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REGULAR ARTICLE

Analysis of the stability of finite subspaces in density functional theory

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Abstract We study the problem of the stability of finite subspaces with respect to the external potential in the formulation of the Hohenberg-Kohn theorem in density functional theory. We provide general procedures to construct potentials that make any finite dimensional subspace unstable, i.e., we construct potentials that acting over functions that belong to the subspace, generate functions that do not belong to that subspace. Explicit calculations of these instability generating potentials are carried out for the particle-in-a-box problem and for the hydrogen atom. We also discuss the consequences of these instabilities on the Kohn–Sham equations, as well as conditions for stability and the relation between instability and nonuniqueness of potentials.

Keywords DFT · Finite subspaces · Hydrogen atom

Dedicated to the memory of Professor Oriano Salvetti and published as part of the Salvetti Memorial Issue.

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1 Introduction

Density functional theory (DFT) [1–14] (for some recent reviews, critical appraisals, and extensions, see Refs. [15–27]) has become the method of choice for electronic structure calculations not only in condensed matter theory but also in quantum chemistry [28–30].

Applications of this theory have relied on the Kohn–Sham (KS) equations [31] where, the effective potentials are obtained as variational derivatives of carefully taylored approximations to the exact exchange-correlation functionals. The use of the orbital paradigm for solving one-particle KS equations is natural in this context, as the KS equations are quite similar, albeit simpler than the Hartree–Fock ones, due to the presence of a local multiplicative potential for exchange and correlation. Most applications make use of finite sets of one-particle primitive functions for expanding the KS atomic, molecular, and crystalline orbitals as well as the one-particle density.

Clearly, practical electronic structure calculations are almost always performed on a subspace of the Hilbert space. Such is the case, for example, when a finite expansion of the N-particle wavefunction is used or when the solutions to a system of N one-particle equations are approximated in a finite basis set. However, when extending the Hohenberg-Kohn approach (or of its alternative constrained-search formulation [32–34]) to finite subspaces it becomes necessary to deal with the problem of determining the conditions guaranteeing the adequateness of this approach in finite subspaces. Some restricted considerations related to this finite subspace problem have been given by Epstein and Rosenthal [35] and by Katriel et al. [36, 37]. More general considerations have been advanced by Harriman [38], and more recently, by Görling and Ernzerhof [39]. Also, this question is basic to

some recent comparisons of the xOEP and HF methods [40–42].

In a previous article [43], we have analyzed the stability conditions that must be satisfied in order for the Hohenberg-Kohn theorem to hold in a subspace. In the present article, we further analyze these stability conditions and show that when they are not fulfilled, it is possible to construct *instability* potentials which differ from each other by more than a constant and which nevertheless associate with the same density. We provide explicit methods for obtaining these potentials and give illustrations of this subspace instability for the particle-in-a-box problem and for the hydrogen atom. As these examples arise in the instability domain, they do not contradict, however, the Hohenberg-Kohn theorem [39, 42]. In addition, from this new perspective, we also discuss the nature of the constraints necessary so that stability conditions be preserved in the subspace. It is shown that these conditions can be imposed by requiring linear dependence among products of one-particle orbitals, much in the manner already presented by Görling et al. [42].

The plan of the article is as follows. In Sect. 2, we briefly review the stability conditions previously obtained by Pino et al. [43]. In Sect. 3, we prove a theorem underlying a constructive method for generating *instability* potentials. In Sect. 4, we apply this method to the case of the particle-in-a-box and the hydrogen atom. In Sect. 5, we discuss the problem of the instability effects that the introduction of finite basis sets brings into the Kohn–Sham equations. We also consider the problem of constructing a subclass of potentials v and v' such that the stability conditions are satisfied. Finally, we discuss the relationship between instability and nonuniqueness of potentials in DFT [44–51]. In Sect. 6 we present some conclusions.

2 The Hohenberg-Kohn theorem in finite subspaces

For a system formed by N-electrons interacting with an "external" potential

$$V(\vec{r}_1,\ldots,\vec{r}_N)=\sum_{i=1}^{N} v(\vec{r}_i). \tag{1}$$

the many-electron Hamiltonian is

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

where

$$\widehat{H}_0=-\frac{1}{2}\sum\nabla^2_{\vec{r}_i}+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{1}{|\vec{r}_i-\vec{r}_j|}. \tag{3}$$

We assume that $v(\vec{r})\in Y$ where $Y=L^{3/2}+L^{\infty}$ is Lieb's class. Hence, $v=v_{3/2}+v_{\infty}$ where $v_{3/2}\in L^{3/2}$ and $|v_{\infty}|$ is a bounded function [for the set of continuous functions $f(x)$, $f(x)\in L^m$ if $\int \mathrm{d}x\,|f(x)|^m<\infty$; in general, $f\in L^m{}_{\mathrm{loc}}$ if $f\in L^m$ and is integrable for any bounded set; also, $f\in H^1$ if f, $\nabla f\in L^2$].

