# UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

## Colegio de Ciencias e Ingenierías

# Stability of finite subspaces in density functional theory: Application to simple atoms
### Proyecto de Investigación
.

# Yessenia Denisse Carrillo Toapanta

## Química

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**Stability of finite subspaces in density functional theory:
Application to simple atoms**

## Yessenia Denisse Carrillo Toapanta

Calificación:

Nombre del profesor, título académico          Javier Torres, Ph.D.

Firma del profesor

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Nombres y apellidos:   Yessenia Denisse Carrillo Toapanta

Código:       00127666

Cédula de Identidad:   1720434529

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# RESUMEN

Examinamos la validez del primer teorema de Hohemberg-Kohn, es decir, la relación uno a uno entre un potencial externo y la densidad de una partícula, cuando esta es aplicada a subespacios finitos y considerar la estabilidad de estos subespacios con respecto a potenciales externas.  Esto se realiza mediante el análisis de la descripción de DFT de algunos átomos simples (ejemplo, H, He, Li y Be) provistos por la solución de la ecuación de Kohn-Sham en un conjunto finito de bases de Gausian. Se muestra que, en el subespacio finito generado a partir del conjunto de bases finitas, es posible construir potenciales externos que difieren de una a otra por más de una constante, pero que se asocian con la misma densidad de una partícula. Llevamos a cabo la construcción específica de estos potenciales para los átomos anteriores usando funciones de onda resultantes a partir de la aplicación del funcional B3LYP. Comentamos el hecho de que estos potenciales de inestabilidad parecen ser prominentes solo en la región exterior del átomo donde la densidad tiende a cero. También se discute las implicaciones que los potenciales de inestabilidad tienen una relación con el formalismo y las ecuaciones de Kohn-Sham.

Palabras clave: primer teorema HK, conjunto de bases finitas, subespacios, espacio de Hilbert.

# ABSTRACT

We examine the validity of the first Hohenberg-Kohn theorem, namely, the one-to-one relationship between an external potential and the 1-particle density, when it is applied to finite subspaces and consider the stability of these subspaces with respect to external potentials. This is done by analyzing the DFT description of some simple atoms (eg, H, He, Li, and Be) provided by the solution of the Kohn-Sham equation in a finite Gaussian basis set. We show that in the finite subspace generated from the finite basis set, it is possible to construct external potentials that differ from one another by more than a constant, but which associate with the same 1-particle density. We carry out the specific construction of these potentials for the above atoms using the wave functions resulting from the application of the B3LYP functional. We comment on the fact that these instability potentials seem to be prominent only in the outer region of the atom where the density tends to zero. We also discuss the implications that the instability potentials have in relation to the Kohn-Sham formalism and equations.

*Key words*: first HK theorem, finite basis set, subspaces, Hilbert space.

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# Stability of finite subspaces in density functional theory: Application to simple atoms

**F. J. Torres**[1,2] (ORCID) | **E. V. Ludeña**[3] | **Y. Carrillo**[1] | **L. Rincón**[1] | **P. Iza**[2] | **D. Zambrano**[2]

[1]Universidad San Francisco de Quito (USFQ), Instituto de Simulación Computacional (ISC-USFQ) and Grupo de Química Computacional y Teórica (QCT-USFQ), Departamento de Química e Ingeniería Química, Diego de Robles s/n Vía Interoceánica, Quito 17-1200-841, Ecuador

[2]Departamento de Física, Facultad de Ciencias Naturales y Matemáticas, Escuela Superior Politécnica del Litoral, ESPOL, Km 30.5 Vía Perimetral, Guayaquil, Ecuador

[3]Center of Nanotechnology Research and Development, CIDNA, Escuela Superior Politécnica del Litoral, ESPOL, Km 30.5 Vía Perimetral, Guayaquil, Ecuador

**Correspondence**
Eduardo Vicente Ludena, Instituto Venezolano de Investigaciones Cientificas, IVIC, Chemistry, Quimica, IVIC, Apartado 21827, Caracas 1020-A, Venezuela.
Email: popluabe@yahoo.es

**Abstract**
We examine the validity of the first Hohenberg-Kohn theorem, namely, the one-to-one relationship between an external potential and the 1-particle density, when it is applied to finite subspaces and consider the stability of these subspaces with respect to external potentials. This is done by analysing the DFT description of some simple atoms (eg, H, He, Li, and Be) provided by the solution of the Kohn-Sham equation in a finite Gaussian basis set. We show that in the finite subspace generated from the finite basis set, it is possible to construct external potentials that differ from one another by more than a constant but which associate with the same 1-particle density. We carry out the specific construction of these potentials for the above atoms using the wave functions resulting from the application of the B3LYP functional. We comment on the fact that these instability potentials seem to be prominent only in the outer region of the atom where the density tends to zero. We also discuss the implications that the instability potentials have in relation to the Kohn-Sham formalism and equations.

**KEYWORDS**
first HK theorem, finite basis set, subspaces, Hilbert space

## 1 | INTRODUCTION

Although methods based on density functional theory (DFT),[1-28] are among those most employed for electronic structure calculations of both crystalline and molecular systems,[29-31] DFT in itself cannot be considered to have reached yet a stage of full elaboration.[15,17,19,32,33] The reason for such statement is that there are still foundational questions not fully clarified at the level of the Hohenberg-Kohn, HK, theorems.[34]

One of these questions has to do with the conditions that must be fulfilled in order to extend the range of validity of the first HK theorem to finite subspaces. It must be mentioned that the latter is not to be considered merely an academic question since the validity of the first HK theorem in finite subspaces is of paramount importance in two particular aspects related to the development and practical application of DFT: (1) it has to be acknowledged, on the one hand, that most DFT approaches (eg, electronic structure calculations) are usually performed in a subspace of the Hilbert space that emerges because the Kohn-Sham N-particle wave function is constructed from Kohn-Sham orbitals, which in turn, are expanded in terms of a finite basis set of well-defined single-particle functions; and, on the other hand, (2) the fulfillment of the first HK theorem is a fundamental requirement for the formulation of the second HK theorem, which states that the exact ground-state energy of an N-Fermion system can be computed by minimizing a universal energy functional solely expressed in terms of 1-electron density, an idea that allows the design and implementation of computational algorithms.

