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FORMULATION OF N- AND υ-REPRESENTABLE DENSITY FUNCTIONAL THEORY. III: EXCITED STATES

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Abstract

The local-scaling transformation version of density functional theory is extended to the treatment of excited states. This is accomplished in the context of the superparticle formulation of Katriel [Int. J. Quant. Chem. 23(1983)1767]. It is shown that for a given superparticle generating wave function, the energy density functional corresponding to the excited-state super-system may be explicitly constructed. The derivation of an Euler–Lagrange equation for the composite excited-state density is discussed. A preliminary calculation for the 2^1S state of helium is reported.

1. Introduction

According to the first Hohenberg–Kohn theorem [1], the exact ground-state one-electron density $\rho_0(\boldsymbol{r})$ for a system of N interacting electrons is in a one-to-one correspondence with the external potential $\upsilon(\boldsymbol{r})$. This implies that if by some means $\rho_0(\boldsymbol{r})$ is known, then the Hamiltonian for this system may be determined and by solving Schrödinger's equation, not only the ground-state energy E_0 and the ground-state wave function Ψ_0 but also all other eigenvalues and eigenfunctions for the excited states may be obtained. In this general sense, therefore, the energies of the excited states may be regarded as functionals of ρ_0 [2].

In terms of N-particle wave functions, a variational principle for a particular excited state can be formulated by requiring that its wave function be orthogonal to all low lying states. Clearly, since the lowest lying eigenstates for given symmetries automatically satisfy this orthogonality constraint, these excited states may be treated in the same way as the ground state. The extension of this fact to density functional theories applicable to these particular states is straightforward and has been discussed by several authors [3–6] in the context of Hohenberg–Kohn based theories [7]. It has been shown [8], however, that it is not possible to formulate a theory for arbitrary excited states by means of a simple generalization of the ground-state approach.

A more general treatment of excited states in terms of N-particle wave functions is based on the Hylleraas–Undheim–MacDonald variational procedure [9,10], which is an extension of the Rayleigh–Ritz variational principle. Its density functional theory counterpart has been developed by Valone and Capitani [11] in the context of a generalization of the constrained-search method of Levy [12].

A closely related approach for a density functional theory treatment of excited states has been advanced by Theophilou [13] (see also refs. [14] and [15]). Essentially, this approach deals with an equally-weighted sum of the first m excited states, leading to a composite one-particle density. The equal-weight restriction has been removed by Kohn [16] and Gross et al. [17], who extended these results to finite-temperature ensembles. Katriel [18] has shown that Theophilou's approach to excited states may be cast as a variational problem for the ground state of a super-system of non-interacting superparticles. All these procedures may be viewed as formulations advanced in the context of the Hohenberg–Kohn theory.

There are, however, other recent formulations of density functional theory which constitute either generalizations of, or alternatives to, the Hohenberg–Kohn version. Particularly relevant in this regard are works related to the pseudo-Schrödinger equation for the density amplitude [19,20] and studies of the exact Kohn–Sham potential [21–23]. We should also mention Yang's "integral" formulation of density functional theory [24,25], Cioslowski's "density-driven" approach [26,27], and Kryachko's et al. "local-scaling" version [28–35]. A common ingredient of the last three approaches is their rigorous handling of the functional N- and υ-representability problem. It has been shown [36] though, that the "density-driven" and "local-scaling" methods are very closely related: the former may be cast in terms of a finite orbital representation of local-scaling transformations.

It is the aim of the present paper to develop an extension of the local-scaling version of density functional theory applicable to excited states (a detailed exposition of the treatment of ground states is given in paper I of this series [32]; some calculations of ground-state wave functions and energies are reported in refs. [37–41]). The extension to excited states is carried out in the context of a superparticle formulation which requires the adoption of a concerted transformation involving the whole super-system one-particle density.

The present development differs from the formalism recently advanced by Koga [42] – also based on the local-scaling version of density functional theory – in that in the latter the emphasis is placed on the direct energy minimization of a particular excited state of a given symmetry. Because in the work reported here the treatment of excited states relies on concerted local-scaling transformations which handles on an equal footing the ground and all excited states of a given symmetry, it is clear that there arise notable differences both at the formal and practical levels between Koga's and the present approach.

Since the mathematics of Katriel's [18] superparticle formulations are well-suited for the treatment of excited states in terms of the local-scaling transformation version of density functional theory, we treat below (section 2) in some detail this superparticle approach. In section 3, we deal with the problem of applying local-scaling transformations to excited states. In section 4, we construct the energy density functional for the superparticle system and finally, in section 5, we discuss the derivation of the Euler–Lagrange equation for the composite density. In section 6, we report a preliminary application of the present method to the calculation of the 1^1S and 2^1S states of the helium atom.

2. The superparticle approach

Consider an N-electron system with the Hamiltonian $\hat{H}$

$$\hat{H}(r_1, \ldots, r_N) = \sum_{i=1}^{N} h(r_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} g(r_i, r_j), \tag{1}$$

where

$$h(r_i) = -\tfrac{1}{2}\nabla_{r_i}^2 + v(r_i) \tag{2}$$

and

$$g(r_i, r_j) = |r_i - r_j|^{-1}. \tag{3}$$

The operator $v(r_i)$ represents the Coulomb interactions between electron i and the fixed nuclei at $\{R_\alpha\}$:

