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Construction of the Pauli potential, Pauli energy, and effective potential from the electron density

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The Kohn-Sham (KS) one-electron Schrödinger equations assume the existence of a one-body effective potential $v_{\text{eff}}(\mathbf{x})$, defined to generate the correct electron density $\rho(\mathbf{x})$ of the ground state. This paper returns to the electron-density description of an N-fermion system. It is best thought of as starting from a given $\rho(\mathbf{x})$, ideally to be obtained from diffraction experiments. A method is then set up that focuses predominantly on the way the "correct" $v_{\text{eff}}(\mathbf{x})$ can be "recovered," if it exists, from such an experimental density. Certainly the method has associated with it one practical disadvantage in common with the KS procedure; an order of N Euler equations have to be solved, with input information $\rho(\mathbf{x})$, though the "unknown" potential $v_{\text{eff}}(\mathbf{x})$ does not now appear. In this program, we have found it most helpful to work with the Pauli potential and energy, which enable the N-fermion problem to be converted to a boson problem for the density amplitude $[\rho(\mathbf{x})]^{1/2}$. The way the above-mentioned Euler equations determine the Pauli potential and energy is worked out explicitly. Examples that embrace the important area of atomic central-field calculations are presented to illustrate the method. As a by-product, the theory developed can afford a direct test as to whether a given electron density is, in fact, representable via a one-body potential $v_{\text{eff}}(\mathbf{x})$.

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I. INTRODUCTION

Density-functional theory formally completes the electron-density method introduced into atomic theory by Thomas [1] and Fermi [2]. This paralleled the approach of Hartree [3], in which each electron in an atom is assigned its own "personal" wave function. In both directions, exchange was subsequently included [4,5].

In a landmark paper, Slater [6] brought these two approaches into contact. In his simplification of the Hartree-Fock method, Slater in fact averaged the exchange energy over the Fermi sea by a procedure which led to a factor $\frac{3}{2}$ different from that implicit in the original work of Dirac [5]. Slater's pioneering construction of a one-body potential to use in self-consistent-field theory was formally completed by Kohn and Sham [7].

While the idea of Thomas and Fermi that the ground state of an N-electron system could be characterized by its electron density $\rho(\mathbf{x})$ was formally proved by Hohenberg and Kohn [8], doubts have remained as to the status of the one-body potential $v(\mathbf{x})$; this is the so-called v-representability problem [9]. Therefore, in the present paper, a different philosophy will be set out. From the outset the basic input will be the ground-state electron density $\rho(\mathbf{x})$; ideally to be taken from diffraction experiments [10]. Similar to the Kohn-Sham (KS) approach, the present work requires the solution of the order of N single-particle Euler equations. These are now, however, characterized solely by the input density $\rho(\mathbf{x})$.

It proves most helpful in the present work to focus, in implementing the above program, on the Pauli potential [11] and energy, and to demonstrate the way in which they can be constructed explicitly from the solution of the above-mentioned Euler equations. The central gain from working with these Pauli quantities is that the N-fermion problem is thereby converted to a boson problem for the density amplitude $[\rho(\mathbf{x})]^{1/2}$.

The layout of the paper is then as follows. After summarizing relevant basic results of density-functional theory in Sec. II, a variational approach to derive Euler equations characterized by the input ground-state density is fully worked out in Sec. III. The determination of the Pauli potential as a functional of $\rho(\mathbf{x})$ is the focus of Sec. IV. In Sec. V, contact is made with a body of earlier work on one-dimensional problems, which embraces the atomic central field case. Section VI constitutes a summary of the main results of the present work. Three examples are presented in Appendices in which the effective potential is constructed from a specified density.

II. FOUNDATIONS OF DENSITY-FUNCTIONAL FORMALISM

A. Fermion form

Consider a system of N fermions (electrons) interacting among themselves via Coulombic repulsion and interacting with some external potential (e.g., due to a nucleus for an atomic problem, or to fixed nuclei in specified positions for molecular and condensed-matter problems). In addition, it will be convenient to assume, with no significant loss of generality, that all electrons have only one (e.g., up) spin polarization.

The existence theorem of Hohenberg and Kohn [8] plus the work of Kohn and Sham [7] allows the ground-state energy $E_{\rm GS}$ and the density $\rho_{\rm GS}(\mathbf{x})$ of the system to be obtained from

$$E_{\rm GS}=\min_{\rho}\{T_s[\rho]+V_{\rm eff}[\rho]\}=T_s[\rho_{\rm GS}]+V_{\rm eff}[\rho_{\rm GS}]\ , \tag{2.1}$$

where the variational density must normalize to the correct number N of electrons:

$$\int d\mathbf{x}\,\rho(\mathbf{x})=N\ . \tag{2.2}$$

The first term occurring in Eq. (2.1) is the kinetic-energy functional for N noninteracting fermions, defined by Levy [12] as

$$T_s[\rho]=\min_{\Psi_\rho}\langle\Psi_\rho|\hat{T}|\Psi_\rho\rangle\ , \tag{2.3}$$

where the search for the minimum, which we carry out explicitly below, is here restricted to single Slater determinants Ψ_ρ which lead to the given density $\rho(\mathbf{x})$:

$$N\int d\mathbf{x}_2\ldots d\mathbf{x}_N|\Psi_\rho(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)|^2=\rho(\mathbf{x}_1)\ , \tag{2.4}$$

while $\hat{T}$ signifies the kinetic-energy operator for N particles. The second term in Eq. (2.1) is the effective potential energy functional

$$V_{\rm eff}[\rho]=E_{\rm es}[\rho]+E_{\rm xc}[\rho]+V[\rho]\ , \tag{2.5}$$

where the terms in order are (i) the classical Coulomb self-interaction energy, (ii) the exchange-correlation energy, and (iii) the external potential energy.

The minimization (2.1) with the constraint (2.2) leads to the Euler-Lagrange equation

$$\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{x})}+v_{\rm eff}[\rho;\mathbf{x}]=\lambda\ , \tag{2.6}$$

where the effective KS potential is given by

$$v_{\rm eff}[\rho;\mathbf{x}]=\frac{\delta V_{\rm eff}[\rho]}{\delta\rho(\mathbf{x})}=v_{\rm es}[\rho;\mathbf{x}]+v_{\rm xc}[\rho;\mathbf{x}]+v(\mathbf{x})\ . \tag{2.7}$$

The last term only in Eq. (2.7), the external potential $v(\mathbf{x})$, is independent of ρ. While $v_{\rm es}[\rho;\mathbf{x}]$ is a known nonlocal functional of ρ, the precise form of the exchange-correlation potential $v_{\rm xc}[\rho;\mathbf{x}]$ and the energy $E_{\rm xc}[\rho]$ is not presently known.

Unfortunately, the definition (2.3) does not provide any constructive algorithm to evaluate $T_s[\rho]$ and $\delta T_s[\rho]/\delta\rho(\mathbf{x})$. In order to circumvent this difficulty, Kohn and Sham assumed that densities $\rho(\mathbf{x})$ which are close to the solution $\rho_{\rm GS}(\mathbf{x})$ are v representable for noninteracting electrons. This results in the KS equations; to be solved iteratively to achieve self-consistency.

The noninteracting N-fermion picture of the system is in evidence at each iteration, when the density distribution used to evaluate $v_{\rm eff}$ is fixed. The original electron-electron interaction, of course, is subsumed in $v_{\rm es}$ and $v_{\rm xc}$ as functionals of ρ.

The aim below is to develop an algorithm which allows the calculation of $T_s[\rho]$ and $\delta T_s[\rho]/\delta\rho(\mathbf{x})$ for arbitrary density distribution $\rho(\mathbf{x})$ which is noninteracting v representable; i.e., under the same assumptions made by KS. We have found it very helpful to use the language of Pauli energy and Pauli potential, which allows the fermion problem to be reduced to boson form explained as follows.

B. Reduction of fermion problem to boson form

In an admittedly very approximate form of the density-functional theory, the Weizsäcker approach, March and Murray [13] already noted that the Euler equation for the density could be transformed into a simple Schrödinger equation for the density amplitude $[\rho(\mathbf{x})]^{1/2}$. However the effective potential entering this equation was $v_{\rm eff}(\mathbf{x})+v_{\rm Pauli}(\mathbf{x})$, where the Pauli potential [11,14] was found within this approximate framework to be

$$v_{\rm Pauli}^{\rm Weiz}=\tfrac{5}{3}c_k[\rho(\mathbf{x})]^{2/3}\ , \tag{2.8}$$

where $c_k=(3/10)(6\pi^2)^{2/3}$ for single occupancy of states. Later workers have generalized this [15–17], and always the essential quantity appearing is the difference between T_s introduced above and the Weizsäcker kinetic energy:

$$T_W[\rho]=\tfrac{1}{8}\int d\mathbf{x}|\nabla\rho(\mathbf{x})|^2\Big/\rho(\mathbf{x})=\tfrac{1}{2}\int d\mathbf{x}|\nabla\rho^{1/2}(\mathbf{x})|^2\ . \tag{2.9}$$

In addition to the Pauli potential defined in Ref. [11], see also Ref. [14], it will be helpful for what follows to define the Pauli energy functional $E_P[\rho]$ as

$$E_P[\rho]=T_s[\rho]-T_W[\rho]\ . \tag{2.10}$$

In following sections we shall discuss how $E_P[\rho]$ and its functional derivative can be evaluated. Therefore, at present, we assume they are known, just as was assumed above for $E_{\rm xc}[\rho]$.

It is to be noted that

$$E_P[\rho]=0\quad\text{for } N=1\ , \tag{2.11}$$

since in this case the ground-state wave function, ϕ_1 say, can be chosen to be real and positive, and then $\rho^{1/2}(\mathbf{x})=\phi_1(\mathbf{x})$, resulting in $T_W[\rho]$ coinciding with $T_s[\rho]$.

In terms of E_p and $V_{\rm eff}[\rho]$ the ground-state problem (2.1) may be rewritten as

$$E_{\rm GS}=\min_{\rho}\{T_W[\rho]+E_P[\rho]+V_{\rm eff}[\rho]\} \tag{2.12}$$

with the constraint (2.2). Furthermore we are led to the equation

$$\frac{\delta T_W[\rho]}{\delta\rho(\mathbf{x})}+v_B[\rho;\mathbf{x}]=\lambda \tag{2.13}$$

with the effective potential for the boson problem given by

$$v_B[\rho;\mathbf{x}]=v_P[\rho;\mathbf{x}]+v_{\rm eff}[\rho;\mathbf{x}] \tag{2.14}$$

where we have now explicitly introduced the Pauli potential already referred to:

$$v_P[\rho;\mathbf{x}]=\frac{\delta E_P[\rho]}{\delta\rho(\mathbf{x})} \tag{2.15}$$

while v_{eff} was as defined in Eq. (2.7).

By performing direct functional differentiation of the Weizsäcker energy in Eq. (2.9) we obtain

$$\frac{\delta T_W[\rho]}{\delta\rho(\mathbf{x})}=\frac{1}{8}\left[\frac{\nabla\rho(\mathbf{x})}{\rho(\mathbf{x})}\right]^2-\frac{1}{4}\frac{\nabla^2\rho(\mathbf{x})}{\rho(\mathbf{x})}=-\frac{1}{2}\frac{\nabla^2[\rho^{1/2}(\mathbf{x})]}{\rho^{1/2}(\mathbf{x})} . \tag{2.16}$$

This allows one to rewrite Eq. (2.13) as

$$-\frac{1}{2}\nabla^2\rho^{1/2}(\mathbf{x})+v_B[\rho;\mathbf{x}]\rho^{1/2}(\mathbf{x})=\lambda\rho^{1/2}(\mathbf{x}) , \tag{2.17}$$

which is of the precise form written by March and Murray [13] in their early study of the Weizsäcker functional, with the Pauli potential approximated there by Eq. (2.8).