When extending the HK first theorem to finite subspaces, particular attention must be paid to the stability conditions that the subspace must satisfy in order to guarantee the fulfillment of this theorem. Some of these restrictions have been given by Epstein et al.,[35] Katriel et al.,[36] Harriman,[37] and more recently by Pino et al.[38,39] According to Pino et al., one way to satisfy these conditions in a finite subspace is to have $\Delta V$, defined as $\hat{H}_{v'} - \hat{H}_v \equiv V' - V$, equal to a constant. However, it must be considered that there may be instability potentials (ie, $\Delta V \neq$ constant) that violate the subspace stability conditions, meaning that in a finite subspace, one can have external potentials $V'$ and $V$ that differ from each other by more than a constant and which still lead to the same 1-particle density.[39] Let us mention that the same non-uniqueness problem emerges when the exchange correlation potential is obtained from the 2-matrix by an inverse method.[40-44]

In the present work, we obtain KS solutions for the simple atoms H, He, Li, and Be by employing the B3LYP functional. The results are then used to generate a subspace of Hilbert space where we construct instability external potentials, that is, potentials that differ from the ordinary Coulomb external potential by more than a constant and which yield, nevertheless, the same ground-state 1-particle density. It must be mentioned that the present represents the first report on the subject that makes use of the DFT description of multielectronic atoms.

The structure of the paper is as follows: In Section 2, we briefly discuss extensions of the first HK theorem to finite subspaces and explicitly describe the procedure to generate instability potentials. In Section 3, we apply this procedure to each one of the atoms considered in this work and present numerical results. In Section 4 we consider the implications of instability potentials on the Kohn-Sham theory. In particular we discuss how these potentials affect the Kohn-Sham equations. Finally, in Section 5, we provide some final remarks and conclusions.

## 2 | CONSTRUCTION OF POTENTIALS ASSOCIATED WITH THE SAME GROUND STATE DENSITY

For the sake of completeness, we present here some aspects of the first HK theorem already discussed in Refs. [38] and [39]. Consider a system formed by $N$ electrons interacting with an external potential

$$V(\mathbf{r_1} \ldots \mathbf{r_N}) = \sum_{i=1}^{N} v(\mathbf{r_i}) \tag{1}$$

whose Hamiltonian is given by

$$\hat{H}_v = \hat{H}_0 + \hat{V} \tag{2}$$

and where the internal Hamiltonian $\hat{H}_0$ is:

$$\hat{H}_0 = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{\mathbf{r_i}}^2 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|} \tag{3}$$

It is important to assume, as noted by Lieb,[45,46] that $v(\mathbf{r}) \in Y$, where $Y$ is Lieb's class, defined by $Y = L^{3/2} + L^{\infty}$. This implies that $v(\mathbf{r}) = v_{3/2}(\mathbf{r}) + v_{\infty}(\mathbf{r})$, with $v_{3/2}(\mathbf{r}) \in L^{3/2}$ and $v_{\infty}(\mathbf{r}) \in L^{\infty}$ (for a set of continuous functions $f(\mathbf{r})$, $f(\mathbf{r}) \in L^m$ if $\int d\mathbf{r} |f(\mathbf{r})|^m < \infty$). If we can associate to the above Hamiltonian a ground state wave function $\Psi_0^v(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N})$, then the ground-state 1-electron density is defined as follows:

$$\rho_0^v(\mathbf{r}) = \int d^3\mathbf{r_1} \int d^3\mathbf{r_2} \ldots \int d^3\mathbf{r_N} |\Psi_0^v(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}|^2 \sum_{i=1}^{N} \delta(\mathbf{r_i} - \mathbf{r}) = N \int d\mathbf{r_2} \ldots \int d\mathbf{r_N} |\Psi_0^v(\mathbf{r}, \mathbf{r_2}, \ldots, \mathbf{r_N})|^2 \tag{4}$$

and, in that case, the first HK theorem states that there exists a one-to-one correspondence between the external potential $v(\mathbf{r_i})$ and the exact ground-state density $\rho_0^v(\mathbf{r})$. In 1983, Lieb[46] pointed out that the original proof of this theorem, carried out by *reductio ad absurdum*, had some inherent difficulties, which implied that a revision of the first HK theorem's proof was required in order to circumvent them. In this vein, an alternative proof was presented by Pino et al.[38] for the case of infinite spaces which was then extended to the case of finite subspaces. In the following, some of the basic aspects of this extension are described:

Consider the external potentials $v(\mathbf{r}) \in Y$ and $v\prime(\mathbf{r}) \in Y$ which define through Equation 2 the Hamiltonians $\hat{H}_v$ and $\hat{H}_{v\prime}$, respectively. Let $F \subset \mathcal{L}_N$ be a finite subspace of the Hilbert space $\mathcal{L}_N$ of the antisymmetric, square-integrable N-electron wave functions, defined by:

$$F = \{\Psi_I^v(x) | I = 0, \ldots, M; \int dx \Psi_I^{v*}(x) \Psi_J^v(x) = \delta_{IJ}; \sum_{I=0} |\Psi_I^v(x)|^2 > 0; x \in \mathbf{R}^N\} \tag{5}$$

where $\Psi_I^v(x) \equiv \Psi_I^v(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N})$. The dimension of $F$ is $M + 1$, and the orthogonal projector in $F$ is defined as:

$$\hat{P}_F = \sum_{I=0}^{M} |\Psi_I^v(x)> <\Psi_I^v(x)| \tag{6}$$

Let $E_0^v(M) \leq \ldots \leq E_M^v(M)$ be the ordered non-zero eigenvalues of $\hat{P}_F \hat{H}_v \hat{P}_F$. Then, the instability potential theorem of Refs. [38] and [39] states that there exists and external potential $v\prime(\mathbf{r}) \in Y$ such that $\hat{P}_F \hat{H}_v \hat{P}_F$ and $\hat{P}_F \hat{H}_{v\prime} \hat{P}_F$ have the same ground state for $\Delta V = V\prime - V \neq$ constant, or in view of Equation 1, $\Delta v = v\prime - v \neq$ constant.

In the subspace $F$, the functions $\{\Psi_I^v\}_{i=0}^{M}$ diagonalize the matrix $\underline{H}^v(M)$, formed by the elements $\underline{H}_{ij}^v(M) = <\Psi_i^v|\hat{H}_v|\Psi_j^v>$. In other words, these elements satisfy:

$$\underline{H}_{IJ}^v(M) = E_I^v(M)\delta_{IJ} \tag{7}$$

Note that these conditions are satisfied by the set $\{\Psi_I^v\}_{I=0}^{M}$ formed by the first $M$ solutions of the Schrödinger equation in the full antisymmetric Hilbert space. But in the present case, we assume that the set $\{\Psi_I^v\}_{I=0}^{M}$ is formed by the N-particle wave functions that diagonalize the Hamiltonian $\hat{H}_v$ over the subspace $F$.

