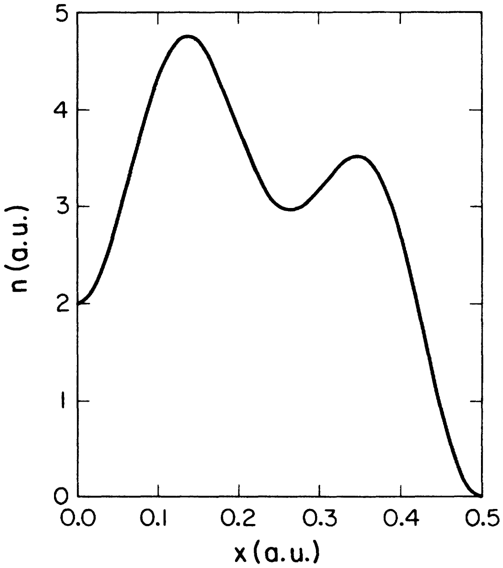

FIG. 1. A three-particle density constructed from the eigenfunctions of a square-well potential of width unity, $n_2=\phi_0^2+\phi_1^2+\phi_3^2$, where $\phi_k=\sqrt{2}\sin[(k+1)\pi x]$ is the kth eigenfunction. This density is the first excited-state density of three noninteracting spinless fermions moving in the square-well potential.

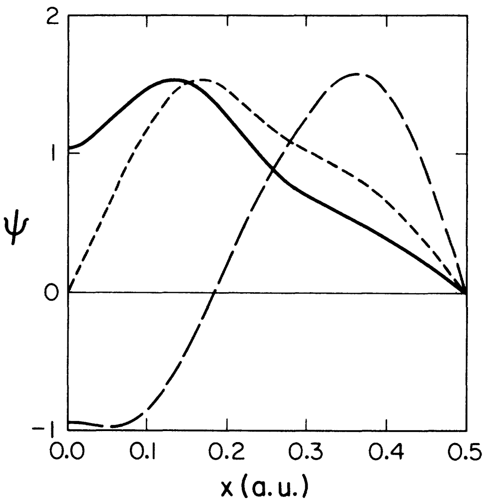

FIG. 2. The solutions to Eqs. (21) and (22) for the three-particle density shown in Fig. 1. The solid curve has no node, the short-dashed curve has one node, and the long-dashed curve has two nodes. They correspond to the lowest, first excited, and second excited single-particle states of the potential shown in Fig. 3.

now consider three-dimensional systems of physical interest restricting attention to systems with spherical symmetry as in these cases Eq. (14) reduces to a one-dimensional form.

We begin by considering a spherical system consisting of two spinless fermions applicable to the Be atom. The two lowest occupied states must be the 1s and 2s, since only in this way can the ground-state density be spherical. With $N=2$ the set (14) reduces to the single differential equation

$$-\frac{1}{2}\frac{d^2u_{2s}}{dr^2}+\left[\frac{1}{2(\rho-u_{2s}^2)^{1/2}}\frac{d^2}{dr^2}(\rho-u_{2s}^2)^{1/2}\right]u_{2s}=\varepsilon_{2s}u_{2s}\ , \qquad (23)$$

where $\varepsilon_{2s}=E_{2s}-E_{1s}$. The form is identical with Eq. (19) for the one-dimensional system but with n replaced by $\rho=4\pi r^2 n$ and $u_{2s}=rR_{2s}$ where r is the radial distance and R_{2s} is the 2s radial wave function.

The transformation which leads to simplifications in the one-dimensional case is also useful here. With $u_{1s}=\sqrt{\rho}\cos\theta$, $u_{2s}=\sqrt{\rho}\sin\theta$, and $-\pi/2\leq\theta\leq\pi/2$, (23) becomes

$$\frac{d^2\theta}{dr^2}+\left[\frac{1}{\rho}\frac{d\rho}{dr}\right]\frac{d\theta}{dr}+\varepsilon_{2s}\sin(2\theta)=0\ . \qquad (24)$$

The boundary conditions are

$$\theta \text{ must have one node only}\ , \qquad (25a)$$

$$\int_0^\infty dr\,\rho\sin^2\theta=\int_0^\infty dr\,\rho\cos^2\theta=1\ , \qquad (25b)$$

$$\theta\rightarrow-\frac{\pi}{2} \text{ as } r\rightarrow\infty\ , \qquad (25c)$$

The last condition follows from the fact that $u_{2s}\rightarrow\sqrt{\rho}$ as $r\rightarrow\infty$. Solution of (24) yields u_{2s} from which V_{eff} can be obtained using

$$V_{\text{eff}}(r)-E_{1s}=\frac{1}{2(\rho-u_{2s}^2)^{1/2}}\frac{d^2}{dr^2}(\rho-u_{2s}^2)^{1/2}\ . \qquad (26)$$

We use Eq. (24) to deduce the effective potentials or the Kohn-Sham potentials of the beryllium atom from both the Hartree-Fock[14] and correlated electron densities[15] (Fig. 4). A beryllium atom has four electrons but in the single-particle picture, these electrons occupy the 1s and

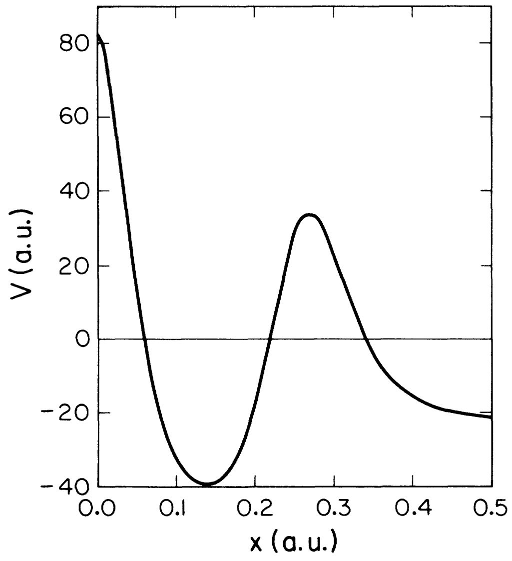

FIG. 3. The effective potential deduced from the three-particle density shown in Fig. 1 which is the ground-state density of this potential.

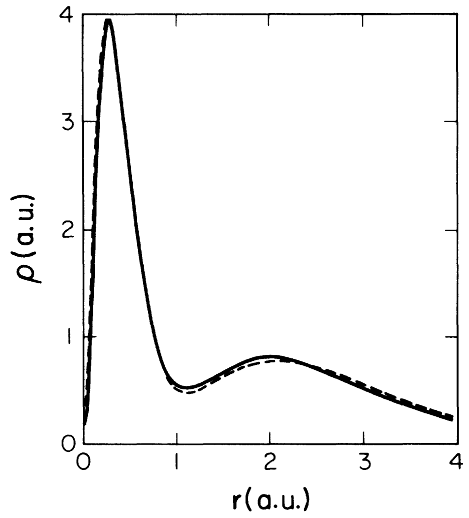

FIG. 4. The Hartree-Fock and configuration-interaction radial densities of beryllium. The solid curve is the configuration-interaction density taken from Ref. 15 and the dashed curve is the Hartree-Fock density taken from Ref. 14.