Because of the importance of the form (2.17) for density functional theory, (see Ref. [11] and, other references cited therein), let us comment on its interpretation. Imagine that the N-particle density $\rho(\mathbf{x})$ in Eq. (2.2) is due to N bosons, instead of N fermions, which in the ground state all occupy the same state, described by the wave function $b(\mathbf{x})$:

$$\rho(\mathbf{x})=N[b(\mathbf{x})]^2 . \tag{2.18}$$

Then Eq. (2.17) turns out to be the Schrödinger-like equation for the boson function $b(\mathbf{x})$:

$$-\frac{1}{2}\nabla^2 b(\mathbf{x})+v_B[Nb^2;\mathbf{x}]b(\mathbf{x})=\lambda b(\mathbf{x}) \tag{2.19}$$

with the constraint

$$\int d\mathbf{x}\, b^2(\mathbf{x})=1 . \tag{2.20}$$

The Lagrange multiplier λ is to be determined from the constraint (2.20). The boundary conditions for the function $b(x)$ are

$$b(\mathbf{x})\rightarrow 0 \quad \text{as } x\rightarrow \text{boundaries of system} . \tag{2.21}$$

It should be noted that Eq. (2.19) represents a second-order differential nonlinear equation. The difficulty with this nonlinearity may be overcome by introducing again the self-consistent scheme of solution.

The ground-state energy of the system in Eq. (2.12) may be written in terms of the eigenvalue $\lambda=\lambda_B$ and the density $\rho_{\mathrm{GS}}(\mathbf{x})$ obtained from Eqs. (2.18)–(2.21) when self-consistency is achieved as

$$\begin{aligned}E_{\mathrm{GS}}&=T_W[\rho_{\mathrm{GS}}]+E_P[\rho_{\mathrm{GS}}]+V_{\mathrm{eff}}[\rho_{\mathrm{GS}}]\\&=N\lambda_B+\left\{E_P[\rho]-\int d\mathbf{x}\,\rho(\mathbf{x})v_P[\rho;\mathbf{x}]\right\}_{\rho_{\mathrm{GS}}}\\&\quad+\left\{V_{\mathrm{eff}}[\rho]-\int d\mathbf{x}\,\rho(\mathbf{x})v_{\mathrm{eff}}[\rho;\mathbf{x}]\right\}_{\rho_{\mathrm{GS}}} .\end{aligned} \tag{2.22}$$

It is to be noted that, as in the prior scheme, the N noninteracting boson picture of the original system is in evidence in each particular step only of the self-consistent procedure.

III. DETERMINATION OF PAULI ENERGY AND EFFECTIVE POTENTIAL AS FUNCTIONALS OF DENSITY

A. Choice of appropriate trial functions

Under the assumption of noninteracting v representability, the density and the kinetic energy of the system can be written as sums of N contributions connected with the single-particle wave functions $\phi_j(\mathbf{x})$. Therefore, according to the definition (2.10) of the Pauli energy, the functional $E_P[\rho]$ in terms of $T_s[\rho]$, Eq. (2.3), and $T_W[\rho]$, Eq. (2.9), can be obtained as a solution of the minimization problem

$$E_P[\rho]=\min_{\phi_1,\ldots,\phi_N}(\tilde{T}_s[\phi_1]+\cdots+\tilde{T}_s[\phi_N]-\tilde{T}_s[\rho^{1/2}]) \tag{3.1}$$

with the following constraints on the trial functions $\phi_j(\mathbf{x})$.

(a) They shall yield the given density $\rho(\mathbf{x})$ through

$$|\phi_1(\mathbf{x})|^2+\cdots+|\phi_N(\mathbf{x})|^2=\rho(\mathbf{x}) ; \tag{3.2}$$

(b) normalization

$$\int d\mathbf{x}|\phi_j(\mathbf{x})|^2=1,\ j=1,\ldots,N ; \tag{3.3}$$

(c) orthogonality

$$\int d\mathbf{x}\,\phi_j^*(\mathbf{x})\phi_k(\mathbf{x})=0,\quad j\neq k,\quad j,k=1,\ldots,N . \tag{3.4}$$

The boundary conditions are

$$\phi_j(\mathbf{x})\rightarrow 0 \quad \text{as } \mathbf{x}\rightarrow\text{boundaries} . \tag{3.5}$$

In Eq. (3.1), the kinetic-energy functional corresponding to a single orbital is defined as

$$\tilde{T}_s[f]=\tfrac{1}{2}\int d\mathbf{x}|\nabla f(\mathbf{x})|^2 . \tag{3.6}$$

Of course the presence of the last Weizsäcker term in Eq. (3.1) does not influence the minimization, which is dictated by Eq. (2.3), because it is performed at fixed density $\rho(\mathbf{x})$.

In order to obtain a fruitful route to determine Euler-Lagrange equations corresponding to Eq. (3.1) with the constraints set out explicitly above, we shall replace the set $\phi_1(\mathbf{x}),\ldots,\phi_N(\mathbf{x})$ of trial functions by another set, into which the condition (3.2) is explicitly incorporated into the structure of these functions. While this can be done in a variety of ways, in this section we shall explore the consequences of explicit choice $\{\chi(\mathbf{x}),K_2(\mathbf{x}),\ldots,K_N(\mathbf{x})\}$, defined in terms of the original set as

$$\chi(\mathbf{x})=[|\phi_1(\mathbf{x})|^2+\cdots+|\phi_N(\mathbf{x})|^2]^{1/2} \tag{3.7}$$

$$\begin{aligned}K_j(\mathbf{x})&=\phi_j(\mathbf{x})/[|\phi_1(\mathbf{x})|^2+\cdots+|\phi_N(\mathbf{x})|^2]^{1/2}\\&=\phi_j(\mathbf{x})/\chi(\mathbf{x}),\quad j=2,\ldots,N .\end{aligned} \tag{3.8}$$

It will be convenient also to define an auxiliary function $K_1(\mathbf{x})$, which however depends on all the independent functions K_j:

$$K_1(\mathbf{x})=\tilde{K}_1(K_2(\mathbf{x}),\ldots,K_N(\mathbf{x}))$$
$$=\{1-[|K_2(\mathbf{x})|^2+\cdots+|K_N(\mathbf{x})|^2]\}^{1/2}\ . \quad (3.9)$$

The inverse transformation between these two sets can be written

$$\phi_j(\mathbf{x})=\chi(\mathbf{x})K_j(\mathbf{x}),\ \ j=2,\ldots,N \quad (3.10)$$

$$\phi_1(\mathbf{x})=\chi(\mathbf{x})\tilde{K}_1(K_2(\mathbf{x}),\ldots,K_N(\mathbf{X}))\ . \quad (3.11)$$

We have chosen above to label the functions $\phi_j(\mathbf{x})$ so that $\phi_1(\mathbf{x})$is the lowest, i.e., nodeless function of the (assumed given) single-particle Hamiltonian leading to the given $\rho(\mathbf{x})$ according to noninteracting v representability. Therefore $\phi_1(\mathbf{x})$ can be chosen to be real and positive; this justifies the correctness of Eq. (3.11) with (3.9), where the square root is to be understood as the arithmetic one.

Since the functions $\phi_j(\mathbf{x})$ are continuous (as representing one-particle wave functions), evidently one must require the same continuity for the density amplitude $\chi(\mathbf{x})=\rho^{1/2}$ and $K_j(\mathbf{x})$. Also, in general, for the same reason, the gradients should be continuous, except at those points (lines, surfaces) where $\nabla\rho(\mathbf{x})$ is discontinuous. This latter property would reflect the presence of singularities in the underlying potential.

Thus, it can be seen that the two sets of trial functions referred to above consist of the same number N of members and the transformations between these two sets are continuous and differentiable. Therefore, by replacing the original set with a new one in the minimization problem (3.1), we have not changed the value of the minimum.

The constraint (3.2) written in terms of the new set of functions is just

$$\chi^2(\mathbf{x})=\rho(\mathbf{x})\ . \quad (3.12)$$

Therefore, in order to satisfy it, the function $\chi(\mathbf{x})$ can be kept fixed at its value $\rho^{1/2}(\mathbf{x})$. Proceeding to rewrite Eq. (3.1) in terms of the new set, we evaluate the functional (3.6) for $f=\phi_j$ given by Eq. (3.10):

$$\tilde{T}_s[\phi_j]=\tilde{T}_s[\chi K_j]=\tfrac{1}{2}\int d\mathbf{x}[\nabla(\chi K_j^*)]\cdot[\nabla(\chi K_j)]$$
$$=\tfrac{1}{2}\int d\mathbf{x}\{(\nabla\chi)^2|K_j|^2+\chi^2|\nabla K_j|^2$$
$$+\tfrac{1}{4}[\nabla(\chi^2)]\cdot[\nabla(|K_j|^2)]\}\ . \quad (3.13)$$

Let us note here that Eq. (3.9) defining K_1 may be rewritten as a sum rule for all K_j including K_1:

$$\sum_{j=1}^{N}|K_j(\mathbf{x})|^2=1\ . \quad (3.14)$$

This allows Eq. (3.13) to be summed over j to yield

$$\sum_{j=1}^{N}\tilde{T}_s[\phi_j]=\tfrac{1}{2}\int d\mathbf{x}\left\{(\nabla\chi)^2+\chi^2\sum_{j=1}^{N}|\nabla K_j|^2+\tfrac{1}{4}[\nabla(\chi^2)]\cdot[\nabla 1]\right\}$$
$$=\tilde{T}_s[\chi]+\tfrac{1}{2}\int d\mathbf{x}\,\chi^2\sum_{j=1}^{N}|\nabla K_j|^2\ . \quad (3.15)$$

This enables us, by using Eqs. (3.12) and (3.15), to rewrite Eq. (3.1) as

$$E_P[\rho]=\min_{K_2,\ldots,K_N}\int d\mathbf{x}\,\rho(\mathbf{x})\sum_{j=1}^{N}\tfrac{1}{2}|\nabla K_j(\mathbf{x})|^2\ , \quad (3.16)$$

where K_1 is given by Eq. (3.9). It is to be noted that the Weizsäcker term is precisely cancelled with the corresponding term present in Eq. (3.15). While the constraint (3.2) is already satisfied, constraints (3.3) and (3.4) remain to be imposed:

$$\int d\mathbf{x}\,\rho(\mathbf{x})|K_j(\mathbf{x})|^2=1,\ \ j=2,\ldots,N \quad (3.17)$$

$$\int d\mathbf{x}\,\rho(\mathbf{x})K_j^*(\mathbf{x})K_k(\mathbf{x})=0,\ \ j\neq k,\ \ j,k=1,\ldots,N\ . \quad (3.18)$$

In Eq. (3.17) the case $j=1$ is omitted, since it is equivalent to the constraint (2.2) minus the sum of all constraints listed in Eq. (3.17).

It is worth emphasizing that the noninteracting kinetic energy T_s, the Weizsäcker energy T_W, and the Pauli energy E_P can be written as integrals of the corresponding energy densities: $e_s(\mathbf{x})$, $e_W(\mathbf{x})$, and $e_P(\mathbf{x})$ which are related by $e_s(\mathbf{x})=e_W(\mathbf{x})+e_P(\mathbf{x})$. These densities are to be identified with integrands occurring in Eqs. (3.1) with (3.6) for ϕ_j corresponding to the minimum. It is obvious from these definitions that $e_s\geq 0, e_W\geq 0$, while Eq. (3.16) demonstrates that $e_P\geq 0$. Therefore we have $E_P>0$ for $N\geq 2$ [and Eq. (2.11) otherwise].

