Differentiability in density-functional theory: Further study of the locality theorem

Ingvar Lindgren* and Sten Salomonson†

Department of Physics, Chalmers University of Technology and the Göteborg University, Göteborg, Sweden

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The locality theorem in density-functional theory (DFT) states that the functional derivative of the Hohenberg-Kohn universal functional can be expressed as a local multiplicative potential function, and this is the basis of DFT and of the successful Kohn-Sham model. Nesbet has in several papers [Phys. Rev. A 58, R12 (1998); ibid. 65, 010502 (2001); Adv. Quant. Chem. 43, 1 (2003)] claimed that this theorem is in conflict with fundamental quantum physics, and as a consequence that the Hohenberg-Kohn theory cannot be generally valid. We have commented upon these works [Comment, Phys. Rev. A 67, 056501 (2003)] and recently extended the arguments [Adv. Quantum Chem. 43, 95 (2003)]. We have shown that there is no such conflict and that the locality theorem is inherently exact. In the present work we have furthermore verified this numerically by constructing a local Kohn-Sham potential for the 1s2s3S state of helium that generates the many-body electron density and shown that the corresponding 2s Kohn-Sham orbital eigenvalue agrees with the ionization energy to nine digits. Similar result is obtained with the Hartree-Fock density. Therefore, in addition to verifying the locality theorem, this result also confirms the so-called ionization-potential theorem.

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I. INTRODUCTION

The locality theorem in density-functional theory is the cornerstone of the density-functional theory (DFT) and the basis for the widely used Hohenberg-Kohn-Sham model [1,2]. This fact, which we shall refer to as the locality theorem, was rigorously proved for a large class of functionals by Lieb and of Ensslin [3,4]. Nesbet has in several papers [Phys. Rev. A 58, R12 (1998); ibid. 65, 010502 (2001); Adv. Quant. Chem. 43, 1 (2003)] claimed that this theorem is in conflict with fundamental quantum physics, and as a consequence that the Hohenberg-Kohn theory cannot be generally valid. We have commented upon these works [Comment, Phys. Rev. A 67, 056501 (2003)] and recently extended the arguments [Adv. Quantum Chem. 43, 95 (2003)]. We have shown that there is no such conflict and that the locality theorem is inherently exact. In the present work we have furthermore verified this numerically by constructing a local Kohn-Sham potential for the 1s2s3S state of helium that generates the many-body electron density and shown that the corresponding 2s Kohn-Sham orbital eigenvalue agrees with the ionization energy to nine digits. Similar result is obtained with the Hartree-Fock density. Therefore, in addition to verifying the locality theorem, this result also confirms the so-called ionization-potential theorem.

where

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*Electronic address: ingvar.lindgren@fy.chalmers.se; http://fy.chalmers.se/~f3ail
†Electronic address: f3asos@fy.chalmers.se
with serious misunderstandings in the current literature, we shall here try to present simple arguments how the present conflict has arisen and how it can be resolved. We shall also present in our opinion particularly strong numerical evidence in favor of the theorem. More mathematical details are given in our recent review in Advances in Quantum Chemistry \[11\] as well as in the article by van Leeuwen \[6\] in the same volume (43), largely devoted to this issue.

II. FUNCTIONAL DERIVATIVES

Generally, a density functional \( F[\rho] \) is defined as a mapping of a normed space of densities\(^1\) \( (M) \) on the space of real numbers \( (\mathcal{R}) \) \[25\],

\[
F[\rho]: M \rightarrow \mathcal{R},
\]

(4)
a mapping that has to be unique in the sense that a certain density corresponds to a single real number.

A. Gâteaux derivative

The Gâteaux or weak differential of a density functional \( F[\rho] \) is defined \([25, p. 46, [26, \text{p. 293, [6, Eq. (60)] as}]

\[
dF[\rho_0, \delta \rho] = \lim_{\lambda \rightarrow 0} \frac{F[\rho_0 + \lambda \delta \rho] - F[\rho_0]}{\lambda}
\]

(5)
or, alternatively,

\[
\delta F[\rho_0, \lambda \delta \rho] = F[\rho_0 + \lambda \delta \rho] - F[\rho_0]
\]

\[
= \lambda dF[\rho_0, \delta \rho] + \omega(\rho_0, \lambda \delta \rho),
\]

