Existence of a density functional for an intrinsic state

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A generalization of the Hohenberg-Kohn theorem for finite systems proves the existence of a density functional (DF) for a symmetry violating intrinsic state, out of which a physical state with good quantum numbers can be projected.

I. INTRODUCTION

Density functional [1] theory (DFT) was initially defined for ground states. These have good quantum numbers. Every nuclear physicist knows that, for instance, the ground state of ^{20}Ne is 0^+ and that its density is, thus, isotropic, not an ellipsoid. Every molecular physicist knows that, for instance, the ground state of the ammonia molecule is a good parity state, not just the pyramid described by the Born-Oppenheimer approximation. In particular, the nuclear DF must generate *spherical* solutions for the some thousand 0^+ nuclear ground states, whether nuclei are intrinsically deformed or not. The same need for isotropic solutions extends to the nonlocal generalization of the DFT [2,3]. But the theory of rotational bands and/or parity vibrations, whether in nuclear, atomic or molecular physics, most often relates ground states to wave packets, often named "intrinsic states," which are symmetry breaking, namely do not transform in an irreducible representation (irrep) of the symmetry group S of the Hamiltonian. Therefore, one may raise the question of DFT for intrinsic states rather than eigenstates.

Given the physical Hamiltonian H with its symmetry group S, calculations providing a "non-S-irrep" state as a solution for minimum energy cannot be labeled as the result of "the" DF. Such a state, labeled intrinsic, is actually just a convenient wave packet, to be subsequently projected onto good quantum numbers to account for physical levels. Such intrinsic calculations should rather exhibit a special Hamiltonian, which might be called an intrinsic Hamiltonian, distinct from the physical one, if such calculations are to be legitimized. Or they should be interpreted as one variety of the Hartree-Fock, Hartree-Bogoliubov, etc. variational approaches. This is implicit or even explicit in calculations with an *energy density* functional, implying nonlocalities, see, for instance, Refs. [4–7]. Energy density and particle density are different concepts.

It turns out that the particle density which has been used for the foundation of DF theory mainly concerns eigenstates of the physical Hamiltonian, in principle at least, while the energy density, used for Skyrme force calculations in nuclear physics for instance, mainly provides intrinsic states. This paper presents a *particle* DF theory for *intrinsic* states, not for eigenstates of the Hamiltonian. We show how the physical Hamiltonian can be reconciled with the proper definition of a DF for an intrinsic state and how the resulting intrinsic state can be accepted as a useful wave packet, out of which states with good quantum numbers can be projected. In particular, in the case of molecules, our approach will consider both the electrons and the nuclei. Our intrinsic state can take into account both kinds of degrees of freedom. Section II describes a functional out of which a variational principle derives for an intrinsic state, and out of which a DF for the intrinsic density is obtained. Section III gives an example of variational equations to be solved in practice. Section IV rewrites the formalism into a slightly simpler form. Section V contains a discussion of our result and suggests an ansatz for intrinsic Hamiltonians.

II. BASIC FORMALISM

For the first argument, dealing with one kind of identical particles only, let H be their physical Hamiltonian and $\phi, \langle \phi | \phi \rangle = 1$, be a trial wave packet, most often not transforming under an irrep of the symmetry group S of H. For instance, for fermions, ϕ may be an arbitrary Slater determinant, but we let ϕ also be a more general wave function, including some amount of correlations. States $\psi \propto P\phi$ with good quantum numbers can then be projected out of ϕ by a projector P, a fixed operator. In the following, we shall systematically use the properties, $P^2 = P$ and $[P, H] = 0$. It may happen that $\langle \phi | P | \phi \rangle$ vanishes, but such cases usually make a domain of zero measure in the usual variational domains, where ϕ evolves. In any case, since H is an operator bounded from below, the functional of $\phi, \langle \phi | PH | \phi \rangle / \langle \phi | P | \phi \rangle$, is bounded from below. Embed now the system in an external, local field, $U = \Sigma_i u(r_i)$. The local, real potential u is taken bounded from below, but is other-