Consider now the Hamiltonian matrix $\underline{H}^{v'}(M)$, associated with the projected Hamiltonian $\hat{P}_F\hat{H}_{v'}\hat{P}_F$. The matrix elements for the first row (and column) are:

$$\underline{H}^{v'}_{0l}(M)=\langle\Psi^v_0|\hat{H}_{v'}|\Psi^v_l\rangle \tag{8}$$

Since the Hamiltonian operators are related through the expression:

$$\hat{H}^{v'}=\hat{H}^v+\Delta V \tag{9}$$

we have

$$\begin{aligned}\underline{H}^{v'}_{0l}(M)&=\langle\Psi^v_0|\hat{H}_v|\Psi^v_l\rangle+\langle\Psi^v_0|\Delta V|\Psi^v_l\rangle\\&=E^v_0(M)\delta_{0l}+\int d^3\mathbf{r}\Delta v(\mathbf{r})\rho_{0l}(\mathbf{r})\end{aligned} \tag{10}$$

where

$$\rho_{0l}(\mathbf{r})=\int d^3\mathbf{r_2}\dots\int d^3\mathbf{r_N}\Psi^v_0(\mathbf{r},\mathbf{r_2},\dots,\mathbf{r_N})\Psi^v_l(\mathbf{r},\mathbf{r_2},\dots,\mathbf{r_N}) \tag{11}$$

The proof by construction of the instability theorem proceeds by taking $\Delta v(\mathbf{r})\in Y$ non-constant and requiring that

$$\int d^3\mathbf{r}\Delta v(\mathbf{r})\rho_{0l}(\mathbf{r})=0,\qquad\text{for}\quad l=0,\dots,M \tag{12}$$

where $\Delta v(\mathbf{r})$ is expressed by means of a linear combination of linearly independent functions $\{h_j(\mathbf{r})\}^{M+1}_{j=0}$ as:

$$\Delta v(\mathbf{r})=\sum^{M+1}_{j=0}c_jh_j(\mathbf{r})=c_{M+1}\sum^{M+1}_{j=0}a_jh_j(\mathbf{r}) \tag{13}$$

where $a_j=c_j/c_{M+1}$. Setting the arbitrary coefficient $c_{M+1}=1$ we can rewrite Equation 12 as:

$$\sum^{M}_{j=0}a_jA_{j,l}=-A_{M+1,l},\qquad\text{for}\quad l=0,\dots,M \tag{14}$$

where

$$A_{j,l}=\int d^3\mathbf{r}h_j(\mathbf{r})\rho_{0l}(\mathbf{r}) \tag{15}$$

$$A_{M+1,l}=\int d^3\mathbf{r}h_{M+1}(\mathbf{r})\rho_{0l}(\mathbf{r}) \tag{16}$$

As Equation 14 defines a set of $M+1$ linear equations with $M+1$ unknowns, this problem can be readily solved by algebraic methods and, as a result, the instability potential can be constructed. In fact, taking into account that the expansion functions $\{h_j(\mathbf{r})\}^{M+1}_{j=0}$ can be chosen at will, this procedure leads to an infinite number of such potentials. This point is illustrated below.

## 3 | NUMERICAL RESULTS AND DISCUSSION

### 3.1 | Generation of the subspace $F$

Although for the present application one may resort to the KS solutions obtained at any level of DFT, namely, from a variety of approximated functionals and finite basis sets, the B3LYP functional as implemented in the G09 suite of programs[47] was employed in this study. Moreover, for the purpose of avoiding the complexity that would arise from the use of Gaussian functions of higher angular momentum, all occupied and virtual KS orbitals of H, He, Li, and Be are represented as a linear combination of $m$ Gaussian s-type atomic functions.

$$\varphi_i(\mathbf{r})=\sum^m_{j=1}C_{ij}g_{js}(\alpha_j,\mathbf{r}) \tag{17}$$

where $g_{js}(\alpha_j,\mathbf{r})$ is given by:

$$g_{js}(\alpha_j,\mathbf{r})=\left(\frac{2\alpha_j}{\pi}\right)^{\frac{3}{4}}e^{-\alpha_j r^2} \tag{18}$$

As mentioned above, a set of 4 un-contracted primitive s-type Gaussian functions ($m=4$), referred to as BS-4G, was adopted to expand the KS atomic orbitals of H, He, Li, and Be. It is important to point out that the use of such a small basis set has the only purpose of proving the concept,

**TABLE 1** Gaussian parameters $\alpha_i$ and normalized orbital expansion coefficients for H, He, Li, and Be atoms for $m = 4$

| Atoms | $\alpha_i$ | $\varphi_{1s}$ | $\varphi_{2s}$ | $\varphi_{3s}$ | $\varphi_{4s}$ |
|---|---|---|---|---|---|
| H | 18.73113696 | 0.08560301 | 0.14791224 | 0.09124998 | 8.08351627 |
|  | 2.825394365 | 0.15269228 | 0.04786874 | $-2.29987410$ | $-1.59092901$ |
|  | 0.64012169 | 0.18289640 | 0.67440467 | 0.76417228 | 0.27810617 |
|  | 0.16127776 | 0.11909453 | $-0.23256445$ | $-0.10294077$ | $-0.03345203$ |
| He | 38.42227406 | 0.17785145 | $-0.12032745$ | $-0.15310403$ | 13.38945322 |
|  | 5.78228472 | 0.63845458 | $-0.34487284$ | $-2.83278342$ | $-2.05169707$ |
|  | 0.37192174 | 0.50321006 | $-1.26681636$ | 0.89222947 | 0.21394200 |
|  | 0.25646476 | $-0.16125861$ | 1.05912669 | $-0.54975310$ | $-0.12895706$ |
| Li | 36.83371926 | 0.73196072 | $-0.15696290$ | $-0.66898376$ | 13.07768411 |
|  | 5.45155505 | 1.02886516 | $-0.23393123$ | $-2.87219243$ | $-2.40905944$ |
|  | 0.95761562 | 0.45945036 | $-0.17176437$ | 0.78017009 | 0.23437529 |
|  | 0.06589269 | 0.00275014 | 0.097160667 | $-0.02219952$ | $-0.00507206$ |
| Be | 71.87209770 | 1.07508452 | $-0.19879652$ | 0.99890851 | 21.51453295 |
|  | 10.62472215 | 1.73530485 | $-0.37403801$ | 4.57846347 | $-3.79846965$ |
|  | 1.67683654 | 0.71275977 | $-0.21637575$ | $-1.12303668$ | 0.31675528 |
|  | 0.10203848 | 0.00099978 | 0.02863460 | 0.028634602 | $-0.0059781$ |