$$v(r_i) = \sum_{\alpha=1}^{A} \frac{Z_\alpha}{|r_i - R_\alpha|}. \tag{4}$$

Let $\Psi_0(\mathbf{r}), \Psi_1(\mathbf{r}), \ldots, \Psi_M(\mathbf{r})$ be its first $M+1$ bound states of the same symmetry (i.e., having the same spectroscopic term) as the ground state $\Psi_0(\mathbf{r})$, where $\mathbf{r}$ is the radius-vector in the $3N$-dimensional space $\mathbb{R}^{3N}$, namely, $\mathbf{r} \equiv (r_1, r_2, \ldots, r_N)$ with $r_i \in \mathbb{R}^3$, $i = 1, 2, \ldots, N$. For a symmetry other than that of the ground state, we assume that $\Psi_0(\mathbf{r})$ represents the lowest state of that symmetry. The spin structure of the given wave functions has been removed for simplicity. Clearly, however, since the set of $M+1$ states corresponds to the same spectroscopic term, they have for the different levels the same spin structure. Let us start by considering $M+1$ samples, or replicas of the given system and by constructing a super-system consisting of these $M+1$ samples ("*superparticles*" or compound particles) which do not interact with each other. So, we may regard this super-system as a quantum mechanical system of dimension $(M+1)3N$ with the super-Hamiltonian

$$\hat{\mathcal{H}}^{(M+1)} = \sum_{i=0}^{M} \hat{H}^{(i)}, \tag{5}$$

where $\hat{H}^{(i)}$ is the Hamiltonian of the ith sample. Since the super-system introduced consists of non-interacting "particles", its lowest bound state can be represented in the form of the $(M+1)$-superparticle Slater determinant wave function

$$\Psi^{(M+1)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{M+1}) = [(M+1)!]^{-1/2} \det[\Psi_0(\mathbf{r}_1)\Psi_1(\mathbf{r}_2), \ldots, \Psi_M(\mathbf{r}_{M+1})], \tag{6}$$

constructed from $M+1$ orthonormalized superorbitals $\Psi_i(\mathbf{r})$, $i = 0, \ldots, M$. Then the energy functional for the given super-system becomes

$$E[\Psi^{(M+1)}] \equiv \left\langle \Psi^{(M+1)} \middle| \hat{H}^{(M+1)} \middle| \Psi^{(M+1)} \right\rangle \equiv \sum_{i=0}^{M} E[\Psi_i]. \tag{7}$$

It is trivially proved that $E[\Psi^{(M+1)}]$ attains its minimum

$$E[\Psi_0^{(M+1)}] = E_0 + E_1 + \ldots + E_M \tag{8}$$

iff $\Psi_0^{(M+1)}$ is given by eq. (6). Then the ground-state one-superparticle density, $\rho_0^{(M+1)}(\mathbf{r})$, takes the form

$$\rho_0^{(M+1)}(\mathbf{r}) = \sum_{i=0}^{M} |\Psi_i(\mathbf{r})|^2. \tag{9}$$

Following Katriel's approach [18], we construct the super-Hamiltonian $\hat{\mathcal{H}}^{(M+1)}$ via the rule given by eq. (5) and define the appropriate class S_{M+1} of admissible superfunctions consisting of $(M+1)$-superparticle Slater determinants. It is clear that $\Psi_i(\mathbf{r})$ describing the ith sample must belong to $\mathcal{L}_N^{(i)} = \mathcal{L}_N \setminus \mathcal{L}_N^{(i-1)}$ to comply with the orthogonality constraint on the superorbitals constituting the $(M+1)$-superparticle Slater determinant. Solving the ground-state variational problem for the given super-system by searching the extremum of $E[\Psi^{(M+1)}]$ over S_{M+1}, one obtains the ground-super-state $\Psi_0^{(M+1)}$ and the associated density $\rho_0^{(M+1)}(\mathbf{r})$ of eq. (9). Subtracting from the latter the density $\rho_0^{(M)}$, given by construction, one determines finally the required $\Psi_M(\mathbf{r}) = [\rho^{(M+1)}(\mathbf{r}) - \rho_0^{(M)}(\mathbf{r})]^{1/2}$ to within a phase factor.

3. A local-scaling transformation treatment of excited states

In order to develop a density functional theory for excited states, we must now transpose Katriel's approach [18] to the local-scaling transformation formalism.

For this purpose, it is necessary, however, that instead of the set $\mathcal{N}_B^N$ of single-particle densities (coming from wave functions and thus possessing the topological properties shown by Bader [43] to be essential ingredients of true densities [32]), we deal with the set $\mathcal{N}_S^{M+1}$ of one-superparticle densities $\rho^{(M+1)}(\mathbf{r})$ defined by eq. (9). Further, we define the generalized group $\tilde{\mathcal{F}}^N \equiv [\times]^{M+1}\mathcal{F}^N$ of local-scaling transformations and its action on $\otimes^{M+1}\mathcal{L}_N$. For a given $\Psi_{i_1}(\mathbf{r}), \Psi_{i_2}(\mathbf{r}), \ldots, \Psi_{i_{M+1}}(\mathbf{r}) \in \otimes^{M+1}\mathcal{L}_N$ and for arbitrary

$$(\widehat{\mathbf{f}^N}, \widehat{\mathbf{f}^N}, \ldots, \widehat{\mathbf{f}^N}) \in \tilde{\mathcal{F}}^N$$

with

$$\widehat{\mathbf{f}^N} \in \mathcal{F}^N,$$

we have

$$\begin{aligned}(\widehat{\mathbf{f}^N}, \widehat{\mathbf{f}^N}, \ldots, \widehat{\mathbf{f}^N})&(\Psi_{i_1}(\mathbf{r}), \Psi_{i_2}(\mathbf{r}), \ldots, \Psi_{i_{M+1}}(\mathbf{r}))\\ &\equiv (\Psi_{i_1\mathbf{f}}(\mathbf{r}), \Psi_{i_2\mathbf{f}}(\mathbf{r}), \ldots, \Psi_{i_{M+1}\mathbf{f}}(\mathbf{r})),\end{aligned} \tag{10a}$$

with

$$(\Psi_{i_1\mathbf{f}}(\mathbf{r}), \Psi_{i_2\mathbf{f}}(\mathbf{r}), \ldots, \Psi_{i_{M+1}\mathbf{f}}(\mathbf{r})) \in \overset{M+1}{\otimes} \mathcal{L}_N, \tag{10b}$$

where

$$\Psi_{i_k\mathbf{f}}(\mathbf{r}) \equiv \widehat{\mathbf{f}^N}\Psi_{i_k}(\mathbf{r}). \tag{10c}$$