$2s$ states, each with two electrons, so that there are only two distinct orbitals and therefore it is equivalent to a system of two spinless fermions.

From the Hartree-Fock density we can find the effect of exchange on the total effective potential by simply subtracting the Hartree potential from the total effective potential obtained by solving Eq. (24) with boundary conditions (25). We then obtain what can be termed the effective exchange potential:

$$V_x = V_{\text{eff}} - V_{\text{H}}^{\text{HF}} , \tag{27}$$

where V_{H}^{HF} is the Hartree potential calculated with the Hartree-Fock density. However, this is not the only definition of the exchange potential in density-functional theory. A more commonly used definition can be found in Ref. 16.

From the configuration-interaction (CI) electron density we can find the effect of exchange and correlation on the total effective potential because, neglecting relativistic corrections and finite nuclear size and mass, the CI electron density is essentially exact. The exchange-correlation potential is then obtained by subtracting the Hartree potential, corresponding to the CI electron density, from the total effective potential deduced from Eq. (24),

$$V_{\text{xc}} = V_{\text{eff}} - V_{\text{H}}^{\text{CI}} . \tag{28}$$

In addition we can also separate the effect of correlation by defining an effective correlation potential as the difference between the exchange-correlation potential and the exchange potential:

$$V_c = V_{\text{xc}} - V_x . \tag{29}$$

In order to determine the absolute potentials, it is necessary to know either E_{1s} or E_{2s}. In principle E_{2s} can be obtained from the asymptotic form of the density but this form deduced from published Hartree-Fock and CI densities is not accurate enough for our purposes. This problem can be avoided in the following way. It can be shown from the many-body Schrödinger equation that for a localized system the asymptotic behavior of the density is given by[17]

$$n \sim e^{-2kr} \sim e^{-2r(-2E_N)^{1/2}} \quad \text{as } r \to \infty , \tag{30}$$

where k is related to the exact ionization energy $E(N-1)-E(N)=\frac{1}{2}k^2$ and E_N is the highest occupied energy. We are therefore able to deduce the exact highest occupied Kohn-Sham eigenvalue from the measured ionization energy and hence fix the absolute value of the V_{eff} corresponding to the CI density. A similar procedure was used to obtain the absolute V_{eff} corresponding to the Hartree-Fock density, where the highest occupied Kohn-Sham eigenvalue is equal to the highest occupied Hartree-Fock eigenvalue.

The solution for θ and the exchange, exchange-correlation, and correlation potentials are shown in Figs. 5 and 6, respectively. The results are in agreement with those obtained by Almbladh and Pedroza[7] as is also the energy difference $E_{2s}-E_{1s}$ for the correlated electron density. The function $\theta(r)$ shown in Fig. 5 corresponds to the CI density but on the scale of the figure the results for the CI and the Hartree-Fock densities are indistinguishable. It is typical of the $\theta(r)$ that we have obtained for a variety of one-dimensional and three-dimensional situations for two spinless fermions being flat at the end points and falling smoothly and monotonically through a single node but otherwise fairly featureless.

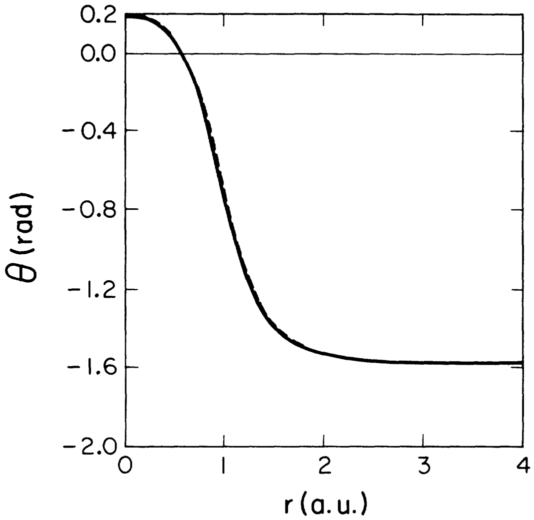

FIG. 5. The solutions to Eq. (14) for the Hartree-Fock and configuration-interaction densities of beryllium shown in Fig. 4. The solid and dashed curves correspond to the configuration-interaction and Hartree-Fock densities, respectively.

We move on from Be which reduces to a system of two spinless fermions and requires the solution of a single

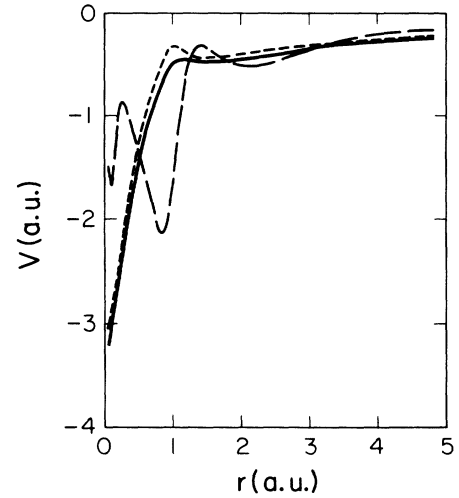

FIG. 6. The effective exchange, exchange-correlation, and correlation potentials of beryllium deduced from the Hartree-Fock and configuration-interaction densities shown in Fig. 4. The solid curve is the exchange-correlation potential, the short-dashed curve is the exchange potential, and the long-dashed curve is the correlation potential which is magnified ten times.

differential equation in our approach to consider systems consisting of a greater number of particles. Solution of the two coupled differential equations for the one-dimensional system consisting of three spinless fermions discussed in the preceding section was not inordinately difficult. These same methods allow us to treat three-dimensional spherical systems of five spinless fermions which covers the case of the ten-electron neon atom discussed next. Specifically we consider a spherically symmetric system with the 1*s*, 2*s*, and 2*p* shells lying lowest in energy and fully occupied by five spinless fermions. The threefold degeneracy of the 2*p* states reduces the number of distinct orbitals to three and we therefore have the two coupled differential equations

$$-\frac{1}{2}\frac{d^2u_{2s}}{dr^2}+\left[\frac{1}{2(\rho-u_{2s}^2-3u_{2p}^2)^{1/2}}\times\frac{d^2}{dr^2}(\rho-u_{2s}^2-3u_{2p}^2)^{1/2}\right]u_{2s}=\varepsilon_{2s}u_{2s}\ , \qquad (31)$$

$$-\frac{1}{2}\frac{d^2u_{2p}}{dr^2}+\left[\frac{1}{2(\rho-u_{2s}^2-3u_{2p}^2)^{1/2}}\times\frac{d^2}{dr^2}(\rho-u_{2s}^2-3u_{2p}^2)^{1/2}+\frac{2}{r^2}\right]u_{2p}=\varepsilon_{2p}u_{2p}\ , \qquad (32)$$