and the generality of the results would not be affected by employing more complex basis sets. In order to explore the validity of the latter statement, larger basis sets were tested for the simple hydrogen atom. The results obtained by employing an un-contracted Pople's 6-311G basis set ($m = 5$) as well as a basis set containing 8 un-contracted Gaussian s-type atomic functions ($m = 8$) are reported as Supporting Information (Figure S1 and Table S1). The values of the exponents $\alpha_i$ that minimize the total electronic energy computed with BS-4G were determined for each atom by means of the Levenberg-Marquardt algorithm implemented in a computational script designed to use directly G09 results. In Table 1, we present the values of the Gaussian parameters $\alpha_i$ and the expansion coefficients $C_{ij}$ used in the present work for the H, He, Li, and Be atoms.

For hydrogen ($^2S$), the set $\{\varphi_i(\mathbf{r})\}$ where $i = 1, \ldots, 4$ of Kohn-Sham orbitals already defines the basis $\Phi^v_{l(i)}$ with $l = 0, \ldots, M$ ($M = 3$) of the subspace $F$ (we emphasize in this notation the dependence on the external potential $v$).

For helium ($^1S$), there are 2 types of antisymmetrized 2-particle functions (ie, $S = 0$) that can be constructed from the set of $\{\varphi_i(\mathbf{r})\}_{i=1}^m$:

$$\Phi^v_{l(ii)}(\mathbf{r_1}, \sigma_1, \mathbf{r_2}, \sigma_2) = \varphi_i(\mathbf{r_1})\varphi_i(\mathbf{r_2})\frac{1}{\sqrt{2}}(\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)) \tag{19}$$

$$\Phi^v_{l(ij)}(\mathbf{r_1}, \sigma_1, \mathbf{r_2}, \sigma_2) = \frac{1}{\sqrt{2}}(\varphi_i(\mathbf{r_1})\varphi_j(\mathbf{r_2}) + \varphi_j(\mathbf{r_1})\varphi_i(\mathbf{r_2}))\frac{1}{\sqrt{2}}(\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)) \tag{20}$$

where $\Phi^v_{l(11)} \equiv \Phi^v_0$ is an approximation to the ground state wave function given in terms of a single determinant, corresponding to the configuration $1s^2$. The index $l(ij)$ spans the $M + 1$ values from 0 to $M$. In this case, since $i, j = 1, \ldots, 4$, with $i \leq j$ it follows that $M = 9$.

For the lithium atom ($^2S$), all the antisymmetrized wave functions formed from the orbital set $\{\varphi_i(\mathbf{r})\}_{i=1}^m$ are Slater determinants given by:

$$\Phi^v_{l(ijk)}(\mathbf{r_1}, \sigma_1, \mathbf{r_2}, \sigma_2, \mathbf{r_3}, \sigma_3) = \frac{1}{\sqrt{6}}\det\begin{vmatrix} \varphi_{is}(\mathbf{r_1})\alpha(\sigma_1) & \varphi_{js}(\mathbf{r_1})\beta(\sigma_1) & \varphi_{ks}(\mathbf{r_1})\alpha(\sigma_1) \\ \varphi_{is}(\mathbf{r_2})\alpha(\sigma_2) & \varphi_{js}(\mathbf{r_2})\beta(\sigma_2) & \varphi_{ks}(\mathbf{r_2})\alpha(\sigma_2) \\ \varphi_{is}(\mathbf{r_3})\alpha(\sigma_3) & \varphi_{js}(\mathbf{r_3})\beta(\sigma_3) & \varphi_{ks}(\mathbf{r_3})\alpha(\sigma_3) \end{vmatrix} \tag{21}$$

with $l(ijk) = 0, \ldots, M$, where $\Phi^v_0 \equiv \Phi_{l(112)}$. The set of Slater determinants $\{\Phi^v_{l(ijk)}\}$ for $l(ijk) = 0, \ldots, M$ which forms the basis of the subspace are generated by spanning over the values of $i, j, k = 1, \ldots, m$ subject to the conditions $i \leq j \leq k$ and $i \neq k$. In the present case for $m = 4$ we have $M = 15$.

Similarly, for beryllium ($^1S$) we have the set of 4-particle single Slater determinants $\{\Phi^v_{l(ijkl)}\}$ where $l(ijkl) = 0, \ldots, M$ and where $\Phi^v_0 \equiv \Phi^v_{l(1122)}$ are generated by spanning over the values $i, j, k, l = 1, \ldots, m$ subject to the conditions $i \leq j \leq k \leq l$ where additionally $i \neq k$ and $j \neq l$. For this 4-particle case, for $m = 4$ we have $M = 18$.

The sets $\{\Phi^v_l\}_{l=0}^M$ for H, He, Li, and Be atoms are used to construct the functions $\{\Psi^v_l\}_{l=0}^M$ such that the latter diagonalize the Hamiltonian matrix. As the functions $\Psi^v_l$ are given as linear combinations of the functions $\Phi^v_l$,
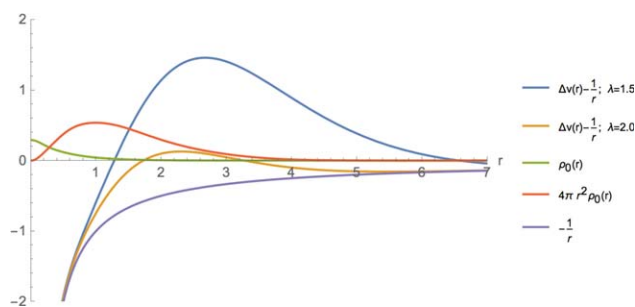
**FIGURE 1** Instability potentials $\Delta v(\mathbf{r}) - \frac{Z}{r}$ (see Equation 13) for H with $\lambda=1.5$ (blue) and $\lambda=2.0$ (orange). The ground state density $\rho_0$ (green) and the radial density $4\pi r^2 \rho_0$ (red) are also presented. For comparison, we also plot the Coulomb external potential $v(r)=-\frac{1}{r}$ (purple)