This action of $\hat{\mathcal{F}}^N$ on $\otimes^{M+1}\mathcal{L}_N$ is consistent, in view of the mapping between $\mathcal{F}$ and $\mathcal{N}_B^N$, with the action of $\tilde{\mathcal{F}} \equiv \otimes^{M+1}\mathcal{F}$ on $\otimes^{M+1}\mathcal{N}_B^N$ when a density $(\rho_{i_1}(r), \rho_{i_2}(r), \ldots, \rho_{i_{M+1}}(r)) \in \otimes^{M+1}\mathcal{N}_B^N$ acted upon by $(\hat{\mathbf{f}}, \hat{\mathbf{f}}, \ldots, \hat{\mathbf{f}}) \in \mathcal{F}$ is transformed as follows:

$$\begin{aligned}(\hat{\mathbf{f}}, \hat{\mathbf{f}}, \ldots, \hat{\mathbf{f}})&(\rho_{i_1}(r), \rho_{i_2}(r), \ldots, \rho_{i_{M+1}}(r))\\ &\equiv (\rho_{i_1\mathbf{f}}(r), \rho_{i_2\mathbf{f}}(r), \ldots, \rho_{i_{M+1}\mathbf{f}}(r)),\end{aligned} \tag{11a}$$

with

$$(\rho_{i_1\mathbf{f}}(r), \rho_{i_2\mathbf{f}}(r), \ldots, \rho_{i_{M+1}\mathbf{f}}(r)) \in \overset{M+1}{\otimes} \mathcal{N}_B^N, \tag{11b}$$

where

$$\rho_{i_k\mathbf{f}}(r) \equiv \hat{\mathbf{f}}\rho_{i_k}(r). \tag{11c}$$

For any element, say $(\rho_{i_1}(r), \rho_{i_2}(r), \ldots, \rho_{i_{M+1}}(r))$, of $\otimes^{M+1}\mathcal{N}_B^N$ one can define the density

$$\rho_I(r) = \sum_{k=1}^{M+1} \rho_{i_k}(r), \tag{12}$$

where $I = \{i_1, \ldots, i_{M+1}\}$, which is clearly an element of $\mathcal{N}_B^{N(M+1)}$. In terms of these densities, eq. (11a) can be rewritten as follows:

$$\rho_{If}(r) = \rho_I(f(r))D\{f(r); r\}, \tag{13}$$

which gives the definition of the usual action of the group $\mathcal{F}$ on $\mathcal{N}_B^{N(M+1)}$.

With respect to the action of $\tilde{\mathcal{F}}^N$ on $\otimes^{M+1}\mathcal{L}_N$ defined by eq. (10a), the class $\otimes^{M+1}\mathcal{L}_N$ is partitioned into the orbits as

$$\overset{M+1}{\otimes} \mathcal{L}_N = \cup_\alpha \mathbf{O}^{[\alpha]}. \tag{14}$$

One may summarize the above in the following theorem [32].

THEOREM

Within every orbital $\mathbf{O}^{[\alpha]} \subset \otimes^{M+1}\mathcal{L}_N$ there exists a one-to-one correspondence between $(M+1)$-superparticle wave functions, belonging to $\mathbf{O}^{[\alpha]}$, and "densities" from $\otimes^{M+1}\mathcal{N}_B^N$, and also for the given and fixed generator

$$(\Psi^{[\alpha]}_{i_1,g}(\mathbf{r}), \Psi^{[\alpha]}_{i_2,g}(\mathbf{r}), \ldots, \Psi^{[\alpha]}_{i_{M+1},g}(\mathbf{r}))$$

of the orbit $\mathbf{O}^{[\alpha]}$, a one-to-one correspondence between the element of $\mathbf{O}^{[\alpha]}$ and local-scaling transformations $\mathbf{f} \in \mathcal{F}$.

Within the given orbit $\mathbf{O}^{[\alpha]} \subset \otimes^{M+1}\mathcal{L}_N$, an arbitrary one-superparticle density $\rho^{(M+1)}(\mathbf{r})$ takes the form:

$$\rho^{[\alpha](M+1)}(\mathbf{r}) = \rho^{[\alpha](M+1)}_{I\mathbf{f},g}(\mathbf{r}) \equiv \sum_{k=1}^{M+1} \left|\Psi^{[\alpha]}_{i_k\mathbf{f},g}(\mathbf{r})\right|^2 \tag{15}$$

for an appropriately chosen $\hat{\mathbf{f}} \in \mathcal{F}$. Comparing eq. (15) with eq. (13), one arrives at the following

COROLLARY

There exists a one-to-one correspondence between the elements of the orbit $\mathbf{O}^{[\alpha]} \in \otimes^{M+1}\mathcal{L}_N$ and densities from $\mathcal{N}_B^{N(M+1)}$.

It is clear that densities of $\mathcal{N}_B^{N(M+1)}$ can be viewed as the reduced analogues of one-superparticle densities, belonging to $\mathcal{N}_S^{M+1}$. Restricting the domain where the energy function $E[\Psi^{(M+1)}]$ can be determined to the given orbit $\mathbf{O}^{[\alpha]} \subset \otimes^{M+1}\mathcal{L}_N$, one obtains the well-defined energy density functional $E_\alpha^{[i]}[\rho(r)]$ given on $\mathcal{N}_B^{N(M+1)}$.