where the term $2/r^2$ is the centrifugal potential for angular momentum $l=1$, and the factor of 3 in $(\rho-u_{2s}^2-3u_{2p}^2)^{1/2}$ accounts for the three spinless fermions in the 2*p* shell. ε_{2s} and ε_{2p} are the 2*s* and 2*p* eigenvalues with respect to the 1*s* eigenvalue. The boundary conditions are

u_{2s} and u_{2p} must have only

one and zero nodes, respectively ; (33a)

$$\int_0^\infty dr\, u_{2s}^2=\int_0^\infty dr\, u_{2p}^2=1\ ; \qquad (33b)$$

$$u_{2p}\to\sqrt{\rho}\ \text{if}\ \varepsilon_{2p}>\varepsilon_{2s}\ \text{or}\ u_{2s}\to\sqrt{\rho}\ \text{if}\ \varepsilon_{2p}<\varepsilon_{2s}\ . \qquad (33c)$$

By doubling these levels to account for electron spin we are able to treat the case of the Ne atom. We have used the available HF (Ref. 14) and CI (Ref. 18) electron densities for Ne for $\rho=4\pi r^2 n$ in (31) and (32) to find the corresponding effective potentials from which local exchange and exchange-correlation potentials were deduced as for Be. The electron density and the resulting potentials are shown in Figs. 7 and 8.

From the effective potentials of neon and beryllium, the exact Kohn-Sham eigenvalues were calculated and the results are shown in Table I. These are compared with the local-density approximation (LDA) and Hartree-Fock eigenvalues. Following Almbladh and von Barth[19] we also list the measured excitation energies. A comparison of the LD and LDX results shows that the introduction of correlation into the local-density approximation lowers the eigenvalues and this will always be the case. However, the exact correlation potential as defined in density-functional theory leads to different effects on the eigenvalues for Be and Ne as can be noted by comparing the columns labeled DF and DFX. Correlation introduced through the density raised the eigenvalues in the case of Ne suggesting an inadequacy in the LDA treatment of correlation. It is also noteworthy that the exact eigenvalues lie below the results of the LDA for both atoms. The measured excitation energies are always intermediate between the exact density functional and the HF eigenvalues although we know of no *a priori* reason for close correspondence except for the highest occupied eigenvalues.

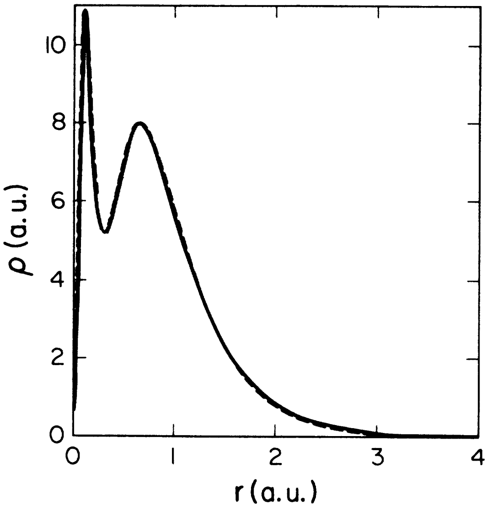

FIG. 7. The Hartree-Fock and configuration-interaction radial densities of neon. The solid curve is the configuration-interaction density taken from Ref. 18 and the dashed curve is the Hartree-Fock density taken from Ref. 14.

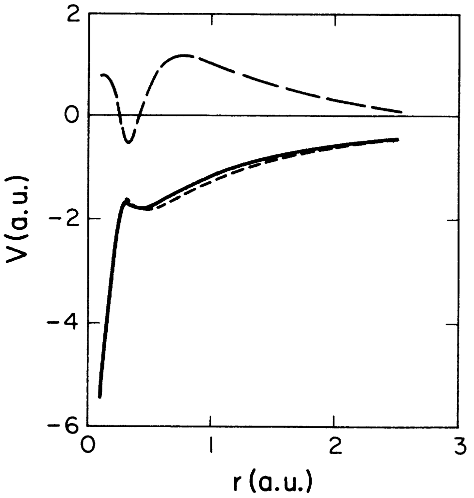

FIG. 8. The effective exchange, exchange-correlation, and correlation potentials of neon deduced from the Hartree-Fock and configuration-interaction densities shown in Fig. 7. The solid curve is the exchange-correlation potential, the short-dashed curve is the exchange potential, and the long-dashed curve is the correlation potential which is magnified 10 times.

TABLE I. The orbital eigenvalues of Be and Ne in various theoretical schemes compared with the measured excitation energies. All the energies shown above are negative and in atomic units. DF refers to the exact density-functional theory, LD to its local-density approximation, HF to the Hartree-Fock approximation, DFX to the exact density-functional theory with exchange only, and LDX refers to its local-density approximation. "Expt." refers to the measured excitation energies. Data for LD, LDX, and Expt. are taken from Ref. 19 and data for HF are taken from Ref. 14.

		DF	LD	HF	DFX	LDX	Expt.
Be	1*s*	4.23	3.86	4.74	4.13	3.79	4.54
	2*s*	0.34	0.21	0.31	0.31	0.17	0.34
	2*p*	0.21	0.08		0.18		
Ne	1*s*	30.82	30.32	32.78	30.84	30.25	31.99
	2*s*	1.65	1.33	1.93	1.72	1.27	1.78
	2*p*	0.79	0.50	0.85	0.85	0.44	0.79
	3*s*	0.18	0.01		0.19		

The exchange and exchange-correlation potentials for both beryllium and neon show characteristic peaks located in the region between the 1*s* and 2*s* shells where $\rho=4\pi r^2 n$ displayed in Figs. 4 and 7 is a minimum. These peaks correspond to the exchange repulsion between electrons of the same spin in the 1*s* and 2*s* shells. The correlation potentials also presented show a double-peak structure for both atoms. The peaks coincide with maxima in the radial densities and serve to disperse antiparallel spin electrons within a shell thereby further lowering the energy. Consistent with the effect of correlation on the eigenvalues noted earlier we see that the correlation potentials for Be and Ne are generally of opposite sign. The behavior of the correlation potential V_c at small distances $\lesssim 0.1$ a.u. should be viewed with caution because V_c is the difference between V_{xc} and V_x which are both large near the nucleus. The behavior of V_x and V_{xc} at large distances ($\gtrsim 3.5$ a.u. for Be and $\gtrsim 2.0$ a.u. for Ne) should also be viewed cautiously because of the inaccuracy in the available densities at large distances and the sensitivity of the potentials to small changes in the initial values of the wave functions and the eigenvalues, typical of atomic problems. For example, the potentials tend erroneously to a constant at very large distances because the asymptotic form of the density is inconsistent with the highest occupied eigenvalues. As far as we know, the exact exchange-correlation potential for Ne has not been obtained before.