$$\Psi_I^v(r_1, \sigma_1, \ldots, r_N, \sigma_N) = \sum_{J=0}^{M} B_{IJ} \Phi_J^v(r_1, \sigma_1, \ldots, r_N, \sigma_N) \tag{22}$$

the variational coefficients of these expansions are determined by diagonalizing the Hamiltonian matrix $\underline{H}^v(\Phi)$ whose elements are $\underline{H}_{IJ}^v(\Phi) = <\Phi_I|\hat{H}_v|\Phi_J^v>$. Clearly since $\underline{H}^v(\Phi)$ is Hermitian it can be diagonalized by means of a unitary transformation

$$\underline{H}^v(M) = \underline{B}\,\underline{H}^v(\Phi)\underline{B}^{-1} \tag{23}$$

where $\underline{B}$ is a unitary matrix satisfying $\underline{B}\,\underline{B}^{-1}=1$ and $\underline{H}^v(M)$ is the matrix defined by Equation 7.

## 3.2 | Calculation of instability potentials

Two elements are necessary for the construction of instability potentials. One is the set of transition densities $\rho_{0I}(\mathbf{r})$ (see Equation 11) and the other is the selection of some expansion set $\{h_j(\mathbf{r})\}_{j=0}^{M+1}$. For the present examples, the expansion functions are defined by $h_j(\mathbf{r})=e^{-\lambda r}r^j$. Furthermore, bearing in mind Equation 22 the elements of the transition matrix are:

$$\rho_{0I}(\mathbf{r}) = \sum_{J=0}^{M} \sum_{K=0}^{M} B_{0J} B_{IK} S_{JK}(\mathbf{r}) \tag{24}$$

where

$$S_{JK}(\mathbf{r}) = \int d\sigma \int d\sigma_2 d^3\mathbf{r}_2 \ldots \int d\sigma_N d^3\mathbf{r_N} \\ \times \Phi_J^v(\mathbf{r}, \sigma, \mathbf{r_2}, \sigma_2 \ldots, \mathbf{r_N}, \sigma_N) \\ \times \Phi_K^v(\mathbf{r}, \sigma, \mathbf{r_2}, \sigma_2, \ldots, \mathbf{r_N}, \sigma_N) \tag{25}$$

For the case of the lithium atom, for example, where $J \equiv J(ijk)$ and $K \equiv K(pqr)$ label the corresponding Slater determinants given by Equation 21, we have the following explicit form of these matrix elements:

$$S_{JK}(\mathbf{r}) = \frac{1}{3}[\varphi_{is}(\mathbf{r})\varphi_{ps}(\mathbf{r})\delta_{jp}\delta_{kr} - \varphi_{is}(\mathbf{r})\varphi_{rs}(\mathbf{r})\delta_{jq}\delta_{kp} \\ + \varphi_{js}(\mathbf{r})\varphi_{qs}(\mathbf{r})\delta_{ip}\delta_{kr} - \varphi_{js}(\mathbf{r})\varphi_{qs}(\mathbf{r})\delta_{ir}\delta_{kp} \\ + \varphi_{ks}(\mathbf{r})\varphi_{rs}(\mathbf{r})\delta_{ip}\delta_{jq} - \varphi_{ks}(\mathbf{r})\varphi_{ps}(\mathbf{r})\delta_{ir}\delta_{jp}] \tag{26}$$

A similar expression may be readily derived also for the case of the beryllium atom, where $J \equiv J(ijkl)$ and $K \equiv K(pqrt)$ label the corresponding Slater determinants.

In Figures 1–4 we present plots for the instability potentials for the H, He, Li, and Be atoms, respectively. These potentials are calculated from Equations 14–16 for different choices of the parameter $\lambda$. For completeness, the external potentials $v=-Z/r$ and the 1-particle density for each one of the atoms considered here are also included.

## 4 | IMPLICATIONS FOR THE KOHN-SHAM EQUATIONS

Since in the present calculation of instability potentials, the 1-electron density is obtained by integration over $N-1$ coordinates of the square of the wave function, at first sight this procedure seems to be quite different from the familiar Kohn-Sham, KS, one where the density is computed as the sum of the squares of the occupied Kohn-Sham orbitals $\{\phi_i^v(\mathbf{r})\}_{i=1}^{N}$ corresponding to an external potential $v(\mathbf{r})$, namely,
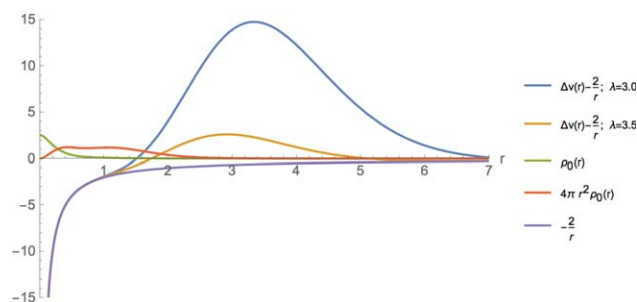
**FIGURE 2** Instability potentials $\Delta v(r) - \frac{Z}{r}$ (see Equation 13) for He with $\lambda=3.0$ (blue) and $\lambda=3.5$ (orange). The ground state density $\rho_0$ (green) and the radial density $4\pi r^2 \rho_0$ (red) are also presented. For comparison, we also plot the Coulomb external potential $v(r) = -\frac{2}{r}$ (purple)

$$\rho_0^v(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i^v(\mathbf{r})|^2 \tag{27}$$

In order to establish the connection between the construction of instability potentials and the Kohn-Sham procedure, let us consider the KS ground state wave function given by the single Slater determinant:

$$\Phi_0^{v,KS}(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{\det}{\sqrt{N!}} \{\phi_i^v(\mathbf{r}_1), \cdots, \phi_i^v(\mathbf{r}_N)\} \tag{28}$$

