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LOCAL-SCALING DENSITY FUNCTIONAL THEORY: PROSPECTS FOR APPLICATIONS TO THE ELECTRONIC STRUCTURE OF ATOMS

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RESUMEN. La versión de Hohenberg-Kohn de la teoría del funcional de la densidad se revisa críticamente. Discutimos algunas de sus deficiencias relacionadas con la representación del multipleto atómico, el cálculo de estados excitados y la N-representabilidad del funcional y de la densidad de una partícula. Se presenta una versión alternativa de la teoría del funcional de la densidad basada en transformaciones de escalamiento local, en donde las deficiencias mencionadas son resueltas. Algunas aplicaciones factibles de esta nueva teoría al cálculo de la estructura electrónica de atómos son discutidas.

ABSTRACT. The Hohenberg-Kohn version of density functional theory is critically reviewed. Some of its shortcomings having to do with atomic multiplet representation, calculation of excited states and N-representability of the functional and of the one-particle density are discussed. An alternative version of density functional theory based on local-scaling transformations, where the above shortcomings are solved, is presented. Some prospective applications of this novel theory to the calculation of electronic structure of atoms is discussed.

Key words: ATOMIC PROCESSES

I. INTRODUCTION

Certainly, with the advent of modern computers, the long sought-for goal of calculating to within spectroscopic accuracy the ground- and excited-state energies of many-electron atoms has become, in principle, attainable. This is so because computers allow us to handle, also in principle, energy calculations based on large configuration interaction (CI) expansions. As is well known[1], any particular atomic state may be adequately approximated by such an expansion provided that, of course, we include a sufficiently large number of configurations. This is just a consequence of the fact that quantum mechanics occurs in Hilbert space.

But in spite of the astonishing improvements undergone by computers in terms of their speed and storage facilities, these devices are still far away from meeting the demands exacted by highly accurate atomic calculations. Configuration interaction expansions are slowly convergent, and therefore an inordinately large number of terms is required to describe properly the Coulomb correlation which is not accounted for by a single determinant ansatz. Since the number of N-particle Slater determinants which can be generated from an orbital basis set $\{\phi_i(\vec{r})\}_{i=1}^{m}$ is $M = \binom{m}{N}$, it is easy to see that for first-row transition metal atoms, taking $m = 2N$ (two basis functions per electron), M is of the order of 10^{17}. As a result, the problem of calculating from first principles the discrete energy spectrum of a transition metal atom, such as for example Fe, both in its neutral and ionized states, is still far from being just a perfunctory application of many-body quantum mechanics in its configuration interaction realization: the full CI problem is just too large to be handled even by the most powerful present-day supercomputers.

In other methods not based on CI expansions, such as many-body perturbation theory, coupled-cluster approaches, etc., the difficulties are still of the same order of magnitude. In consequence, all direct *ab–initio* methods capable of providing an accurate description of atomic electronic structure, become in practice highly limited by computational constraints. For this reason, a number of approximate approaches have been developed which, either by incorporating empirically obtained spectral data or by setting up particular methods geared at describing accurately certain aspects of the atomic many-body problem, have by-passed the difficulties encountered in direct $ab-initio$ techniques. But, without doubt, there is still need for an accurate, low-cost and strictly quantum-mechanical approach to the calculation of the discrete energy spectra of neutral atoms and their ions.

In the last few years, Hohenberg-Kohn based density functional theory[2] has emerged as a suitable alternative to the traditional ways of dealing with the quantum mechanical many-particle problem. It has met with considerable success in applications to condensed matter systems and in the elucidation of the electronic structure and nuclear dynamics of molecules[3–5]. There have been some difficulties in applying this theory to the calculation of the discrete spectrum of atoms because in its initial formulation it was chiefly developed as a ground-state theory. This limitation has been removed, however, in some recent versions designed to handle excited states[6,7].

Notwithstanding all these advances, there remain some unsolved problems in the Hohenberg-Kohn based density functional theory[8]. One is the particularly poor way of handling electronic state multiplicities. Another is related to the fact that the exact exchange-correlation functional remains unknown such that for practical applications approximate expressions must be used. But more seriously, it is a theory whose energy functional is not "N-representable" regardless of the kind of approximation introduced for the exchange-correlation term. This means that in this theory there does not exist a one to one correspondence between the energy as a functional of the one-particle density $\rho(\vec{r},\sigma)$ and the usual quantum mechanical energy expressed as a functional of the N-particle wavefunction $\Phi(\vec{r}_1,\sigma_1,\ldots,\vec{r}_N,\sigma_N)$. This lack of "functional N-representability" does away with the strict upper bound character of the theory, and hence, as has been confirmed by calculations, ground-state energies lower than the exact ones have quite often been obtained[9].

A different formulation of density functional theory, which removes the difficulties present in the Hohenberg-Kohn versions, has recently been advanced by Kryachko and coworkers[10]. It is based on the use of local-scaling transformations. In the present article, the prospects of applying this theory to electronic structure calculations of atoms is analyzed. For this purpose, in Section II we critically review some of the difficulties present in the Hohenberg-Kohn versions, in particular with respect to non-N-representability, multiplicity and excited state problems. In Section III we review the local-scaling version of density functional theory, placing special emphasis on the fact that in its context the functional N-representability problem is solved. We discuss how in this theory the multiplet structure can be handled and how it is possible to advance a CI formulation in terms of locally scaled orbitals. Finally, we indicate how this theory can be used for the calculation of a specific excited state.

II. LIMITATIONS OF HOHENBERG-KOHN-BASED VERSIONS OF DENSITY FUNCTIONAL THEORY

II.1. Symmetry and energy variation in quantum mechanics

In the context of quantum mechanics, the stationary state of a many-body system is fully characterized by a wavefunction $\Psi_k \in \mathcal{L}_N$ (where $\mathcal{L}_N$ is the N-particle antisymmmetric Hilbert space) which is an eigenfunction of the set $\{\widehat{O}_i\}_{i=1}^{K}$ of commuting operators. In atomic physics, within the $L-S$ coupling scheme, this set of commuting operators contains the Hamiltonian $\widehat{H}$, the angular momentum and spin operators $\widehat{L^2}$, $\widehat{S^2}$, $\widehat{L}_z$, $\widehat{S}_z$ and the parity operator $\widehat{\Pi}$. In general, a single Slater determinant cannot be a common eigenfunction of these operators; in fact, such eigenfunctions must be expressed as linear combinations of Slater determinants.