B. Euler-Lagrange equations for functions $K_j(\mathbf{x})$

The minimization (3.16) with the constraints (3.17), following the introduction of Lagrange multipliers λ_j, leads to

$$\frac{\delta}{\delta K_l^*(\mathbf{x})}\left[\sum_{j=1}^{N}\tilde{E}_P[\rho,K_j,K_j^*]-\sum_{j=2}^{N}\lambda_j(S[\rho,K_j,K_j^*]-1)\right]=0\ ,$$
$$l=2,\ldots,N \quad (3.19)$$

where

$$\tilde{E}_P[\rho,K_j,K_j^*]=\tfrac{1}{2}\int d\mathbf{x}\,\rho(\mathbf{x})[\nabla K_j^*(\mathbf{x})]\cdot[\nabla K_j(\mathbf{x})]\ , \quad (3.20)$$

$$S[\rho,K_j,K_j^*]=\int d\mathbf{x}\,\rho(\mathbf{x})K_j^*(\mathbf{x})K_j(\mathbf{x})\ . \quad (3.21)$$

In Appendix A it is demonstrated that all contributions except that due to $\tilde{E}_P[\rho,K_1,K_1]$ can be evaluated in a fairly straightforward way. This latter term is also calculated there, and this enables another central result of the present approach to be obtained from Eq. (3.19), namely,

$$-\tfrac{1}{2}\nabla^2 K_l-\tfrac{1}{2}(\rho^{-1}\nabla\rho)\cdot\nabla K_l+v_c[\rho,\tilde{K}_1(K_2,\ldots,K_N)]K_l =\lambda_l K_l,\quad l=2,\ldots,N\ , \tag{3.22}$$

where the quantity v_c in Eq. (3.22) is obtained explicitly as a function of $\mathbf{x}$ in terms of the particle density $\rho(\mathbf{x})$, the function $K_1(\mathbf{x})$, and their low-order gradients. Precisely, the result for v_c is

$$v_c[\rho,K_1;\mathbf{x}]=\tfrac{1}{2}K_1^{-1}(\mathbf{x})\nabla^2 K_1(\mathbf{x}) +\tfrac{1}{2}[\rho^{-1}(\mathbf{x})\nabla\rho(\mathbf{x})]\cdot[K_1^{-1}(\mathbf{x})\nabla K_1(\mathbf{x})]\ . \tag{3.23}$$

Equation (3.22) constitutes a system of $(N-1)$ second-order differential coupled equations for the functions $K_l(\mathbf{x})$. The coupling arises through the potential v_c, Eq. (3.23), which depends on all functions K_j via $\tilde{K}_1$, Eq. (3.9). This is, however, a local type of dependence, because in effect $v_c(\mathbf{x})$ is a function of $K_1(\mathbf{x})$, its gradient and its Laplacian, together with the density ρ and its gradient, solely at the point $\mathbf{x}$. To complete the integration of the differential equations (3.22), one must specify the boundary conditions on $K_l(\mathbf{x})$. This is done in Appendix B.

To conclude this section, let us also comment that the requirement of weighted orthogonality of the functions K_j expressed in Eq. (3.18) was not included in the variational approach because it was anticipated that these conditions will be fulfilled by functions resulting from the solution. This is demonstrated in Appendix C.

C. Existence of solution of Eq. (3.22): The effective potential

Having specified the boundary conditions, we can integrate the system (3.22) of $(N-1)$ differential equations for arbitrarily chosen parameters λ_j and then their proper values can be determined with the aid of the constraints (3.17). In other words, this is a typical eigenvalue-eigenfunction problem. Because these equations (3.22) have a nonlinear coupled character, it may perhaps be questioned whether their solution exists. Below, we answer this is in the affirmative, by making use of our general assumption about the noninteracting v representability of $\rho(\mathbf{x})$ [which is involved in Eqs. (3.22) and (3.17)]. This assumption means that $\rho(\mathbf{x})$ can be written in terms of one-particle wave functions $\phi_j(\mathbf{x})$ of some one-electron Hamiltonian:

$$-\tfrac{1}{2}\nabla^2\phi_j(\mathbf{x})+v_{\rm eff}(\mathbf{x})\phi_j(\mathbf{x})=\varepsilon_j\phi_j(\mathbf{x})\ , \tag{3.24}$$

$$\int d\mathbf{x}\,\phi_j(\mathbf{x})\phi_k(x)=\delta_{jk}\ , \tag{3.25}$$

$$\rho(\mathbf{x})=\sum_{j=1}^{N}|\phi_j(\mathbf{x})|^2\ . \tag{3.26}$$

Although by assumption the potential $v_{\rm eff}(\mathbf{x})$ exists, its form is not known *a priori*. Using Eqs. (3.8) and (3.9), let us therefore construct functions $K_j(\mathbf{x})$, $j=1,\ldots,N$ from the functions $\phi_j(\mathbf{x})$, $j=1,\ldots,N$, which satisfy Eqs. (3.24)–(3.26). Then it can be directly verified that the functions $K_j(\mathbf{x})$ thereby obtained satisfy boundary conditions and Eqs. (3.22) and (3.17), and (3.18) having eigenvalues

$$\lambda_l=\varepsilon_l-\varepsilon_1;\quad l=1,\ldots,N\ . \tag{3.27}$$

In this way, it has been demonstrated that there exists a solution $\{\lambda_j[\rho],K_j[\rho;\mathbf{x}],\ j=2,\ldots,N\}$ of a system of $(N-1)$ equations (3.22) with constraints (3.17), (3.18) and the desired boundary conditions (found in Appendix B). It should be noted that the solution is a functional of $\rho(\mathbf{x})$, because this density enters these equations quite explicitly.

In terms of the above-mentioned solution, we can obtain functions $\phi_j(\mathbf{x})$ by employing Eqs. (3.10) and (3.11) with (3.12). But this also means that the effective potential can be obtained, since from Eq. (3.24) we have

$$v_{\rm eff}(\mathbf{x})=\varepsilon_1+\tfrac{1}{2}\frac{\nabla^2\phi_1(\mathbf{x})}{\phi_1(\mathbf{x})}\ . \tag{3.28}$$

In fact any one of the functions $\phi_l(\mathbf{x})$ can be used for that reason, but the nodeless function $\phi_1(\mathbf{x})$ can be expected usually to be the most convenient. Therefore the effective potential which generated the given $\rho(\mathbf{x})$ is obtained in terms of the above solution as

$$v_{\rm eff}[\rho;\mathbf{x}]+\text{const}=v_{\rm eff}[\rho;\mathbf{x}]-\varepsilon_1=\tilde{v}_{\rm eff}(\mathbf{x}) =2^{-1}\nabla^2\{\rho^{1/2}(\mathbf{x})K_1[\rho;\mathbf{x}]\}/\{\rho^{1/2}(\mathbf{x})K_1[\rho;\mathbf{x}]\}\ , \tag{3.29}$$

where K_1 is given by Eq. (3.9).

It is important to note here that the problem of calculating the effective potential from the particle density for one-dimensional systems was solved by Werden and Davidson [18] in quite a different way.

In any practical application, having some particle density $\rho(\mathbf{x})$, we may not know in advance whether it has the property of being noninteracting v representable. Nevertheless, we can attempt to solve the systems of Eqs. (3.22), along with (3.17), utilizing this density $\rho(\mathbf{x})$. If a solution is found, then surely $\rho(\mathbf{x})$ is v representable, with the potential given by Eq. (3.29). Otherwise, it does not belong to this class. Of course, such categorical conclusions can be drawn only in the case when the input density together with the solution of the system of equations are represented analytically (see examples given in Appendix E). In the case of numerical input and solution, the conclusions are conditional on the accuracy and reliability of the code employed.

D. Pauli energy

According to Eq. (3.16), the Pauli energy can be written in terms of the density plus the functions K_j found above as

$$E_P[\rho]=\int d\mathbf{x}\,\rho(\mathbf{x})\sum_{j=1}^{N}\tfrac{1}{2}|\nabla K_j[\rho;\mathbf{x}]|^2\ . \tag{3.30}$$

This can also be expressed in terms of the eigenvalues λ_j. To obtain this form let us first multiply both sides of Eq. (3.22) by $K_l^*(\mathbf{x})$. We then obtain

$$-(2\rho)^{-1}K_l^*\nabla\cdot(\rho\nabla K_l)+v_c|K_l|^2=\lambda_l|K_l|^2\ ,$$
$$l=2,\ldots,N\ . \quad (3.31)$$

Next, we take the complex conjugate of this equation and then average the two equations to find

$$-(4\rho)^{-1}[K_l^*\nabla\cdot(\rho\nabla K_l)+K_l\nabla\cdot(\rho\nabla K_l^*)]$$
$$+v_c|K_l|^2=\lambda_l|K_l|^2 \quad (3.32)$$

which may be transformed to

$$-(4\rho)^{-1}\nabla\cdot(\rho\nabla|K_l|^2)+2^{-1}|\nabla K_l|^2+v_c|K_l|^2$$
$$=\lambda_l|K_l|^2,\ l=2,\ldots,N\ . \quad (3.33)$$

Actually it is readily shown from Eq. (3.23) that Eq. (3.22) and therefore Eq. (3.33) holds also for $l=1$ with $\lambda_1=0$. Now we perform the sum of Eqs. (3.33) from $l=1$ to N, using the sum rule (3.14), to find

$$\tfrac{1}{2}\sum_{l=1}^{N}|\nabla K_l|^2+v_c=\sum_{l=2}^{N}\lambda_l|K_l|^2\ . \quad (3.34)$$

Substituting this result into Eq. (3.30) we obtain

$$E_P[\rho]=\left[\sum_{l=2}^{N}\lambda_l\right]-\int d\mathbf{x}\,\rho(\mathbf{x})v_c(\mathbf{x})\ , \quad (3.35)$$

and after substitution of Eq. (3.23) for v_c and some manipulation the result is

$$E_P[\rho]=\left[\sum_{l=2}^{N}\lambda_l\right]-\frac{1}{2}\int d\mathbf{x}\,\rho(\mathbf{x})\left[\frac{\nabla K_1(\mathbf{x})}{K_1(\mathbf{x})}\right]^2\ . \quad (3.36)$$

To this result, we have to add the requirement that the proper solution $\{\lambda_j,K_j,\ j=2,\ldots,N\}$ or $\{\varepsilon_j,\ \phi_j,\ j=1,\ldots,N\}$ should correspond to the following enumeration of the eigenvalues

$$0=\lambda_1<\lambda_2\leq\cdots\leq\lambda_{N-1}\leq\lambda_N\leq\lambda_k,\quad N<k \quad (3.37)$$

in order to ensure the absolute minimum of the variational procedure. It should be noted that the ordering (3.37) is equivalent to the similar ordering of ε_l—the eigenvalues of a one-electron problem, Eq. (3.24), because of the relation (3.27).

IV. DETERMINATION OF PAULI POTENTIAL AS FUNCTIONAL OF DENSITY

Having determined the Pauli energy E_P as a functional of the density, we turn to one of the main results of the present work, namely, the calculation of the Pauli potential v_P, as the functional derivative of E_P:

$$v_P[\rho;\mathbf{x}]=\frac{\delta E_P[\rho]}{\delta\rho(\mathbf{x})}\ . \quad (4.1)$$

According to Eq. (3.30), using Eq. (3.20), the Pauli energy is

$$E_P[\rho]=\sum_{j=1}^{N}\tilde{E}_P[\rho,K_j[\rho],K_j^*[\rho]]\ , \quad (4.2)$$

where $\{\lambda_j[\rho],K_j[\rho;\mathbf{x}],\ j=2,\ldots,N\}$ represents the solution of the eigenvalue problem posed in Eqs. (3.22), (3.17), (3.37), and boundary conditions (Appendix B) and where K_1 is given in terms of this solution by Eq. (3.9). It follows from Eqs. (4.1) and (4.2) that one can write the Pauli potential v_P as a sum of two contributions, namely,

$$v_P[\rho;\mathbf{x}]=v_P^{\mathrm{dir}}(\mathbf{x})+v_P^{\mathrm{ind}}(\mathbf{x})\ , \quad (4.3)$$

where the direct contribution is given by

$$v_P^{\mathrm{dir}}(\mathbf{x})=\sum_{j=1}^{N}\frac{\delta\tilde{E}_P[\rho,K_j,K_j^*]}{\delta\rho(\mathbf{x})}\ . \quad (4.4)$$

In Eq. (4.3) the indirect piece (i.e., via $K_l[\rho]$, $l=2,\ldots,N$, as independent functions) is

$$v_P^{\mathrm{ind}}(\mathbf{x})=\sum_{l=2}^{N}\int d\mathbf{y}\left[\frac{\delta K_l^*[\rho;\mathbf{y}]}{\delta\rho(\mathbf{x})}\times\frac{\delta}{\delta K_l^*(\mathbf{y})}\left[\sum_{j=1}^{N}\tilde{E}_P[\rho,K_j,K_j^*]\right]+\mathrm{c.c.}\right]\ . \quad (4.5)$$

From the definition (3.20) we obtain immediately

$$v_P^{\mathrm{dir}}(\mathbf{x})=\sum_{j=1}^{N}\tfrac{1}{2}|\nabla K_j(\mathbf{x})|^2\ . \quad (4.6)$$