From Table I we note that the 1*s* and 2*s* states lie lowest in the case of Be and the 1*s*, 2*s*, and 2*p* states lie lowest in the case of Ne. We therefore conclude that all the densities for Be and Ne that we have considered are *v*-representable, i.e., they are ground-state densities of the effective potentials that we have deduced.

The densities that we have considered so far including the one-dimensional densities have been found to be *v*-representable, but as shown by Levy[5] and Lieb,[6] not all densities are *v*-representable. They have shown that densities constructed from linear combinations of degenerate ground-state densities are not the ground-state densities of any potentials. These densities look physically reasonable and smooth and by no means pathological.

In order to develop a qualitative understanding of how the non-*v*-representability arises it is instructive to consider the difference between the one- and three-dimensional cases. Without loss of generality, let us fix our attention on a two-fermion case. In one dimension, the crucial features that the energy eigenfunctions in one dimension can be ordered with increasing energy according to the number of nodes[11] and the absence of degeneracy in one dimension guarantee the *v*-representability of the density if a solution to (19) exists (except for some special cases to be discussed later). Thus if a solution is found with the lowest number of nodes, the density is *v*-representable. This is in contrast to the three-dimensional case where the existence of a solution to Eq. (24) with the lowest possible number of nodes does not necessarily guarantee the *v*-representability of the density because the eigenfunctions cannot be ordered according to the number of nodes and the solution found may not correspond to the ground state. Only eigenfunctions belonging to the same angular momentum can be ordered as in one dimension.

It is fitting at this point to consider a non-*v*-representable density to illustrate this point. The density is one of the class introduced by Levy[5] and Lieb[6] and is constructed as follows:

$$n(r)=R_{1s}^2+\alpha R_{2s}^2+\beta R_{2p}^2 , \tag{34}$$

where R_{nl} is the radial hydrogenic wave function for $Z=2$ and $\alpha+\beta=1$.

No difficulties were encountered in solving Eq. (24) for θ and deducing the effective potentials for a number of values of α between 0 and 1. However, when the single-particle energy eigenvalues were calculated from the effective potentials, the 2*p* state was found to be lower than the 2*s* state for all α except when $\alpha=1$ in which case the 2*s* and 2*p* states became accidentally degenerate (see Fig. 12). This means that the densities given by (34) were not *v*-representable because the lowest two-particle state that corresponds to a spherically symmetric density is the 1*s*-2*s* state, but in fact the lowest two-particle state is the 1*s*-2*p* state which is triply degenerate and does not correspond to a spherically symmetric density. This is typical of non-*v*-representable densities with spherical symmetry and an example of a density in Eq. (34) with $\alpha=0.25$ is shown in Fig. 9. The corresponding solution of Eq. (24) and the effective potential are shown in Figs. 10 and 11,

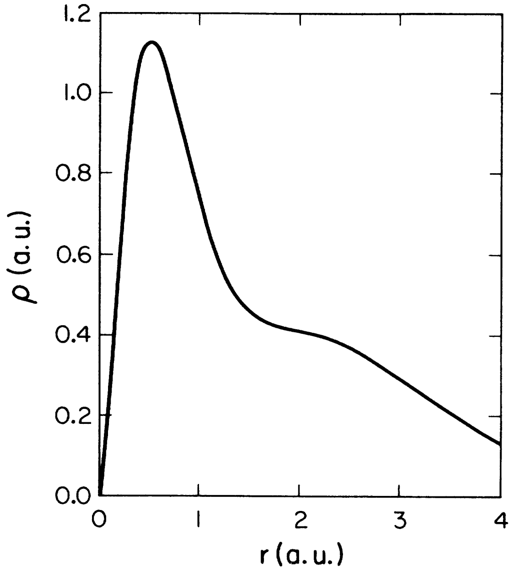

FIG. 9. A two-particle ensemble density constructed from a linear combination of degenerate ground-state densities of a hydrogenic atom of $Z=2$ with equal weight, i.e., the density is given by $\rho=4\pi r^2(R_{1s}^2+\frac{1}{4}R_{2s}^2+\frac{3}{4}R_{2p}^2)$, where R_{nl} is the radial wave function of the hydrogenic atom.

respectively. The splitting in energy between the 2s and 2p states is shown in Fig. 12.

As a final example we consider densities of the form $\sim e^{-ar}$. For one fermion the densities are of course v-representable. We consider in the following the two- and five-fermion cases. The two-fermion case corresponds to occupied 1s and 2s states whereas the five-fermion case corresponds to occupied 1s, 2s, and 2p states.

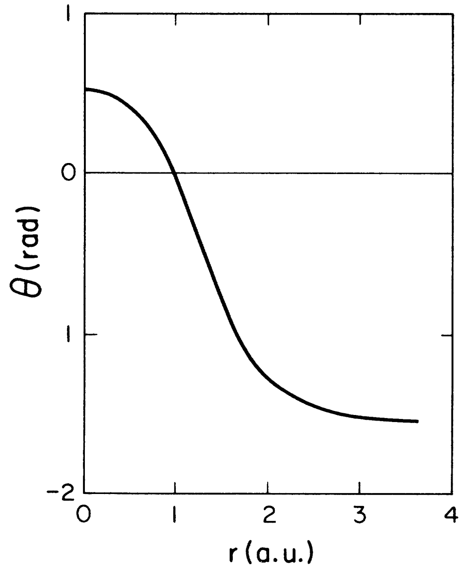

FIG. 10. The solution to Eq. (24) corresponding to the ensemble density shown in Fig. 9.

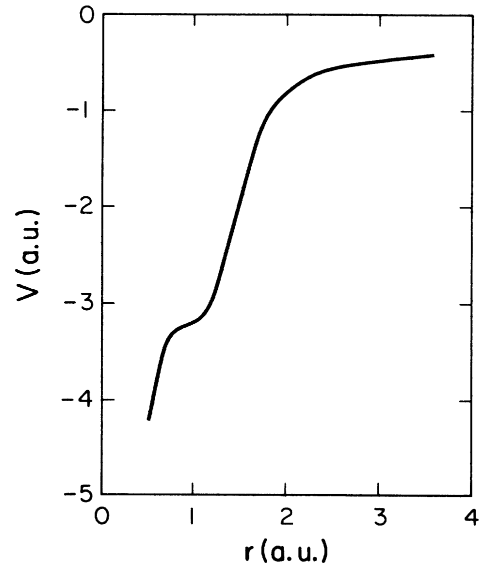

FIG. 11. The effective potential deduced from the ensemble density shown in Fig. 9. The arbitrary constant in the potential is adjusted so that the potential goes to zero at infinity.