When such a system possesses a ground-state wavefunction Ψ_0^v the associated one-electron density $\rho_0^v(\vec{r})$ is defined by

$$\rho_0^v(\vec{r}_1)=N\int d^3\vec{r}_2\cdots\int d^3\vec{r}_N|\Psi_0^v(\vec{r}_1,\ldots,\vec{r}_N)|^2, \tag{4}$$

and, in that case, the Hohenberg-Kohn theorem states that there exists a one-to-one correspondence between an external potential $v(\vec{r})$ and the exact ground-state density $\rho_0^v(\vec{r})$.

The original proof of this theorem [1] was carried out by *reductio ad absurdum* based on the assumption that although Ψ_0^v and $\Psi_0^{v'}$ associate with the same density $\rho_0^v=\rho_0^{v'}=\rho_0$ they satisfy different Schrödinger equations. As pointed out by Lieb, this assumption implies that Ψ_0^v and $\Psi_0^{v'}$ cannot vanish in a set of positive measure. As this condition introduces some difficulties, an alternative proof was advanced by Pino et al. [43], where the above assumption is dropped. This new approach, in turn, allowed both a straightforward extension of the Hohenberg-Kohn theorem to subspaces and an examination of the conditions that must be satisfied in subspaces. For completeness, we review here the main results for subspaces obtained in Ref. [43].

Theorem 2 (infinite-dimensional subspaces) of Ref. [43] states that when F is an infinite subspace of the antisymmetric N-particle Hilbert space in the domains of $\widehat{H}_v$ and $\widehat{H}_{v'}$, and the following conditions are satisfied: (a) v, v' in Y, (b) ρ_0^v and $\rho_0^{v'}$ are the ground state densities of the restrictions $\widehat{H}_v|_F$ and $\widehat{H}_{v'}|_F$, respectively, and (c) the ground state wavefunction Ψ_0^v of $\widehat{H}_v$ vanishes at most on a Lebesgue's zero-measure set of $\mathbb{R}^{3N}$, then the Hohenberg-Kohn theorem is valid provided that F is stable under the action of $\widehat{H}_v$ and $\widehat{H}_{v'}$, i.e., $(\widehat{H}_vF\subset F$ and $\widehat{H}_{v'}F\subset F)$.

Similarly, using the fact that a multiplicative operator $\widehat{V}$ associated to a scalar potential V is defined by $(\widehat{V}(\Psi))(x):=V(x)\Psi(x)$, Theorem 3 (finite-dimensional subspaces) of [43] states that when F is a finite-dimensional subspace of $L^2(\mathbb{R}^n)$ $(n\geq 1)$, i.e.,

$$F=\left\{u_i(x)\middle| i=1,\ldots,M;\int \mathrm{d}x u_i(x)u_j^*(x)=\delta_{ij};\sum_{i=1}^{M}|u_i(x)|^2>0;x\in\mathbb{R}^n\right\} \tag{5}$$

and $V(x)$ is a continuous real-valued potential, then

$$(\widehat{V}(F)\subset F)\Longrightarrow(V(x)=\text{const on }\mathbb{R}^n)$$

A consequence of this theorem is

$$V(x)\psi_i(x)=\lambda_i\psi_i(x),\quad i=1,\ldots,M. \tag{6}$$

which implies that addition of a constant potential does not alter either the one-particle density or the ordering of the eigenvalues.

Thus, according to Theorem 3 of Ref. [43] one way to satisfy the stability conditions of Theorem 2 of Ref. [43] in the case when F is finite dimensional is to have $\Delta V = \text{const}$. However, there may be *instability* potentials (defined as those potentials with $\Delta V \neq \text{const}$ that violate the subspace stability conditions) which arise in finite dimensional spaces when the assumption $\Delta V(F) \subset F$ is relaxed. This is made more explicit in the next section.

3 Constructive method for generating instability potentials

For a given external potential $v \in Y$ and a finite subspace F of Hilbert space, we devise in the present subsection a general method for generating single particle external potentials v' (with $v' - v \neq \text{const}$) that do not fulfill the stability conditions on the finite subspace and that, hence, associate with the same ground-state density ρ_0^v of v.

Theorem (Instability potentials) Let $v \in Y$, and F as in Eq. 5 with finite dimension, $\dim F = M + 1 > 1$. Let $\hat{P}_F = \sum_{n=0}^{M} |\Psi_n^v\rangle\langle\Psi_n^v|$ be the orthogonal projector on F, and let $E_0^v(M) \leq \cdots \leq E_M^v(M)$ be the ordered eigenvalues of $\hat{P}_F \widehat{H}_v \hat{P}_F$. Suppose that there exists k for which the strict inequality $E_0^v(M) < E_k^v(M)$ is satisfied. Then, there exists a potential $v' \in Y$ such that $\hat{P}_F \widehat{H}_{v'} \hat{P}_F$ and $\hat{P}_F \widehat{H}_v \hat{P}_F$ have the same ground state, for $\Delta v \equiv v' - v \neq \text{constant}$.