In order to calculate v_P^{ind} let us first add and subtract the term

$$\sum_{j=2}^{N}\lambda_j(S[\rho,K_j,K_j^*]-1) \quad (4.7)$$

in the expression within the brackets in Eq. (4.5). After that, use may be made of Eq. (3.19), which is fulfilled by the functions belonging to its solution. Thus the only term which remains is that connected with Eq. (4.7):

$$v_P^{\int}(\mathbf{x})=\sum_{l=2}^{N}\int d\mathbf{y}\left[\frac{\delta K_l^*[\rho;\mathbf{y}]}{\delta\rho(\mathbf{x})}\times\frac{\delta}{\delta K_l^*(\mathbf{y})}\left[\sum_{j=2}^{N}\lambda_j S[\rho,K_j,K_j^*]\right]+\mathrm{c.c.}\right]\ . \quad (4.8)$$

Next we use the fact that only independent functions K_l and K_j are involved in Eq. (4.8); there being no K_1 there. Hence the summation over j can be removed:

$$v_P^{\mathrm{ind}}(\mathbf{x})=\sum_{l=2}^{N}\lambda_l\int d\mathbf{y}\left[\frac{\delta K_l^*[\rho;\mathbf{y}]}{\delta\rho(\mathbf{x})}\frac{\delta S[\rho,K_l,K_l^*]}{\delta K_l^*(\mathbf{y})}+\mathrm{c.c.}\right]\ . \quad (4.9)$$

After inserting the functional derivative of S, Eq. (A1), we have

$$v_P^{\text{ind}}(\mathbf{x})=\sum_{l=2}^{N}\lambda_l\int d\mathbf{y}\left[\frac{\delta K_l^*[\rho;\mathbf{y}]}{\delta\rho(\mathbf{x})}\rho(\mathbf{y})K_l(\mathbf{y})+\frac{\delta K_l[\rho;\mathbf{y}]}{\delta\rho(\mathbf{x})}\rho(\mathbf{y})K_l^*(\mathbf{y})\right]$$
$$=\sum_{l=2}^{N}\lambda_l\int d\mathbf{y}\,\rho(\mathbf{y})\frac{\delta}{\delta\rho(\mathbf{x})}(|K_l[\rho;\mathbf{y}]|^2)\ . \tag{4.10}$$

Now let us calculate the functional derivative of both sides of the constraint in Eq. (3.17):

$$\frac{\delta}{\delta\rho(\mathbf{x})}\int d\mathbf{y}\,\rho(\mathbf{y})|K_l[\rho;\mathbf{y}]|^2$$
$$=|K_l[\rho;\mathbf{x}]|^2+\int d\mathbf{y}\,\rho(\mathbf{y})\frac{\delta}{\delta\rho(\mathbf{x})}(|K_l[\rho;\mathbf{y}]|^2)=0\ . \tag{4.11}$$

Employing this result in Eq. (4.10) we obtain

$$v_P^{\text{ind}}(x)=-\sum_{l=2}^{N}\lambda_l|K_l(\mathbf{x})|^2\ . \tag{4.12}$$

Collecting direct and indirect contributions, we have finally the Pauli potential v_P in the form

$$v_P[\rho;\mathbf{x}]=\sum_{j=1}^{N}(\tfrac{1}{2}|\nabla K_j[\rho;\mathbf{x}]|^2-\lambda_j[\rho]|K_j[\rho;\mathbf{x}]|^2)\ . \tag{4.13}$$

Of course, any arbitrary constant can be added to Eq. (4.13), because, according to Eq. (2.2), the integral of $\delta\rho(\mathbf{x})$ is zero.

Equation (4.13) is, as already mentioned, one of the principal results of the present work. It shows that $v_P(\mathbf{x})$ is made up of two parts. Clearly the first term in Eq. (4.13) is positive everywhere; one might loosely refer to this direct contribution therefore as a "repulsive" potential. However, one has a balance between this and an "attractive" term, since λ_j in Eq. (4.13) is, according to (3.37), positive. It is worth emphasizing that through Eq. (4.13) the Pauli potential has been expressed solely in terms of the solution $\{\lambda_j[\rho],K_j[\rho;\mathbf{x}],\ j=2,\ldots,N\}$ of the eigenvalue problem connected with the determination of the Pauli energy $E_P[\rho]$.

By analogy with the case of the Pauli energy, other forms of Eq. (4.13) for the Pauli potential v_P are possible. Thus, if we make use of Eqs. (3.34) and (3.23), then Eq. (4.13) reduces to

$$v_P[\rho;\mathbf{x}]=-v_c[\rho,K_1[\rho];\mathbf{x}]$$
$$=-\frac{1}{2}\left[\frac{\nabla^2K_1}{K_1}+\left[\frac{\nabla\rho}{\rho}\right]\cdot\left[\frac{\nabla K_1}{K_1}\right]\right]\ , \tag{4.14}$$

where $K_1=K_1[\rho;\mathbf{x}]$ is given in terms of the solution via Eq. (3.9).

It is of some interest at this point to calculate the combination occurring in the expression (2.22) for the ground-state energy reduced to the boson problem

$$E_P[\rho]-\int d\mathbf{x}\,\rho(\mathbf{x})v_P[\rho;\mathbf{x}]=\sum_{l=2}^{N}\lambda_l[\rho]\ . \tag{4.15}$$

This result was obtained directly from Eqs. (3.35) and (4.14).

Results similar to those obtained in Secs. III and IV in terms of variational functions $K_j(\mathbf{x})$ are exhibited in Appendix D in terms of conventional single-particle wave functions. Simple illustrative examples of the solution of the system of Eqs. (3.22) for some particular one- and two-dimensional densities $\rho(\mathbf{x})$ and subsequent derivation of the effective potential and Pauli quantities are given in Appendix E. The purpose of the final Appendix F is to demonstrate explicitly that the Pauli potential can be written in terms of the particle density and the kinetic-energy density in the case of the one-dimensional harmonic oscillator problem.

V. ONE-DIMENSIONAL CASE: RELATION TO HYPERSPHERICAL FUNCTIONS

A. Variational problem in terms of $K_j(\mathbf{x})$

So far the methods devised have been applicable to problems of any dimensionality and arbitrarily low symmetry. In this section contact will be established between these more general methods and an earlier body of work on one-dimensional problems. This latter class can, of course, embrace central field problems, after separating the wave function into a product of radial and angular (spherical harmonic) functions.

Let us note that for the one-dimensional case all eigenvalues of the single-particle Hamiltonian (3.24) are nondegenerate while the eigenfunctions can be chosen to be real. If they are enumerated according to the following ordering of the eigenvalues

$$\varepsilon_1<\varepsilon_2<\cdots<\varepsilon_N<\varepsilon_{N+1}<\cdots \tag{5.1}$$

then the jth eigenfunction has exactly $j-1$ nodes $x_{j,k}$ lying between the boundaries (called proper nodes)

$$\phi_j(x_{j,k})=0,\quad k=1,2,\ldots,j-1\ , \tag{5.2}$$

while the boundary conditions (3.5) can be viewed as two additional (improper) nodes, say

$$x_{1,0}=x_{2,0}=\cdots=x_{j,0}=\cdots=\text{lower boundary}\ ;$$
$$x_{1,1}=x_{2,2}=\cdots=x_{j,j}=\cdots=\text{upper boundary} \tag{5.3}$$

(both infinite or finite boundaries may occur). The proper nodes of the $(j+1)$th eigenfunction lie between the nodes of the jth function

$$x_{j,0}<x_{j+1,1}<x_{j,1}<x_{j+1,2}<x_{j,2}<\cdots<x_{j,j-1}<x_{j+1,j}<x_{j,j}\ . \tag{5.4}$$

If the minimization problem (3.1) for E_P is solved for the one-dimensional case in terms of $K_j(x)$, Eq. (3.8), then the requirement (3.37), which asserts that in order to have the solution at the absolute minimum, it should embrace the N lowest eigenvalues, can be replaced by the requirement that the set of eigenfunctions forming the solution should include these only, which have $0,1,\ldots,N-1$ proper nodes, according to the property (5.2) with (5.1); it is obvious from Eq. (3.8) that the proper nodes of $K_j(x)$ coincide with the nodes of $\phi_j(\mathbf{x})$. The new requirement is much more convenient for numerical implementation than the previous form.

B. Variational problem in terms of phase functions

Following Dawson and March [19], and also Nalewajski and Kozlowski [20,21], we shall explore a set of trial functions $[\theta_j(x),\ j=1,\ldots,N-1]$, called phase functions, as variational functions for the minimization problem (3.1), suitable for the one-dimensional case. In these terms, the set $\{K_j(x)\}$ or $\{\phi_j(x)\}$, $j=1,\ldots,N$ introduced in Sec. III is given as the so-called hyperspherical functions:

$$K_1(x)=\rho^{-1/2}\phi_1=\tilde{K}_1(\theta_1)=\cos[\theta_1(x)] \tag{5.5}$$

$$\begin{aligned}K_j(x)=\rho^{-1/2}\phi_j&=\tilde{K}_j(\theta_1,\theta_2,\ldots,\theta_j)\\&=\sin(\theta_1)\sin(\theta_2)\cdots\sin(\theta_{j-1})\\&\qquad\times\cos(\theta_j),\quad j=2,3,\ldots\ .\end{aligned} \tag{5.6}$$

By definition, for an N-particle system we put

$$\theta_N(x)=0\ , \tag{5.7}$$

thus leaving $(N-1)$ functions $\theta_j(x)$, $j=1,\ldots,N-1$, independent.

The definition (5.5)–(5.7) ensures that the basic property (3.14) is fulfilled for arbitrary x:

$$\sum_{j=1}^{N} K_j^2(x)=\sum_{j=1}^{N}\tilde{K}_j^2(\theta_1,\ldots,\theta_j)=1\ . \tag{5.8}$$

In order to define the opposite transformation $\{K_j\}\rightarrow\{\theta_j\}$ or $\{\phi_j\}\rightarrow\{\theta_j\}$ in a unique way we assume, without loss of generality, that $K_j(x)>0$ for x close to the lower boundary. Then the above transformations are given by the following.

(i) For $j=1$ and $N=3,4,\ldots$,

$$\theta_1(x)=\arccos[K_j(x)]=\arccos(\phi_1/\rho^{1/2})\ , \tag{5.9}$$

$$0<\theta_1(x)<\pi/2\ . \tag{5.10}$$

(ii) For $j=2,\ldots,N-2$ and $N=4,5,\ldots$,

$$\begin{aligned}\theta_j(x)&=\arccos[K_j/(K_j^2+K_{j+1}^2+\cdots+K_N^2)^{1/2}]\\&=\arccos[\phi_j/(\phi_j^2+\phi_{j+1}^2+\cdots+\phi_N^2)^{1/2}]\ ,\end{aligned} \tag{5.11}$$

$$0<\theta_j(x)<\pi\ . \tag{5.12a}$$

The function $\theta_j(x)$ oscillates around the level $\pi/2$, satisfying

$$\theta_j(x_{j,k})=\pi/2\quad\text{for } k=1,2,\ldots,j-1\ , \tag{5.12b}$$

which follows from the property (5.2).

(iii) For $j=N-1$ and $N=2,3,\ldots$, the function $\theta_{N-1}(x)$ is determined by the following complex equation:

$$\begin{aligned}\exp[i\theta_{N-1}(x)]&=[K_{N-1}(x)+iK_N(x)]/[K_{N-1}^2(x)+K_N^2(x)]^{1/2}\\&=[\phi_{N-1}(x)+i\phi_N(x)]/[\phi_{N-1}^2(x)+\phi_N^2(x)]^{1/2}\ ,\end{aligned} \tag{5.13}$$

$$-(2N-3)\pi/2<\theta_{N-1}(x)<\pi/2\ . \tag{5.14a}$$

The $\theta_{N-1}(x)$ is a decreasing (on average) function of x, having the following particular values at nodes of ϕ_{N-1} and ϕ_N:

$$\theta_{N-1}(x_{N,k})=-(k-1)\pi,\quad k=1,2,\ldots,N-1\ ; \tag{5.14b}$$

$$\theta_{N-1}(x_{N-1,k})=-(k-\tfrac{1}{2})\pi,\quad k=1,2,\ldots,N-2\ ; \tag{5.14c}$$

which follow from the properties (5.2) and (5.4).

In all cases (i), (ii), and (iii) we have

$$0<\theta_j(x)<\pi/2\quad\text{for } x \text{ close to } x_{j,0}\ . \tag{5.15}$$

The established conditions (5.10), (5.12), and (5.14), which must be imposed on the variational functions $\theta_j(x)$, guarantee that the functions $\phi_l(\mathbf{x})$ expressed in terms of $\theta_j(x)$ have the required number of nodes as in Eq. (5.2). In this case, of course, positions of the nodes are not known *a priori*, so their number and ordering only is important.