With densities of the form $\sim e^{-ar}$ it is possible to scale the set of Eqs. (24), (31), and (32) by substituting $x=ar$. For example, Eq. (24) becomes

$$\frac{d^2\tilde{\theta}}{dx^2}+\left(\frac{2}{x}-1\right)\frac{d\tilde{\theta}}{dx}+\left(\frac{\varepsilon_{2s}}{a^2}\right)\sin(2\theta)=0\ . \tag{35}$$

The normalization condition becomes

$$\int_0^\infty dx\, x^2 e^{-x}\sin^2\tilde{\theta}=1 \tag{36}$$

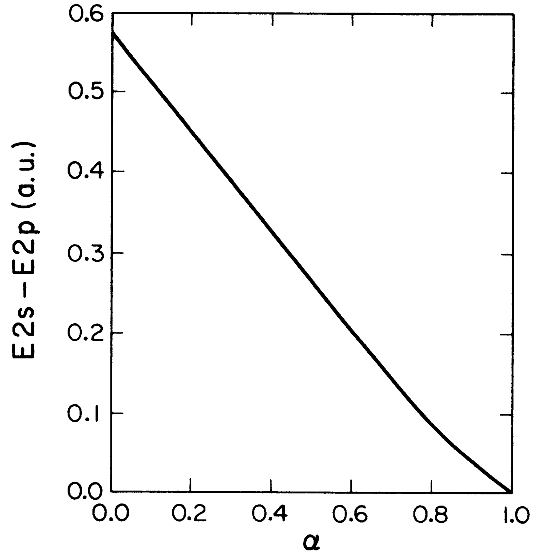

FIG. 12. The energy splitting between the 2s and 2p states as a function of the coefficient α in Eq. (34). $\alpha=1$ corresponds to the Coulomb potential in which the 2s and 2p states become accidentally degenerate.

and the effective potential can be scaled according to

$$V_{\text{eff}}(r)=a^2\tilde{V}_{\text{eff}}(x)\ . \tag{37}$$

In fact, with densities that scale according to $\rho(r)=a^3\tilde{\rho}(x)$, $r=x/a$, and if $\tilde{\rho}(x)$ is independent of a, it is possible to scale (14) for any number of particles. It can also be shown that the effective potential can be scaled according to (37). For these densities, it is therefore necessary to find V_{eff} for only one value of a. The density that we are considering, $\rho\sim e^{-ar}$, is but one example.

Having found the effective potentials for two and five spinless fermions, we can use these to solve the single-particle Schrödinger equations which can be similarly scaled. We find for the two-fermion case that for $a>0$, $\varepsilon_{1s}<\varepsilon_{2p}<\varepsilon_{3d}<\varepsilon_{2s}$ which implies that densities of the form $\sim e^{-ar}$ are not v-representable for two spinless fermions because the spherically symmetric $1s2s$ state is not the ground state. However, for the five-fermion case we find that for $a>0$, ε_{1s}, ε_{2s}, and ε_{2p} are the three lowest states with $\varepsilon_{1s}<\varepsilon_{2p}<\varepsilon_{2s}$, i.e., densities of the form $\sim e^{-ar}$ are v-representable for five spinless fermions.

These results clearly suggest a strong dependence on the number of particles for a density to be v-representable. This is already evident from the fact that any positive density for one particle is always v-representable and the densities of Levy and Lieb which may be constructed for any number of particles ≥ 2 are not v-representable. Figure 13 compares the effective potentials for the exponential density for two particles deduced for the $1s2s$ case and for the $1s2p$ case.

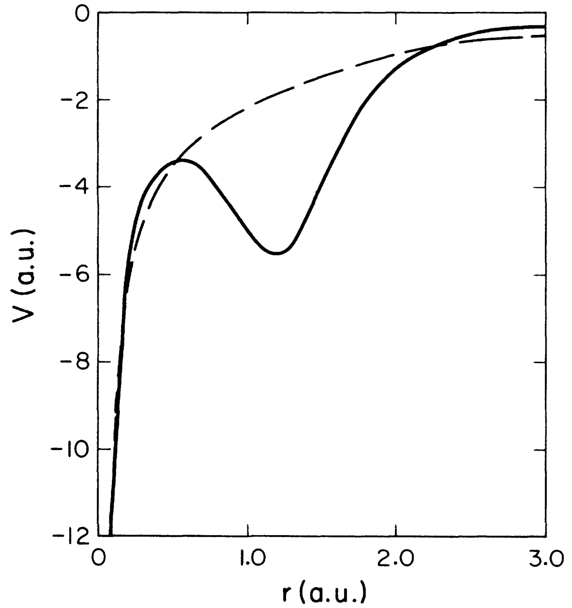

FIG. 13. Effective potentials deduced from the spherical density $n=ce^{-ar}$ with $a=2$. The solid curve follows by assuming that the $1s$ and $2s$ states are lowest in energy; this proves not to be the case showing that the density is not v-representable. The dashed curve follows by assuming that the $1s$ and $1p$ states are lowest in energy; this is the case showing that the density is a Levy-Lieb density.

There arises the question whether the exponential density for two particles, which we have found to be non-v-representable, is actually a linear combination of degenerate ground-state densities of some potential, that is, a Levy-Lieb density.[20] To investigate this question, we assume that the density is constructed from the $1s$ and $2p$ states of some spherically symmetric potential V for which these two states are the lowest:

$$\rho=u_{1s}^2+u_{2p}^2\ , \tag{38}$$

i.e., we take the density to be a linear combination of degenerate ground-state densities of the potential V. We wish to find out whether this potential really has as its two lowest states the $1s$ and $2p$ states.

Following a similar procedure of deducing an effective potential from a given density as described in Sec. II and assuming that the density is given by (38), we arrive at the following equation:

$$\frac{d^2\theta}{dr^2}+\left[\frac{1}{\rho}\frac{d\rho}{dr}\right]\frac{d\theta}{dr}+\left[\varepsilon_{2p}-\frac{1}{r^2}\right]\sin(2\theta)=0\ , \tag{39}$$

where $0\leq\theta\leq\pi/2$ and

$$\begin{aligned} u_{1s}&=\sqrt{\rho}\cos\theta\ ,\\ u_{2p}&=\sqrt{\rho}\sin\theta\ . \end{aligned} \tag{40}$$

We were able to solve Eq. (39) for θ with the boundary condition $\theta\rightarrow\pi/2$ as $r\rightarrow\infty$, and the usual normalization condition on u_{1s} and u_{2p}, and the effective potential was easily constructed from either u_{1s} or u_{2p}. With this potential, we then solved the single-particle Schrödinger equations and found that the $1s$ and $2p$ states were indeed the two lowest states. This means that the exponential density for two particles is a Levy-Lieb density. All the spherically symmetric non-v-representable densities that we have considered are Levy-Lieb densities and it is not inconceivable that all spherically symmetric densities are either v-representable or Levy-Lieb densities.

IV. THE v-REPRESENTABILITY OF A TWO-PARTICLE DENSITY IN ONE DIMENSION

In this section, the problem of v-representability is discussed and a proof of the v-representability of any positive density for two spinless fermions in one dimension is offered and the exceptions enumerated.