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wise arbitrary. In particular, it may usually have none of the symmetries of H. Then, given u, the following functional of ϕ,

$$\mathcal{F}[\phi] = \frac{\langle\phi|PH|\phi\rangle}{\langle\phi|P|\phi\rangle} + \langle\phi|U|\phi\rangle, \quad (1)$$

is bounded from below. To find the lowest energy with the quantum numbers specified by P one can use a constrained search [8], in which one first considers only states that show a given density profile $\tau(r)$, then one lets τ vary,

$$\mathrm{Inf}_\phi\left[\frac{\langle\phi|PH|\phi\rangle}{\langle\phi|P|\phi\rangle} + \langle\phi|U|\phi\rangle\right]$$
$$= \mathrm{Inf}_\tau\left[\left(\mathrm{Inf}_{\phi\to\tau}\frac{\langle\phi|PH|\phi\rangle}{\langle\phi|P|\phi\rangle}\right) + \int dr\tau(r)u(r)\right]. \quad (2)$$

The process goes in two steps, namely, (i) a minimization within a given particle density profile, $\tau(r) \equiv \langle\phi|c_r^\dagger c_r|\phi\rangle$, for N particles, with $c_r^\dagger$ and c_r the usual creation and annihilation operators at position r, then, (ii) a minimization with respect to the profile. The inner minimization clearly defines a DF, $F[\tau] \equiv \mathrm{Inf}_{\phi\to\tau}(\langle\phi|PH|\phi\rangle/\langle\phi|P|\phi\rangle)$.

Actually, it is more general [9–13] to use many-body density matrices $\mathcal{B}$ in N-body space, meaning mixed as well as pure states, and yielding a density $\tau(r)$ in one-body space,

$$\mathrm{Inf}_\tau\left[\mathrm{Inf}_{\mathcal{B}\to\tau}\left(\frac{\mathrm{Tr}\,\mathcal{B}PH}{\mathrm{Tr}\,\mathcal{B}P} + \mathrm{Tr}\,\mathcal{B}U\right)\right], \quad (3)$$

but we shall use wave functions in the following, namely, $\mathcal{B} = |\phi\rangle\langle\phi|$, for obvious pedagogical reasons. We shall assume that this Inf_ϕ actually defines an absolute minimum, Min_ϕ, reached at some solution Φ of the corresponding variational principle. Moreover, we shall assume, temporarily at least, that the solution Φ is unique. Uniqueness is not obvious, however, if only because many ϕ's can give the same $P|\phi\rangle$, and, when u vanishes, this variational principle, Eq. (2), reduces to the well-known "variation after projection" [14] method for Hartree-Fock calculations for instance.

Anyhow, τ and u are clearly conjugate in a functional Legendre transform, with $\delta F/\delta\tau = -u$. Finally, if $\rho(r)$ denotes the profile of Φ when $u\to0$, then the lowest energy with good quantum numbers is nothing but $F[\rho]$. The minimization, with respect to τ, of the functional, $F[\tau]$, provides simultaneously the density of the intrinsic (unprojected) state and the projected energy. Notice, incidentally, that $F[\tau]$ depends on the choice of the variational set of trial functions ϕ where the "inner minimization" is performed. Furthermore, it obviously depends on P.

A more general argument is possible, with more than one kind of identical particles. Trial states can be, for instance, products of determinants, one for each kind of fermions, and permanents, one for each kind of bosons. Consider for instance the ammonia molecule, with (i) its active electrons, (ii) its three protons, and (iii) its nitrogen ion. It is trivial to include a center-of-mass trap into H to factorize into a spherical wave packet the center of mass motion of this self-bound system and avoid translational degeneracy problems. The complete Hamiltonian H, trial states ϕ, and density operators $\mathcal{B}$ depend on and describe simultaneously the electron, proton, and nitrogen ion coordinates and momenta. A DF in just the electronic density space, however, results from the definition,

$$\mathcal{F}[\tau] = \mathrm{Inf}_{\mathcal{B}\to\tau}\frac{\mathrm{Tr}\,\mathcal{B}PH}{\mathrm{Tr}\,\mathcal{B}P}, \quad (4)$$

where P projects good quantum numbers for the whole system and traces are taken over all degrees of freedom, while τ is set as only an electronic density. Interactions between heavy degrees of freedom, between heavy and electronic ones, and between electrons, are taken into account by the trace in the numerator. No Born-Oppenheimer approximation is needed for this "global" definition. For the sake of simplicity, however, we return in the following to the case of one kind of particles only. Most considerations which follow have obvious generalization for multicomponent systems.