Proof We first consider the proof for the case when the ground state degeneracy is one. We take for F the orthonormal basis set of eigenvectors of $\widehat{H}_v$: Ψ_0^v,..., Ψ_M^v. In this basis, the matrix elements of $\widehat{H}_{v'}$ are $H_{ij}^{v'} = \langle\Psi_i^v|\widehat{H}_{v'}|\Psi_j^v\rangle$. In particular using $\widehat{H}_{v'} = \widehat{H}_v + \Delta V$ one has

$$H_{0i}^{v'} = \delta_{0i} E_0^v + \int \Delta v \rho_{0i} \tag{7}$$

where $\rho_{ji}(\vec{r}) = N \int \Psi_j^{v*} \Psi_i^v \mathrm{d}\vec{r}_2 \ldots \mathrm{d}\vec{r}_N$. Note that $\rho_{ji} \in L^1(\mathbb{R}^3)$ by Schwartz inequality. The first step is to take $\Delta v \in Y$, nonconstant, such that

$$\int \Delta v \rho_{0i} = 0, \quad \text{for} \quad i = 0, \ldots, M. \tag{8}$$

This can be done as follows: take $(h_j)_{j=0\ldots M+1}$ to be a set of $M + 2$ (nonconstant) linearly independent functions of $L^1 \cap L^\infty \subset Y$ (because for all $p \in [1, \infty)$, $L^1 \cap L^\infty \subset L^p$). If we search for Δv as a linear combination of the h_j, i.e.,

$$\Delta v(\vec{r}) = \sum_{j=0}^{M+1} c_j h_j(\vec{r}) \tag{9}$$

then Eq. 8 is equivalent to an homogeneous system of $M + 1$ linear equations with $M + 2$ unknowns. Thus, we can find at least one nonzero set (c_0,..., c_{M+1}), giving a solution for Δv. If Δv is constant, then it must be zero because $\Delta v \in L^1$, but this is not possible in view of the fact that the (h_j)'s are linearly independent.

At present we know that the matrix $H^{v'}$ [representative of the operator $\hat{P}_F \widehat{H}_{v'} \hat{P}_F$ in the (Ψ_i^v) basis] has the eigenvalue E_0^v with the eigenvector Ψ_0^v at least. We still do not know if it is the ground state eigenvector of $H^{v'}$. The second step is to take Δv sufficiently small such that this becomes true. Let us rename the preceding Δv as Δw and look for $\Delta v = \lambda\, \Delta w$ where $\lambda > 0$. First, note that Eq. 8 is still verified. Second, we know that the eigenvalues of a matrix depend continuously on the coefficients: here the eigenvalues of $H^{v'}$ depend continuously on λ. Thus, for λ small enough, $E_0^{v'}$,..., $E_M^{v'}$ will approach E_0^v,..., E_M^v. The fact that $E_1^v > E_0^v$ implies that for λ small enough, all $E_1^{v'}$,..., $E_M^{v'}$ will lie *strictly above* E_0^v. This proves that $E_0^{v'} = E_0^v$, and hence that Ψ_0^v is the ground state of $H^{v'}$.

However, when Δv is not small we cannot, in general, make assertions about the ordering of the eigenvalues, because they depend on the calculated coefficients. In those cases it is useful to perform numerical analysis for some concrete cases, see examples in next section.

In the case of $k > 1$ ground-state degeneracy, we take a set of $k \times (M + 1) + 1$ functions h_j, and find a Δv such that

$$\int \Delta v \rho_{ij} = 0 \quad \text{for} \quad i = 0, \ldots, k-1 \quad \text{and} \quad j = 0, \ldots, M. \tag{10}$$

Then Ψ_0^v,..., Ψ_{k-1}^v are all ground state eigenvectors of $\widehat{H}_{v'}|_F$, with the same eigenvalue E_0^v. □

The above "instability potential" theorem, therefore, provides a method for associating in a finite subspace the same ground state densities with potentials that differ by more than a constant, (i.e., $\Delta v = v' - v$ nonconstant). Clearly, however, this does not imply a violation of the Hohenberg-Kohn theorem, because these potentials are unstable in the finite subspace. Note in addition, that we are constructing a space F which is unstable by $H_{v'}$, and furthermore obtain a particular ordering of the eigenvalues of $P_F\, H_{v'}\, P_F$.