Usually, it is quite simple to construct eigenfunctions of the subset of commuting operators which does not contain $\widehat{H}$. In fact, using this subset, Hilbert space $\mathcal{L}_N$ can be decomposed into disjoint subspaces

$\mathcal{L}_N^j[\{o_i\}]$ such that $\mathcal{L}_N = \cup_{j=1}\mathcal{L}_N^j[\{o_i\}]$ where $[\{o_i\}_{i=1}^{K-1}]$ is the set of $K-1$ eigenvalues of the subset of operators which commute with $\widehat{H}$. The superindex j labels a particular symmetry, i.e., a particular combination of o_i's which characterize a spectroscopic term.

The eigenfunctions of $\widehat{H}$ can be obtained either by solving the Schrödinger equation $\widehat{H}\Psi_k^j = E_k^j\Psi_k^j$ for each symmetry j or by dealing with its equivalent variational principle for the energy functional $E[\Phi] \equiv \langle\Phi|\widehat{H}|\Phi\rangle/\langle\Phi|\Phi\rangle$. In terms of the variational principle, the energy spectrum is generated as follows:

$$
\begin{aligned}
E_o^j &= \inf_{\Phi^j \in \mathcal{L}_N^j[\{o_i\}]} \left\{ E[\Phi^j] \right\} = E[\Phi^j]_{\Phi^j=\Psi_o^j} \\
&\ \vdots \\
E_m^j &= \inf_{\substack{\Phi^j \in \mathcal{L}_N^j[\{o_i\}] \\ \langle\Phi^j|\Psi_o^j\rangle = \cdots = \langle\Phi^j|\Psi_{m-1}^j\rangle = 0.}} \left\{ E[\Phi^j] \right\} = E[\Phi^j]_{\Phi^j=\Psi_m^j}
\end{aligned}
\tag{1}
$$

In actual practice, it is impossible to perform the above minimization in a Hilbert space $\mathcal{L}_N^j[\{o_i\}]$ corresponding to a particular symmetry j. The reason is that these are infinite dimensional spaces, and thus a proper minimization would require that we write $\Phi_m^j = \sum_{I=1}^{\infty} C_{mI}\,\Phi_I^j$. But when we restrict the infinite sum to a finite one, it is no longer feasible to enforce the orthogonality constraints on a given trial function $\Phi_m^j = \sum_{I=1}^{M} C_{mI}\,\Phi_I^j$ with respect to the *exact* wavefunctions $\Psi_o^j, \cdots, \Psi_{m-1}^j$ because these exact wavefunctions are unknown. In this case, it becomes necessary to perform the variation subject to the constraints of Hamiltonian orthogonality, namely, $\langle\Phi_m^j|\widehat{H}|\Phi_o^j\rangle = \cdots = \langle\Phi_m^j|\widehat{H}|\Phi_{m-1}^j\rangle = 0$.

We have stressed here the importance of the above considerations in straightforward quantum mechanics because they embody a minimum set of requirements which must be fulfilled by any other theory—approximate or not—designed to deal with the many-particle problem. With this in mind, let us look at the Hohenberg-Kohn version of density functional theory.

II.2. The Hohenberg-Kohn formalism and the v-representability problem

The basic assumption in the Hohenberg-Kohn formalism concerns the existence of an energy functional

$$\mathcal{E}_v[\rho_o^{v\prime}(\vec{r})] = E[\Psi_o^{v\prime}] \equiv \langle\Psi_o^{v\prime}|\widehat{H}|\Psi_o^{v\prime}\rangle \tag{2}$$

satisfying the variational principle

$$\mathcal{E}_v[\rho_o^{v\prime}(\vec{r})] \geq \mathcal{E}_v[\rho_o^{v}(\vec{r})] = E_o^v. \tag{3}$$

In these expressions $\rho_o^v(\vec{r})$ is the exact ground-state density obtained from the exact ground-state wavefunction Ψ_o^v satisfying the Schrödinger equation $\widehat{H}_v\Psi_o^v = E_o^v\Psi_o^v$, where $\widehat{H}_v = \widehat{T} + \widehat{U} + \sum_{i=1}^N v(\vec{r}_i)$. Similarly, $\rho_o^{v\prime}(\vec{r})$ comes from $\Psi_o^{v\prime}$ which is the ground-state wavefunction for $\widehat{H}_{v\prime} = \widehat{T} + \widehat{U} + \sum_{i=1}^N v\prime(\vec{r}_i)$. The non-equivalence between $\rho_o^v(\vec{r})$ and $\rho_o^{v\prime}(\vec{r})$ is guaranteed by the theorem[2a] which states that there exists a one to one correspondence between $\rho_o^v(\vec{r})$ and the external potential $v(\vec{r})$. Thus, any other external potential $v\prime(\vec{r})$ implies the existence of a one-particle density $\rho_o^{v\prime}(\vec{r})$ which differs from $\rho_o^v(\vec{r})$ by more than a constant. The Hohenberg-Kohn minimum principle leading to the exact ground-state energy is therefore:

$$E_o^v = \inf_{\rho_o^{v\prime}(\vec{r}) \in \mathcal{A}_v} \{\mathcal{E}_v[\rho_o^{v\prime}(\vec{r})]\} \tag{4}$$

where the set $\mathcal{A}_v$ contains all one-particle densities which integrate to the total number of particles N and which come from ground-state wavefunctions $\{\Psi_o^{v\prime}\}$ (one-particle densities belonging to $\mathcal{A}_v$ are said to be pure-state "v-representable"[8]). The problem with the variational principle given by Eq.(4) is that although Hohenberg and Kohn[2a] proved that at the extreme point of variation $E^v_o = \mathcal{E}_v[\rho^v_o(\vec{r})]$ they did not provide either a way to construct $\mathcal{E}_v[\rho^{v\prime}_o(\vec{r})]$ or to explicitly define the set $\mathcal{A}_v$.