It is to be noted that we order the functions K_j in a different manner from that adopted in the work of Dawson and March [19] and of Nalewajski and Kozlowski [20].

The minimization problem (3.16) for the Pauli energy rewritten in terms of $\theta_j(x)$ via the transformation (5.5)–(5.7) is

$$E_P[\rho]=\min_{\theta_1,\ldots,\theta_{N-1}}\tfrac{1}{2}\int dx\,\rho\{[\theta_1']^2+[\sin(\theta_1)\theta_2']^2+\cdots+[\sin(\theta_1)\cdots\sin(\theta_{j-1})\theta_j']^2+\cdots\} \tag{5.16}$$

(the number of terms being $N-1$). Here and elsewhere we write

$$f'(x)=\frac{df(x)}{dx},\quad f''(x)=\frac{d^2f(k)}{dx^2},\ldots . \tag{5.17}$$

The normalization constraints

$$\int dx\,\rho(\mathbf{x})\tilde{K}_j^2(\theta_1(\mathbf{x}),\ldots,\theta_j(\mathbf{x}))=1,\quad j=1,\ldots,N \tag{5.18}$$

have to be imposed, only $(N-1)$ of them, however, being independent due to Eqs. (5.8) and (2.2). The orthogonality constraints (3.18)

$$\int d\mathbf{x}\,\rho(\mathbf{x})\tilde{k}_j(\theta_1(\mathbf{x}),\ldots,\theta_j(\mathbf{x}))\tilde{K}_k(\theta_1(\mathbf{x}),\ldots,\theta_k(\mathbf{x}))=0,\quad j\neq k \tag{5.19}$$

are fulfilled by the solutions, as has already been demonstrated.

It turns out that the Euler-Lagrange equations for the problem (5.16) and (5.18) are

$$\frac{\delta}{\delta\theta_l(x)}\left[\tfrac{1}{2}\int dy\,\rho(y)\{[\theta_1'(y)]^2+\cdots+[\sin(\theta_1)\cdots\sin(\theta_{N-2})\theta_{N-1}']^2\}\right.$$
$$\left.-\sum_{j=2}^{N}\lambda_j\left[\int dy\,\rho(y)\tilde{K}_j^2(\theta_1(y),\ldots,\theta_j(y))-1\right]\right]=0,\quad l=1,\ldots,N-1 \tag{5.20}$$

where the λ_j are the Lagrange multipliers connected with the constraints (5.18). Because the integrands in Eqs. (5.20) depend solely on the zeroth and first derivatives of the variational functions θ_l, Eqs. (5.20) lead to a system of $(N-1)$ second-order differential nonlinear coupled equations. We shall not write these down explicitly for arbitrary N as the detail proliferates. Rather the example $N=2$ will be discussed in some detail in Sec. V E and the example $N=3$ in Appendix E2.

The boundary conditions necessary to solve such equations are

$$\theta_j'(x)\rightarrow 0 \quad \text{as} \quad x\rightarrow \text{boundary} . \tag{5.21}$$

These conditions follow directly from Eq. (B8) via the transformations (5.9), (5.11) or (5.13). Both infinite and finite (e.g., at $x=0$ for a radial equation problem [22,23] referred to above) boundaries are covered by Eq. (5.21).

Therefore, for any N, a system of equations and constraints [(5.20), (5.18), (5.21), (5.10), (5.12), and (5.14)], involving the given density $\rho(\mathbf{x})$, defines an eigenproblem which can be solved numerically, leading to the unique solution

$$\{\lambda_{j+1}[\rho],\theta_j[\rho;x],j=1,\ldots,N-1\} . \tag{5.22}$$

Next, using Eqs. (5.5)–(5.7), this solution can be transformed into

$$\{\lambda_j[\rho],K_j[\rho;x],j=1,\ldots,N\} . \tag{5.23}$$

Here $\lambda_1=0$ is added, see Eq. (3.27), and then, using Eqs. (D2), (D6), (3.10), and (3.12), transformed into

$$\{\lambda_j[\rho],\psi_j[\rho;x],j=1,\ldots,N\} . \tag{5.24}$$

C. Pauli quantities

This will allow the use of the forms for the Pauli energy and potential derived in Secs. III and IV. In particular, using Eqs. (3.29) and (5.5), we have for the effective potential in terms of ρ and θ_1 only

$$v_{\text{eff}}[\rho;x]+\text{const}=\tilde{v}_{\text{eff}}[\rho;x]=\frac{1}{2}\frac{[\rho^{1/2}\cos(\theta_1)]''}{\rho^{1/2}\cos(\theta_1)} . \tag{5.25}$$

Using Eq. (4.14) we have for the Pauli potential

$$v_P[\rho;x]=\tfrac{1}{2}(\theta_1')^2+\tfrac{1}{2}\tan(\theta_1)\left[\theta_1''+\frac{\rho'}{\rho}\theta_1'\right] . \tag{5.26}$$

The basic expression for the Pauli energy coming from Eq. (5.16) with the solution (5.22) is

$$E_P[\rho]=\int dx\tfrac{1}{2}\rho\{[\theta_1']^2+\cdots$$
$$+[\sin(\theta_1)\cdots\sin(\theta_{N-2})\theta_{N-1}']^2\} . \tag{5.27}$$

Using Eq. (4.15) it can be written in terms of all eigenvalues and one function $\theta_1(x)$ [via Eq. (5.26)]:

$$E_P[\rho]=\left[\sum_{l=2}^{N}\lambda_l[\rho]\right]+\int dx\,\rho(x)v_P[\rho;x] . \tag{5.28}$$

D. Differential form of virial theorem

It should be mentioned that for one-dimensional systems there exists an interesting differential form of the virial theorem given by March and Young [24] and by Baltin [25]. This relates derivatives of the kinetic-energy density $e_s(x)$ and the effective potential $v_{\text{eff}}(x)$, namely,

$$e_s'(x)+\tfrac{1}{2}\rho(x)v_{\text{eff}}'(x)-\tfrac{1}{8}\rho'''(x)=0 , \tag{5.29}$$

where e_s is defined in terms of single-particle solutions $\psi_j[\rho;x]$ as

$$e_s[\rho;x]=\sum_{j=1}^{N}\tfrac{1}{2}[\psi_j'(x)]^2;\quad T_s[\rho]=\int dx\,e_s[\rho;x] \tag{5.30}$$

[to be compared with Eqs. (D8) and (3.6), remembering that $E_P=T_s-T_W$; see also the last paragraph of Sec. III A]. Below we shall use Eq. (5.29) to obtain v_P' in terms of e_s' and ρ. Let us differentiate Eq. (D24) using also Eq. (2.16):

$$v_P' = \frac{1}{2}\left[\frac{(\rho^{1/2})''}{\rho^{1/2}}\right]' - v_{\text{eff}}' \ . \tag{5.31}$$

Into Eq. (5.31) we shall now insert v_{eff}' from Eq. (5.29) to find

$$v_P'(x) = \frac{2}{\rho(x)}\{e_s'(x) - [\rho^{1/2}(x)]'[\rho^{1/2}(x)]''\} \ . \tag{5.32}$$

E. Two-level results

For compactness, the remainder of this section will be restricted to the two-level problem. In this case, only one eigenfunction $\theta_1(x) = \theta(x)$ and one eigenvalue $\lambda_2 = \lambda$ are to be determined. Equation (5.20) then simplifies to

$$\frac{\delta}{\delta\theta(x)}\int dy\, \rho(y)\{\tfrac{1}{2}[\theta'(y)]^2 - \lambda \sin^2[\theta(y)]\} = 0 \ . \tag{5.33}$$

Therefore the Euler equation is (see Harriman [26], also Nagy and March [22])

$$\theta'' + \frac{\rho'}{\rho}\theta' + \lambda \sin(2\theta) = 0 \ . \tag{5.34}$$

This is to be solved subject to the conditions

$$\theta'(x) \to 0 \quad \text{as} \quad x \to \text{boundary} \tag{5.35}$$

and the constraints

$$\int dx\, \rho(x) \sin^2[\theta(x)] = 1 \tag{5.36}$$

and [see Eq. (5.14)] that $-\pi/2 < \theta(x) < \pi/2$, that $\theta(x)$ must have one node and that $\lambda > 0$.

Equations (5.34)–(5.36) can be readily solved numerically for given density $\rho(x)$, leading to the solution $\lambda_2 = \lambda[\rho]$, $\theta_1 = \theta[\rho;x]$. Then from Eqs. (5.25)–(5.28) one can find the Pauli quantities, as well as the effective potential v_{eff}.

VI. SUMMARY

Following the early work of Stoddart *et al.* [10] on Be metal, in which the Bragg reflection experiments of Brown [27] were used to construct an input charge density $\rho(\mathbf{x})$, the philosophy of the present work has similarly centered on the use of an experimental ground-state density within the general framework of density-functional theory. For general N-electron atomic and molecular systems, without invoking any simplifications due to the possible existence of symmetry, $N-1$ Euler equations (3.22) have been derived. The first stage of practical implementation of the present method must be the solution of the eigenvalue problem posed by these equations, for a given input $\rho(\mathbf{x})$. Provided these equations have physical solutions (which is the test of potential representability of the input density), it is then demonstrated explicitly how the eigenvalues and eigenfunctions can be used to construct the Pauli potential and energy, as well as the KS potential. Some examples are given to illustrate the approach. It does not need stressing that it is now of the utmost importance to have high-quality electron densities for atoms, molecules, and condensed matter from x-ray and/or electron scattering experiments. Standard quantum-chemical procedures using extensive basis sets should then be adequate to solve the Euler equations (3.22) derived here. These have the merit of "locality," in the sense that the functions $K_j(\mathbf{x})$, plus gradient and Laplacian, together with the input density and its gradient, alone enter these equations at a single position vector $\mathbf{x}$. Solutions of these equations, when they can be found for a given input density, then demonstrate v representability of that density. In terms of them the Pauli potential, energy and effective one-body potential can all be extracted.

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APPENDIX A: INTERMEDIATE STEPS IN DERIVATION OF THE EULER EQUATIONS (3.22) FOR $K_j(\mathbf{x})$

The results below have been employed in passing from Eq. (3.19) to (3.22).

$$\frac{\delta}{\delta K_l^*(\mathbf{x})} S[\rho, K_l, K_l^*] = \rho(\mathbf{x}) K_l(\mathbf{x}); \quad l = 2, \ldots, N \tag{A1}$$

and

$$\begin{aligned}\frac{\delta}{\delta K_l^*(\mathbf{x})}\widetilde{E}_P[\rho, K_l, K_l^*] &= \left[-\nabla\cdot\frac{\partial}{\partial(\nabla K_l^*)} + \frac{\partial}{\partial K_l^*}\right]\{\rho(\mathbf{x})\tfrac{1}{2}[\nabla K_l^*(\mathbf{x})]\cdot[\nabla K_l(\mathbf{x})]\} \\ &= -\tfrac{1}{2}\rho(\mathbf{x})\nabla^2 K_l(\mathbf{x}) - \tfrac{1}{2}[\nabla\rho(\mathbf{x})]\cdot[\nabla K_l(\mathbf{x})], \quad l = 2, \ldots, N \ .\end{aligned} \tag{A2}$$

The term presenting the most difficulty will now be written as

$$\begin{aligned}\widetilde{E}_P[\rho, K_1, K_1] &= \int d\mathbf{x}\, \mathcal{L}_1 \\ &= \tfrac{1}{8}\int d\mathbf{x}\, \rho(\mathbf{x})[K_1^2(\mathbf{x})]^{-1}\{\nabla[K_1^2(\mathbf{x})]\}^2\end{aligned} \tag{A3}$$

but [see Eq. (3.14)]

$$\nabla[K_1^2(\mathbf{x})] = \sum_{j=2}^{N}(-K_j\nabla K_j^* - K_j^*\nabla K_j) \ . \tag{A4}$$

It follows that

$$\frac{\partial \mathcal{L}_1}{\partial K_l^*}=\tfrac{1}{8}\rho\{2[\nabla K_1^2]\cdot[-\nabla K_l](K_1^2)^{-1}+[\nabla(K_1^2)]^2K_1^{-4}K_l\}$$

$$=\frac{-\rho}{2}K_1^{-1}(\nabla K_1)\cdot(\nabla K_l)+\frac{\rho}{2}(K_1^{-1}\nabla K_1)^2K_l \qquad \text{(A5)}$$

and

$$\frac{\partial \mathcal{L}_1}{\partial(\nabla K_l^*)}=\frac{\rho}{4}K_1^{-2}[\nabla(K_1^2)](-K_l)=-\frac{\rho}{2}K_1^{-1}(\nabla K_1)K_l\ . \qquad \text{(A6)}$$

Also

$$-\nabla\cdot\left[\frac{\partial \mathcal{L}_1}{\partial(\nabla K_l^*)}\right]$$

$$=\tfrac{1}{2}(\nabla\rho)\cdot(K_1^{-1}\nabla K_1)K_l-\frac{\rho}{2}(K_1^{-1}\nabla K_1)^2K_l$$

$$+\frac{\rho}{2}(K_1^{-1}\nabla^2K_1)K_l+\frac{\rho}{2}(K_1^{-1}\nabla K_1)\cdot\nabla K_l\ . \qquad \text{(A7)}$$

Using these steps, the Euler equations (3.22) for the functions K_l follow.

