Finite-basis-set implementation of subspace density-functional theory for excited states

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The aim of this paper is to study the peculiarities arising in a finite-basis-set implementation of the subspace density-functional theory (SDFT) for the excited states of molecules. The accuracy of different basis-set calculations is discussed within the framework of the local-density approximation. Small basis sets with adjustable parameters, optimized for each subspace energy, were found to provide a balanced description of states. On the contrary, basis sets adjusted to the ground state yield a poor approximation for the excited states. For the molecules under consideration (H_2, HeH, and LiH), the SDFT accuracy for excited states compares well with ground-state density-functional theory calculations. Despite the limited basis set used the excitation energies calculated are in agreement with the more accurate ones obtained within the wave-function formalism by the configuration interaction methods.

Many excited-state density-functional theories (DFT's) appeared since the introduction of the subspace theory in 1979 [1]. Depending on the class of problems that one has to deal with, some theories are more appropriate than others. As noted in Ref. [2], the subspace theory is very appropriate for degenerate states as it makes use of the whole space of degeneracy, characterized by certain irreducible representation of the symmetry group of the Hamiltonian, giving densities having the symmetry of the external potential. This, in effect, gives Kohn and Sham (KS) potentials that have the same transformation properties as the external potential [3]. This advantage is absent in the case of the general ensemble theory developed by Kohn, Oliveira, and Gross [4]. In fact, in their applications these authors restricted themselves to the equiensemble theory, which is identical to the subspace theory. Single excited state DFTs have also appeared [5], whereas time depended DFT is another method widely used for deriving information about excitations spectra [6].

The major problem in these theories is the derivation of a good exchange and correlation energy function $E_{xc}(\rho)$ and potential $V_{xc}(\mathbf{r},\rho)$. An attempt was made initially by Kohn [7], but the nonlocal character of this potential did not encourage many applications. Successful functional forms of $E_{xc}(\rho)$ for excited-state theories have been derived by Nagy [8], who showed the accuracy of her functional forms by doing numerical applications for atoms and molecules. In a recent paper it was shown that $E_{xc}(\rho)$ for subspaces have the same functional form as those of the ground state [9]. Thus one can use the already existing literature on the ground-state functionals, where considerable progress has been made recently [8,5,10].

The subspace density-functional theory for excited states has been tested recently for atoms [9], using the local-density approximation for $V_{xc}(\mathbf{r},\rho)$ [11]. The energies found compare well in accuracy with those of the ground-state DFT of Kohn and co-workers [12]. In applying the theory to atoms, we had to deal with the single variable r, the electron-nucleus distance. Thus one could apply numerical procedures to solve the KS equations. However, for the case of molecules, the advantage of the spherical symmetry is missing

and one has to apply other methods. One of the popular methods is to use finite basis-set expansion employed in almost all contemporary molecular-structure calculations, i.e., each occupied KS orbital $\phi_i(\mathbf{r})$, $i=1,2,...,N$ is presented by a linear combination of the basis functions $g_k(\mathbf{r})$, $k=1,2,...,m$. Thus

$$\phi_i(\mathbf{r})=\sum_{k=1}^{m} C_{ik}g_k(\mathbf{r}). \tag{1}$$

In doing so one faces the problems of selecting the functions $g_k(\mathbf{r})$. The accuracy of calculations is ultimately determined by the degree of completeness of the basis set. At present, the effects due to a basis-set truncation are widely recognized as the main source of error in *ab initio* calculations (see, e.g., [13] and references therein). Usually a process of trial and error in the choice of the basis set is needed. For ground-state (GS) calculations much progress has been achieved and useful computational experience has been accumulated [14,15], but for the excited states (ESs), the situation is far less satisfactory and this problem is open to discussion.

In this paper we are testing subspace density-functional theory (SDFT) for the case of molecules and discuss various aspects of constructing the basis sets that could provide a flexible scheme to treat in a balanced way the GS and ESs and give reasonable values for the energy differences, e.g., excitation energies. In the present application, attention was focused on simple molecules H_2, HeH, and LiH, which can be adequately described by a small number of basis functions. The calculations were carried out for eigenstates having the same symmetry as the GS as, in general, the minimum principle can be restricted on states transforming according to the irreducible representation of the symmetry group of the Hamiltonian [9]. For these molecules the basis functions $g_k(\mathbf{r})$ have the form

$$g_k(\mathbf{r})=\exp\{-\zeta_k[(x^2+y^2+(z-z_k)^2]\}, \quad k=1,2,...m. \tag{2}$$

TABLE I. Total energies of the ground and excited states for the molecules H_2, LiH, and HeH using the Hartree-Fock (HF) and local-density approximation (LDA) (nuclear separation $R = 1.4$ bohr for H_2, $R = 3.014$ bohr for LiH and $R = 1.5$ bohr for HeH; error is given for the LDA values; all values are in a.u.).