Let us stress here that in the Hohenberg-Kohn formalism no mention is made of the symmetry problem. According to our previous discussion, a Hamiltonian $\widehat{H}_v$ must commute with the operators $\widehat{L^2}$, $\widehat{S^2}$, $\widehat{L}_z$, $\widehat{S}_z$ and $\widehat{\Pi}$. This requirement certainly imposes restrictions on the kinds of admissible external potentials, and confines $v(\vec{r})$ to belong to the set $\mathcal{V}$ of external potentials such that $\widehat{H}_v$ has a ground state Ψ^v_o which is a common eigenstate of the operators $\{\widehat{O}_i\}^{K-1}_{i=1}$ yielding for a given symmetry the same eigenvalues $\{o_i\}^{K-1}_{i=1}$ for all $v(\vec{r}) \in \mathcal{V}$ (i.e., the variation must proceed with conservation of the state symmetry).

At this point we must address a more general question (already implied in Eq.(2)) of whether we can establish a one to one correspondence between an energy functional $E[\Phi]$ and the energy functional $\mathcal{E}[\rho_\Phi]$, such that the variation of $E[\Phi]$ with respect to a wavefunction $\Phi \in \mathcal{L}_N$ becomes equivalent to the variation of its counterpart $\mathcal{E}[\rho_\Phi]$ with respect to the one-particle density $\rho_\Phi(\vec{r}) \in \mathcal{N}_\Phi$, where $\mathcal{N}_\Phi$ is the set of densities coming from wavefunctions $\Phi \in \mathcal{L}_N$, namely, the set of "N-representable" densities[8]. It is clear that unless we introduce some additional constraints to these variations, it is not possible to establish this one to one correspondence. The reason is that there is a many to one correspondence between N-particle wavefunctions $\Phi \in \mathcal{L}_N$ and one-particle densities $\rho_\Phi(\vec{r}) \in \mathcal{N}_\Phi$. This fact, of course, has consequences on the energy expressions. Consider, for example, a particular one-particle density $\rho_1(\vec{r}) \in \mathcal{N}_\Phi$ which comes from any one of the wavefunctions $\Phi^{[1]}_{\rho_1}$, $\Phi^{[2]}_{\rho_1}, \cdots$ belonging to $\mathcal{L}_N$ (in Hilbert space there is an infinite number of functions which yield the same one-particle density). Now, since each one of these functions (which for simplicity we assume to be non-degenerate) yields a different value for the energy functional, we have $E[\Phi^{[1]}_{\rho_1}] \neq E[\Phi^{[2]}_{\rho_1}] \neq \cdots$. If we assume that there is a one to one correspondence between the energy as a functional of the N-particle wavefunction and the energy as a functional of the one-particle density, we obtain:

$$\begin{aligned} E[\Phi^{[1]}_{\rho_1}] &\Longleftrightarrow \mathcal{E}[\rho_1] \\ &\vdots \\ E[\Phi^{[k]}_{\rho_1}] &\Longleftrightarrow \mathcal{E}[\rho_1]. \end{aligned} \tag{5}$$

If the right-hand side is just a functional of $\rho_1(\vec{r})$, then it must have the same value. On the other hand, the left-hand side expressions are all different. Hence we must conclude that the above equivalences are ill-defined.

How does the energy functional $\mathcal{E}_v[\rho^{v\prime}_o(\vec{r})]$ stand in relation the usual energy functional $E[\Phi]$ with $\Phi \in \mathcal{L}_N$? Notice that according to Eq.(2) $\mathcal{E}_v[\rho^{v\prime}_o(\vec{r})]$ is equal to $E_v[\Psi^{v\prime}_o]$. Furthermore, in terms of the wavefunction-dependent energy functionals, the variational principle is $E_v[\Psi^{v\prime}_o] \geq E_v[\Psi^v_o] \equiv E^v_o$. However, the variation cannot span all wavefunctions Φ in Hilbert space (of a given symmetry). The constrained variational principle of Hohenberg and Kohn requires that the wavefunctions be restricted to the subspace $\mathcal{L}_N(v) \subset \mathcal{L}_N$ containing all wavefunctions $\{\Psi^{v\prime}_o\}$ which are ground-state solutions of Hamiltonians $\{\widehat{H}_{v\prime}\}$ with $v\prime \in \mathcal{V}$. Therefore, the equality stated by Eq.(2) cannot be met by every wavefunction $\Phi \in \mathcal{L}_N$, but only by wavefunctions belonging to the more restricted subspace $\mathcal{L}_N(v) \subset \mathcal{L}_N$. This introduces an implicit condition on the energy functional $\mathcal{E}_v[\rho^{v\prime}_o(\vec{r})]$, namely that it be v-representable: it must stand in a one to one correspondence with $E_v[\Psi^{v\prime}_o]$. In wavefunction language, the Hohenberg-Kohn constrained energy variation is

$$E^v_o = \inf_{\Phi \in \mathcal{L}_N(v) \subset \mathcal{L}_N} \{E_v[\Phi]\}. \tag{6}$$

But, curiously enough, it cannot be carried out in practice—not even at the wavefunction level—because the conditions which define $\mathcal{L}_N(v)$ in terms of arbitrary wavefunctions $\Phi \in \mathcal{L}_N$ remain unknown.

II.3. The functional and density N-representability problems

It has been known, almost from the very beginning of quantum mechanics that, under certain approximations, $E[\Phi]$ for $\Phi \in \mathcal{L}_N$ may be expressed as a functional $\mathcal{E}[\rho(\vec{r})]$. This fact has acted as an incentive to the different attempts whose aim has been to express the energy as an exact functional of the one-particle density. Purportedly, a sound justification for this project is given by the Hohenberg-Kohn theorems[2a]. But, as we have mentioned above, the functional and the density v-representability problems have not been solved in the Hohenberg-Kohn formalism, and hence, these theorems do not guarantee[8] that there exists a one to one correspondence between and arbitrary functional $\mathcal{E}_v[\rho(\vec{r})]$ and $E_v[\Phi]$ with $\Phi \in \mathcal{L}_N$.