Consider the orthogonal projector $\hat{P}_F$ of Equation 6 defined in terms of the finite set of $N$-particle functions $\{\Psi_i^v\}_{i=0}^M$ and assume that $\Psi_0^v \equiv \Phi_0^{v,KS}$ and all remaining functions $\Psi_i^v$, $i=1, \cdots, M$ are orthogonal to $\Psi_0^v$ and, in addition, diagonalize the matrix $\underline{H}^v(M)$ whose elements are $\underline{H}_{ij}^v(M) = \langle \Psi_i^v | \hat{H}_v | \Psi_j^v \rangle$, where $\hat{H}_v$ is the $N$-particle Hamiltonian of Equation 2. Following the same recipe as in Section 2 we can construct, in the present case, instability potentials that satisfy Equation 12 and which, in particular, comply with the condition:

$$\int d^3\mathbf{r} \Delta v(\mathbf{r}) \rho_{00}(\mathbf{r}) \equiv \int d^3\mathbf{r} \Delta v(\mathbf{r}) \rho_0^v(\mathbf{r}) = 0 \tag{29}$$

Let us now show how this result has bearing on KS procedure. Consider the KS Hamiltonian

$$\hat{H}_v^{KS} = \hat{T} + V_s \tag{30}$$

where $\hat{T} = \sum_{i=1}^N \hat{t}(\mathbf{r}_i)$ with $\hat{t}(\mathbf{r}_i) = -(1/2)\nabla_{\mathbf{r}_i}^2$ and $V_s = V + V_{Coul} + V_{xc}^{KS} = \sum_{i=1}^N v_s(\mathbf{r}_i)$. If $V = \sum_{i=1}^N v(\mathbf{r}_i)$ is the external potential then the KS Hamiltonian for an external potential $V\prime$ may be written as:

$$\hat{H}_{v\prime}^{KS} = \hat{T} + V_s' = \hat{H}_v^{KS} + \Delta V \tag{31}$$

where $\Delta V = V\prime - V = \sum_{i=1}^N \Delta v(\mathbf{r})$ with $\Delta v(\mathbf{r}) = v\prime(\mathbf{r}) - v(\mathbf{r})$. These KS Hamiltonians satisfy the Schrödinger equations

$$\hat{H}_v^{KS} \Phi_0^{v,KS} = E_0^v \Phi_0^{v,KS} \tag{32}$$

$$\hat{H}_{v\prime}^{KS} \Phi_0^{v\prime,KS} = E_0^{v\prime} \Phi_0^{v\prime,KS} \tag{33}$$

In view of the fact that the KS Hamiltonian is the sum of 1-particle operators and that the KS wave function is a single Slater determinant, Equation 32 is equivalent to the system of KS single particle equations $\hat{h}_v^{KS}(\mathbf{r})\phi_i^v(\mathbf{r}) = \epsilon_i^v \phi_i^v(\mathbf{r})$ where $\hat{h}_v^{KS}(\mathbf{r}) = \hat{t}(\mathbf{r}) + v_s(\mathbf{r})$. Note that $E_0^v = \sum_{i=1}^N \epsilon_i^v$.
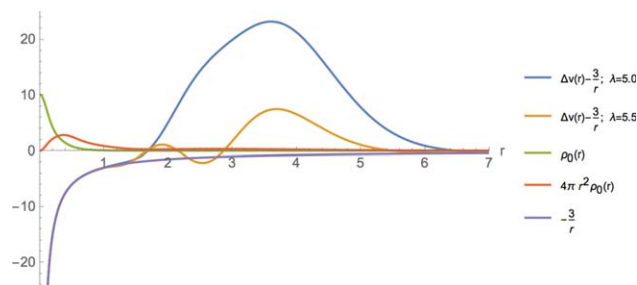
Let us consider



**FIGURE 3** Instability potentials $\Delta v(r) - \frac{Z}{r}$ (see Equation 13) for Li with $\lambda=5.0$ (blue) and $\lambda=5.5$ (orange). The ground state density $\rho_0$ (green) and the radial density $4\pi r^2 \rho_0$ (red) are also presented. For comparison, we also plot the Coulomb external potential $v(r) = -\frac{3}{r}$ (purple)
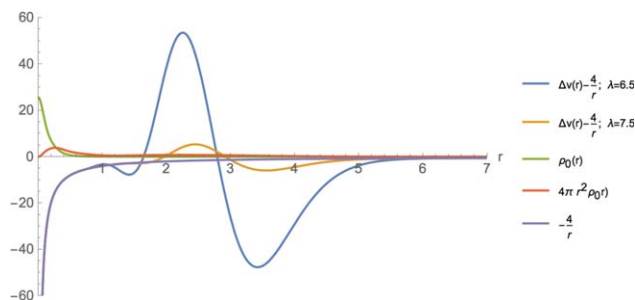
**FIGURE 4** Instability potentials $\Delta v(\mathbf{r}) - \frac{Z}{r}$ (see Equation 13) for Be with $\lambda=6.5$ (blue) and $\lambda=7.0$ (orange). The ground state density $\rho_0$ (green) and the radial density $4\pi r^2 \rho_0$ (red) are also presented. For comparison, we also plot the Coulomb external potential $v(r)=-\frac{4}{r}$ (purple)

$$<\Phi_0^{v,KS}|\hat{H}_{v'}^{KS}|\Phi_0^{v,KS}>=<\Phi_0^{v,KS}|\hat{H}_v^{KS}|\Phi_0^{v,KS}> \\ +<\Phi_0^{v,KS}|\Delta V|\Phi_0^{v,KS}> \tag{34}$$

Bearing in mind Equation 29 we have:

$$<\Phi_0^{v,KS}|\Delta V|\Phi_0^{v,KS}>=\int d^3\mathbf{r}\Delta v(\mathbf{r})\rho_0^v(\mathbf{r})=0 \tag{35}$$

Thus, we obtain from Equation 34

$$<\Phi_0^{v,KS}|\hat{H}_{v'}^{KS}|\Phi_0^{v,KS}>=E_0^v \tag{36}$$

Similarly, we have:

$$<\Phi_0^{v',KS}|\hat{H}_v^{KS}|\Phi_0^{v',KS}>=E_0^{v'} \tag{37}$$

We use these results to show by *reductio ad absurdum* that for a $\Delta v(\mathbf{r})$ obtained by the procedure indicated in this section and satisfying Equation 29, necessarily the wavefunctions corresponding to different potentials must be equal, namely, $\Phi_0^{v,KS}=\Phi_0^{v',KS}$.