	H_2		LiH		HeH		
Method[a]	$^1\Sigma_g^+$	$2^1\Sigma_g^+$	$X^1\Sigma^+$	$A^1\Sigma^+$	$X^2\Sigma^+$	$A^2\Sigma^+$	$C^2\Sigma^+$
HF	−1.133	−0.599	−7.966	−7.716	−3.217	−2.975	−2.959
LDA	−1.135	−0.654	−7.914	−7.786	−3.205	−3.061	−2.978
Exact[b]	−1.174	−0.681	−8.070	−7.936	−3.264	−3.114	−3.056
Error %	2.3	4.0	1.9	1.9	1.8	1.7	2.2

[a]Basis set optimized for each individual HF and LDA subspace energies, respectively.
[b]Exact values were taken from precise *ab initio* calculations based on configuration interaction approach (see text).

Unlike the traditional atom-centered basis sets widely used in molecular calculations, we employed the basis functions whose exponents (ζ_k) and positions (z_k) were determined by invoking the variational principle. For the hydrogen molecular ion, such a basis set of 25 functions was found to support an accuracy in both the GS and ES energies at the submicron Hartree level [16,17]. These functions showed also good performance in ES calculations based on Hartree-Fock (HF) and perturbational schemes [18]. The main disadvantage is that the minimum principle results to a nonlinear optimization that requires much higher computational time than usual methods employing the same number of basis functions. Despite the difficulty of determining nonlinear parameters, one expects sufficient accuracy with a smaller number of basis functions. Besides, the use of such basis sets allows one to hope that error due to incompleteness is comparable for different states and, therefore, it is possible to see a trend in the behavior of energies stipulated without basis-set truncation effects.

For the correlation energy $E_{xc}(\rho)$ and the exchange and correlation potential $V_{xc}(\rho)$, we used the local-density approximation (LDA) [11] as in Ref. [9]. The reason for using this $V_{xc}(\rho)$ was to avoid at this stage complications arising from nonlocal forms. Calculations for the H_2 molecule were carried out at the nuclear separation distance $R = 1.4$ bohr in the GS ($^1\Sigma_g^+$) and ES ($2^1\Sigma_g^+$), for LiH at $R = 3.014$ bohr in the GS ($X^1\Sigma^+$) and the first ES ($A^1\Sigma^+$), and for HeH at $R = 1.5$ bohr in the GS ($X^2\Sigma^+$) and the ESs ($A^2\Sigma^+$ and $C^2\Sigma^+$). The basis sets consisting of nine functions were used for both H_2 and LiH. But because of symmetry in H_2, unlike the case of LiH, one basis function should be centered on the bond midpoint, that is ($z_9 = 0$). The remainder are distributed in pairs at $\pm z_k$. For the HeH molecule a basis set contained 14 s Gaussians.

To make clear the influence of a basis set on energy eigenvalues, we performed calculations using different basis sets: (i) optimized for the HF energy, (ii) optimized for the LDA GS energy, and (iii) specifically optimized for the subspace LDA (GS+ES) energy. The exponents and positions of the basis sets are available from the authors on request. As expected, the results of our calculations showed that a good basis set for LDA is not good for the HF scheme and vice versa. The best energy values were achieved with the basis sets specifically optimized for each individual subspace LDA

energy. These results are presented in Table I where the HF results are included for comparison. The ES HF energy was determined using the same scheme as the ES LDA one, but with $E_{xc} = E_{xc}^{HF}$. We compare also our results with those of precise *ab initio* calculations based on the configuration interaction approach obtained by Kolos and Roothaan for H_2 [19], by Langhoff and Chong for LiH [20] and by Petsalakis *et al.* for HeH [21]. Certainly, it is difficult to hope that the poor LDA potential and limited basis sets will yield good results for the absolute values of the energies. Nevertheless, we can observe that the SDFT implementation provides a balanced description of states, i.e., the SDFT accuracy of the ES molecular calculations compares with that of the GS LDA calculations. Indeed, Table II, where the vertical excitation energies are listed, shows that the SDFT leads to reasonable results for the energy differences, whereas the HF approximation gives worse results for both the ES energy and the excitation energy.

Thus, one may conclude that it is a success of the theory and its implementation the fact that for the molecules under consideration we have small deviations of the excitation energies from the precise ones.

TABLE II. Vertical excitation energies in the excited states for H_2, LiH, and HeH (error is given for the LDA values; all values are in a.u.)

	H_2	LiH	HeH	
Method[a]	$2^1\Sigma_g^+$	$A^1\Sigma^+$	$A^2\Sigma^+$	$C^2\Sigma^+$
HF	0.534	0.250	0.242	0.258
LDA	0.481	0.128	0.144	0.218
Exact[b]	0.493	0.134	0.150	0.208
Error %	2.4	4.5	4.0	4.8

[a]Basis set optimized for each individual HF and LDA subspace energies, respectively.
[b]Exact values were taken from precise *ab initio* calculations based on configuration interaction approach (see text).

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