(6)

where

\[
\lim_{\lambda \rightarrow 0} \frac{\omega(\rho_0, \lambda \delta \rho)}{\lambda} = 0.
\]

(7)

In principle, this differential depends on the direction \( \delta \rho \), and it needs to be neither linear nor continuous in \( \delta \rho \). Generally, it can be expressed as

\[
dF[\rho_0, \delta \rho] = \int dr F'(\rho_0, \delta \rho, r) \delta \rho(r),
\]

(8)

where \( F'(\rho_0, \delta \rho, r) \) is a function of \( r \)—not necessarily continuous—and a functional of \( \rho \) as well as of \( \delta \rho \). If the differential is linear and continuous in \( \delta \rho \), then \( F' \) must be independent of \( \delta \rho \), and the differential can be expressed as

\[
dF[\rho_0, \delta \rho] = \int dr F'([\rho_0], r) \delta \rho(r).
\]

(9)

\( F'([\rho_0], r) \) is here a local, finite, multiplicative function of \( r \) that is single valued for given \( \rho_0 \) and conventionally referred to as the Gâteaux derivative of the functional \( F \) at the density \( \rho_0 \) \([25, p. 46, [6, Eq. (61)]\):

\[\text{B. Fréchet derivative}\]

The Fréchet or strong differential \( dF[\rho_0, \delta \rho] \) can be defined \([25, p. 37, [26, \text{p. 292]} as]

\[
\delta F[\rho_0, \delta \rho] = F[\rho_0 + \delta \rho] - F[\rho_0] = dF[\rho_0, \delta \rho] + \omega(\rho_0, \delta \rho),
\]

(11)

where

\[
\lim_{\|\delta \rho\| \rightarrow 0} \frac{\omega(\rho_0, \delta \rho)}{\|\delta \rho\|} = 0.
\]

(12)

Here, the limit has to be uniform in the neighborhood of the density \( \rho_0 \). The Fréchet differential can also be expressed in the form (9) with the derivative in the form of a local potential function \([25, p. 41]\).

The criterion for Fréchet differentiability (12) is stronger than the corresponding Gâteaux criterion (7). If the Gâteaux derivative exists in the neighborhood of a density and is uniformly continuous in this neighborhood, then the Gâteaux derivative at that density is also a Fréchet derivative \([25, p. 47, [26, \text{p. 295}]\). This requires that the functional is defined also for unnormalized densities. In DFT it is possible to stay within the normalization domain, and then Gâteaux differentiability is sufficient.

In the next section we shall summarize the basics of the Kohn-Sham model as a background of the locality analysis. (For further details regarding the basic theory, see, e.g., Refs. \[20,21,27,6\].)

III. HOHENBERG-KOHN-SHAM MODEL

A. Hohenberg-Kohn theorem

The Hohenberg-Kohn universal functional \([1] \) is in the constrained-search formulation given by\(^2\)

\[
F_{\text{HK}}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle = T_{\text{HK}}[\rho] + W_{\text{HK}}[\rho].
\]

(13)

Here, \( \hat{T} \) and \( \hat{W} \) represent the kinetic-energy and electron-electron-interaction operators of the \( N \)-electron system, respectively:

\[
\hat{T} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2, \quad \hat{W} = \sum_{i<j}^{N} \frac{1}{|r_i - r_j|}.
\]

(14)

The normalized wave function \( \Psi \) belongs to the Sobolev space \( H^1(\mathcal{R}^3)\) \([28,5,11,6]\), and the corresponding functional is defined for all \( N \)-representable densities \([21]\).

The HK energy functional of a system with an external, local potential \( v(r) \) is

\[\text{This is known as the Levy-Lieb functional and is sometimes denoted } F_{\text{LL}}[\rho].\]
\[ E_v[\rho] = F_{\text{HK}}[\rho] + \int dr \rho(r) v(r), \]

and the energy \( E_{v0} \), and the electron density \( \rho_0(r) \), of the ground state (or the lowest eigenstate of certain symmetry [29]) are obtained by minimizing this functional over normalized densities [21]:

\[ E_{v0} = \min_{\rho \rightarrow N} E_v[\rho] = E_v[\rho_0]. \]

As in our previous works [10,11], we shall extend the definition of the HK functional (13) in a straightforward way by allowing the wave functions to vary also outside the normalized domain of the Sobolev space, which is needed in order to be able to apply the Euler-Lagrange procedure. The minimization then leads to the Euler-Lagrange, (EL) equation

\[ \frac{\delta F_{\text{HK}}[\rho]}{\delta \rho(r)} + v(r) = \mu, \]

where \( \mu \) is the Lagrange parameter for the normalization constraint, \( \int dr \rho(r) = N \).