It is illustrative, nonetheless, to show how these approximate functionals arise. For this purpose, let us first write $E[\Phi]$ as a functional of the reduced 1- and 2-matrices $D^1(x_1, x_1')$ and $D^2(x_1, x_2; x_1, x_2)$ and of the density $\rho(x_1)$ (x stands for the space and spin coordinates: $x \equiv \vec{r}, s$):

$$E[\Phi] = \frac{1}{2}\int d^4x_1 \nabla_{\vec{r}_1}\nabla_{\vec{r}_1'} D^1_\Phi(x_1, x_1')|_{x_1=x_1'} + \int d^4x_1 v(\vec{r}_1)\rho_\Phi(x_1) + \frac{1}{2}\int d^4x_1 \int d^4x_2 \frac{D^2_\Phi(x_1, x_2; x_1, x_2)}{|\vec{r}_1 - \vec{r}_2|} \tag{7}$$

where the 1-matrix is defined by

$$D^1_\Phi(x_1; x_1') \equiv N \int d^4x_2 \cdots \int d^4x_N \Phi^*(x_1, x_2, \ldots, x_N)\Phi(x_1', x_2, \ldots, x_N) \tag{8}$$

and where similarly, the 2-matrix is given by

$$D^2_\Phi(x_1, x_2; x_1, x_2) \equiv \frac{N(N-1)}{2} \int d^4x_3 \cdots \int d^4x_N \Phi^*(x_1, x_2, \ldots, x_N)\Phi(x_1, x_2, \ldots, x_N). \tag{9}$$

The one particle density is just the diagonal part of the 1-matrix: $\rho(x) \equiv D^1(x; x)$. Both these reduced matrices are non-local operators which may be written as products of a local part times a non-local part proper:

$$D^1_\Phi(x_1; x_1') \equiv \rho_\Phi^{1/2}(x_1)\rho_\Phi^{1/2}(x_2)\widetilde{D}^1_\Phi(x_1; x_1')] \tag{10}$$

where $\widetilde{D}^1_\Phi$ is the non-local part of the 1-matrix[11] and

$$D^2_\Phi(x_1, x_2; x_1, x_2) \equiv \frac{1}{2}\rho_\Phi(x_1)\rho_\Phi(x_2)[1 + \mathrm{f}^{XC}(x_1, x_2; x_1, x_2)]. \tag{11}$$

In Eq.(11), the term $\mathrm{f}^{XC}(x_1, x_2; x_1, x_2)$ is the non-local exchange-correlation factor. The energy functional $E[\Phi]$ may be *exactly* written as

$$\begin{aligned} E[\Phi] = {} & \frac{1}{8}\int d^4x_1 \frac{[\nabla_{\vec{r}_1}\rho_\Phi(x_1)]^2}{\rho_\Phi(x_1)} + \frac{1}{2}\int d^4x_1\, \rho_\Phi(x_1)\nabla_{\vec{r}_1}\nabla_{\vec{r}_1'}\widetilde{D}^1_\Phi(x_1, x_1')|_{x_1=x_1'} + \int d^4x_1 v(\vec{r}_1)\rho_\Phi(x_1) \\ & + \frac{1}{2}\int d^4x_1 \int d^4x_2 \frac{\rho_\Phi(x_1)\rho_\Phi(x_2)}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{2}\int d^4x_1 \int d^4x_2 \frac{\rho_\Phi(x_1)\rho_\Phi(x_2)\mathrm{f}^{XC}_\Phi(x_1, x_2)}{|\vec{r}_1 - \vec{r}_2|}. \end{aligned} \tag{12}$$

The origin of density functional theory goes back to Thomas and Fermi whose energy functional can be obtained as an approximation to the energy expression given by Eq.(12). In fact, it can be shown[12] that, since in the context of the homogeneous electron gas model

$$\frac{1}{2}\int d^4x_1\, \rho_\Phi(x_1)\nabla_{\vec{r}_1}\nabla_{\vec{r}_1'}\widetilde{D}^1_\Phi(x_1, x_1')|_{x_1=x_1'} \simeq \frac{3}{10}(3\pi)^{2/3}\int d^3\vec{r}\rho(\vec{r})^{5/3}\,, \tag{13}$$

the Thomas-Fermi energy functional arises when one approximates the non-local part of the kinetic energy according to Eq.(13) and disregards at the same time the contributions coming from the exchange-correlation factor. The explicit form of the Thomas-Fermi energy density functional is

$$E[\Phi] \sim \mathcal{E}_{TF}[\rho(\vec{r})] \equiv \frac{3}{10}(3\pi)^{2/3}\int d^3\vec{r}\rho(\vec{r})^{5/3} + \int d^3\vec{r}v(\vec{r})\rho(\vec{r}) + \frac{1}{2}\int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}. \tag{14}$$

But let us notice that this simplification prevent us from finding a $\Phi \in \mathcal{L}_N$ such that $\mathcal{E}_{TF}[\rho(\vec{r})]$ is equal to $E[\Phi]$. In other words, $\mathcal{E}_{TF}[\rho(\vec{r})]$ does not comply with the condition of *functional* N-representability. Furthermore, this same difficulty is present in *all* approximate functionals (obtained from gradient expansions, constructed by including cut-off functions, local and non-local, etc.) which appear in the various realizations of the Hohenberg-Kohn-based density functional theory[9].

An important formal extension of the Hohenberg-Kohn formulation which, in principle, solves the N-representability problem is provided by the constrained variation two-step approach of Levy and Lieb[13]. In the first step, for a *fixed* one-particle density, $\rho(\vec{r})$, the following functional is defined:

$$F[\rho(\vec{r}), \Phi_\rho^{min}] = \min_{\Phi_\rho \in \mathcal{L}_N} \{\langle \Phi_\rho \,|\, \widehat{T} + \widehat{V}_{ee} \,|\, \Phi_\rho \rangle\}. \tag{15}$$

Notice that this definition hinges on the possibility of finding an N-representable one-particle density, namely, a $\rho(\vec{r})$ that comes from the wavefunctions $\{\Phi_\rho \in \mathcal{L}_N\}$. Fortunately, the conditions that make a density N-representable are known. Using $F[\rho(\vec{r}), \Phi_\rho^{min}]$, the energy can then be expressed as a functional of both the density and the optimal wavefunction:

$$\mathcal{E}[\rho(\vec{r}); \Phi_\rho^{min}] = F[\rho(\vec{r}), \Phi_\rho^{min}] + \int d^3\vec{r}\, v(\vec{r})\rho(\vec{r}) \tag{16}$$

with $\Phi_\rho \Longrightarrow \rho(\vec{r}) \in \mathcal{N}_\Phi$ where $\mathcal{N}_\Phi$ is the set of N-representable one-particle densities. The functional N-representability problem is solved because there is a one to one correspondence between the functional $\mathcal{E}[\rho(\vec{r}); \Phi_\rho^{min}]$ and $E[\Phi_\rho^{min}]$ for a *fixed* $\rho(\vec{r})$. Therefore, the usual variational inequality