III. VARIATIONAL EQUATIONS

Let $\delta\phi$ be an infinitesimal variation of the trial function in its allowed domain. Then, at first order, one obtains

$$\delta\mathcal{F} = \frac{\langle\delta\phi|PH|\phi\rangle}{\langle\phi|P|\phi\rangle} + \langle\delta\phi|U|\phi\rangle - \frac{\langle\delta\phi|P|\phi\rangle\langle\phi|PH|\phi\rangle}{(\langle\phi|P|\phi\rangle)^2}$$
$$+ \frac{\langle\phi|PH|\delta\phi\rangle}{\langle\phi|P|\phi\rangle} + \langle\phi|U|\delta\phi\rangle - \frac{\langle\phi|P|\delta\phi\rangle\langle\phi|PH|\phi\rangle}{(\langle\phi|P|\phi\rangle)^2}.$$
$$(5)$$

If one defines the "gradient operator"

$$\mathcal{G} = \frac{PH}{\langle\phi|P|\phi\rangle} + U - \frac{P\langle\phi|PH|\phi\rangle}{(\langle\phi|P|\phi\rangle)^2}, \quad (6)$$

then, obviously, $\delta\mathcal{F} = \langle\delta\phi|\mathcal{G}|\phi\rangle + \langle\phi|\mathcal{G}|\delta\phi\rangle$. Note, incidentally, that $\mathcal{G}$ is Hermitian.

At the minimum position Φ, the variation $\delta\mathcal{F}$ vanishes for any $\delta\phi$. Replace $\delta\phi$ by $i\delta\phi$ to see that the difference, $-\langle\delta\phi|\mathcal{G}|\Phi\rangle + \langle\Phi|\mathcal{G}|\delta\phi\rangle$, vanishes as well. Then, trivially, at Φ, both $\langle\delta\phi|\mathcal{G}|\Phi\rangle$ and $\langle\Phi|\mathcal{G}|\delta\phi\rangle$ vanish simultaneously,

$$\langle\delta\phi|\mathcal{G}|\Phi\rangle = \langle\Phi|\mathcal{G}|\delta\phi\rangle = 0, \quad \forall\ \delta\phi. \quad (7)$$

In the special case of Slater determinants, let $|ph\rangle \equiv c_p^\dagger c_h|\Phi\rangle$ denote any particle-hole state built upon $|\Phi\rangle$ as the "reference vacuum" for quasiparticles. Here $c^\dagger$ and c are the familiar fermionic creation and annihilation operators, respectively. Then the particle-hole matrix elements of $\mathcal{G}$ vanish,

$$\langle ph|\mathcal{G}|\Phi\rangle = 0, \quad \forall\ ph. \quad (8)$$

As long as a solution of this stationarity condition, Eq. (8), is not reached, the matrix elements, $\langle ph|\mathcal{G}|\phi\rangle$, define the direction of the gradient of $\mathcal{F}$ in the hyperplane tangent to the manifold of Slater determinants. A gradient descent algorithm, $|\delta\phi\rangle = -\eta\Sigma_{ph}|ph\rangle\langle ph|\mathcal{G}|\phi\rangle$, where η is a small step parameter, then leads to the solution. Notice, however, that the ph representation is covariant with ϕ. The ph basis has to be recalculated at each step. Being state dependent, $\mathcal{G}$ must also be recalculated at each step.

IV. SIMILAR THEORY, WITH A LAGRANGE MULTIPLIER

The slightly complicated gradient operator, Eq. (6), leads to a variational condition, Eq. (7), which combines the matrix elements of three operators, namely PH, P, and U. Define the number $\lambda = \langle \Phi | PH | \Phi \rangle / \langle \Phi | P | \Phi \rangle$ as a yet unknown Lagrange multiplier; it can be considered as an arbitrary parameter and shall be adjusted self-consistently later, when Φ is reached. Then Eq. (7) also reads

$$\langle \delta\phi | (PH - \lambda P + \langle \Phi | P | \Phi \rangle U) | \Phi \rangle = 0. \qquad (9)$$

If ϕ were completely unrestricted, namely if $\delta\phi$ were completely general, this equation, Eq. (9), would mean that Φ is an eigenstate of the operator $\mathcal{G}$. Since intrinsic states are understood to belong to restricted sets of states, the result Φ is only an approximate eigenstate of $\mathcal{G}$.