If we omit the electron-interaction part \( \hat{W} \) of the HK functional (13), then the EL equation (17) is quite analogous to the Thomas-Fermi equation for noninteracting electrons, Eq. (3). The kinetic part \( T_{\text{HK}}[\rho] \) of the HK functional (13) is then the kinetic-energy functional of the exact Thomas-Fermi model, which thus is a direct consequence of the HK theorem.

**B. Kohn-Sham model**

In the Kohn-Sham (KS) model, the interacting system is replaced by a system of noninteracting electrons, moving in the local Kohn-Sham potential \( v_{\text{KS}}(r) \):

\[ \left[ -\frac{1}{2} \nabla^2 + v_{\text{KS}}(r) \right] \phi_i(r) = \epsilon_i \phi_i(r). \]

The analog of the energy functional (15) is then

\[ E_v[\rho] = T_{\text{KS}}[\rho] + \int dr \rho(r) v_{\text{KS}}(r), \]

where

\[ T_{\text{KS}}[\rho] = \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} | \Phi \rangle, \]

and \( \Phi \) is a single-Slater-determinantal wave function in the same functional space as previously. Minimizing the energy functional leads in analogy with the Euler-Lagrange equation (17) to

\[ \frac{\delta T_{\text{KS}}[\rho]}{\delta \rho(r)} + v_{\text{KS}}(r) = \mu. \]

The two equations lead to the same solution if, apart from an additive constant,

\[ v_{\text{KS}}(r) = \frac{\delta F_{\text{HK}}[\rho]}{\delta \rho(r)} - \frac{\delta F_{\text{KS}}[\rho]}{\delta \rho(r)} + v(r). \]

If this potential were known, solving the KS equations self-consistently would, in principle, yield the exact electron density and, if the HK functional (15) were known, the exact total energy of the ground state—or the lowest state of a given symmetry. In addition, it has been shown that the eigenvalue of the highest occupied KS orbital yields the exact ionization energy [30–32,24].

A crucial point in the KS procedure is that the functionals involved are differentiable and that the functional derivative is in the form of a local potential function. This is now a well-established fact. In the standard DFT procedure, the variations are restricted to normalized densities, and then Gâteaux differentiability is sufficient. The Gâteaux differentiability of the functional (13) was rigorously demonstrated two decades ago by Englisch and Enßlisch [3,4], based upon works of Lieb [5], and the derivative was shown to be in the form of a local potential function.\(^3\) These results have recently been carefully confirmed by van Leeuwen [6]. By extending the definitions to unnormalized densities, as mentioned above, we have demonstrated that the functionals involved have a Gâteaux derivative according to the definition (9) above also in the extended domain. This derivative is—at least for practical purposes—also a Fréchet derivative\(^4\) [10,11,33].

**IV. NESBET’S LOCALITY DILEMMA AND ITS SOLUTION**

A. The problem

In his efforts to demonstrate that standard DFT is in conflict with fundamental physics, Nesbet considers the ground state—or lowest state of given symmetry—of a system of noninteracting electrons. For a two-electron system this can be represented by a determinantal wave function \( \Phi(r_1,r_2) \), composed of spin-orbitals with the space part satisfying the single-electron Schrödinger equation

\[ [\hat{\imath} + v(r)] \phi_i(r) = \epsilon_i \phi_i(r), \]

with \( \hat{\imath} \) being the kinetic-energy operator \( \hat{\imath} = -\frac{1}{2} \nabla^2 \) and \( v(r) \) a local external potential. For the kinetic energy and electron density of the system Nesbet uses the expressions

\[ T = \langle \phi_1 | \hat{\imath} | \phi_1 \rangle + \langle \phi_2 | \hat{\imath} | \phi_2 \rangle, \]

\[ \rho(r) = \rho_1(r) + \rho_2(r) = |\phi_1(r)|^2 + |\phi_2(r)|^2. \]

valid for normalized orbitals. By making small orbital changes \( \delta \phi \), the kinetic energy of the ground state is to leading order changed by [Eq. (9) in [18]]

\(^3\)The proof concerns the so-called Lieb functional, usually denoted \( F_\text{L}[\rho] \), which in the case of nondegenerate ground states we are concerned with here is identical to the functional (13).