$$E_o \equiv E[\Psi_o] \leq E[\Phi_\rho^{min}] \equiv \mathcal{E}[\rho(\vec{r}); \Phi_\rho^{min}] \tag{17}$$

is satisfied. Furthermore, when $\Phi_\rho^{min} = \Psi_o$ it follows that $\rho(\vec{r}) = \rho_o(\vec{r})$, and thus the exact ground-state energy is attained:

$$E_o = \mathcal{E}[\rho_o(\vec{r}); \Psi_o]. \tag{18}$$

In the Levy-Lieb reformulation of the Hohenberg-Kohn theory, functional N-representability is guaranteed if, and only if, upon variation, the energy density functional corresponding to $\rho'(\vec{r}) = \rho(\vec{r}) + \delta\rho(\vec{r})$ is $\mathcal{E}[\rho(\vec{r}) + \delta\rho(\vec{r}); \Phi^{min}_{\rho+\delta\rho}]$. In order to comply with this requirement it is necessary to devise a method for calculating for each modified density $\rho'(\vec{r})$ the corresponding functional $F[\rho(\vec{r}) + \delta\rho(\vec{r}), \Phi^{min}_{\rho+\delta\rho(\vec{r})}]$. Until recently, it had not been possible to compute this "dynamic" energy functional. This problem has been solved by Cioslowski[14]. It turns out[15], however, that Cioslowski's method is just a finite basis representation of the local-scaling transformation approach of Kryachko and coworkers[10]. In conclusion, the use of approximate functionals is not warranted by the Levy-Lieb reformulation. Because these functionals are not N-representable, they do not replace strict quantum mechanical methods. At best they may be regarded as useful "black boxes", much more in the category of the semi-empirical molecular orbital methods in quantum chemistry.

II.4. The atomic multiplet and excited state problems

Just about all practical applications of the Hohenberg-Kohn formalism have been fully realized or are connected, in one way or another, to the Kohn-Sham equations[2b]. These one-particle equations are in spirit similar to the Slater Hartree-Fock equations[16] which are derived from a single Slater determinant; but where the exchange non-local potential is replaced by a local potential which is a functional of the one-particle density. Explicitly the Kohn-Sham equations are given by

$$[-\frac{1}{2}\nabla^2 + v(\vec{r}) + v^{KS}_{Coulomb}([\rho]; \vec{r}) + v^{KS}_{XC}([\rho]; \vec{r})]\psi_i^{KS}(\vec{r}) = \mathcal{E}_i^{KS}\phi_i^{KS}(\vec{r}) \tag{19}$$

where $v(\vec{r})$ is the electron-nuclear potential. The remaining Coulomb and exchange-correlation potentials are given by

$$\begin{aligned} v^{KS}_{Coulomb}([\rho]; \vec{r}) &= \int d^3\vec{r}\,' \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \\ v^{KS}_{XC}([\rho]; \vec{r}) &= \frac{\delta}{\delta\rho} E^{KS}_{XC}[\rho(\vec{r})] \end{aligned} \tag{20}$$

In this last expression, $E_{XC}^{KS}[\rho(\vec{r})]$ contains the usual exchange correlation energy minus the kinetic energy functional for a non-interacting system possessing the same density as that of the interacting system (see Section III.3). By solving these equations one obtains a set $\{\psi_i^{KS}(\vec{r})\}_{i=1}^{N}$ of Kohn-Sham single particle orbitals and their respective energies $\{\mathcal{E}_i^{KS}(\vec{r})\}_{i=1}^{N}$. Since the density is $\rho(\vec{r}) = \sum_{i=1}^{N} |\psi(\vec{r})|^2$ the total energy

$$E^{KS} = \sum_{i=1}^{N} \mathcal{E}_i^{KS} - \frac{1}{2}\int d^3\vec{r} \int d^3\vec{r}\prime \frac{\rho(\vec{r})\rho(\vec{r}\prime)}{|\vec{r}-\vec{r}'|} + E_{XC}^{KS}[\rho(\vec{r})] - \int d^3\vec{r}\rho(\vec{r})v_{XC}^{KS}([\rho];\vec{r}) \tag{21}$$

is completely defined by these quantities. In practice, however, the energy is calculated by the transition state method[17].

The atomic multiplet problem arises because only the first N orbitals enter in the calculation of the energy. In turn, these correspond to the orbitals which define the single Slater determinant for the non-interacting system. But because the expectation value of a single Slater determinant yields an energy which is a weighted average of the energies of spectroscopic states, when one chooses a given set of occupation numbers for the Kohn-Sham orbitals, one is effectively selecting a single determinantal state. This means that the energy calculated by Eq.(21) corresponds to this weighted average. As an example, a single determinant $\Phi = \det[\psi_{1s}(1)\alpha(1)\psi_{2s}(2)\beta(2)]/\sqrt{2}$ of He yields an energy

$$E[\Phi] = \frac{1}{2}[E(2^1\mathrm{S}) + E(2^3\mathrm{S})]. \tag{22}$$

In order to extricate from this expression the energy for the first excited state 2^1S, one can compute the energy of 2^3S using the single Slater determinant $\Phi(\ 2^3\mathrm{S}\ ) = \det[\psi_{1s}(1)\alpha(1)\psi_{2s}(2)\alpha(2)]/\sqrt{2}$ and solve for $E(2^1\mathrm{S})$ in Eq.(22).

As the original proof of the Hohenberg-Kohn theorem assumed pure ground states, there arises the problem of how to justify this procedure for ensembles containing excited states. Much of the extension of density functional theory to excited states is based on the work of Theophilou[6] for equi-ensembles. More recently, however, Gross, Oliveira and Kohn[7] have introduced a formalism for unequally weighted ensembles. Practical applications of these theoretical developments suffer, however, from the same kind of difficulty already present in the ground state, namely, the lack of a well defined procedure for the construction of the ensemble energy functional. Again, one must maintain a one to one correspondence between the ensemble functional given in terms of wavefunctions in Hilbert space and the energy density functional. In other words, one must deal with an ensemble N-representability problem for the energy functional. Approximate functionals invalidate the variational inequalities upon which these extensions of the Hohenberg-Kohn formalism are based. In particular, the use of the quasi-local density approximation, whereby ensemble averages are replaced by thermal averages in the construction of the exchange-correlation energy functional, cannot be justified by resorting to basic principles. Moreover, it has been shown[18] that no currently available version of the exchange-correlation functional is able to account for the interconfiguration energies of iron series atoms.