Katriel's approach suggests a reduction of all orbits $\mathbf{O}^{[\alpha]} \subset \otimes^{M+1} \mathcal{L}_N$ to those belonging to $\mathbf{S}_{M+1}$. One can identify the class $\mathbf{S}_{M+1}$ as that one consisting of the elements of the type

$$(\Psi_{i_1}(\mathbf{r}), \Psi_{i_2}(\mathbf{r}), \ldots, \Psi_{i_{M+1}}(\mathbf{r})) \in \bigotimes^{M+1} \mathcal{L}_N,$$

for which $\Psi_{i_k}(\mathbf{r}) \in \mathcal{L}_N^{(i_k)}$, with $k = 1, 2, \ldots, M+1$, and where $\mathcal{L}^{(i)} = \mathcal{L}_N \setminus \mathcal{L}_N^{(i-1)}$. Using this definition for $\mathbf{S}_{M+1}$, it is fairly easy to prove that $\tilde{\mathcal{F}}^N(\mathbf{S}_{M+1}) \subseteq \mathbf{S}_{M+1}$. In other words, the concept of an orbit in $\otimes^{M+1} \mathcal{L}_N$ is also well-defined in $\mathbf{S}_{M+1}$. In particular, $\mathbf{S}_{M+1}$ contains the generalized Hohenberg–Kohn, or proper orbit $\mathbf{O}^{[HK]}$ possessing the element $(\Psi_0(\mathbf{r}), \Psi_1(\mathbf{r}), \ldots, \Psi_M(\mathbf{r}))$, made up by the exact first $M+1$ states.

4. The energy density functional for excited states

For the purpose of deriving the explicit form of $\mathbf{E}_\alpha[\rho(r)]$ with $\rho(r) \in \mathcal{N}_B^{N(M+1)}$, for an arbitrary orbit $\mathbf{O}^{[\alpha]}$ in $\mathbf{S}_{M+1}$, we choose a generator $(\Psi_{i_1,g}(\mathbf{r}), \Psi_{i_2,g}(\mathbf{r}), \ldots, \Psi_{i_{M+1},g}(\mathbf{r}))$. Since an operator $\hat{\mathbf{f}}^N$ changes each one of the generating wave functions $\Psi_{i_k,g}(\mathbf{r})$ into $\Psi_{i_k,\rho}(\mathbf{r})$, i.e. $\Psi_{i_k,\rho}(\mathbf{r}) = \hat{\mathbf{f}}^N \Psi_{i_k,g}(\mathbf{r})$, (cf. eq. (10c)), in view of eq. (7) we have

$$\mathbf{E}[\rho^{[\alpha]}(r)] \equiv \sum_{k=1}^{M+1} \left\langle \Psi_{i_k,\rho}^{[\alpha]} \middle| \hat{H} \middle| \Psi_{i_k,\rho}^{[\alpha]} \right\rangle \equiv \sum_{k=1}^{M+1} \mathbf{E}^{[\alpha]}\left[\rho_{i_k}^{[\alpha]}(r)\right], \tag{16}$$

where $\rho^{[\alpha]}(r) \in \mathcal{N}_B^{N(M+1)}$ is defined by

$$\rho^{[\alpha]}(r) = \sum_{k=1}^{M+1} \hat{\mathbf{f}} \rho_{i_k,g}^{[\alpha]}(r) = \sum_{k=1}^{M+1} \rho_{i_k}^{[\alpha]}(r). \tag{17}$$

The transformation function $f_{g,\rho}^{\alpha}(r, \theta, \phi)$ is generated by spanning the function

$$f_{g,\rho}^{\alpha}(r, \theta_0, \phi_0) = \left[\int_0^r \mathrm{d}r' \frac{3r'^2 \rho(r', \theta_0, \phi_0)}{\rho_{I,g}^{(\alpha)}(f_{g,\rho}^{\alpha}(r', \theta_0, \phi_0), \theta_0, \phi_0)} \right]^{1/3}, \tag{18}$$

with

$$\rho_{I,g}^{[\alpha]} \equiv \sum_{k=1}^{M+1} \rho_{i_k,g}^{[\alpha]}(r) \tag{19}$$

over all angles θ_0 and ϕ_0. The energy expression given by eq. (16) can be expanded as follows

$$\mathbf{E}\left[\rho_{i_k}^{[\alpha]}(r)\right] = \sum_{k=1}^{M+1} \left(\mathbf{T}^{[\alpha]}\left[\rho_{i_k}^{[\alpha]}(r)\right] + \mathbf{E}_{\mathrm{Coulomb}}^{[\alpha]}\left[\rho_{i_k}^{[\alpha]}(r)\right] + \mathbf{E}_{\mathrm{XC}}^{[\alpha]}\left[\rho_{i_k}^{[\alpha]}(r)\right] + \mathbf{U}_{\mathrm{en}}^{[\alpha]}\left[\rho_{i_k}^{[\alpha]}(r)\right] \right). \tag{20}$$

Let us consider the explicit form of the various terms appearing in eq. (20). By definition, the kinetic energy operator is given by

$$\mathrm{T}^{[\alpha]}\left[\rho^{[\alpha]}_{i_k}(r)\right] \equiv \tfrac{1}{2}\int \mathrm{d}^3 r\, \nabla_r \nabla_{r'}\, \gamma^{[\alpha]}_{i_k,\rho}(r,r')\Big|_{r=r'} . \tag{21}$$