Let us assume that $\Phi_0^{v,KS} \neq \Phi_0^{v',KS}$. By the variational principle we have the strict inequalities

$$<\Phi_0^{v',KS}|\hat{H}_v^{KS}|\Phi_0^{v',KS}> \gg E_0^{v'} \tag{38}$$

$$<\Phi_0^{v,KS}|\hat{H}_{v'}^{KS}|\Phi_0^{v,KS}> \gg E_0^{v} \tag{39}$$

Making use of Equations 36 and 37 and adding Equations 38 and 39 we are led to the contradiction

$$E_0^{v'}+E_0^v>E_0^{v'}+E_0^v \tag{40}$$

Hence, we conclude that $\Phi_0^{v,KS}=\Phi_0^{v',KS}$. In view of these results, Equation 33 becomes:

$$\hat{H}_{v'}^{KS}\Phi_0^{v,KS}=E_0^v\Phi_0^{v,KS} \tag{41}$$

In terms of the KS equations, these results also imply that in addition to the KS 1-particle equation $\hat{h}_v^{KS}(\mathbf{r})\phi_i^v(\mathbf{r})=\epsilon_i^v\phi_i^v(\mathbf{r})$, the following KS equation also holds: $\hat{h}_{v'}^{KS}(\mathbf{r})\phi_i^v(\mathbf{r})=\epsilon_i^v\phi_i^v(\mathbf{r})$, where $\hat{h}_{v'}^{KS}(\mathbf{r})=\hat{h}_v^{KS}(\mathbf{r})+\Delta v(\mathbf{r})$.

## 5 | FINAL REMARKS AND CONCLUSIONS

We have shown in the present work that it is possible to construct instability potentials, that is, external potentials which differ from the external Coulomb potential $v(r)=-\frac{Z}{r}$ by more than a constant but which nonetheless, correspond to the same ground state density. The existence of these potentials in finite subspaces of Hilbert space does not contradict, however, the first Hohenberg-Kohn theorem as this theorem holds in an infinite Hilbert space. But the present results are pertinent to the usual applications of the Kohn-Sham theory, where the search for optimal Kohn-Sham orbitals is carried out in finite spaces.

Since in the proof of the instability theorem is carried out in the domain of a finite Hilbert space generated by *N*-particle wave functions, the direct relationship between these potentials and the Kohn-Sham formulation of DFT, based on the concept of 1-particle density and of functionals of the density, is not evident. For this reason we have included in Section 4 a discussion where the connection between instability potentials and the Kohn-Sham equations is examined. As it is shown, the Kohn-Sham Hamiltonians given by Equations 30 and 31 corresponding to an external potential *v* and to an instability potential *v'*, respectively, lead to Schrödinger equations having the same wave functions and the same eigenvalues. In turn, since these Schrödinger equations for the Kohn-Sham Hamiltonians can be reduced to the 1-particle Kohn-Sham equations, it is seen that there exist instability potentials for the Kohn-Sham equations that yield the same ground state orbitals and energies as those obtained from the Coulomb external potentials. In consequence, one may in principle construct instability potentials that when applied to the Kohn-Sham equations do not modify either the energy or the 1-particle density.

The work presented here is precisely an attempt to bridge the theoretical result concerning the existence of these instability potentials with an endeavor to actually calculate them for some simple atomic systems. In fact, we have used solutions to the Kohn-Sham equations for the H ($^2S$), He ($^1S$), Li ($^2S$), and Be ($^1S$) atoms obtained with the application of the B3LYP functional, in order to construct instability potentials in the particular $N$-particle subspaces $F$ generated for each atom from the set BS-4G comprising 4 primitive Gaussians. The choice of this simple basis set is made for convenience and in no way it does affect the validity of this demonstration. The reason is that in the proof of the instability potential theorem (see Section above) no restriction is placed on $M$, the size of the finite subspace. However, the effect of increasing the basis set in the present proof is reported for the simple hydrogen atom as Supporting Information (Figure S1 and Table S1) where it can be observed that the value of $r$ for which $v'$ ($r$) and the Coulomb potential become different depends on $m$. The values of $r$ where $v'(r)-1/r$ begin to be sizeable are $r > 0.35$, $r > 0.55$, and $r > 0.7$ for $m = 4$, $m = 5$, and $m = 8$, respectively. It is important to note that the latter behavior suggests that the larger the value of $m$ the larger the value of $r$ for which the difference $v'(r)-1/r$ becomes significant, which implies that, at the limit $m \rightarrow \infty$, $v'(r) = -1/r$ for the whole $r$ domain. The latter observations are expected to hold also for He, Li, and Be.

From an examination of the instability potentials obtained with $m = 4$ (Figures 1–4), it is seen that they do not differ noticeably from the corresponding Coulomb ones in the region where the atomic densities are sizeable. In fact, these potentials show strong differences from the nuclear Coulomb ones only in the regions where the densities are strongly decaying (tending to zero). This characteristic seems to imply that these potentials have a significant effect only in regions where the physics of the systems does not seem to be affected. A possible interpretation is that in finite subspaces these instability potentials determine boundaries to a cage where the system is confined. The region where these different boundaries arise is sufficiently far away as not to affect, apparently, the properties of the system.

The lack of a one-to-one correspondence between the density and the potentials has also been observed for the case of Kohn-Sham exchange-correlation potentials $v_{xc}^{KS}$. In the case of finite basis sets, when these potentials are extracted from densities they show a plurality of results. The same is true in the case of the application of density-to-potential mapping techniques when the densities are expressed in terms of Gaussian orbitals. This situation contrasts, of course, with those in which the $v_{xc}^{KS}$ potentials are obtained directly from reconstruction methods involving wavefunction.[42–44] We would like to emphasize, however, that the possibility of generating instability potentials discussed in the present work is of an entirely different nature. In fact, only general properties of $N$-particle subspaces of Hilbert space are used in the proof of the instability potential theorem as well as in the actual construction of potentials. For this reason, the determination of instability potentials does not hinge on characteristics of any particular basis set, or particular DFT functional; nor does it rest on particular methods to solve the inverse problem of going from densities to potentials. It is true, however, that the particular form that the instability potential adopts depends on the type of finite subspace chosen. But, as discussed in Section , for each subspace there is the possibility of generating an infinite number of instability potentials just by selecting, for example, different values for the parameter $\lambda$.

## ACKNOWLEDGEMENTS

## REFERENCES

[1] P. Hohenberg, W. Kohn, *Phys. Rev* **1964**, *136*, 864.