III. VARIATIONAL PRINCIPLE IN LOCAL-SCALING DENSITY FUNCTIONAL THEORY

We deal here with the formulation of a novel version of density functional theory[10] where particular care has been taken to comply with the N-representability conditions, both of the density and the energy functional; and where provisions have been made to satisfy the symmetry conditions on states stipulated by strict quantum mechanics.

III.1. Local-scaling transformations

Some well-known transformations in quantum mechanics, which keep the directions of the coordinate system unchanged but modify all points of $\mathcal{R}^3$ by the same amount; are the scaling transformations[19]:

$$\vec{r} \equiv (x, y, z) \quad \xrightarrow{\hat{f}_\lambda} \quad \vec{f}(\vec{r}) \equiv (\lambda x, \lambda y, \lambda z)\ . \tag{23}$$

However, we can envision more general transformations which, while keeping the directions unchanged, expand or contract each point of three-dimensional space according to:

$$\vec{r} \equiv (x, y, z) \quad \xrightarrow{\hat{f}} \quad \vec{f}(\vec{r}) \equiv \left(\frac{f(\vec{r})}{r}x, \frac{f(\vec{r})}{r}y, \frac{f(\vec{r})}{r}z\right) . \tag{24}$$

For obvious reasons these are called local-scaling transformations. In density functional theory these transformations become important because they carry a trial density into a final density (which can be the exact density) preserving its topological features[19].

The effect of a local-scaling transformation on a trial density $\rho(\vec{r})$ is given by

$$\rho(\vec{r}) \quad \xrightarrow{f} \quad \hat{f}(\rho(\vec{r})) \equiv \rho_f(\vec{r}) = J\{\vec{f}(\vec{r});\vec{r}\}\rho(\vec{f}(\vec{r})) \tag{25}$$

where $\rho_f(\vec{r})$ is the transformed density and $J\{\vec{f}(\vec{r});\vec{r}\}$ is the Jacobian of the transformation. As has been shown elsewhere[10], when the Jacobian of the local-scaling transformation is explicitly calculated about a single center, Eq.(25) is transformed into a first-order differential equation which along a chosen path $\Omega_o \equiv (\theta_o, \phi_o)$:

$$\frac{df^3(r,\theta_o,\phi_o)}{dr} = \frac{3r^2\rho_f(r,\theta_o,\phi_o)}{\rho(f(r,\theta_o,\phi_o),\theta_o,\phi_o)}. \tag{26}$$

Clearly, the total transformation is obtained by solving this equation over all paths.

Since there exists a one to many correspondence between a one-particle density and the set $\left\{\Phi_\rho^{[k]}(1,\ldots,N); \quad k = 1,2,\ldots\right\}$ of N-particle wavefunctions $\Phi_\rho^{[k]}$ that yield the same density $\rho(\vec{r})$, when the transformation is applied by means of the N-particle operator $\widehat{F}^N \equiv \underbrace{\hat{f}\ldots\hat{f}}_{\text{N}-\text{times}}$ to a particular wavefunction $\Phi_\rho^{[k]}$ from this set, one gets the new wavefunction $\Phi_f^{[k]} \equiv \widehat{F}^N\Phi_\rho^{[k]}$ which is explicitly given by

$$\Phi_f^{[k]}(\vec{r}_1,\ldots,\vec{r}_N) = \prod_{i=1}^{N} J\left\{\vec{f}(\vec{r}_i);\vec{r}_i\right\}^{1/2}\Phi_\rho^{[k]}(\vec{f}(\vec{r}_1),\ldots,\vec{f}(\vec{r}_N)). \tag{27}$$

An important consequence of this transformation is that each one of the transformed wavefunctions from this set is in a one to one correspondence with the transformed one-particle density $\rho_f(\vec{r}) \equiv \rho_{\Phi_f^{[k]}}(\vec{r})$. This implies that, starting from any one of the N-particle wavefunctions of this set, a class of N-particle wavefunctions (or an "orbit" $\mathcal{O}_\mathcal{L}^{[k]}$) is generated such that every wavefunction $\Phi_f^{[k]}(\vec{r}) \in \mathcal{O}_\mathcal{L}^{[k]}$ is in a one to one correspondence with a one-particle density $\rho_f(\vec{r})$. As one can clearly see, therefore, these transformations partition Hilbert space $\mathcal{L}_N$ into disjoint subsets of N-particle wavefunctions or orbits.

III.2. The local-scaling variational principle

Within the orbit structure of $\mathcal{L}_N$, the many to one correspondence between wavefunctions and one-particle densities is eliminated. Hence, the the variational problem can be transformed into a double search: intra-orbit optimization of the energy by varying the one-particle density $\rho(\vec{r})$ coupled to a scanning over all orbits,

$$E_o \equiv \inf_{\substack{\text{over all orbits} \\ \mathcal{O}_\mathcal{L}^{[k]}\subset\mathcal{L}_N}} \left\{ \inf_{\substack{\Phi_f^{[k]}\in\mathcal{O}_\mathcal{L}^{[k]} \\ \Phi_f^{[k]}\Longrightarrow\rho_f}} \left\{\mathcal{E}[\rho_f(\vec{r});\Phi_g^{[k]}]\right\}\right\}. \tag{28}$$

Furthermore, in this formalism, within each orbit we can write explicitly the following expression for the energy density functional:

$$\begin{aligned}\mathcal{E}[\rho_f(\vec{r});\Phi_g^{[k]}] =& \frac{1}{8}\int d^3\vec{r}\frac{[\nabla_{\vec{r}}\rho_f(\vec{r})]^2}{\rho_f(\vec{r})} + \frac{1}{2}\int d^3\vec{r}\rho_f(\vec{r})\nabla_{\vec{r}}\nabla_{\vec{r}'}\widetilde{D}_g^{1[k]}(\vec{f}_{g,f}^{[k]}(\vec{r});\vec{f}_{g,f}^{[k]}(\vec{r}'))|_{\vec{r}'=\vec{r}} \\ &+ \int d^3\vec{r}\rho_f(\vec{r})\,v(\vec{r}) + \frac{1}{2}\int d^3\vec{r}\rho_f(\vec{r})\mathcal{E}_{XC,g}^{[k]}(([\rho_f(\vec{r})];\vec{f}(\vec{r}))\end{aligned} \tag{29}$$

where the exchange-correlation energy density is

$$\mathcal{E}^{[k]}_{XC,g}(([\rho_f(\vec{r})];\vec{f}(\vec{r}))\equiv\int d^3\vec{r}'\frac{\rho_f(\vec{r})(1+\mathbf{f}^{[k]}_{XC,g}(\vec{f}^{[k]}_{g,f}(\vec{r});\vec{f}^{[k]}_{g,f}(\vec{r}'))}{|\vec{r}-\vec{r}'|}\,. \tag{30}$$