There are two kinds of v-representability: noninteracting and interacting. By a noninteracting v-representable density we mean a density which can be generated as a ground-state density of a noninteracting system of particles moving in some effective local potential. A density is called interacting v-representable if it is a ground-state density of an interacting system such as electrons, moving in a local external potential. Clearly, all ground-state densities of real electronic systems must be interacting v-representable, but they are not necessarily noninteracting v-representable. We shall be concerned with the question of noninteracting v-representability for which we shall use the term v-representability.

The question of v-representability is relevant to the use of the Kohn-Sham scheme[2] for calculating the ground-state energies of electronic systems. In developing the scheme, it is implicitly assumed that the ground-state density of an interacting electronic system is also a ground-state density of an auxiliary noninteracting system moving in an effective local potential. But we have seen from several examples that the existence of such an effective potential cannot be taken for granted for an arbitrary density. We do not believe that this invalidates the Kohn-Sham scheme but rather it provides motivation for studying v-representability.

We consider first the v-representability problem for one-dimensional systems. An important feature in one dimension is the fact that the energy eigenfunctions can be ordered with increasing energy according to the number of nodes of the eigenfunctions.[11] Thus the lowest state has no node, the first excited state has one node, the second two nodes, and so on. The other important feature is the absence of degeneracy in one dimension. As a consequence, if we can construct a potential from a given N-particle density such that the squares of the N lowest eigenfunctions selected according to the number of nodes sum to the given density then it immediately follows that the density is v-representable simply because there are no other possible lower states. The ordering of the eigenfunctions according to the number of nodes, the absence of degeneracy, and the examples given earlier all point to the suggestion that any one-dimensional density is v-representable.

In contrast to the one-dimensional case, we have seen that not all densities in three dimensions are v-representable. Let us now consider the differences between one- and three-dimensional systems that allow a three-dimensional density to be non-v-representable. We restrict ourselves to the spherically symmetric case. In three dimensions, the energy eigenfunctions cannot be ordered with increasing energy according to the number of nodes of the radial eigenfunctions. Only for a fixed angular momentum quantum number can such ordering be accomplished. Furthermore, the presence of spherical symmetry results in degeneracy. The requirement of spherical symmetry on the density forces us to consider only the lowest eigenfunctions which yield spherically symmetric densities but these eigenfunctions are not necessarily the lowest eigenfunctions of the corresponding potential from which they are generated.

To illustrate the preceding discussion, let us return to the two examples of non-v-representable densities presented earlier. The two densities are spherically symmetric and under the assumption that they come from spherically symmetric potentials, we have no choice but to take the 1s and 2s states to construct the density because they are the two lowest possible states that would yield a spherically symmetric density. There is no difficulty in deducing the effective potentials whose 1s and 2s states yield the given densities but these are not the lowest states of the potentials. It happens that the triply degenerate 2p states lie lower than the 2s state which results in degenerate ground states, with necessarily nonspherical densities. Hence the two densities are not v-representable.

The tentative conclusion that can be drawn from the discussion and the examples is that the v-representability problem arises from the degeneracy associated with the symmetry which is allowed in dimensions greater than 1. While it is possible to construct from a given density an effective potential which has the given density as its lowest possible state density of the given symmetry, there is no guarantee that this is the ground-state density. On the other hand, the absence of degeneracy seems to be the responsible factor causing the one-dimensional densities discussed earlier to be v-representable. In what follows, we set out to prove the v-representability of any density in one dimension for two spinless fermions.

The idea behind the proof is as follows. Suppose from a given two-particle density it is possible to find a solution to Eq. (19) satisfying the boundary conditions (20). This means that we have found a potential such that the eigenfunctions with zero and one node yield the given density. These two eigenfunctions are necessarily the two lowest possible states and therefore the given density is the ground-state density of the deduced potential, i.e., it is v-representable. There are certain conditions that the density must satisfy but for the moment we assume that they are fulfilled. Thus if we can show that there is always a solution to Eq. (19) satisfying the conditions (20) then we will have accomplished our goal.

We proceed by recasting the problem into a variational principle and noting that the existence of a solution to the differential equation (19) is established by showing the existence of a minimizing function of the corresponding functional. Equation (19) is the Euler-Lagrange equation of the following (kinetic energy) functional:

$$T[\theta]=\frac{1}{2}\int_0^L dx\, n(x)\left[\frac{d\theta}{dx}\right]^2 , \tag{41}$$

subject to the constraint

$$\int_0^L dx\, n\sin^2\theta=\int_0^L dx\, n\cos^2\theta=1 , \tag{42}$$

i.e., $(\delta/\delta\theta)(T-\varepsilon_1\int_0^L dx\, n\sin^2\theta)=0$ yields Eq. (19) with the Lagrange undetermined multiplier identified as $\varepsilon_1=E_1-E_0>0$. In the following, we wish to prove that for an arbitrary positive density it is always possible to find a function θ with only one node which minimizes $T(\theta)$ subject to the constraint (42). This will establish the existence of a solution of (19) with its accompanying conditions and thereby v-representability of a density.

We first obtain some useful results from Eq. (19) regarding the behavior of the solution which are required to determine the space in which $T[\theta]$ is defined. Multiplying Eq. (19) by $n(x)$ and integrating yields

$$n\frac{d\theta}{dx}=-\varepsilon_1\int_0^x dx\, n\sin(2\theta) , \tag{43}$$

since $n(x)$ and $d\theta/dx$ vanish at the boundaries. Furthermore, since θ is confined to $-\pi/2\le\theta\le\pi/2$ and is required to have one node it follows from (43) that

$d\theta/dx \leq 0$ if $\theta(0)$ is taken to be positive. It can also be shown directly from (19) that

$$\int_0^L dx\, n \sin(2\theta)=0 \,,$$

which is equivalent to the statement of orthogonality between $\psi_0=\sqrt{n}\,\cos\theta$ and $\psi_1=\sqrt{n}\,\sin\theta$.

We now consider a discrete lattice of M points and write Eq. (19) as a difference equation

$$\frac{\theta_{i+1}-2\theta_i+\theta_{i-1}}{h^2}+\left[\frac{n_{i+1}-n_i}{hn_i}\right]\frac{\theta_{i+1}-\theta_i}{h}+\varepsilon_1\sin(2\theta_i)=0, \quad i=1,2,\ldots,M \tag{44}$$

where h is the interval. Because the slope of θ at the boundaries is zero, we can set $\theta_0=\theta_1$ and $\theta_{M+1}=\theta_M$. The functional $T[\theta]$ becomes a function of M variables $\theta_1,\theta_2,\ldots,\theta_M$,

$$T(\theta_1,\theta_2,\ldots,\theta_M)=\tfrac{1}{2}\sum_{i=1}^{M} hn_i\left[\frac{\theta_{i+1}-\theta_i}{h}\right]^2 . \tag{45}$$

We want to show that there exists $(\theta_1,\theta_2,\ldots,\theta_M)$ such that $T(\theta_1,\theta_2,\ldots,\theta_M)$ is a minimum.