Since the transformed 1-matrix is related to the generating 1-matrix by means of the transformation

$$\gamma^{[\alpha]}_{i_k,\rho}(r,r') = \left[D\left\{f^{[\alpha]}_{g,\rho}(r);r\right\}D\left\{f^{[\alpha]}_{g,\rho}(r');r\right\}\right]^{1/2} \gamma^{[\alpha]}_{i_k,\rho}\left(f^{[\alpha]}_{g,\rho}(r'), f^{[\alpha]}_{g,\rho}(r')\right), \tag{22}$$

where $D\{f^{[\alpha]}_{g,\rho}(r);r'\}$ is the Jacobian of the transformation, we obtain for the kinetic energy term [32]

$$\begin{aligned}\mathrm{T}^{[\alpha]}\left[\rho^{[\alpha]}_{i_k}(r)\right] &= \tfrac{1}{2}\int \mathrm{d}^3 r\left[\nabla_r\left(\rho^{[\alpha]}_{i_k}(r)\right)^{1/2}\right]^2 \\ &\quad + \tfrac{1}{2}\int \mathrm{d}^3 r\,\rho^{[\alpha]}_{i_k}(r)\left[\nabla_r \nabla_{r'}\,\tilde{\gamma}^{[\alpha]}_{i_k,g}\left(f^{[\alpha]}_{g,\rho}(r), f^{[\alpha]}_{g,\rho}(r')\right)\right]_{r=r'} .\end{aligned} \tag{23}$$

In the above expression, the transformed density satisfies the equation

$$\rho^{[\alpha]}_{i_k}(r) \equiv D\left\{f^{[\alpha]}_{g,\rho}(r);r\right\}\rho^{[\alpha]}_{i_k,g}\left(f^{[\alpha]}_{g,\rho}(r)\right) \tag{24}$$

and $\tilde{\gamma}^{[\alpha]}_{i_k,g}$ is the non-local part of the 1-matrix [43]. Similarly, we have the following expressions for the remaining energy terms:

$$\mathrm{E}^{[\alpha]}_{\mathrm{Coulomb}}\left[\rho^{[\alpha]}_{i_k}(r)\right] = \tfrac{1}{2}\int \mathrm{d}^3 r \int \mathrm{d}^3 r'\, \frac{\rho^{[\alpha]}_{i_k}(r)\rho^{[\alpha]}_{i_k}(r')}{\left|r-r'\right|}, \tag{25}$$

$$\mathrm{U}^{[\alpha]}_{\mathrm{en}}\left[\rho^{[\alpha]}_{i_k}(r)\right] = \int \mathrm{d}^3 r\, \upsilon(r)\rho^{[\alpha]}_{i_k}(r), \tag{26}$$

$$\mathrm{E}^{[\alpha]}_{\mathrm{XC}}\left[\rho^{[\alpha]}_{i_k}(r)\right] = \tfrac{1}{2}\int \mathrm{d}^3 r\,\rho^{[\alpha]}_{i_k}(r)\mathcal{E}^{\mathrm{XC}[\alpha]}_{i_k,g}\left(\left[\rho^{[\alpha]}_{i_k}(r)\right]; f^{[\alpha]}_{g,\rho}(r)\right). \tag{27}$$

In eq. (27), $\mathcal{E}^{\mathrm{XC}[\alpha]}_{i_k,g}$ is defined by

$$\mathcal{E}^{\mathrm{XC}[\alpha]}_{i_k,g}\left(\left[\rho^{[\alpha]}_{i_k}(r)\right]; f^{[\alpha]}_{g,\rho}(r)\right) = \tfrac{1}{2}\int \mathrm{d}^3 r'\, \frac{\rho^{[\alpha]}_{i_k}(r')\mathcal{F}^{\mathrm{XC}[\alpha]}_{i_k,g}\left(f^{[\alpha]}_{g,\rho}(r); f^{[\alpha]}_{g,\rho}(r')\right)}{\left|r-r'\right|}, \tag{28}$$

where $\mathcal{F}^{\mathrm{XC}[\alpha]}_{i_k,g}$ is the exchange-correlation factor [44] corresponding to the generating wave function $\Phi^{[\alpha]}_{i_k,g}(\mathbf{r})$.

Notice that for a given and known generator

$$(\Phi^{[\alpha]}_{i_1,g}(\mathbf{r}),\dots,\Phi^{[\alpha]}_{i_M,g}(\boldsymbol{r})) \in \otimes^{M+1}\mathcal{L}_N,$$

we may actually construct the nonlocal term

$$\tilde{\gamma}^{\mathrm{XC}[\alpha]}_{i_k,g}(f^{[\alpha]}_{g,\rho}(\boldsymbol{r}); f^{[\alpha]}_{g,\rho}(\boldsymbol{r}'))$$

arising from the 1-matrix, as well as the nonlocal exchange-correlation factor

$$\mathcal{F}^{\mathrm{XC}[\alpha]}_{i_k,g}(f^{[\alpha]}_{g,\rho}(\boldsymbol{r}); f^{[\alpha]}_{g,\rho}(\boldsymbol{r}')).$$

This is done by first computing

$$\tilde{\gamma}^{[\alpha]}_{i_k,g}(\boldsymbol{r};\boldsymbol{r}') \text{ and } \mathcal{F}^{\mathrm{XC}[\alpha]}_{i_k,g}(\boldsymbol{r};\boldsymbol{r}')$$

and then replacing $\boldsymbol{r}$ and $\boldsymbol{r}'$ by their counterparts

$$f^{[\alpha]}_{g,\rho}(\boldsymbol{r}) \text{ and } f^{[\alpha]}_{g,\rho}(\boldsymbol{r}'),$$

respectively.