To avoid the cumbersome coefficient, $\langle \Phi | P | \Phi \rangle$, which multiplies U, it is convenient to define the auxiliary operator,

$$\mathcal{H} = PH - \lambda P + W, \qquad (10)$$

where $W = \Sigma_i w(r_i)$ is, like U, an arbitrary, local, real, external field, bounded from below. It is obvious that $\mathcal{G}$ and $\mathcal{H}$ define a common solution Φ if u and w are suitably proportional to each other, $w = \langle \Phi | P | \Phi \rangle u$. In the following, however, we set $\mathcal{H}$ *ab initio*. It is an operator bounded from below. We are interested in its "almost ground state" Ξ and assume that this state is unique. A connection between a solution Ξ in this section and a solution Φ in the previous section can easily be tested later.

Define again a constrained search for the lowest energy,

$$\mathrm{Inf}_{\phi} \langle \phi | \mathcal{H} | \phi \rangle = \mathrm{Inf}_{\tau} (\mathrm{Inf}_{\phi \to \tau} \langle \phi | \mathcal{H} | \phi \rangle)$$

$$= \mathrm{Inf}_{\tau} \left(F_{\lambda}[\tau] + \int dr \tau(r) w(r) \right), \qquad (11)$$

where the λ-dependent DF, F_{λ}, is defined as

$$F_{\lambda}[\tau] \equiv \mathrm{Inf}_{\phi \to \tau} \langle \phi | (PH - \lambda P) | \phi \rangle. \qquad (12)$$

It is again convenient, for pedagogy at least, to assume that this Inf_{ϕ} induces an absolute minimum, reached at a position Ξ in the variational space. The same assumption states that, given λ, the absolute minimum of $F_{\lambda}[\tau]$ is

$$F_{\lambda}[\sigma] = \langle \Xi | (PH - \lambda P) | \Xi \rangle, \qquad (13)$$

where σ is the density of Ξ. Let $\mathcal{E}$ denote this energy, $\mathcal{E}(\lambda) \equiv \langle \Xi | (PH - \lambda P) | \Xi \rangle$. A simple manipulation then gives

$$\frac{d\mathcal{E}}{d\lambda} = - \langle \Xi | P | \Xi \rangle. \qquad (14)$$

A Legendre transform, using λ and $\langle \Xi | P | \Xi \rangle$ as conjugate variables, is thus available to return the matrix element $\langle \Xi | PH | \Xi \rangle$ as a function of the matrix element $\langle \Xi | P | \Xi \rangle$. Then one has just to locate the minimum of their ratio.

Note again that the theory depends on the variational space where ϕ evolves. But, in any case, one obtains simultaneously the density of $\bar{\bar{\Xi}}$, the best intrinsic state, and the energy of its projected state $P | \bar{\bar{\Xi}} \rangle$.

V. SUMMARY, DISCUSSION, AND CONCLUSION

If only because of the need for spin densities [15] in the description of polarizable systems, the problem of symmetry conservation, or restoration, in DF theory has already received much attention in atomic and molecular physics [16–19]. It has been revisited here, in the spirit of the projected Hartree-Fock method with variation *after* projection [14]: a variational principle for the density of an intrinsic state, without symmetry, optimizes the energy of a state with good quantum numbers. The idea was already introduced in the context of particle number projection [20]. We have shown in Secs. II and IV that our approach allows generalizations of the Hohenberg-Kohn existence theorem.

It can be stressed that the present approach is concerned with the density of an intrinsic state, not that of an eigenstate. This is a major difference with all the other DF theories that we are aware of. Note, in particular, how our functional differs from a functional of a symmetrized [16] density.

We showed in Sec. IV that a way to define the intrinsic Hamiltonian amounts to a linear combination, $\mathcal{H} = -\lambda P + PH$, of the projector P on the desired quantum numbers, and the laboratory Hamiltonian multiplied by that same P. Here, a subtle question must be raised, that of the nature of the intrinsic state. The more flexible the trial functions for this state, the better the projected state and the lower the projected energy. However, full flexibility contradicts simplicity, and, moreover, uniqueness of the intrinsic state; many different packets $|\phi\rangle$ can give the same $P|\phi\rangle$. Symmetry projection brings correlations which, therefore, *must* be absent from the intrinsic state. This is why variational domains for intrinsic states must *necessarily* be much narrower than the full Hilbert space.

In practice, fortunately, intrinsic states are confined to nonlinear, curved [21] manifolds, such as coherent states, Slater determinants, etc., which do not make linear subspaces. The intrinsic state, therefore, is not an exact eigenstate of $\mathcal{H}$. It just minimizes a related quantity, the projected energy. It must be concluded that DF theory for an intrinsic state necessarily depends on two factors, namely, (i) obviously the quantum numbers to be projected out, but also (ii) the variational space retained for this intrinsic state.

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