We must now specify the space in which $T(\theta_1,\theta_2,\ldots,\theta_M)$ is defined. The normalization condition and the orthogonality relation are given, respectively, by

$$\sum_{i=1}^{M} n_i h \sin^2\theta_i=1 \,, \tag{46}$$

$$\sum_{i=1}^{M} n_i h \sin(2\theta_i)=0 \,. \tag{47}$$

The condition $d\theta/dx \leq 0$ and $-\pi/2\leq\theta\leq\pi/2$ implies that

$$\frac{\pi}{2}\geq\theta_1\geq\theta_2\geq\cdots\geq\theta_M\geq-\frac{\pi}{2} \,. \tag{48}$$

The overlap between the three M-dimensional spaces (46), (47), and (48) is the space where $T(\theta_1,\theta_2,\ldots,\theta_M)$ is defined. Because the space defined by (48) is a closed one, so is the overlap space. The conditions (46)–(48) ensure that θ has only one node. The overlap region exists or the set of functions in which $T(\theta_1,\theta_2,\ldots,\theta_M)$ is defined is not empty if there is at least one function that satisfies all the required conditions. Such a function is readily given by

$$\theta=\frac{\pi}{2}\left[1-\int_0^x dx\, n\right] . \tag{49}$$

This is a special form of more general orthonormal functions introduced by Harriman[21] which are constructed from a density alone.

We are now in a position to invoke the Weierstrass theorem[22] which states that any function of a finite number of variables defined in a closed region must have a minimum inside the region or on its boundary. Since $T(\theta_1,\theta_2,\ldots,\theta_M)$ is a function of a finite number of variables and is defined within a closed region then it follows from the Weierstrass theorem that there exists $(\theta_1,\theta_2,\ldots,\theta_M)$ such that $T(\theta_1,\theta_2,\ldots,\theta_M)$ is a minimum, i.e., there exists a solution to the difference equation (44) satisfying the appropriate boundary conditions.

There remains the step of going from the discrete lattice to the continuum at which a problem may arise if the minimizing function is not unique. However, we know from the theorem of Hohenberg and Kohn[1] that if there is a solution to the differential equation that satisfies the conditions (46)–(49) then it is the only one. For if we managed to find more than one solution then there would be two potentials giving the same ground-state densities.

Thus we have shown with the use of the Weierstrass and Hohenberg-Kohn theorems that there exists a unique solution to the differential equation (19) satisfying the conditions (20) for any $n(x)$. An alternative proof is given in the Appendix. We now proceed to discuss the conditions that $n(x)$ must satisfy to be v-representable.

The above proof shows that from a given arbitrary density it is always possible to find ψ_0 and ψ_1 such that $n(x)=\psi_0^2+\psi_1^2$ with ψ_0 and ψ_1 satisfying the single-particle Schrödinger equations with the same effective potential and having zero and one node, respectively. We have implicitly assumed that the density is positive definite except at the boundaries. A negative density is clearly physically unacceptable and a zero of a density at some point implies the presence of a singularity in the potential at that point which divides the system into two separate systems.

We also require the density to be twice differentiable because otherwise the effective potential will be divergent and the Slater determinant formed from ψ_0 and ψ_1 will not necessarily be the ground state. We illustrate this circumstance by considering a density that varies like $\sim x^{2q}$ near one of the boundaries, with q a positive constant. The effective potential and the corresponding ψ_0 and ψ_1 can be deduced but the leading term in the potential for small x has the form

$$V_{\text{eff}}\sim q(q-1)x^{-2} \,.$$

Consequently the potential is attractive and diverges at the boundary if $q<1$. If such an effective potential is treated variationally trial functions can always be chosen which yield an expectation value of the potential energy $E_v\rightarrow-\infty$ and therefore the expectation value of the energy is unbounded from below and ψ_0,ψ_1 do not give the two-particle ground state. Densities that vary like $\sim x^{2q}$ at a boundary with $q<1$ are evidently not v-representable. Fortunately it is easy to exclude pathological cases of this sort by merely requiring that the density is twice differentiable.

In summary the two-particle density $n(x)$ is v-representable if it is twice differentiable and positive definite except at the boundary.

V. CONCLUSIONS

We have presented a systematic method for deriving from a given arbitrary density, the effective single-particle potential which has that density for its ground state. For a system of N spinless fermions, the solution takes the form of $(N-1)$ nonlinear differential equations which are equivalent to the set of single-particle Schrödinger equations, but the single-particle wave functions are determined from the ground-state density instead of from the potential.

We have applied the method to beryllium and neon atoms to find the effective exchange and exchange-correlation potentials from the HF and CI densities, respectively. We have also used the method to investigate the question of v-representability by considering examples of densities for a small number of particles in one dimension and in three dimensions with spherical symmetry. As has been shown by Levy and Lieb, not all three-dimensional densities are v-representable and this we verify by considering a particular example of a Levy-Lieb density. In contrast to the three-dimensional cases, all the one-dimensional densities that we have considered are v-representable and we have presented a proof of the v-representability in one dimension of any two-fermion density which must satisfy certain criteria.

Although the proof is only for a two-particle system, it seems clear that the same idea used in the proof can be carried over to any number of particles in one dimension. The problem of showing the v-representability of an N-particle density in one dimension is equivalent to showing the existence of a set of N minimizing functions, with the lowest number of nodes, to the kinetic-energy functional subject to orthonormality constraints on the functions. The crucial factor distinguishing the one- and three-dimensional cases is that in one dimension the single-particle states can be ordered in increasing energy according to the number of nodes in the wave function whereas no such unique ordering is possible in three dimensions. Tentatively, we suggest that any one-dimensional density is v-representable.

The question of v-representability in two or more dimensions has not been settled yet. It could be that all non-v-representable densities are necessarily Levy-Lieb densities. Indeed, all the densities we found to be non-v-representable are Levy-Lieb densities. An exception to this seemed to be an exponential density for two particles which we found to be non-v-representable for any value of the decay constant but on closer examination these densities proved to be Levy-Lieb densities although they had not been initially constructed as such.

We have restricted ourselves to spherically symmetric potentials but it is not inconceivable that there exist nonspherical potentials with spherically symmetric ground-state densities. From the HK theorem such a density could not be a ground-state density or a Levy-Lieb density for a spherically symmetric potential. The non-v-representable densities that we have considered, however, cannot be the ground-state densities of nonspherical potentials because they are Levy-Lieb densities.

Further applications of the method to other atomic systems can be readily made. The isoelectronic series of Be, B^+, etc., falls within the scope of two-particle systems and analysis amounts to solving a single nonlinear differential equation. Extension to spin-polarized systems may be illustrated with Li. The minority spin potential can be easily obtained and the majority spin potential can be found by solving a single differential equation as in the case of Be. The isoelectronic series of Ne, Na^+, Mg^{2+}, etc., falls within a three-particle system and larger atoms such as Mg and spin-polarized Na correspond to having three or more coupled differential equations.