In is important to remark that in view of eqs. (17) and (18), the transformation function $f^{[\alpha]}_{g,\rho}(\boldsymbol{r})$ depends upon the complete set $\{\rho^{[\alpha]}_{i_k}(\boldsymbol{r})\}^{M+1}_{k=1}$ of one-particle densities corresponding to the ground state ($k = 1$) and to M excited states ($k = 2, \dots, M + 1$). This relationship may be represented by

$$f^{[\alpha]} \equiv f^{[\alpha]}\left(\left[\left\{\rho^{[\alpha]}_{i_k}(\boldsymbol{r})\right\}^{M+1}_{k=1}\right];\boldsymbol{r}\right). \tag{29}$$

Equation (29) embodies the main idea of the energy density functional theory devised here to deal with the bound spectrum. All prototype wave functions of the ground plus excited states are deformed coherently into their optimal variational representations by means of a unique local-scaling transformation which preserves throughout this deformation the orthogonality of the wave functions.

5. Variational equations for the one-particle densities

The energy functional given by eq. (16), whose components are determined by eqs. (23)–(27), is a well-defined functional of the set $\{\rho^{[\alpha]}_{i_k}(\boldsymbol{r})\}^{M+1}_{k=1}$ of one-particle densities. However, the variation is of the constrained type since it is required that the variational one-particle densities $\{\rho^{[\alpha]}_{i_k}(\boldsymbol{r})\}$ come from the generating one-particle densities $\{\rho^{[\alpha]}_{i_k,g}(\boldsymbol{r})\}$ via the concerted transformation given by eq. (24). This is a finite subsidiary condition [45] which may be incorporated in the variational principle through the Lagrange multplier functions $\{\omega_{i_k}(\mathbf{r})\}$. Once the normalization condition has been included, the stationary variational principle may be written as

$$\frac{\delta}{\delta\rho^{[\alpha]}_{i_k}(\mathbf{r})}\Bigg[\sum_{k=1}^{M+1}\Big(\mathrm{E}^{[\alpha]}\big[\rho^{[\alpha]}_{i_k}(\mathbf{r})\big]-\mu^{[\alpha]}_{i_k}\Big[\int \mathrm{d}^3 r\rho^{[\alpha]}_{i_k}(\mathbf{r})-N\Big]$$

$$+\int \mathrm{d}^3\omega_{i_k}(\mathbf{r})\Big[\rho^{[\alpha]}_{i_k}(\mathbf{r})-D\big(f^{[\alpha]}_{g,\rho}(\mathbf{r});\mathbf{r}\big)\rho^{[\alpha]}_{i_k}\big(f^{[\alpha]}_{g,\rho}(\mathbf{r});\mathbf{r}\big)\Big]\Big)\Bigg]=0, \qquad (30)$$

for $k = 1, \ldots, M+1$.

Before proceeding to the variation, let us notice that also by virtue of eq. (29), the nonlocal component $\tilde{\gamma}^{[\alpha]}_{i_k,g}$ of the 1-matrix, appearing in the energy expression through eq. (23), depends upon the whole set of one-particle densities:

$$\tilde{\gamma}^{[\alpha]}_{i_k,g}(f^{[\alpha]}_{g,\rho}(\mathbf{r}); f^{[\alpha]}_{g,\rho}(\mathbf{r}')) \equiv \tilde{\gamma}^{[\alpha]}_{i_k,g}\Big([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}]; \mathbf{r},\mathbf{r}'\Big) \qquad (31)$$

Similarly, the following relation holds for the exchange-correlation factor:

$$\mathcal{F}^{\mathrm{XC}[\alpha]}_{i_k,g}(f^{[\alpha]}_{g,\rho}(\mathbf{r}); f^{[\alpha]}_{g,\rho}(\mathbf{r}')) \equiv \mathcal{F}^{\mathrm{XC}[\alpha]}_{i_k,g}\Big([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}]; \mathbf{r},\mathbf{r}'\Big). \qquad (32)$$

This fact allows us to write

$$\mathcal{E}^{\mathrm{XC}[\alpha]}_{i_k,g}([\rho^{[\alpha]}_{i_k}(\mathbf{r})]; f^{[\alpha]}_{g,\rho}(\mathbf{r})) \equiv \mathcal{E}^{\mathrm{XC}[\alpha]}_{i_k,g}\Big([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}]; \mathbf{r}\Big). \qquad (33)$$

The same applies to $D(f^{[\alpha]}_{g,\rho}(\mathbf{r});\mathbf{r})$, the Jacobian of the transformation and to the transformed density $\rho^{[\alpha]}_{i_k}(f^{[\alpha]}_{g,\rho}(\mathbf{r}))$. Carrying out the variation stipulated by eq. (30), we are led to the system of coupled Euler–Lagrange equations:

$$-\frac{1}{8}\left[\frac{\nabla_r\rho^{[\alpha]}_{i_k}(\mathbf{r})}{\rho^{[\alpha]}_{i_k}(\mathbf{r})}\right]^2-\frac{1}{4}\frac{\nabla^2_r\rho^{[\alpha]}_{i_k}(\mathbf{r})}{\rho^{[\alpha]}_{i_k}(\mathbf{r})}+v^{T[\alpha]}_{i_k,g}\Big([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}];\mathbf{r}\Big)$$

$$+\ v(\mathbf{r})+v^{\mathrm{H}[\alpha]}_{i_k,g}\Big([\rho^{[\alpha]}_{i_k}(\mathbf{r})];\mathbf{r}\Big)+v^{\mathrm{XC}[\alpha]}_{i_k,g}\Big([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}];\mathbf{r}\Big) \qquad (34)$$

$$=\mu^{[\alpha]}_{i_k}-\omega_{i_k}(\mathbf{r})\left[1+\frac{\delta D}{\delta\rho^{[\alpha]}_{i_k}(\mathbf{r})}\rho^{[\alpha]}_{i_k}(f^{[\alpha]}_{g,\rho}(\mathbf{r}))+D\frac{\delta\rho^{[\alpha]}_{i_k}(f^{[\alpha]}_{g,\rho}(\mathbf{r}))}{\delta\rho^{[\alpha]}_{i_k}(\mathbf{r})}\right],$$

for $k = 1, \ldots, M+1$.