\(^4\)This holds for calculations with finite basis set, where the kinetic energy has a finite upper bound, but it may not be rigorously true when the number of dimensions is infinite. (See Ref. [11] for a more detailed discussion.)
\[ dT = \int dr [\varepsilon_1 - v(r)] \delta \rho_1(r) + \int dr [\varepsilon_2 - v(r)] \delta \rho_2(r), \]  
(26) 

where 
\[ \delta \rho_\alpha(r) = \delta \phi_\alpha^*(r) \phi_\alpha(r) + \text{c.c.} \]

This is neither of the form (9) nor of the form (8) outside the domain of normalized orbitals [where \( \int dr \delta \rho_\alpha(r) \neq 0 \)] when the eigenvalues are different. Therefore, \( dT \) cannot be a differential of a density functional in this region, and no density-functional derivative exists, as we have demonstrated before [10]. Instead, Nesbet introduces orbital-dependent derivatives
\[ \frac{\delta T}{\delta \rho_\alpha(r)} = \varepsilon_\alpha - v(r) \]  
(27)

and interprets them as Gâteaux derivatives, which is obviously neither in accordance with the standard definition (9) above nor with the extended definition (8).

In spite of the fact that \( T \) is not a density functional in the extended domain, Nesbet applies the chain rule [see, e.g., Ref. [18], Eq. (13)]
\[ \frac{\delta T}{\delta \rho_\alpha} = \frac{\delta T}{\delta \rho_\alpha^*} \frac{\delta \rho_\alpha^*}{\delta \rho_\alpha} + \frac{\delta T}{\delta \rho_\alpha^*} \frac{\delta \rho_\alpha^*}{\delta \rho_\alpha}. \]  
(28)

Since Nesbet assumes that \( \rho(r) = \sum \rho_\alpha(r) \) according to Eq. (25), this simplified version of the chain rule can be used [cf. Eq. (35) below]. Together with the result (27) this leads to a conflict with the TF equation (3), if the orbital energies are different:
\[ \varepsilon_1 \neq \varepsilon_2 \Rightarrow \frac{\delta T}{\delta \rho_1} \neq \frac{\delta T}{\delta \rho_2}. \]  
(29)

The reason for the conflict is that the kinetic-energy expression (24), which obviously is an orbital functional, is not a density functional outside the domain of normalized orbitals when the eigenvalues are different. Therefore, the chain rule (28) cannot be used in that region, and the conflict is only apparent, as we have demonstrated before [10,11] and emphasized also by Holas and March [8]. We shall now indicate how this conflict can be resolved.

**B. The solution**

In the treatment of Nesbet the density variations are allowed to go outside the normalization domain. At the same time it is emphasized that the kinetic-energy expression should be an orbital as well as a density functional, which, of course, has to be the case also in the extended domain.

The kinetic energy and the electron density are not a priori defined outside the normalization domain, and we have to choose a proper extension. A natural extension is simply to use the standard expressions also outside the normalization [10,11].
\[
\frac{\delta T}{\delta \phi_i(r)} = \left[ \frac{\delta T}{\delta \rho(r)} (\phi_2 | \phi_2) + (\phi_2 | \frac{\delta T}{\delta \rho} | \phi_2) \right] \phi_i(r). \tag{36}
\]
This is compared with the direct orbital derivation [10]

\[
\frac{\delta T}{\delta \phi_i(r)} = \left[ (e_1 + e_2 - \nu(r)) (\phi_2 | \phi_2) - (\phi_2 | \nu | \phi_2) \right] \phi_i(r),
\]
and identification yields the same expression for the derivative as before, Eq. (33). Thus, by using proper expressions and using the chain rule in a proper way, the conflict observed by Nesbet between direct orbital derivation and the chain rule has disappeared.

### C. Comments

The basic claim of Nesbet is that “density functional derivatives of the Hohenberg-Kohn universal functional cannot be equivalent to local potential functions, as assumed in established literature [20,21], for more than two electrons in a compact electronic system” [34], and it is concluded that “the TF theory is not equivalent to Kohn-Sham theory, even if the exact Hohenberg-Kohn universal functional were known and used” [17].