Let us remark, moreover, that in general, it is possible to construct other instability potentials by taking less than the $M + 2$ functions (h_j) considered in the preceding proof. Suppose that $E_0^v < E_1^v$. Then, for the first step in the proof of Theorem 3 we can require that

$$\int \Delta v \rho_{0i} = 0, \quad \text{for} \quad i = 1, \ldots, M, \tag{11}$$

where there is no condition for $i = 0$. In order to find a $\Delta v \neq 0$ we can expand Δv as a linear combination of $M + 1$ functions (h_j). Subsequently, we can take a Δv sufficiently small such that using the same arguments as in the previous proof, we will have a value $E_0^{v'}$ lying close to (but remaining different from) that of E_0^v, for the same ground state $\Psi_0^{v'} = \Psi_0^v$. In this case, the ordering of the eigenvalues cannot be guaranteed either when Δv is not small enough.

4 Numerical results and discussion

4.1 Instability potentials for particle-in-a-box

Let us consider the well-known problem of a particle in a one-dimensional box with infinite potential walls where the inner region is defined by $x \in [0, +\pi]$. Clearly the simplest way to define the subspace F is in terms of the finite subset formed by the first $M + 1$ exact eigenfunctions $\{\Psi_n^v(x)\}_{n=0}^M$ of the particle-in-a-box problem,

$$\Psi_n^v(x) = \begin{cases} \sqrt{\frac{2}{\pi}}\sin(n+1)x & \text{if } x \in [0,+\pi] \quad \text{for} \quad n = 0,\ldots,M. \\ 0 & \text{otherwise} \end{cases} \tag{12}$$

We carry out the present calculations using this exact set. But, in addition, due to the fact that in realistic problems the exact eigenfunctions are not known and necessarily one must rely on approximations to these exact wave functions, we also deal in the present case with approximate forms of these eigenfunctions. In this vein, we start from the nonorthogonal set $\{p_i(x) = x\prod_{k=1}[(k/i)\pi - x]\}_{i=1}^K$ and obtain by Schmidt orthonormalization the set $\{u_i(x)\}_{i=1}^K$ which by construction satisfies the boundary conditions $u_i(0) = 0$ and $u_i(\pi) = 0$. We then use this set $\{u_i(x)\}_{i=1}^K$ in order to provide a finite matrix representation of the particle-in-a-box Hamiltonian $\widehat{H}_v$ and obtain, by matrix diagonalization, the approximate eigenfunctions $\{\widetilde{\Psi}_n^v(x) = \sum_{j=1}^K c_{nj}u_j(x)\}_{n=0}^{K-1}$.

We now assume that the subspace F is formed by the first $M + 1$ approximate eigenfunctions, namely, by the set $\{\widetilde{\Psi}_n^v(x)\}_{n=0}^M$, and require that the conditions imposed by Eq. 8 be satisfied. We take as basis functions for expanding $\Delta v(x)$, the set of $M + 2$ positive powers of x: $\{h_{j-1}(x) = x^j\}$, $j = 1,\ldots, M + 2$. These functions obviously belong to Lieb's class (Y) because of the finiteness of the interval. Thus, $\Delta v = \sum_{j=0}^{M+1} c_j h_j(x) \equiv c_{M+1}\sum_{j=0}^{M+1} a_j h_j(x)$ where $a_j \equiv c_j/c_{M+1}$. Calculating the matrix elements, and solving the system of equations—taking c_{M+1} equal to unity—we obtain the desired new potential. Let us remark that an infinite number of potentials are generated upon multiplication by the freely specifiable parameter c_{M+1}.

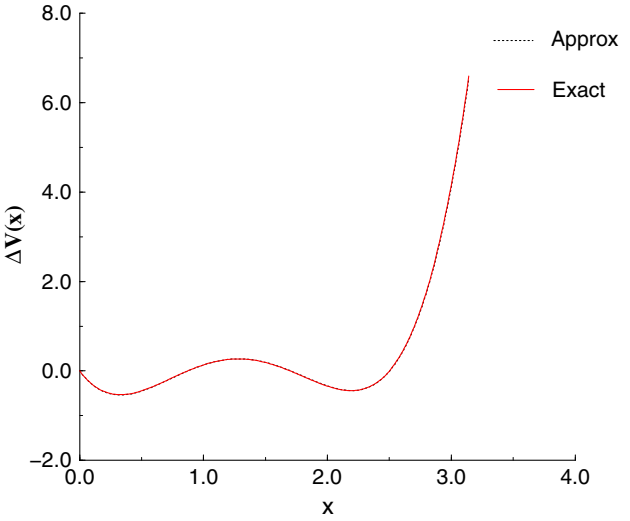

Fig. 1 Graphical representation of the potential v' generated through Eq. 8 for a set of three exact and three approximate particle-in-a-box eigenfunctions ($M = 2$ and $c_{M+1} = 1$)