APPENDIX B: BOUNDARY CONDITIONS ON EULER EQUATIONS (3.22) FOR $K_j(\mathbf{x})$

In order to integrate the differential equations (3.22), one must, of course, specify the boundary conditions for the functions $K_l(\mathbf{x})$. These have to be derived from the properties of a given input density $\rho(\mathbf{x})$ as the only information available about the system.

If $\rho(\mathbf{x})$ happens to be a periodic function

$$\rho(\mathbf{x}+\mathbf{R}_i)=\rho(\mathbf{x})\ , \qquad \text{(B1)}$$

where $\mathbf{R}_i$ represent the periods (e.g., the edges of a large box) then the boundary conditions are found from the conditions that the functions $K_l(\mathbf{x})$ must exhibit the same periodicity

$$K_l(\mathbf{x}+\mathbf{R}_i)=K_l(\mathbf{x}),\quad l=1,2,\ldots\ . \qquad \text{(B2)}$$

Of course, in this case, all integrations must be carried out over an irreducible region, defined by the translations.

If $\rho(\mathbf{x})$ is aperiodic, then, for $\mathbf{x}\rightarrow\infty$, $\rho(\mathbf{x})$ must tend to zero fast enough to ensure the convergence of all integrals involved. The boundary conditions for this case will be established by taking the limit of a finite-region case. Suppose that the system under consideration is enclosed in a spherical box of radius R much greater than any important physical length in the system. This means that an additional potential, infinitely repulsive at $|\mathbf{x}|=R$, is imposed. The density of the system, written in spherical coordinates, in the vicinity of the boundary must take the form

$$\rho(r,\theta,\phi)=\rho(R-\xi,\theta,\phi)=c(\theta,\phi)\xi^n[1+O(\xi)]\ , \qquad \text{(B3)}$$

where $n\geq 2$. As to the form of the functions $K_j(r,\theta,\phi)$, they must be nonzero at $r=R$ because of the property (3.14) valid at any r. Hence one can write

$$K_j(R-\xi,\theta,\phi)=K_j(R,\theta,\phi)-\frac{\partial}{\partial R}K_j(R,\theta,\phi)\xi+O(\xi^2)\ . \qquad \text{(B4)}$$

Next we must turn to analyze Eq. (3.22) in the vicinity of the boundary. Using Eqs. (B3) and (B4) we have for the second term in Eq. (3.22)

$$(\rho^{-1}\nabla\rho)\nabla K_j=c^{-1}(\theta,\phi)\xi^{-n}nc(\theta,\phi)\xi^{n-1}$$

$$\times\frac{\partial K_j(R,\theta,\phi)}{\partial R}+O(\xi^0)$$

$$=n\xi^{-1}\frac{\partial K_j(R,\theta,\phi)}{\partial R}+O(\xi^0)\ . \qquad \text{(B5)}$$

As follows from the expansion (B4), all terms in Eqs. (3.22) and (3.23) other than those calculated in Eq. (B5) for $j=l$ and $j=1$ are of the order of ξ^0 as ξ tends to zero. Therefore we must require that

$$\frac{\partial K_j(R,\theta,\phi)}{\partial R}=0 \qquad \text{(B6)}$$

in order to have the terms arising from Eq. (B5) finite too. Equation (B6) is therefore the boundary condition sought, with respect to the radial variable. As a function of θ and ϕ, the function K_j is periodic with a period 2π. Therefore conditions analogous to Eq. (B2) are to be applied

$$K_j(R,\theta+2\pi,\phi)=K_j(R,\theta,\phi)=K_j(R,\theta,\phi+2\pi)\ . \qquad \text{(B7)}$$

Now the general case of the infinite domain can be realized as the limit when the box radius R tends to infinity. Thus the following boundary conditions are found:

$$\lim_{r\rightarrow\infty}\frac{\partial \log[K_j(r,\theta,\phi)]}{\partial r}=0 \qquad \text{(B8)}$$

and

$$\lim_{r\rightarrow\infty}K_j(r,\theta+2\pi,\phi)=\lim_{r\rightarrow\infty}K_j(r,\theta,\phi)$$

$$=\lim_{r\rightarrow\infty}K_j(r,\theta,\phi+2\pi)\ . \qquad \text{(B9)}$$

This completes the specification of the conditions under which the Euler equations (3.22) are to be solved for a given input density $\rho(\mathbf{x})$.

APPENDIX C: ORTHOGONALITY RELATIONS

This brief Appendix is concerned with weighted orthogonality of the functions K_l. Let us start from the Euler equations (3.22) satisfied by K_l. As remarked in the text, the case $l=1$ with $\lambda_1=0$ can be included because of Eq. (3.23). Then we multiply both sides by $\rho(\mathbf{x})K_j^*(\mathbf{x})$, $j\neq l$, and integrate through the whole of space. After additional integration by parts we then obtain

$$\int d\mathbf{x}\tfrac{1}{2}[\rho(\nabla K_j^*)\cdot(\nabla K_l)+2\rho v_cK_j^*K_l]=\lambda_l\int d\mathbf{x}\,\rho K_j^*K_l\ . \qquad \text{(C1)}$$

A further equation can now be obtained from Eq. (C1) by interchanging the indices j and l and taking the complex conjugate. The left-hand side is then identical with that of Eq. (C1) and by subtraction we find

$$0=(\lambda_l-\lambda_j)\int d\mathbf{x}\,\rho K_j^* K_l;\quad j\neq l;\quad j,l=1,2,\ldots,N\ . \tag{C2}$$

Therefore orthogonality as in Eq. (3.18) is established for states belonging to different eigenvalues. In the case of degenerate eigenvalues, corresponding eigenfunctions can be orthogonalized.

APPENDIX D: PAULI ENERGY AND POTENTIAL USING CONVENTIONAL SINGLE-PARTICLE WAVE FUNCTIONS

As mentioned in Sec. III, the Pauli energy may be obtained from a minimization technique by employing various possible sets of trial functions. In this Appendix, our purpose is to explore the set $\{\chi,\psi_2,\ldots,\psi_N\}$, which is related to the original set $\{\phi_1,\ldots,\phi_N\}$ in the following way:

$$\chi(\mathbf{x})=[|\phi_1(\mathbf{x})|^2+\cdots+|\phi_N(\mathbf{x})|^2]^{1/2}, \tag{D1}$$

$$\psi_j(\mathbf{x})=\phi_j(\mathbf{x}),\quad j=2,\ldots,N\ . \tag{D2}$$

As done previously, we take the $\phi_j(\mathbf{x})$ to be labeled such that ϕ_1 corresponds to the ground state, so that it is a nodeless function, chosen to be real and positive. Therefore the inverse transformation is

$$\phi_1(\mathbf{x})=\{\chi^2(\mathbf{x})-[|\psi_2(\mathbf{x})|^2+\cdots+|\psi_N(\mathbf{x})|^2]\}^{1/2}\ , \tag{D3}$$

$$\phi_j(\mathbf{x})=\psi_j(\mathbf{x}),\quad j=2,\ldots,N \tag{D4}$$

with the arithmetic square root used in Eq. (D3). The constraint (3.2) may evidently be rewritten as

$$\chi^2(\mathbf{x})=\rho(\mathbf{x}) \tag{D5}$$

and it is therefore automatically fulfilled if the function $\chi(\mathbf{x})$ is fixed as $\rho^{1/2}(\mathbf{x})$; that is χ is the usual density amplitude. It will prove convenient to define also an auxiliary function $\psi_1(\mathbf{x})$ depending on $\rho(\mathbf{x})$ and all independent functions $\psi_j(\mathbf{x})$:

$$\begin{aligned}\psi_1(\mathbf{x})&=\tilde{\psi}_1(\rho(\mathbf{x}),\psi_2(\mathbf{x}),\ldots,\psi_N(\mathbf{x}))\\&=[\rho(\mathbf{x})-(|\psi_2|^2+\cdots+|\psi_N|^2)]^{1/2}\ .\end{aligned} \tag{D6}$$

In terms of this function, Eq. (D4) is valid also for $j=1$ when the constraint (D5) is imposed. We can rewrite Eq. (D6) as a sum rule involving ψ_1 as well as all the independent ψ_j as

$$\rho(\mathbf{x})=[\psi_1(\mathbf{x})]^2+|\psi_2(\mathbf{x})|^2+\cdots+|\psi_N(\mathbf{x})|^2\ . \tag{D7}$$

The original minimization problem (3.1)–(3.4) can now be rewritten in terms of a new set of trial functions as

$$\begin{aligned}E_P[\rho]=\min_{\psi_2,\ldots,\psi_N}&(\tilde{T}_s[\psi_1]+\tilde{T}_s[\psi_2]\\&+\cdots+\tilde{T}_s[\psi_N]-\tilde{T}_s[\rho^{1/2}])\end{aligned} \tag{D8}$$

with the usual normalization and orthogonality conditions on $\psi_j(\mathbf{x})$.

After introduction of Lagrange multipliers $\lambda_j, j=2,\ldots,N$, connected with the normalization constraints, we find from Eq. (D8) the result

$$\frac{\delta}{\delta\psi_l^*(\mathbf{x})}\left\{T_s[\psi_1]-T_s[\rho^{1/2}]+\sum_{j=2}^{N}\left[T_s[\psi_j]-\lambda_j\left[\int d\mathbf{x}|\psi_j|^2-1\right]\right]\right\}=0\ . \tag{D9}$$

Contributions from the terms in the square brackets can be obtained in standard fashion. Special attention is needed though for $\tilde{T}_s[\psi_1]$ [see Eqs. (3.6) and (D6)] which may be rewritten as

$$\tilde{T}_s[\psi_1]=\int d\mathbf{x}\,\mathcal{L}_1=\int d\mathbf{x}\,8^{-1}(\psi_1^2)^{-1}[\nabla(\psi_1^2)]^2\ , \tag{D10}$$

where, according to Eq. (D7)

$$\delta(\psi_1^2)=\nabla\rho+\sum_{j=2}^{N}(-\psi_j\nabla\psi_j^*-\psi_j^*\nabla\psi_j)\ . \tag{D11}$$

Thus one has

$$\begin{aligned}\frac{\partial\mathcal{L}_1}{\partial\psi_l^*}&=8^{-1}(\psi_1^2)^{-2}\psi_l[\nabla(\psi_1^2)]^2+8^{-1}(\psi_1^2)^{-1}2\nabla(\psi_1^2)(-1)\cdot\nabla\psi_l\\&=2^{-1}\psi_1^{-2}(\nabla\psi_1)^2\psi_l-2^{-1}(\psi_1^{-1}\nabla\psi_1)\cdot(\nabla\psi_l)\end{aligned} \tag{D12}$$

$$\frac{\partial\mathcal{L}_1}{\partial(\nabla\psi_l^*)}=8^{-1}\psi_1^{-2}2[\nabla(\psi_1^2)](-1)\psi_l=-2^{-1}\psi_1^{-1}(\nabla\psi_1)\psi_l \tag{D13}$$

and

$$\begin{aligned}-\nabla\cdot\left[\frac{\partial\mathcal{L}_1}{\partial(\nabla\psi_l^*)}\right]&=-2^{-1}\psi_1^{-2}(\nabla\psi_1)^2\psi_l+2^{-1}\psi_1^{-1}(\nabla^2\psi_1)\psi_l\\&\quad+2^{-1}(\psi_1^{-1}\nabla\psi_1)\cdot(\nabla\psi_l)\ .\end{aligned} \tag{D14}$$

The sum of Eqs. (D12) and (D14) provides the variational derivative

$$\frac{\delta\tilde{T}_s[\psi_1]}{\delta\psi_l^*(\mathbf{x})}=\frac{1}{2}\left[\frac{\nabla^2\psi_1(\mathbf{x})}{\psi_1(\mathbf{x})}\right]\psi_l(\mathbf{x})\ . \tag{D15}$$

After evaluating the remaining terms in Eq. (D9), we obtain finally the desired Euler-Lagrange equation as

$$-\tfrac{1}{2}\nabla^2\psi_l(\mathbf{x})+\tilde{v}_c[\tilde{\psi}_1(\rho,\psi_2,\ldots,\psi_N);\mathbf{x}]\psi_l(\mathbf{x})=\lambda_l\psi_l(\mathbf{x})\ ,\quad l=2,\ldots,N\ , \tag{D16}$$

where

$$\tilde{v}_c[\psi_1;\mathbf{x}]=\frac{1}{2}\frac{\nabla^2\psi_1(\mathbf{x})}{\psi_1(\mathbf{x})} \tag{D17}$$

with ψ_1 defined by Eq. (D6).