Reference is made to the “well-known failure” of Thomas-Fermi theory to describe the atomic shell structure. This failure is unknown to us—unless, of course, it refers to the trivial case of the original approximation (2) from the 1920s. According to the HK theorem, an exact kinetic-energy functional does exist (\(T_{HK}[\rho]\), in Eq. (13)), but to our knowledge no approximation to the functional beyond the original approximation has been constructed and tested.

A related question addressed by Nesbet is that the Euler-Lagrange equation, like the TF equation (3) or the HK equation (17), with a single Lagrange parameter cannot lead to electronic shell structure. In a recent paper [35] it is stated that “the exclusion principle requires independent normalization of the orbital partial densities”. Without such independent normalization Nesbet claims that the electronic wave function will collapse to the lowest single-electron state.

In the Appendix we have given an elementary counterargument by deriving the standard Hartree-Fock equations for a two-electron system with a single parameter for the normalization of the total wave function. This obviously leads to shell structure, and there is no collapse into the lowest electronic state [12]. Parameters for normalization of individual shells are not needed if orbital overlap integrals are included in the expression to be minimized.

The standard way of deriving the HF equations is, of course, to introduce Lagrange multipliers for the orthonormality condition. Here, however, we want to emphasize that there exist two equivalent ways of performing a minimization by means of orbital variations, either by enforcing orthonormality by means of Lagrange multipliers, omitting orbital normalization and overlap integrals, or by maintaining these integrals together with a single Lagrange parameter for the overall normalization (and performing the orthonormalization afterwards, if desired). In our DFT work we used the latter method.

The reason for the failure of standard DFT is according to Nesbet that the treatment is restricted to normalized densities [34,36]. The Euler-Lagrange procedure requires the functional to be defined also in infinitesimal neighborhoods of such densities. This is regarded as a crucial limitation of the \textit{Hohenberg-Kohn theory}. It is assumed that the normalization constraint “hides” the additional parameters needed to generate shell structure. The conclusion is that a correct theory can only be developed using functional derivatives of orbital densities with \textit{nonlocal} potentials.

We have shown [10,11] that restricting the treatment to normalized densities constitutes no limitation. Extending the treatment to the unnormalized domain leads to identical results—no “hidden” parameters are uncovered.

That DFT is complete without any additional parameters has also been demonstrated among others by Perdew and Levy [24], who emphasize that “the exact functionals themselves (and not extraneous constraints) are responsible for the shell structure.”

Our analysis reconfirms the well-established result that \textit{DFT with local potential is inherently exact}. The same conclusion, using different lines of arguments, is reached by Holas and March in their recent analysis [9].

### V. Numerical Demonstration of Locality

As a further demonstration of the validity of the locality theorem, we have, using the method of van Leeuwen and Baerends [37], constructed numerically the local Kohn-Sham potential for the 1s2s2p3s state of neutral helium—a state often used by Nesbet to demonstrate the breakdown of this principle. Our starting point is the density generated by an accurate many-body wave function, obtained by means of our all-order pair procedure [38]. The potential is constructed so that the Kohn-Sham orbitals generate the many-body density very accurately. The energy eigenvalue of the 2s Kohn-Sham orbital is then found to be \(-0.175229388\) a.u., which agrees with the negative of the many-body ionization energy, \(-0.175229389\) a.u., within our numerical accuracy of nine digits [39]. This \textit{result verifies that a single local potential can generate essentially exact results, also for electrons with different energy eigenvalues, and that there is no conflict between the locality theorem and the exclusion principle}, as claimed by Nesbet. Related results (with less numerical accuracy) have been obtained by many groups in the past [31,40–47]. In addition to verifying the locality theorem, our result represents another numerical verification of the so-called ionization-potential theorem, stating that the eigenvalue of the highest occupied Kohn-Sham orbitals agrees with the negative of the corresponding ionization energy [30–32,24,48].

We have obtained similar result with the Hartree-Fock density, which also can be reproduced by a local Kohn-Sham potential. The eigenvalue of the KS 2s orbital then agrees with the HF value with essentially the same accuracy as in the previous case. This demonstrates that it is possible to represent exchange—in the DFT sense—by a local potential.