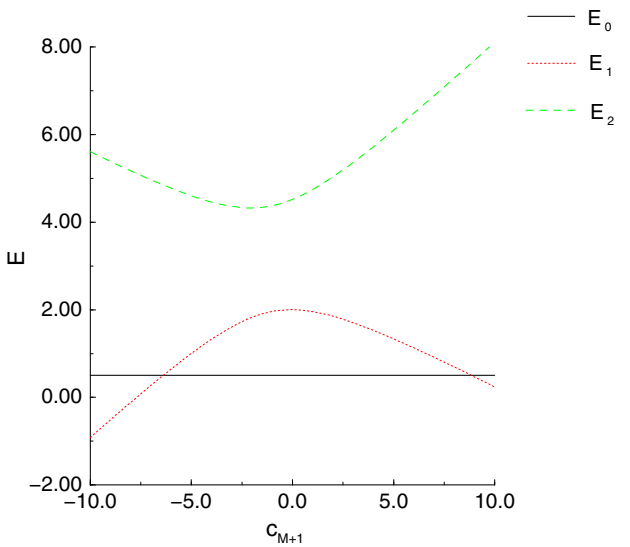

Fig. 2 Numerical behavior of the eigenvalues versus c_{M+1} for the instability potential corresponding to three approximate particle-in-a-box wavefunctions and potentials v' generated through Eq. 8

The potentials depicted in Fig. 1 correspond to solutions to Eq. 8 for both the exact and the approximate particle-in-a-box wavefunctions (for the latter we have made the choice of $c_{M+1} = 1$). Also, for the present numerical examples, we have selected $K = 6$ and $M = 2$. Thus, the subspace F is spanned by the three approximate eigenfunctions $\widetilde{\Psi}_0^v$, $\widetilde{\Psi}_1^v$ and $\widetilde{\Psi}_2^v$ expanded in terms of six u_i basis functions.

In Fig. 2 we show the behavior of the first three eigenvalues for $M = 2$ varying c_{M+1} from -10 to 10 for the case of the approximate wavefunctions. It can be seen that E_0 remains unaltered at the value of $E_0 = 0.5$.

However, we observe that it is not the lowest eigenvalue throughout the whole range considered as there are regions where E_1 attains a lower value. Hence, it is only in the region where E_0 is the lowest eigenvalue that the present procedure yields *bona fide* instability potentials for the given finite subspace.

In Fig. 3, we show the behavior of the eigenvalues obtained when $\Delta v(x)$ is determined by solving the system of equations given by Eq. 11. Note that in this case, E_0 does not remain constant but is modified by the choice of the parameter c_M. In this case, E_0 remains as the lowest eigenvalue within the range considered.

4.2 Instability potentials for the hydrogen atom

We determine families of instability potentials based on the nonrelativistic hydrogen atom problem, as shown in Fig. 5. In this case, the basis set $\{\Psi_n^v(x)\}_{n=0}^M$ is formed by the first $M+1$ hydrogenic eigenfunctions (which are bounded and quadratically integrable): $\Psi_n(r) \equiv R_{n+1,0}(r)$ for $n = 0,..., M$. Expanding the potential difference $\Delta v(r)$ in terms of these very same eigenfunctions, i.e., setting $h_{n-1}(r) \equiv R_{n,0}(r)$ for $n = 1,..., M+2$, and applying Eq. 8 we computed the potential differences shown in Fig. 4 for $M = 2$. In Fig. 5 it can be observed that the ordering of the eigenvalues for $M = 2$ is maintained throughout the range of c_{M+1} between -10 and 10.

5 Some further considerations on instability potentials

In order to illustrate the variational difficulties arising from the finiteness of the space consider, for example, the problem of minimizing the Hamiltonian matrix for $\widehat{H}_v$ over the finite subspace F. As a result of this minimization, one obtains a finite set of $M+1$ approximate antisymmetric N-particle wavefunctions $\{\widetilde{\Psi}_0^v, \ldots, \widetilde{\Psi}_M^v\}$. The energy minimum corresponds to the expectation value of $\widehat{H}_v$ with respect to the lowest wave function $\widetilde{\Psi}_0^v$. But if Eq. 8 is then used in order to determine v', it follows that $\int \Delta v \rho_{00} = 0$ and hence that the lowest energy is also given as the expectation value of $\widehat{H}_{v'}$ with respect to $\widetilde{\Psi}_0^v$. Explicitly, we have, therefore,