Equation (D16) represents a system of $(N-1)$ second-order differential coupled equations for the functions $\psi_l(\mathbf{x})$. The coupling arises through the potential $\tilde{v}_c$, Eq. (D17), which depends on $\rho, \psi_2, \ldots, \psi_N$ in a local way. This system, together with normalization constraints and boundary conditions (the same as for conventional wave functions) can be solved numerically, leading to the solution $\{\lambda_l[\rho], \psi_l[\rho;\mathbf{x}], l=2,\ldots,N\}$.

By comparison of (D16) with the system of Eqs. (3.24) for $\phi_l(\mathbf{x})$, resulting from the assumption of noninteracting v representability for $\rho(\mathbf{x})$, one readily sees that $\psi_l(\mathbf{x})$ coincides with $\phi_l(\mathbf{x})$, while the eigenvalues are related by

$$\lambda_l = \varepsilon_l - \varepsilon_1 \ . \tag{D18}$$

The effective potential turns out to be equivalent to the present coupling potential

$$\tilde{v}_c(\mathbf{X}) = \tilde{v}_{\text{eff}}(\mathbf{x}) = v_{\text{eff}}(\mathbf{x}) + \text{const} \tag{D19}$$

[see Eqs. (3.28) and (3.29)].

It is easy to establish also the equivalence between the present solution $\{\lambda_l[\rho], \psi_l[\rho;\mathbf{x}],\ l=2,\ldots,N\}$ and that discussed in Sec. III, $\{\lambda_l[\rho],\ K_l[\rho;\mathbf{x}],\ l=2,\ldots,N\}$, via the relation

$$\psi_l(\mathbf{x}) = \rho^{1/2}(\mathbf{x}) K_l(\mathbf{x}) \ . \tag{D20}$$

The eigenvalues remain the same, while the relation between the coupling potentials (D17) and (3.23) is

$$v_c = \tilde{v}_c + \frac{1}{8}\left[\frac{\nabla\rho}{\rho}\right]^2 - \frac{1}{4}\frac{\nabla^2\rho}{\rho} = \tilde{v}_c + \frac{\delta T_W[\rho]}{\delta\rho} \ . \tag{D21}$$

Again one can obtain the Pauli energy and potential in terms of the eigenvalues; in view of the procedure set out in the main text we omit the details. In the representation used in this Appendix, one form of the Pauli potential that follows is

$$v_P[\rho;\mathbf{x}] = \frac{1}{\rho(\mathbf{x})}\left[\sum_{j=1}^{N} \tfrac{1}{2}|\nabla\psi_j[\rho;\mathbf{x}]|^2 - \lambda_j[\rho]|\psi_j[\rho;\mathbf{x}]|^2\right] - \frac{1}{8}\left[\frac{\nabla\rho(\mathbf{x})}{\rho(\mathbf{x})}\right]^2 , \tag{D22}$$

where $\lambda_1 = 0$ and

$$\psi_1[\rho;\mathbf{x}] = \{\rho(\mathbf{x}) - (|\psi_2[\rho;\mathbf{x}]|^2 + \cdots + |\psi_N[\rho;\mathbf{x}]|^2)\}^{1/2} \ . \tag{D23}$$

An alternative form of the Pauli potential [11] is [see Eqs. (4.14), (D21), and (D19)]

$$v_P(\mathbf{x}) = \left[\frac{1}{4}\frac{\nabla^2\rho}{\rho} - \frac{1}{8}\left[\frac{\nabla\rho}{\rho}\right]^2\right] - \tilde{v}_{\text{eff}}[\rho] \tag{D24}$$

or equivalently

$$v_P(\mathbf{x}) = \frac{1}{2}\frac{\nabla^2[\rho^{1/2}(\mathbf{x})]}{\rho^{1/2}(\mathbf{x})} - \frac{1}{2}\frac{\nabla^2\psi_1[\rho;\mathbf{x}]}{\psi_1[\rho;\mathbf{x}]} \ . \tag{D25}$$

Also with the aid of Eq. (D21) and the relation between v_P and potential v_c, see Eq. (4.14), one can write

$$v_P[\rho;\mathbf{x}] = -\frac{\delta T_W[\rho]}{\delta\rho(\mathbf{x})} - v_{\text{eff}}[\rho;\mathbf{x}] + \text{const} \tag{D26}$$

or in terms of the boson potential $v_B(\mathbf{x})$, Eq. (2.14),

$$\frac{\delta T_W[\rho]}{\delta\rho(\mathbf{x})} + v_B[\rho;\mathbf{x}] = \text{const} \ , \tag{D27}$$

i.e., the boson problem Eq. (2.13).

It is to be noted that the present result (D22) is close to the result of Bartolotti and Acharya [28] (BA). For comparison, consider all functions ψ_l to be real, as tacitly assumed by BA, and also let us write

$$\rho_j(\mathbf{x}) = \psi_j^2(\mathbf{x}) \ . \tag{D28}$$

In this case, Eq. (D22) can be rewritten as

$$v_P(\mathbf{x}) = \frac{1}{8\rho}\left[\sum_{j=1}^{N}\frac{(\nabla\rho_j)\cdot(\nabla\rho_j)}{\rho_j} - \frac{(\nabla\rho)\cdot(\nabla\rho)}{\rho}\right] - \frac{1}{\rho}\left[\sum_{j=1}^{N}\lambda_j\rho_j\right] . \tag{D29}$$

Thus Eqs. (D29) and (14) of BA, taken for a particular spin polarization, differ only by a constant.

APPENDIX E: EXAMPLES TO OBTAIN EFFECTIVE POTENTIAL AND PAULI QUANTITIES FROM A GIVEN PARTICLE DENSITY

1. One-dimensional problem in semi-infinite domain

The following particle density, defined in the one-dimensional domain $(0,\infty)$, is the given input information

$$\rho(r) = 32r^2[(1-2r)^2 - 8\exp(-4r)]\exp(-4r) \ . \tag{E1}$$

This function exhibits two maxima: a narrow one at $r=0.28$ with $\rho=2.35$ and a broad one at $r=1.28$ where $\rho=0.78$, separated by a shallow minimum of value $\rho=0.57$ at $r=0.79$. By integration, this $\rho(r)$ corresponds to a number of particles

$$N = \int_0^\infty dr\, \rho(r) = 2 \ . \tag{E2}$$

Therefore we can use the formalism given in Sec. V E, dealing with the two-level problem in terms of a phase function. Thus one has to determine one eigenfunction $\theta_1(r) = \theta(r)$ and one eigenvalue $\lambda_2 = \lambda$ from the Euler-Lagrange equation (5.34). Let us rewrite it here in the form

$$-(\theta'' + \theta'\rho'/\rho)/\sin(2\theta) = \lambda \ . \tag{E3}$$

The boundary conditions (5.35) are

$$\theta'(0) = 0;\ \lim_{r\to\infty}\theta'(r) = 0 \ , \tag{E4}$$

the constraints on the range and nodes

$$-\pi/2 < \theta(r) < \pi/2,\quad \theta(r_{2,1}) = 0 \ , \tag{E5}$$

and no normalization [Eq. (5.36)]

$$\int_0^\infty dr\, \rho(r)\sin^2[\theta(r)] = 1 \ . \tag{E6}$$

We now assert that the desired solution of the above problem is

$$\theta(r)=\arctan[R(r)] , \tag{E7}$$

where

$$R(r)=8^{-1/2}(1-2r)\exp(2r) . \tag{E8}$$

The following relations, derived from Eq. (E7), will be useful for verification of the solution:

$$\sin(\theta)=R/(1+R^2)^{1/2} , \tag{E9}$$

$$\cos(\theta)=1/(1+R^2)^{1/2} , \tag{E10}$$

$$\theta'=R'/(1+R^2) , \tag{E11}$$

and

$$\theta''=R''/(1+R^2)-2R(R')^2/(1+R^2)^2 . \tag{E12}$$

It can be seen from Eqs. (E7) and (E11) that Eqs. (E4) and (E5) are fulfilled, with $r_{2,1}=\frac{1}{2}$. Condition (E6) is readily checked with the help of Eq. (E9). By inserting Eqs. (E9)–(E12) into the left-hand side (LHS) of Eq. (E3) we obtain after some algebra a constant value

$$\lambda=-\frac{1}{2}\left[\frac{R''}{R}+\frac{2(1-4r)}{r}\frac{R'}{R}\right]=6 . \tag{E13}$$

The one-particle wave functions [see Eqs. (5.5)–(5.7)], corresponding to the solution obtained, are

$$\phi_1(r)=\rho^{1/2}K_1=\rho^{1/2}\cos(\theta)=16r\exp(-4r) \tag{E14}$$

and

$$\phi_2(r)=\rho^{1/2}K_2=\rho^{1/2}\sin(\theta)$$
$$=8r(2)^{-1/2}(1-2r)\exp(-2r) . \tag{E15}$$

Therefore the given density $\rho(r)$ has been generated by the one-particle Hamiltonian with the effective potential [see Eqs. (3.28) and (3.29)]

$$\tilde{v}_{\text{eff}}(r)=(1/2)\phi_1''/\phi_1=-4/r+8=v_{\text{eff}}(r)-\varepsilon_1 , \tag{E16}$$

which is the Coulomb potential with $Z=4$, shifted by a constant 8. So, if, in addition, we allow for double occupancy of the levels, the above example simulates the radial equation problem of Be, but with the electron-electron interaction switched off. Its eigenenergies given by

$$\varepsilon_l=-Z^2/(2l^2) \tag{E17}$$

are consistent with $\varepsilon_1=-8$ seen in Eq. (E16) and $\lambda=\lambda_2=\varepsilon_2-\varepsilon_1=6$ from Eq. (E13).

The phase function $\theta(r)$, Eq. (E7), has a maximum $\theta=0.34$ at $r=0$, from which it decreases monotonically, going through zero at $r=\frac{1}{2}$, then $\theta=-1.21$ at 1.0, -1.55 at 2 and approaches the asymptotic value $-\pi/2$ for large r.

The Pauli energy can be evaluated numerically according to Eq. (3.30), using Eqs. (E14) and (E15), as

$$E_P=\frac{1}{2}\int_0^\infty dr\,\rho(r)\{[K_1'(r)]^2+[K_2'(r)]^2\} , \tag{E18}$$

while the Pauli potential, according to Eq. (4.13), is

$$v_P(r)=\tfrac{1}{2}(K_1')^2+\tfrac{1}{2}(K_2')^2-6K_2^2 . \tag{E19}$$

This function starts from $v_P=-\frac{2}{3}$ at $r=0$, increases (quadratically for small r) to the maximum 3.50 at $r=0.65$, then goes through zero at $r=0.81$ and further decreases to -4.34 at $r=1$, to -5.95 at 1.5, and eventually approaches the asymptotic value -6 for large r.