The latter result is in sharp contrast to the conclusions drawn, for instance, by Nesbet and Colle [52–54,19], who
conclude that the Kohn-Sham model with a local potential can never be exact and, in particular, that a local potential can never be better than the optimized-potential method of Talman and Shadwick [55]. This potential in turn yields higher ground-state energy than the Hartree-Fock model, as measured by the expectation value of the Hamiltonian \( \langle \Psi | \hat{H} | \Psi \rangle \), and this is supposed to confirm the failure of the locality theorem for exchange. A comparison of this kind is, of course, of no value, since the energy in DFT is given by the HK energy functional—not by \( \langle \Psi | \hat{H} | \Psi \rangle \). Needless to say, though, a local potential can never in all respects reproduce the nonlocal exchange.

Our results provide counterexamples to Nesbet’s conclusions drawn in several papers [19,36], that a correct theory can only be developed using orbital-functional theory with nonlocal potentials. We have demonstrated that density-functional theory with local potential is exact—but, of course, not identical to orbital-functional theory with nonlocal potential.

VI. SUMMARY

In summary, we have reconfirmed that the locality theorem is virtually exact, implying that the derivatives of large classes of density functionals are strictly local. The conflict with the exclusion principle, claimed by Nesbet, is only apparent and is eliminated by using expressions that are density functionals also outside the orbital normalization. Our conclusion is supported by accurate numerical results.

Note added. Recently we became aware of a very recent paper by Harbola [49], based upon works of Görling [50] and of Levy and Nagy [51], which deals with a problem quite similar to that considered in Sec. V.

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APPENDIX: FERMI-DIRAC STATISTICS WITH A SINGLE LAGRANGE MULTIPLIER

In this appendix we want to demonstrate in an elementary way that it is possible to satisfy the conditions for Fermi-Dirac statistics in a variational procedure with only a single Lagrange multiplier. We shall do that by minimizing the expectation value of the Hamiltonian \( \langle \Psi | \hat{H} | \Psi \rangle \) under the condition that the total wave function \( \Psi \) be normalized, \( \langle \Psi | \Psi \rangle = 1 \), and show that this leads to the standard Hartree-Fock equations. No additional parameters are needed. Fermi-Dirac statistics is enforced by demanding that the two-electron wave function is antisymmetric.

Generally, the solution of the problem is found by demanding that

\[
L[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle - E \langle \Psi | \Psi \rangle
\]

be stationary with \( E \) being the Lagrange multiplier for the normalization of \( \Psi \). This leads to the Schrödinger equation

\[
\hat{H} \Psi = E \Psi, \quad \langle \Psi | \Psi \rangle = 1.
\]

We consider now a two-electron system in a state where the electrons are in different orbitals, such as the lowest triplet state \( 1s2s^3S \). The antisymmetric wave function can be expressed in terms of spin-orbitals \( \phi_a \) and \( \phi_b \):

\[
\Psi_{\text{HF}}(1,2) = \frac{1}{\sqrt{2}}(\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)).
\]

The Hamiltonian \( \hat{H} \) is here

\[
\hat{H} = h_0(1) + h_0(2) + \frac{1}{r_{12}}.
\]

Using Eq. (A3), the functional (A1) now becomes an orbital functional

\[
L[\Psi_{\text{HF}}] = L[\phi_a, \phi_b] = \langle a | h_0 | a \rangle \langle b | b \rangle + \langle a | a \rangle \langle b | h_0 | b \rangle - \langle a | h_0 | b \rangle \langle b | a \rangle - \langle a | b | h_0 | a \rangle
\]

\[
+ \left\langle ab \frac{1}{r_{12}} ab \right\rangle - \left\langle ab \frac{1}{r_{12}} ba \right\rangle - E(\langle a | a \rangle \langle b | b \rangle - \langle a | b | a \rangle),
\]

which should be stationary under independent small variations of the orbitals. So the conditions \( \delta L / \delta \phi_a = 0 \) and \( \delta L / \delta \phi_b = 0 \) lead to the orbital equations

\[
h_0 | a \rangle \langle b | + | a \rangle \langle h_0 | b \rangle | b \rangle - h_0 | b \rangle \langle b | a \rangle - | b \rangle \langle h_0 | a \rangle
\]