Notice that the implicit dependence of this energy functional through the transformation function is a necessary ingredient for maintaining the N-representability of the functional. This dependence, however, modifies the form of the functional at each step of the variation such that it becomes a "dynamic" functional. For this reason, it is easily seen that the usual "static" approximate functionals appearing in the Hohenberg-Kohn versions of density functional theory cannot maintain N-representability at all steps of variation. Nevertheless, such a condition is fulfilled by the dynamic functional introduced by Cioslowski in the "density-driven" method. But, as it turns out, this method can be reformulated as a finite-basis representation of the local-scaling version of density functional theory.

Within each orbit $\mathcal{O}^{[i]}_{\mathcal{L}}\subset\mathcal{L}_N$ the following ground-state variational principle holds:

$$\delta\left\{\mathcal{E}[\rho(\vec{r});\Phi^{[i]}_g]-\mu^{[i]}\left(\int d^3\vec{r}\rho(\vec{r})-N\right)\right\}=0,\qquad \rho(\vec{r})\in\mathcal{N}_\Phi \tag{31}$$

where $\mu^{[i]}$ is the Lagrange multiplier which incorporates the normalization condition on the density. The Euler-Lagrange equation for the density is:

$$-\frac{1}{8}\left[\frac{\nabla_{\vec{r}}\rho(\vec{r})}{\rho(\vec{r})}\right]^2-\frac{1}{4}\frac{\nabla^2_{\vec{r}}\rho(\vec{r})}{\rho(\vec{r})}+v^{[i]}_{T,g}([\rho(\vec{r})];\vec{r})+v(\vec{r})+v_{Coulomb}([\rho(\vec{r})];\vec{r})+v^{[i]}_{XC,g}([\rho(\vec{r})];\vec{r})=\mu^{[i]} \tag{32}$$

where $v^{[i]}_{T,g}$ is the potential arising from the non-local part of the kinetic energy, $v_{Coulomb}$ is the Hartree potential and $v^{[i]}_{XC,g}$, is the exchange-correlation potential. Notice that $v^{[i]}_{T,g}$ and $v^{[i]}_{XC,g}$ are potentials which depend upon the orbit generating wavefunction $\Phi^{[i]}_g$.

Among the orbits into which Hilbert space is decomposed, there exists a particular one (which we have called the Hohenberg-Kohn orbit) to which the exact ground-state wavefunction belongs. Let us consider within this orbit a generating wavefunction $\Phi^{[HK]}_g$, which is different from the exact ground-state wavefunction. Clearly then, by applying Eq.(32), the exact density can be obtained. Furthermore, a local-scaling transformation from the orbit generating one-particle density to the exact one would allow us in turn to obtain the exact wavefunction $\Psi^{[HK]}_o$ and hence the exact energy E_o.

III.3. Symmetry adapted Kohn-Sham-type equations

It is possible, as we have seen above, to get to the exact result if we start already from the Hohenberg-Kohn orbit and vary the density according to Eq.(32). But it is also possible to perform this variation with respect to the single particle orbitals $\{\psi_i(\vec{r})\}^N_{i=1}$, provided that the one-particle density which appears in the density functional $\mathcal{E}[\rho(\vec{r});\Phi^{[HK]}_g]\equiv E[\Phi^{[HK]}_\rho]$ of Eq.(29) is expanded in terms of these orbitals. This leads to the following equivalence:

$$\mathcal{E}[\rho(\vec{r});\Phi^{[HK]}_g]\equiv\mathcal{E}[\{\psi_i(\vec{r})\}^N_{i=1};\Phi^{[HK]}_g]\,. \tag{33}$$

Adding and substracting the kinetic energy term $-\frac{1}{2}\sum^N_{i=1}\langle\psi_i(\vec{r})\,|\,\nabla^2_{\vec{r}}\,|\,\psi_i(\vec{r})\rangle$, the energy functional given by Eq.(29) becomes:

$$\begin{aligned}\mathcal{E}[\{\psi_i(\vec{r})\}^N_{i=1};\Phi^{[HK]}_g]\equiv&-\frac{1}{2}\sum^N_{i=1}\langle\psi_i(\vec{r})\,|\,\nabla^2_{\vec{r}}\,|\,\psi_i(\vec{r})\rangle+\int d^4x_1v(\vec{r}_1)\rho(x_1)\\&+\frac{1}{2}\int d^4x_1\int d^4x_2\frac{\rho(x_1)\rho(x_2)}{|\vec{r}_1-\vec{r}_2|}+\mathcal{E}_{XC}[\rho(\vec{r});\widetilde{\Phi}^{[HK]}_g]\end{aligned} \tag{34}$$

where the "exchange-correlation" energy in the Hohenberg-Kohn orbit appearing in the above equation differs from the usual one because it includes in this case a kinetic energy difference:

$$\begin{aligned}\mathcal{E}_{XC}[\rho(\vec{r});\Phi_g^{[HK]}] \equiv \frac{1}{2}\int d^4x_1 \nabla_{\vec{r}_1}\nabla_{\vec{r}_1'} D_\rho^{1[HK]}(x_1,x_1')|_{x_1=x_1'} + \frac{1}{2}\sum_{i=1}^{N}\langle\psi_i(\vec{r})\,|\,\nabla_{\vec{r}}^2\,|\,\psi_i(\vec{r})\rangle \\ + \frac{1}{2}\int d^4x_1\int d^4x_2 \frac{\rho(x_1)\rho(x_2)\mathrm{f}_{XC,g}^{[HK]}(\vec{f}_{g,\rho}^{[HK]}(\vec{r});\vec{f}_{g,\rho}^{[HK]}(\vec{r}'))}{|\vec{r}-\vec{r}'|}\end{aligned} \tag{35}$$