2. One-dimensional problem in finite domain

The following density, defined in the range (0,2), is the given input information:

$$\rho(x)=S^2(14C^4+2S^2) , \tag{E20}$$

where

$$S(x)=\sin(\pi x/2),\quad C(x)=\cos(\pi x/2) . \tag{E21}$$

This function has one maximum $\rho=2$ at $x=1$, two maxima $\rho=2.16$ at $x=0.41$ and 1.59, separated by two minima $\rho=1.47$ at $x=0.71$ and 1.29, and quadratically approaches zero at the boundaries.

By integration, this $\rho(x)$ corresponds to a number of particles

$$N=\int_0^2 dx\,\rho(x)=3 . \tag{E22}$$

Using the formalism of phase functions, developed in Sec. V B, we have to determine two functions $\theta_1(x)$ and $\theta_2(x)$ and two eigenvalues λ_2 and λ_3 by solving the system of two Euler-Lagrange equations, Eq. (5.20), for $l=1,2$, which can be written in the form

$$\theta_1''=-(\rho'/\rho)\theta_1'+[\tfrac{1}{2}(\theta_2')^2-\lambda_2$$
$$+(\lambda_2-\lambda_3)\sin^2(\theta_2)]\sin(2\theta_1) , \tag{E23}$$

$$\theta_2''=-\left[\frac{\rho'}{\rho}+2\cot(\theta_1)\theta_1'\right]\theta_2'+(\lambda_2-\lambda_3)\sin(2\theta_2) . \tag{E24}$$

We now assert that the desired solution of the above equations with the boundary conditions (5.21) is

$$\lambda_2=(3/8)\pi^2,\quad \lambda_3=(5/8)\pi^2 , \tag{E25}$$

$$\theta_1(x)=\arccos[(14C^4+2S^4)^{-1/2}] , \tag{E26}$$

$$\theta_2(x)=\begin{cases}\arctan[2C-(2C)^{-1}], & \text{for } 0\le x<1\\ -\pi/2, & \text{for } x=1\\ -\pi+\arctan[2C-(2C)^{-1}], & \text{for } 1<x\le 2 .\end{cases} \tag{E27}$$

We see that θ_1 satisfies Eq. (5.10), and θ_2 Eq. (5.14) with $x_{2,1}=1$, $x_{3,1}=\frac{2}{3}$ and $x_{4,1}=\frac{4}{3}$. The function θ_1 has two maxima $\theta_1=1.30$ at the boundaries and a minimum $\theta_1=\pi/4$ at $x=1$. The function θ_2 decreases monotonically from 0.98 at $x=0$ to -4.12 at $x=2$.

Having the solution (E25)–(E27) in analytical form, Eq. (E23) and (E24) can be verified, in principle analytically. But the expressions became so unwieldy that instead of performing that task we checked them numerically at a large number of points. With differentiations performed numerically, excellent agreement was obtained.

Substituting the solution (E26) and (E27) into Eqs. (5.5)–(5.7), we find

$$\phi_1(x)=\rho^{1/2}\cos(\theta_1)=\sin(\pi x/2)\ , \tag{E28}$$

$$\phi_2(x)=\rho^{1/2}\sin(\theta_1)\cos(\theta_2)=\sin(\pi x)\ , \tag{E29}$$

and

$$\phi_3(x)=\rho^{1/2}\sin(\theta_1)\sin(\theta_2)=\sin(3\pi x/2)\ . \tag{E30}$$

Therefore the given density $\rho(x)$ has been generated by the potential

$$\tilde{v}_{\text{eff}}(x)=\tfrac{1}{2}\phi_1''/\phi_1=-\pi^2/8=v_{\text{eff}}(x)-\varepsilon_1\ . \tag{E31}$$

This corresponds to the empty well potential

$$v_{\text{eff}}(x)=\begin{cases}+\infty, & x<0\\ 0, & 0\le x\le 2\\ +\infty, & 2<x\ .\end{cases} \tag{E32}$$

3. Two-dimensional problem in infinite domain

The input information this time is the following density in the infinite (x,y) plane:

$$\rho(x,y)=\rho_0(x,y)D(x,y) \tag{E33}$$

with

$$\rho_0(x,y)=\pi^{-1}\exp(-x^2-y^2) \tag{E34}$$

and

$$D(x,y)=1+2(x^2+y^2)+4x^2y^2\ . \tag{E35}$$

This function exhibits the symmetry of a square. By integration, it corresponds to four particles. Therefore according to Sec. III, we must determine three functions K_l and eigenvalues λ_l, $l=2,3,4$, from the system of Eqs. (3.22). These can be rewritten as

$$\begin{aligned}&-\tfrac{1}{2}(K_l^{-1}\nabla^2K_l-K_1^{-1}\nabla^2K_1)\\&\quad-\tfrac{1}{2}\rho^{-1}(\nabla\rho)\cdot(K_l^{-1}\nabla K_l-K_1^{-1}\nabla K_1)=\lambda_l,\quad l=2,3,4\end{aligned} \tag{E36}$$

where

$$K_1=(1-K_2^2-K_3^2-K_4^2)^{1/2}\ . \tag{E37}$$

Again, we assert that the solution of the system (E36), with the boundary conditions (B8) and (B9), is

$$\begin{aligned}&K_1=D^{-1/2},\quad K_2=2^{1/2}xD^{-1/2}\ ,\\&K_3=2^{1/2}yD^{-1/2},\quad K_4=2xyD^{-1/2}\ .\end{aligned} \tag{E38}$$

By inserting Eqs. (E38) and (E33)–(E35) into the LHS of Eq. (E36), we obtain some functions of (x,y), which after lengthy algebra reduce to constant values equal to

$$\lambda_2=\lambda_3=1,\quad \lambda_4=2\ , \tag{E39}$$

proving that the solution (E38) satisfies Eqs. (E36). To find the effective potential according to Eqs. (3.28) and (3.29), we must determine

$$\phi_1=\rho^{1/2}K_1=\rho_0^{1/2} \tag{E40}$$

[Eqs. (3.11), (3.12), (E38), and (E33) were used here]. Thus

$$\begin{aligned}\tilde{v}_{\text{eff}}(x,y)&=\tfrac{1}{2}(\nabla^2\phi_1)/\phi_1\\&=\tfrac{1}{2}(x^2+y^2)-1\\&=v_{\text{eff}}(x,y)-\varepsilon_1\ .\end{aligned} \tag{E41}$$

It is seen that the given density was therefore generated by an isotropic two-dimensional harmonic oscillator potential. The two-dimensional eigenfunctions $\phi_l(x,y)=\rho^{1/2}K_l$, $l=1,2,3,4$, given by Eqs. (E38) and (E33), can be written in terms of the eigenfunctions of the one-dimensional oscillator

$$\psi_1(x)=\pi^{-1/4}\exp(-x^2/2),\quad \psi_2(x)=2^{1/2}x\psi_1(x) \tag{E42}$$

(the eigenvalues are $\frac{1}{2}$ and $\frac{3}{2}$, respectively), as

$$\begin{aligned}&\phi_1(x,y)=\psi_1(x)\psi_1(y),\quad \phi_2(x,y)=\psi_2(x)\psi_1(y)\ ,\\&\phi_3(x,y)=\psi_1(x)\psi_2(y),\quad \phi_4(x,y)=\psi_2(x)\psi_2(y)\ .\end{aligned} \tag{E43}$$

The corresponding eigenvalues are

$$\varepsilon_1=\tfrac{1}{2}+\tfrac{1}{2}=1;\ \varepsilon_2=\varepsilon_3=\tfrac{3}{2}+\tfrac{1}{2}=2;\ \varepsilon_4=\tfrac{3}{2}+\tfrac{3}{2}=3 \tag{E44}$$

which is in agreement with ε_1 in Eq. (E41) and with Eq. (E39) where $\lambda_l=\varepsilon_l-\varepsilon_1$. Because the eigenvalues (E44) are constructed from the lowest eigenvalues of the one-dimensional oscillator problem, the requirement (3.37) is fulfilled.

It should be noted here that the ground state of the system of four electrons, generated by the potential $v_{\text{eff}}(x,y)$ in Eq. (E41), happens to be triply degenerate. To see this, we may replace the fourth function of the solution (E43) by $\psi_1(x)\psi_3(y)$ or $\psi_3(x)\psi_1(y)$; the energy remains unchanged since the corresponding eigenvalue is $\frac{1}{2}+\frac{5}{2}=3$ also.

APPENDIX F: PAULI POTENTIAL OF HARMONIC OSCILLATOR POTENTIAL WITH *N* OCCUPIED LEVELS IN ONE DIMENSION

As shown by Lawes and March [29] (LM), the kinetic-energy density $t(x)$, defined now by

$$t(x)=-\tfrac{1}{2}\sum_{l=1}^{N}\psi_l\psi_l'' \tag{F1}$$

for a linear harmonic oscillator with N occupied levels is given by

$$\begin{aligned}t(x)=&\tfrac{1}{12}\psi_N^2[x^4-x^2(4N+1)+2N+4N^2]\\&-\tfrac{1}{12}\psi_N'^2(x^2+1-2N)+\tfrac{1}{6}x\psi_N\psi_N'\ .\end{aligned} \tag{F2}$$

It will be useful to introduce the quantity

$$W_N(x)=v_{\text{eff}}(x)-\varepsilon_N=\tfrac{1}{2}x^2-(N-\tfrac{1}{2})\ , \tag{F3}$$

occurring in the Schrödinger equation for the Nth state:

$$\psi_N''=2W_N\psi_N \; . \tag{F4}$$

Thus Eq. (F2) written in terms of W_N becomes

$$12t=(4W_N^2-6W_N+2)\psi_N^2-2W_N(\psi_N')^2+2x\psi_N\psi_N' \; . \tag{F5}$$

We plan to eliminate ψ_N and ψ_N' from the relation between W_N and t; to do so we need two more equations. They are Eq. (2.2) of LM, written in terms of W_N

$$2\rho=(1-2W_N)\psi_N^2+(\psi_N')^2 \tag{F6}$$

and the derivative of Eq. (2.4) of LM, written in terms of W_N using Eq. (F4)

$$\rho''=(2W_N-1)\psi_N^2+(\psi_N')^2-2x\psi_N\psi_N' \; . \tag{F7}$$

Then one can verify readily the identity

$$12t+(2W_N-1)2\rho+\rho''=0 \; . \tag{F8}$$

Solving Eq. (F8) and forming $v_{\rm eff}$ from Eq. (F3) we have

$$v_{\rm eff}=-\frac{3t}{\rho}-\frac{\rho''}{4\rho}+N \; . \tag{F9}$$

In order to obtain the Pauli potential using Eq. (D22), let us take the Schrödinger equation for the lth state

$$-\frac{1}{2}\psi_l\psi_l''+v_{\rm eff}\psi_l^2=\varepsilon_l\psi_l^2 \tag{F10}$$

and sum it over all N states. Then using the definition (F1) we have

$$t+v_{\rm eff}\rho=\sum_{l=1}^{N}\varepsilon_l\psi_l^2 \tag{F11}$$

and employing Eqs. (F9) and (D18) with $\varepsilon_1=\frac{1}{2}$ we obtain

$$\sum_{l=1}^{N}\lambda_l\psi_l^2=-2t-\tfrac{1}{4}\rho''+(N-\tfrac{1}{2})\rho \; . \tag{F12}$$

Of course, the price paid for achieving the summation over l is the introduction of the kinetic-energy density t as well as ρ and its derivatives.

The Pauli potential according to Eq. (D22) is

$$\begin{aligned} v_P=v_P^{\rm dir}+v_P^{\rm ind}&=\left[\frac{t}{\rho}+\frac{\rho''}{4\rho}-\frac{1}{8}\left(\frac{\rho'}{\rho}\right)^2\right] \\ &\quad+\left[\frac{2t}{\rho}+\frac{\rho''}{4\rho}-\left(N-\frac{1}{2}\right)\right] \\ &=\frac{3t}{\rho}+\frac{\rho''}{2\rho}-\frac{1}{8}\left(\frac{\rho'}{\rho}\right)^2+\text{const} \; . \end{aligned} \tag{F13}$$

The same result may be obtained in an alternative manner from Eq. (D24) with (F9) and (3.29).

It is worth remarking in this context that for this specific example Eq. (F2) expresses $t(x)$ in terms of the wave function of the highest occupied level N.

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