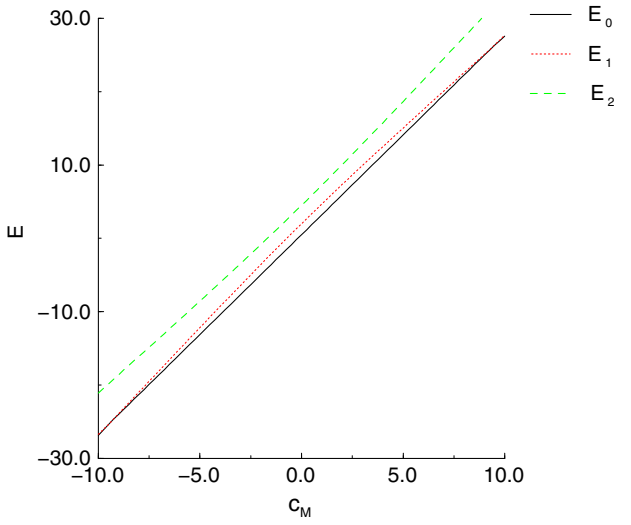

Fig. 3 Numerical behavior of the eigenvalues versus c_{M+1} for the instability potential corresponding to three approximate particle-in-a-box wavefunctions and a potential v' generated through Eq. 11

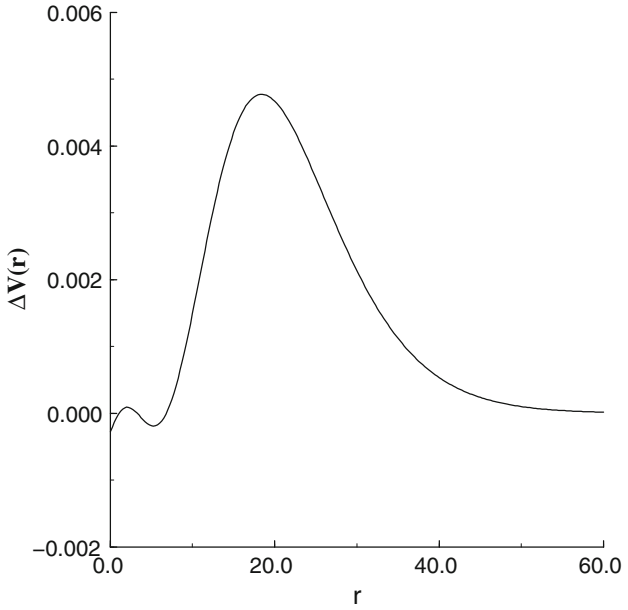

Fig. 4 Graphical representation of the potential difference $\Delta v(r)$ generated via Eq. 8 for the hydrogen atom ($M = 2$ and $c_{M+1} = 1$)

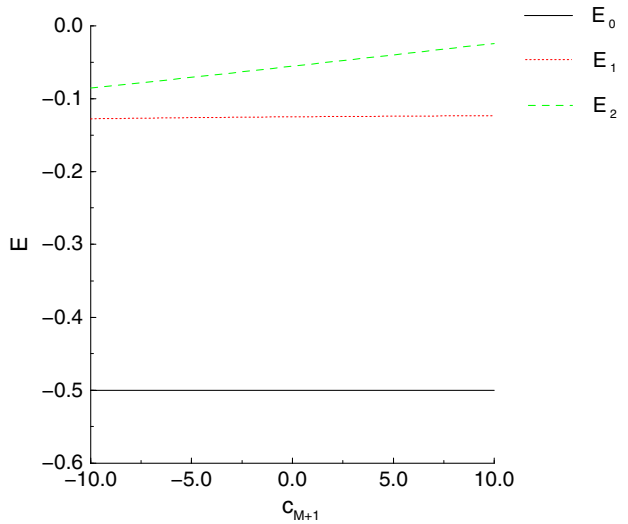

Fig. 5 Numerical behavior of the hydrogen atom eigenvalues versus c_{M+1} for $M = 2$ corresponding to Δv generated by means of Eq. 8

$$\min_{\Psi^v \in F}\left\{\left\langle \Psi^v|\widehat{H}_v|\Psi^v\right\rangle\right\} = \left\langle \widetilde{\Psi}^v_0|\widehat{H}_v|\widetilde{\Psi}^v_0\right\rangle = \left\langle \widetilde{\Psi}^v_0|\widehat{H}_{v'}|\widetilde{\Psi}^v_0\right\rangle \tag{13}$$

This implies that any density functional for the energy $\mathcal{E}_v[\rho] \equiv \langle\Psi|\widehat{H}_v|\Psi\rangle(\Psi \to \rho)$ is not uniquely defined in a finite space F as there can be, in principle, an infinite number of Hamiltonians that differ in their external potential by more than a constant but lead to the same minimum $E^v_0(M) = \mathcal{E}_v[\rho^v_0] = \mathcal{E}_{v'}[\rho^v_0]$ in F.