When Eq.(34) is varied with respect to these orbitals, we obtain the Kohm-Sham-type equations:

$$(-\frac{1}{2}\nabla_{\vec{r}}^2 + v(\vec{r}) + v_H(\vec{r}) + v_{XC}^{[HK]}([\rho];\vec{r})))\psi_k(\vec{r}) = \epsilon_k\psi_k(\vec{r}) \tag{36}$$

where

$$v_{XC}^{[IIK]}([\rho];\vec{r})) = \frac{\delta\mathcal{E}_{XC}[\rho(\vec{r});\Phi_g^{[HK]}]}{\delta\rho(\vec{r})}\ . \tag{37}$$

Clearly, in order to solve the above Kohn-Sham equations within the "exact" orbit, one must have some way of constructing a generating function for this orbit. But this in itself is a formidable problem: it is certainly as difficult to find this wavefunction as it is to find the exact one. Nevertheless, it is possible within the local-scaling transformation version of density functional theory to consider Kohn-Sham-type equations in other approximate orbits. The advantages are that orbit generating wavefunctions can be easily constructed in approximate orbits. Furthermore, as has been discussed elsewhere[10e], an "orbit-jumping" procedure can be implemented for improving the quality of the approximation. One should emphasize that one does not need to calculate this orbit-generating wavefunction, but merely one may guess it through the selection of a random set of parameters. This procedure has been tested for the simple case of a two-configuration wavefunction for the helium atom[20], and it has been shown that for this case it does not matter what random parameters are selected in order to define the orbit generating wavefunction; upon a density transformation which carried the initial density into the Hartree-Fock one, the energy of these transformed random wavefunctions was always better than the Hartree-Fock one and differed by little from the corresponding wavefunction whose parameters had been optimized. Furthermore, also starting from orbit generating wavefunctions defined by random parameters, an orbit-jumping scheme was tested involving parameter optimization at constant density. This procedure rapidly led to convergence in the case of a two-configuration wavefunction for helium[21].

The symmetry of the physical system must be reflected in the choice of the orbit generating wavefunction. Clearly, the resulting energy depends upon how much "physics" we have incorporated into this wavefunction, as the construction of the exchange-correlation functional as well as the non-local part of the kinetic energy depend upon this choice. Fortunately, in the local-scaling scheme there is no restriction requiring that the wavefunction be a single Slater determinant. In addition, if one chooses to solve the variational problem for the density via Kohn-Sham-type equations, it is not necessary to restrict the density to be represented by a sum of just N single-particle orbitals $\{\psi_i(\vec{r})\}$. It could in principle involve all the m orbitals (with $m > N$) which enter in the construction of the orbit generating wavefunction.

III.4. Configuration interaction and a local-scaling treatment of excited states

The technology for performing configuration interaction calculations with a few hundred, or even a few thousand, configuration state functions is at present available both for atoms and for molecules. What remains totally out of reach is the handling of a full CI treatment even for systems containing less than thirty electrons. For some medium-size systems, even when only the valence electrons are considered, these problems become just too large. Thus, for example, in the case of Cr_2 the inclusion of a number of the order of 10^8 configurations would be required for a full CI treatment of the valence electrons[3b].

In terms of a configuration interaction treatment of a many-body system, the local-scaling transformation version of density functional theory can be envisioned as a method for creating density adapted orbitals which drastically reduce the size of the configuration interaction expansion required to give an energy value of a certain accuracy. Let us assume that, taking advantage of the CI technology already available, we start from an orbit-generating wavefunction corresponding to a limited configuration interaction expansion , where the Slater determinants $\{\Phi_I(\vec{r}_1, \cdots, \vec{r}_N)\}_{I=1}^{M}$ are constructed from a given initial one-particle set $\{\psi_i^g(\vec{r})\}_{i=1}^{m}$. Since we require that our treatment satisfies the symmetry requirements on the wavefunctions, we construct from these Slater determinants the configuration state functions $\{D_I(\vec{r}_1, \cdots, \vec{r}_N)\}_{I=1}^{M'}$ which are eigenfunctions of the operators $\widehat{L^2}$, $\widehat{S^2}$, $\widehat{L}_z$, $\widehat{S}_z$ and $\widehat{\Pi}$. By diagonalizing the CI matrix corresponding to this limited CI expansion, one can obtain CI expansion coefficients for all M' states of the same symmetry. This means that we can start with M' orbit-generating wavefunctions $\{\Phi_j^g\}_{j=1}^{M'}$ where the one with lowest energy corresponds to the ground state and the rest to excited states. Explicitly we have

$$\Phi_j^g(\vec{r}_1, \cdots, \vec{r}_N) = \sum_{I=1}^{M} C_{I,j}\, D_I(\vec{r}_1, \cdots, \vec{r}_N)\ . \tag{38}$$

Each one of the above wavefunction yields a one-particle density $\rho_j^g(\vec{r})$.

The set formed by the ground and excited states may be regarded as a supersystem whose density is $\rho_T^g(\vec{r}) = \frac{1}{M'}\sum_{j=1}^{M'} \rho_j^g(\vec{r})$. Let us assume that this supersystem evolves in a concerted fashion from an initial supersystem wavefunction (which is the antisymmetrized product of the state wavefunctions) toward a final wavefunction of the same type, and that the driving force for this evolution is a concerted local scaling transformation which takes $\rho_T^g(\vec{r})$ into $\rho_T^f(\vec{r}) = \frac{1}{M'}\sum_{j=1}^{M'} \rho_j^f(\vec{r})$. For practical applications, one can assume a certain parametric form for $\rho_T^f(\vec{r})$. This concerted density transformation yields the transformed orbitals $\{\psi_i^f(\vec{r})\}_{i=1}^{m}$. Introducing the new orbital set into the CI matrix and calculating the new eigenvalues and eigenfunctions, one can successively tune the parameters upon which $\rho_T^f(\vec{r})$ depends until finally one attains the optimal convergence for the type of generating wavefunction chosen[22]. Another way of dealing with this problem is to optimize the energy of a particular excited state eigenvalue with respect to the variational parameters of $\rho_T^f(\vec{r})$. This latter procedure[23] has led to very good results for the first excited state of the helium atom.

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