An important problem in density-functional theory is the construction of the kinetic-energy functional for noninteracting systems. For the case of two fermions, the exact kinetic-energy functional would be obtained if the solution to Eq. (19) were known analytically as a functional of the density. We have been unable to achieve analytic solution, and transformation of the differential equation (19) to a form in which the density becomes the independent variable which would serve our purpose is not always possible. An approach for obtaining an approximate kinetic-energy functional is to make use of the variational property of the kinetic-energy functional. In the case of two fermions for instance, the general behavior of the solution θ to Eq. (19) can be deduced and may be used to construct an approximate trial solution.

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APPENDIX: ALTERNATIVE PROOF OF THE EXISTENCE OF A SOLUTION TO EQ. (19)

We first introduce some definitions.

1. $f(x)\in L_p$ if $(\int dx\, |f|^p)^{1/p}<\infty$.
2. $f(x)\in W_p^{(1)}$ if f and $df/dx\in L_p$.
3. A sequence $\{x_n\}$ of elements of a Hilbert space H is said to converge weakly to a limit x in H if $(x_n,y)\to(x,y)$ for all y in H. This weak convergence is denoted by $x_n \overset{w}{\to} x$.
4. A set E in a Hilbert space H is called weakly closed if it contains all its weak limit points, i.e., if $x_n\in E$ and $x_n \overset{w}{\to} x$, then $x\in E$.
5. A functional U defined on a Hilbert space H is called weakly lower semicontinuous at the point $x\in H$ if for any sequence $\{x_n\}$ that converges weakly to x, $U[x]\le \lim_{n\to\infty} U[x_n]$.

We also need the following theorems.

1. For $f\in W_2^{(1)}$, the functional $U[f]=\int dx\,(df/dx)^2$ is a weakly lower semicontinuous functional.
2. If a functional U is weakly lower semicontinuous on a bounded weakly closed set E in a Hilbert space, then U assumes its minimum on E.
3. In $W_2^{(1)}$, $U=\int dx\,(df/dx)^2\to\infty$ as $\|f\|\to\infty$. It is therefore sufficient to consider U on bounded subsets of $W_2^{(1)}$.

Choose $\theta\in W_2^{(1)}$ so that $T[\theta]=\int dx\, n(d\theta/dx)^2<\infty$. Clearly, since $n(x)$ is positive everywhere then

$$0\le T<\infty \ .$$

This means that T has a greatest lower bound:

$$d=\inf_{\theta\in W_2^{(1)}}\{T[\theta]\}\ .$$

We may choose a sequence $\{\theta_n\}$ such that

$$\lim_{n\to\infty}T[\theta_n]=d\ .$$

Proof: Let $T[u]=d$. Then $T[\theta]=d+\epsilon$, $\epsilon>0$ if $\theta\neq u$. Let $\epsilon=a/n$ and $T[\theta_n]=d+a/n$. Then $\lim_{n\to\infty}T[\theta_n]=d$. Therefore $\{\theta_n\}$ form a minimizing sequence.

Let S be the Hilbert space consisting of those elements of $W_2^{(1)}$ that satisfy the boundary conditions $\theta'(0)=\theta'(L)=0$. Theorem 3 allows us to consider T on bounded subsets of S. Let E denote the set of elements of S that satisfy

$$\int dx\, n\sin^2\theta=1 \quad\text{and}\quad \int dx\, n\sin(2\theta)=0\ ,$$
$$-\frac{\pi}{2}\le\theta\le\frac{\pi}{2}\ . \qquad (1)$$

We show that E is weakly closed. Let θ_n satisfy (1) and let $\theta_i\xrightarrow{w}\theta$. We must show that θ satisfies (1):

$$\begin{aligned}
&\left|\int dx\, n[\cos(2\theta)-\cos(2\theta_i)]\right|\\
&\quad=2\left|\int dx\, n\sin(\theta+\theta_i)\sin(\theta-\theta_i)\right|\\
&\quad\le 2\max(n)\left|\int dx\,\sin(\theta+\theta_i)\sin(\theta-\theta_i)\right|\\
&\quad\le 2\max(n)\int dx\,|\sin(\theta-\theta_i)|\\
&\quad\le \max(n)\int dx\,|\theta-\theta_i|\\
&\quad\to 0 \text{ as } \theta_i\xrightarrow{w}\theta\ .
\end{aligned}$$

Hence $\int dx\, n\cos(2\theta)=0$ giving $\int dx\, n\sin^2\theta=1$. In a similar fashion, it can be shown that the second condition is also satisfied. Thus there exists an element θ in E that furnishes T with an absolute minimum on E. [E is weakly closed and $E\in$(bounded subsets of S)$\to E$ is a bounded weakly closed set. T is weakly lower semicontinuous on S and $E\in S\to T$ is weakly lower semicontinuous on E. Theorem 2 is then invoked.] For definitions and theorems in this Appendix, see Refs. 23 and 24.

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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] M. Levy, Proc. Nat. Acad. Sci. USA **76**, 6062 (1979).

[4] See, for example, *Theory of Inhomogeneous Electron Gas*, edited by S. Lundgvist and N. H. March (Plenum, New York, 1983).

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

[6] E. M. Lieb, in *Physics as a Natural Philosophy*, edited by A. Shimony and H. Feshbach (MIT Press, Cambridge, Mass., 1982).

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

[8] S. M. Werden and E. R. Davidson, in *Local Density Approximations in Quantum Chemistry and Physics*, edited by J. P. Dahl and J. Avery (Plenum, New York, 1982).

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

[10] F. Aryasetiawan and M. J. Stott, Phys. Rev. B **34**, 4401 (1986).

[11] P. M. Morse and M. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Pt. I, Chap. 6.3.

[12] Equation (19) has also been obtained by March and Nalewajski in their attempt to establish an exact relationship between n and V_{eff}. See N. H. March and R. F. Nalewajski, Phys. Rev. A **35**, 525 (1987).

[13] A. Erdelyi, Z. Angew. Math. Mech. **14**, 235 (1934).

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

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

[16] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).

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

[18] A. V. Bunge and A. O. Esquivel, Phys. Rev. A **34**, 853 (1986).

[19] C.-O. Almbladh and U. von Barth, in *Density Functional Methods in Physics*, edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1984).

[20] M. Levy (private communication).

[21] J. E. Harriman, Phys. Rev. A **24**, 680 (1981).

[22] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1953), Vol. 1.

[23] S. L. Sobolev, *Applications of Functional Analysis in Mathematical Physics* (American Mathematical Society, Providence, 1963).

[24] I. Tadjbakhsh, in *Bifurcation Theory and Non-linear Eigenvalue Problems*, edited by J. B. Keller and S. Antman (Benjamin, New York, 1969).