5.1 Instability potentials and the Kohn–Sham equations

Consider now that we replace $\widehat{H}_v$ of Eq. 2 by the Kohn–Sham Hamiltonian

$$\widehat{H}^{KS}_s \equiv \widehat{T} + \widehat{V}_s \tag{14}$$

where $V_s = \sum_{i=1}^N v_s(\vec{r}_i)$ and where $\widehat{T} = \sum_{i=1}^N \hat{t}(\vec{r}_i)$, with $\hat{t}(\vec{r}) = -(1/2)\nabla^2_{\vec{r}}$. Let us denote the optimal Kohn–Sham ground-state determinantal wavefunction by

$$\Psi^{v(KS)}_0 = \frac{\det}{\sqrt{N!}}\{\phi^{KS}_1(\vec{r}_1),\ldots,\phi^{KS}_N(\vec{r}_N)\} \tag{15}$$

By definition, this wavefunction satisfies the Schrödinger equation $\widehat{H}^{KS}_s\Psi^{v(KS)}_0 = E^{v(KS)}_0\Psi^{v(KS)}_0$. In view of the fact that the Hamiltonian operator $\widehat{H}^{(KS)}_v$ is separable, we can rewrite this equation as the set of N single-particle equations for the Kohn–Sham orbitals:

$$(\hat{t} + v_s)\phi^{KS}_i = \mathcal{E}^{KS}_i\phi^{KS}_i. \tag{16}$$

A procedure for generating instability potentials for the Kohn–Sham case can be readily set up by following the same of argument as in the instability potential theorem, replacing $\widehat{H}_v$ by $\widehat{H}^{KS}_v$ and Ψ^v_0 by $\Psi^{v(KS)}_0$. Note that the condition on the density difference becomes:

$$\int \Delta v_s\rho^{KS}_{0i} = 0, \quad \text{for} \quad i = 0,\ldots,M. \tag{17}$$

where $\Delta v_s = v'_s - v_s \neq$ constant and $\rho^{KS}_{ji}(\vec{r}) = N\int \Psi^{v(KS)*}_j\Psi^{v(KS)}_i d\vec{r}_2\ldots d\vec{r}_N$. We conclude, as before, that the ground state Kohn–Sham wavefunction $\Psi^{v(KS)}_0$ is also an eigenfunction of the Kohn–Sham Hamiltonian $\widehat{H}^{KS}_{v'}$, namely, $\widehat{H}^{KS}_{v'}\Psi^{v(KS)}_0 = E^{v(KS)}_0\Psi^{v(KS)}_0$. Clearly, therefore, although v_s and v'_s differ by more than a constant, they associate with the same density $\rho^{v(KS)}_0$. Moreover, because the Kohn–Sham Hamiltonian is separable, we obtain again the Kohn–Sham equations:

$$(\hat{t} + v'_s)\phi^{KS}_i = \mathcal{E}^{KS}_i\phi^{KS}_i. \tag{18}$$

Thus, we have shown that in the case of the Kohn–Sham equations, the instability potentials can be generated by the same procedure given above. In other words, the calculated effective or exchange-correlation potentials are unique up to any set of functions that projects the basis set out of itself, and those functions can always be constructed. The present approach leads, essentially, to the same conclusions initially established by Harriman [38] and later on by several other workers [39, 41, 42] where these instability conditions are related to the linear independence of finite sets of products of occupied and virtual orbitals.

In view of the unavoidable fact that given some physical potential it is always possible to construct potentials differing from the physical one by more than a constant, another question one may ask is whether these new potentials are physically acceptable. For example, as Savin et al. [52] have found, when certain changes are made on the potentials, such as shifts in small regions, or the introduction of rapid oscillations, then the density is not affected. Although these are potentials that differ in more than a constant their physical significance in relation to the Coulomb many-body problem is not readily apparent (i.e., the particle might not be affected by the rapid oscillations of the potentials [52]).

5.2 Stability conditions for the potentials

An interesting question has to do with whether, given an F, it is possible to construct a subclass of potentials v, $v' \in Y$ such that F is stable under the action of their corresponding Hamiltonians. For such a subclass, we would have a true example of the application of the Hohenberg-Kohn theorem in a finite subspace F. Let us mention that the arisal of unphysical potentials has been regarded [41] as the manifestation of an ill-posed problem resulting from the use of unbalanced (and, hence, unsuitable) basis sets. A proposed solution relies on the introduction of a modified functional that incorporates a regularizing smoothness measure to filter out the unphysical potentials.