[2] P. Hohenberg, W. Kohn, L. J. Sham, *Quantum Chem* **1990**, *21*, 7.

[3] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford **1989**.

[4] R. M. Dreizler, E. K. U. Gross, *Density Functional Theory*, Springer, Berlin **1990**.

[5] E. S. Kryachko, E. V. Ludeña, *Energy Density Functional Theory of Many Electron Systems*, Kluwer, Dordrecht **1990**.

[6] N. H. March, *Electron Density Theory of Atoms and Molecules*, Academic Press, New York **1992**.

[7] J. Cioslowski, Ed. *Many-Electron Densities and Reduced Density Matrices*, Kluwer, Dordrecht **2000**.

[8] E. K. U. Gross, R. M. Dreizler, Eds. *Density Functional Theory, NATO ASI Series*, Vol. *B337*, Plenum, New York **1995**.

[9] J. M. Seminario, P. Politzer, Eds. *Modern Density Functional Theory: A Tool for Chemistry*, Elsevier, Amsterdam **1995**.

[10] J. F. Dobson, G. Vignale, M. P. Das, *Electronic Density Functional Theory. Recent Progress and New Directions*, Plenum Press, New York **1998**.

[11] D. P. Chong, Eds. *Recent Advances in Density Functional Methods*, World Scientific, Singapore **1995**.

[12] P. Geerlings, F. de Proft, W. Langenaeker, Eds. *Density Functional Theory. A Bridge between Chemistry and Physics*, VUB University Press, Brussels **1999**.

[13] R. F. Nalewajski, Ed. Density functional theory, in *Topics in Current Chemistry*, Vols. *180/183*, Springer, Berlin **1996**.

[14] K. D. Sen, Ed. *Reviews in Modern Quantum Chemistry: A Celebration of the Contribution of Robert G. Parr*, World Scientific, Singapore **2002**.

[15] H. Eschrig, *The Fundamentals of Density Functional Theory*, Teubner, Sttutgart **1996**.

[16] R. van Leeuwen, *Adv. Quantum Chem* **2003**, *43*, 24.

[17] E. V. Ludeña, *J. Mol. Struct. (THEOCHEM)* **2004**, *709*, 25.

[18] W. Yang, P. W. Ayers, Q. Wu, *Phys. Rev. Lett* **2004**, *92*, 146404.

[19] A. Görling, *J. Chem. Phys* **2005**, *123*, 062203.

[20] P. W. Ayers, *Phys. Rev. A* **2006**, *73*, 012513.

[21] S. Rohra, A. Görling, *Phys. Rev. Lett* **2006**, *97*, 013005.

[22] W. Kutzelnigg, *J. Mol. Struct. (THEOCHEM)* **2006**, *768*, 163.

[23] F. Illas, I. D. P. R. Moreira, J. M. Bofill, M. Filatov, *Theor. Chem. Acc* **2006**, *116*, 587.

[24] P. W. Ayers, S. Liu, *Phys. Rev. A* **2007**, *75*, 022514.

[25] J. Schirmer, A. Dreuw, *Phys. Rev. A* **2007**, *75*, 022513.

[26] S. F. Sousa, P. A. Fernandes, M. J. Ramos, *J. Phys. Chem. A* **2007**, *111*, 10439.

[27] A. Cohen, P. Mori-Sánchez, W. Yang, *Science* **2008**, *321*, 792.

[28] W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim **2000**.

[29] J. Kohanoff, N. I. Gidopoulos, Density functional theory: basics, new trends and applications, in *Handbook of Molecular Physics and Quantum Chemistry* (Ed: S. Wilson), Molecular Electronic Structure, Wiley, Chichester **2003**, p. 532, Vol. *2*.

[30] G. E. Scuseria, V. N. Staroverov, Progress in the Development of Exchange-Correlation Functionals, in *Theory and Application of Computational Chemistry: The First 40 Years* (Eds: C. E. Dykstra, G. Frenkling, K. S. Kim, G. E. Scuseria), Elsevier, Amsterdam **2005**, p. 669.

[31] W. Kohn, L. J. Sham, *Phys. Rev* **1965**, *140*, 1133.

[32] P. W. Ayers, M. Levy, *J. Chem. Sci* **2005**, *117*, 507.

[33] P. W. Ayers, S. Golden, M. Levy, *J. Chem. Phys* **2006**, *124*, 054101.

[34] E. S. Kryachko, E. V. Ludeña, *Phys. Reports* **2014**, *544*, 123.

[35] S. T. Epstein, C. M. Rosenthal, *J. Chem. Phys* **1976**, *64*, 247.

[36] J. Katriel, C. J. Appellof, E. R. Davidson, *Int. J. Quantum Chem* **1981**, *19*, 293.

[37] J. E. Harriman, *Phys. Rev. A* **1983**, *27*, 632.

[38] R. Pino, O. Bokanowski, E. V. Ludeña, R. L. Boada, *Theor. Chem. Acc* **2007**, *118*, 557.

[39] R. Pino, O. Bokanowski, E. V. Ludeña, R. L. Boada, *Theor. Chem. Acc* **2009**, *123*, 189.

[40] M. E. Mura, P. J. Knowles, C. A. Reynolds, *J. Chem. Phys* **1997**, *106*, 9659.

[41] P. R. T. Schipper, O. V. Gritsenko, E. J. Baerends, *Theor. Chem. Acc* **1997**, *98*, 16.

[42] A. A. Kananenka, S. V. Kohut, A. P. Gaiduk, I. G. Ryabinkin, V. N. Staroverova, *J. Chem. Phys* **2013**, *139*, 074112.

[43] I. G. Ryabinkin, S. V. Kohut, V. N. Staroverov, *Phys. Rev. Lett* **2015**, *115*, 083001.

[44] R. Cuevas-Saavedra, V. N. Staroverov, *Mol. Phys* **2016**, *114*, 1050.

[45] E. H. Lieb, Density functionals for coulomb systems, in *Physics as a Natural Philosophy: Essays in Honor of Laszlo Tisza on His 75th Birthday* (Eds: A. Shimony, H. Feshbach), MIT, Cambridge **1982**, p. 111.

[46] E. H. Lieb, *Int. J. Quantum Chem* **1983**, *24*, 243.

[47] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision E.01*, Gaussian, Inc., Wallingford **2009**.

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