\[
+ \left\langle b \frac{1}{r_{12}} b \right\rangle | a \rangle - \left\langle b \frac{1}{r_{12}} a \right\rangle | b \rangle = E(\langle a | b \rangle - | b \rangle \langle a | b \rangle), \quad (A6a)
\]

\[
h_0 | b \rangle \langle a | + | b \rangle \langle h_0 | a \rangle | a \rangle - h_0 | a \rangle \langle a | b \rangle - | a \rangle \langle h_0 | b \rangle
\]

\[
+ \left\langle a \frac{1}{r_{12}} a \right\rangle | b \rangle - \left\langle a \frac{1}{r_{12}} b \right\rangle | a \rangle
\]

\[
= E(\langle b | a \rangle - | a \rangle \langle b | a \rangle), \quad (A6b)
\]

while \( \delta L / \delta \phi_a = 0 \) and \( \delta L / \delta \phi_b = 0 \) lead to equivalent complex conjugate equations.

Although the normalized two-electron wave function is unique (up to a phase factor of modulus 1), the orbitals are not. They need not be individually normalized and/or orthogonal. If we have found orbitals that satisfy the equations above, however, we can easily transform them to become orthonormal without changing the two-electron wave function. Denoting the transformed orbitals again as \( | a \rangle \) and \( | b \rangle \) for brevity, we insert their properties
\[ \langle a | a \rangle = \langle b | b \rangle = 1, \quad (A7a) \]
\[ \langle a | b \rangle = \langle b | a \rangle = 0, \quad (A7b) \]

into Eqs. (A6a) and (A6b) to obtain
\[ h_0|a\rangle + \frac{1}{r_{12}} \langle a | h_0 | b \rangle - \frac{1}{r_{12}} \langle b | h_0 | a \rangle = 0, \quad (A8a) \]
\[ h_0|b\rangle + \frac{1}{r_{12}} \langle b | h_0 | a \rangle - \frac{1}{r_{12}} \langle a | h_0 | b \rangle = 0, \quad (A8b) \]

which are equivalent to the familiar HF equations
\[ h_0|a\rangle + \frac{1}{r_{12}} \langle a | b \rangle = e_a|a\rangle + e_{ab}|b\rangle, \quad (A9a) \]
\[ h_0|b\rangle + \frac{1}{r_{12}} \langle b | a \rangle = e_b|b\rangle + e_{ab}|a\rangle, \quad (A9b) \]

if we denote some combinations of constants as
\[ e_a = E - \langle b | h_0 | b \rangle, \quad (A10a) \]
\[ e_b = E - \langle a | h_0 | a \rangle, \quad (A10b) \]

\[ e_{ab} = \langle a | h_0 | b \rangle = e^*_{ba}. \quad (A10c) \]

By projecting Eq. (A8a) onto \( \langle a | \) or Eq. (A8b) onto \( \langle b | \)
the value of the Lagrange multiplier \( E \) becomes
\[ E = \langle a | h_0 | a \rangle + \langle b | h_0 | b \rangle + \left( \frac{1}{r_{12}} \langle a | b \rangle - \frac{1}{r_{12}} \langle b | a \rangle \right), \quad (A11) \]

which shows that \( E \) corresponds to the total energy, \( E = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle \). By inserting this value into Eqs. (A10a) and (A10b) we also get the orbital energies \( e_a \) and \( e_b \):
\[ e_a = \langle a | h_0 | a \rangle + \left( \frac{1}{r_{12}} \langle a | b \rangle - \frac{1}{r_{12}} \langle b | a \rangle \right), \quad (A12a) \]
\[ e_b = \langle b | h_0 | b \rangle + \left( \frac{1}{r_{12}} \langle b | a \rangle - \frac{1}{r_{12}} \langle a | b \rangle \right). \quad (A12b) \]

An alternative form of the total energy (A11) is therefore
\[ E = e_a + e_b - \left( \frac{1}{r_{12}} \langle a | b \rangle - \frac{1}{r_{12}} \langle b | a \rangle \right). \quad (A13) \]

Note that it is not possible to introduce the simplification—i.e., orbitals transformed into orthonormal orbitals—already in Eq. (A5), before the variation. That would not lead to meaningful orbital equations. It is the variation of the overlap integrals that is responsible for making the orbital energies \( e_a \) and \( e_b \) different.

I. LINDGREN AND S. SALOMONSON

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