In the above equation, v^T is a potential which originates from the nonlocal contribution to the kinetic energy functional and is defined by

$$v^{T[\alpha]}_{i_k,g}\left([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}];\mathbf{r}\right) = \tfrac{1}{2}\nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}\tilde{\gamma}^{[\alpha]}_{i_k,g}\left([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}];\mathbf{r},\mathbf{r}'\right)\Big|_{\mathbf{r}=\mathbf{r}'}$$
$$+\ \tfrac{1}{2}\rho^{[\alpha]}_{i_k}(\mathbf{r})\frac{\delta}{\delta\rho^{[\alpha]}_{i_k}(\mathbf{r})}\left(\nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}\tilde{\gamma}^{[\alpha]}_{i_k,g}\left([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}];\mathbf{r},\mathbf{r}'\right)\right)\Big|_{\mathbf{r}=\mathbf{r}'}. \tag{35}$$

The potential v^{XC} which arises from the exchange-correlation term is given by

$$v^{\mathrm{XC}[\alpha]}_{i_k,g}\left([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}];\mathbf{r}\right) = \tfrac{1}{2}\mathcal{E}^{\mathrm{XC}[\alpha]}_{i_k,g}\left([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}];\mathbf{r}\right)$$
$$+\ \rho^{[\alpha]}_{i_k}(\mathbf{r})\frac{\delta\mathcal{E}^{\mathrm{XC}[\alpha]}_{i_k,g}\left([\{\rho^{[\alpha]}_{i_k}(\mathbf{r})\}_{k=1}^{M+1}];\mathbf{r}\right)}{\delta\rho^{[\alpha]}_{i_k}(\mathbf{r})}. \tag{36}$$

The potential v^{H} is the usual Hartree potential produced by the charge distribition $\rho^{[\alpha]}_{i_k}(\mathbf{r})$

$$v^{\mathrm{H}[\alpha]}_{i_k}\left([\rho^{[\alpha]}_{i_k}(\mathbf{r})];\mathbf{r}\right) = \int \mathrm{d}^3r'\,\frac{\rho^{[\alpha]}_{i_k}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{37}$$

Due to the presence of coupling terms in v^T and v^{XC}, this system of equations must be solved self-consistently.

6. Preliminary calculations

The practical meaning of the set of Euler–Lagrange equations given by eqs. (34) is the following. Each one of the equations corresponds to the variation of the energy of state Ψ_i with respect to its particular one-particle density $\rho_i(\mathbf{r})$. All other densities $\rho_j(\mathbf{r})$ for $j \neq i$ remain fixed, while $\rho_i(\mathbf{r})$ is varied. However, these remaining densities influence the variation through their contribution to the total density which is precisely the one being transformed by the concerted local-scaling procedure.

In order to avoid at this initial stage the numerical work involved in solving directly eqs. (34), we have selected to deal rather with the equivalent variational principle given by eq. (30). In what follows, we report preliminary calculations for the 1^1S and 2^1S states of helium. The simplest approximation to these states is

$$\Phi(1^1\mathrm{S}) \equiv \Phi_0(1,2) = [1s(r_1)1s(r_2)] \times \text{spin part}, \tag{38a}$$

$$\Phi(2^1\mathrm{S}) \equiv \Phi_1(1,2) = \frac{1}{\sqrt{2}}[1s(r_1)2s(r_2) + 2s(r_1)1s(r_2)] \times \text{spin part}, \tag{38b}$$

where the orthonormal functions $1s(r)$ and $2s(r)$ are

$$1s(r) = \left[\frac{\alpha^3}{\pi}\right]^{1/2} e^{-\alpha r}, \tag{39a}$$

$$2s(r) = B(1 - \lambda\beta r)e^{-\beta r}, \tag{39b}$$

in which

$$B = \left[\frac{\beta^3}{\pi(3\lambda^2 - 3\lambda + 1)}\right]^{1/2}, \tag{39c}$$

$$\lambda = \frac{\alpha + \beta}{3\alpha}. \tag{39d}$$

However, as any linear combination of $\Phi_0(1,2)$ and $\Phi_1(1,2)$ also describes a ^{1}S state, we take as the generating wave functions for these states the following ones:

$$\Psi_0^g(1,2) = C_{00}\Phi_0(1,2) + C_{01}\Phi_1(1,2), \tag{40a}$$

$$\Psi_1^g(1,2) = C_{10}\Phi_0(1,2) + C_{11}\Phi_1(1,2). \tag{40b}$$

In general, the choice of parameters α, β, $C_{00} \ldots C_{11}$ for these generating wave functions is arbitrary. We consider here three alternative choices based on the solution of a 2 × 2 configuration interaction problem generated by these wave functions. These choices are characterized by minimizations of $E_0 + E_1$ (case A), E_0 (case B), and E_1 (case C), respectively. The results are listed in table 1.

Table 1

Optimal parameters for generating wave functions.