Explicitly, these stability conditions guaranteeing the fulfillment of the Hohenberg-Kohn theorem in a finite space are given by $\widehat{H}_vF \subset F, \widehat{H}_{v'}F \subset F$, and $\Delta VF \subset F$. Moreover, for all N-particle functions $\Psi^v_n \in F$ (with $n = 0,\ldots, M$) and $\Psi^v_m \in F^c$ (with $m = M+1,\ldots, \infty$ and where F^c denotes the complement of F), the stability conditions are satisfied provided that

$$\langle\Psi^v_n|\Delta V|\Psi^v_m\rangle = 0 \quad \text{for} \quad n = 0,\ldots,M+1, \quad \text{and} \quad m = M+1,\ldots,\infty \tag{19}$$

Now, making the same considerations as those leading to Eq. 8 we can rewrite Eq. 19 as:

$$\int d^3\vec{r}\rho_{nm}(\vec{r})\Delta v(\vec{r}) = 0 \quad \text{for} \quad n = 0,\ldots,M+1, \quad \text{and} \quad m = M+1,\ldots,\infty \tag{20}$$

Assume that the infinite set $\{\phi_i(\vec{r})\phi_j(\vec{r})\}$ is linearly dependent, for at least some set $\{a_{ij}\}$ (for a proof of this statement, see Ref. [42]), i.e.,

$$\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} a_{ij}\phi_i(\vec{r})\phi_j(\vec{r}) = 0 \tag{21}$$

For an arbitrary function $f(\vec{r})$ we have from Eq. 21 that

$$\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} a_{ij}f_{ij} = 0 \quad \text{where} \quad f_{ij} = \int \mathrm{d}^3\vec{r}\phi_i(\vec{r})\phi_j(\vec{r})f(\vec{r}) \tag{22}$$

Expanding the transition 1-matrix

$$D^1_{nm}(\vec{r},\vec{r}') = \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} c_{ij}^{nm}\phi_i(\vec{r})\phi_j(\vec{r}') \tag{23}$$

and using $\rho_{nm}(\vec{r}) = D^1_{nm}(\vec{r},\vec{r})$ we obtain for the stability condition

$$\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} c_{ij}^{nm}\Delta v_{ij} = 0 \quad \text{where}$$

$$\Delta v_{ij} = \int \mathrm{d}^3\vec{r}\phi_i(\vec{r})\phi_j(\vec{r})\Delta v(\vec{r}) \tag{24}$$

Now, since Δv is arbitrary we can set it as

$$\Delta v_{ij} = \frac{f_{ij}a_{ij}}{c_{ij}^{nm}} \tag{25}$$

Hence, it follows that the stability condition holds provided that the potential difference is defined through the matrix elements defined by Eq. 25, and that the set $\{\phi_i(\vec{r})\phi_j(\vec{r})\}$ satisfies the linear dependency condition given by Eq. 21.

5.3 Instability versus nonuniqueness of potentials

A concept related to instability but, however, logically disjoint from it, is that of nonuniqueness of potentials. Whereas the former arises due to the fact that the action of a potential on a wavefunction belonging to a subspace produces a wavefunction which does not belong to the same subspace, the latter means that the potentials are not uniquely determined by the densities. Nonuniqueness of potentials arises in the case of density functional theories for spin and magnetic systems as well as for current-carrying and superconducting systems [44–51].

Nonuniqueness, as has been shown by Capelle et al. [51], occurs when there is a set formed by more than one density characterizing a given system such that the densities in this set determine just a manifold of ground-state wavefunctions and not specific ground-state ones. Furthermore, the wave functions belonging to this manifold can be ground states in more than one set of external potentials. Hence, nonuniqueness is a general property of particular quantum systems and is not directly related to whether the state of the system is represented in a subspace or in the full Hilbert space. However, as initially shown by Harriman [38] and as is illustrated in the present work, nonuniqueness may also occur when there is only one density characterizing the system provided that the system is represented in a finite subspace and that the instability conditions discussed above hold. It is in this particular situation, hence, that we may talk about an inestability-generated nonuniqueness. For the reasons discussed above, we expect that this type of instability-generated nonuniqueness will also be present in the finite orbital set treatment of Kohn–Sham equations, even in the case when spin is present.

6 Conclusions

In the present study, by utilizing an extension of the Hohenberg-Kohn theorem to finite subspaces, we have been able: (1) to analyze the subspace stability conditions related to the potential; (2) to devise explicit methods for generating potentials that violate subspace stability; (3) to provide numerical examples of instability potentials for simple problems; (4) to discuss some consequences of subspace instability for the numerical evaluation of exact Kohn–Sham exchange-correlation potentials, (5) to relate the stability conditions to linear dependence of finite basis sets, and, (6) to clarify the connection between instability and nonuniqueness of the potentials.

The present study brings into focuss the problem of establishing practical criteria for guaranteeing subspace stability in finite basis set applications Hohenberg-Kohn–Sham theory as well as of setting up physical criteria that would allow us to discern between spurious and truly physical potentials. This problem is of paramount importance, as recent discussions have shown [40–42]. In this context, the present results might prove useful for gaining control over the error $\Delta v = v - v'$ that arises when one works in a finite-dimensional space F (supposing $\rho_v = \rho_{v'}$ for the ground-state densities of the matrix-representation of the operators H_v and $H_{v'}$). The "distance" between F and the whole space should probably be useful in this endeavor. However, it is not yet clear how this distance should be defined and used in order to measure and control the error Δv.

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