	Type of minimization		
	A	B	C
α_{opt}	1.801425	2.201973	1.984940
β_{opt}	0.571686	1.659025	0.518140
C_{00}	0.996310	0.926135	0.992422
C_{01}	- 0.085830	- 0.377193	- 0.122876
C_{10}	0.085830	0.377193	0.122876
C_{11}	0.996310	0.926135	0.992422
E_0^g	- 2.839950	- 2.877037	- 2.768638
E_1^g	- 2.124237	- 0.810173	- 2.142608
$E_0^g + E_1^g$	- 4.964187	- 3.687210	- 4.911246

The concerted reference density is

$$\rho^{\mathrm{g}}(r) = \rho_0^{\mathrm{g}}(r) + \rho_1^{\mathrm{g}}(r), \tag{41a}$$

where $\rho_0^{\mathrm{g}}(r)$ and $\rho_1^{\mathrm{g}}(r)$ correspond to Ψ_0^{g} and Ψ_1^{g}, respectively. The concerted object density is

$$\rho^{\mathrm{f}}(r) = \rho_0^{\mathrm{f}}(r) + \rho_1^{\mathrm{f}}(r), \tag{41b}$$

where the individual components are parametrized according to

$$\rho_0^{\mathrm{f}}(r) = N_0[\mathrm{e}^{-a_0 r} + b_0\mathrm{e}^{-c_0 r} + d_0\mathrm{e}^{-e_0 r}] \tag{42a}$$

and

$$\rho_1^{\mathrm{f}}(r) = N_1[\mathrm{e}^{-a_1 r} + b_1\mathrm{e}^{-c_1 r} + d_1\mathrm{e}^{-e_1 r}]. \tag{42b}$$

In the above expressions, $a_0 - e_0$ and $a_1 - e_1$ are variational parameters and N_0 and N_1 are normalization constants. In all cases, the minimization via the concerted local-scaling transformation was carried out for the highest eigenvalue of the 2×2 CI problem, namely, for E_1 keeping $\rho_0^{\mathrm{f}}(r)$ fixed to the near-Hartree–Fock density [38]. The results of these calculations are given in table 2. It is seen from this table that in case A, which represents a "balanced" situation for both states, the concerted local-scaling transformation improves E_1 from its generating wave function value of $E_1^{\mathrm{g}} = -2.124237$ to $E_1^{\mathrm{LS}} = -2.137995$ Hartrees. This is achieved, however, at the expense of E_0 which goes from $E_0^{\mathrm{g}} = -2.839950$ to $E_0^{\mathrm{LS}} = -2.797951$ Hartrees, thus leading to a higher total energy. This fact is perhaps related to the highly

Table 2

Optimal density parameters and energy values (Hartrees) for local-scaled transformed wave functions.

	Type of generating wave function			
	A	B	C	C*[a)]
a_1	4.15662	4.25909	4.20207	4.20960
b_1	-5.44509×10^{-2}	3.14279×10^{-2}	-4.71447×10^{-2}	-4.59400×10^{-2}
c_1	2.40593	1.46969	2.28153	2.25866
d_1	1.15266×10^{-3}	9.91051×10^{-6}	0.92015×10^{-3}	0.87669×10^{-3}
e_1	1.03665	0.51749	0.99782	0.98932
E_0^{LS}	-2.797951	-2.862835	-2.775102	-2.769790
E_1^{LS}	-2.137995	-1.801722	-2.142541	-2.142692
$E_0^{\mathrm{LS}} + E_1^{\mathrm{LS}}$	-4.935946	-4.664557	-4.917643	-4.912482

[a)] In C*, $\beta_{\mathrm{opt}} = 0.493221$.

restricted nature of the wave functions Ψ_0 and Ψ_1 in the present treatment. If one of them is improved by a concerted local-scaling transformation, there is simply not enough flexibility in the expansions given by eqs. (40) to allow for a concomitant improvement of the other. In case B, the generating wave function is heavily loaded toward the 1^1S ground state and represents poorly the 2^1S excited state. For this reason, concerted local-scaling greatly improves E_1 from $E_1^g = -0.810173$ to $E_1^{LS} = -1.801722$ Hartrees, while it only slightly diminishes E_0. However, in case C, where the generating wave function already favors the 2^1S state, the concerted local-scaling transformation actually raises the value of E_1 from $E_1^g = -2.142608$ to $E_1^{LS} = -2.142541$ Hartrees. Taking into consideration the fact that the value $E_1^g = -2.142608$ should have remained unmodified by the local-scaling transformation $f(r) = r$, we see that the reason why this value changes in the present case is the particular choice of the object density $\rho_0^f(r)$ which does not correspond to that of the generating wave function Ψ_0^g but to the near-Hartree–Fock wave function [38]. This choice, therefore, creates a bias toward the lowest eigenvalue E_0 and leads to this anomalous result. Clearly, a way to remedy this situation is to increase the flexibility of the wave function. For this purpose, in case C* we have selected a generating wave function which has the same α_{opt} as in C but which has an exponent β optimized with respect to the excited state energy E_1^{LS} ensuing from the concerted local-scaling transformation. As a result, we obtain $E_1^{LS} = -2.142692$ Hartrees, which is lower than $E_1^g = -2.142608$ Hartrees of case C. This shows that the local-scaling transformation version of density functional theory can indeed lead to values of the energy for excited states which are lower than those obtained from trial wave functions with optimized parameters. However, the present results also show that the flexibility that the generating wave functions must possess in order to approximate both states at the same time is crucial for the successful application of the concerted local-scaling method.

The present method differs markedly from the direct optimization of an excited state through the use of local-scaling transformations proposed by Koga [42]. In that case, the flexibility of the generating wave functions is not a prerequisite for a successful optimization because only a given excited state is optimized at the time. In the present case, the fact that optimization is carried out by a concerted local-scaling transformation guarantees, in principle, that all energy eigenvalues can be approximated as closely as desired. But clearly, the price one must pay to render this method useful in practice is to increase the size of the configuration interaction expansion representing the generating wave function. However, the point is that since local-scaling transformations do lower the energy of configuration interaction wave functions (with optimized parameters) without adding new configurations, one can hope to treat excited states of atoms without having to resort to unduly long CI expansions. Of course, one should also remark that a direct numerical solution of eqs. (34) is also an alternative route for solving the excited state problem within the local-scaling version of density functional theory.

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