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Highly Excited States from a Time Independent Density Functional Method

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Abstract: A constrained optimized effective potential (COEP) methodology proposed earlier by us for singly low-lying excited states is extended to highly excited states having the same spatial and spin symmetry. Basic tenets of time independent density functional theory and its COEP implementation for excited states are briefly reviewed. The amended Kohn–Sham-like equations for excited state orbitals and their specific features for highly excited states are discussed. The accuracy of the method is demonstrated using exchange-only calculations for highly excited states of the He and Li atoms.

Keywords: excited state; orthogonality constraints; optimized effective potential

1. Introduction

Most of the practical calculations of excited states are carried out via time-dependent density functional theory (DFT), in which transition energies are obtained from the poles of dynamic linear response properties. Despite its tremendous success, the present time-dependent DFT based schemes suffer from a number of shortcomings which restrict their applicability, in particular, for describing both double or multiple excitations and Rydberg states. Earlier, a constrained optimized effective potential (COEP) method has been proposed to compute singly low-lying excitation energies of atomic and molecular systems [1,2]. This method is along a line of the variational time independent DFT (TI-DFT) bifunctional formulation of Levy and Nagy [3,4] for individual excited states and easily implements an asymptotic projection method [5,6] for taking orthogonality constraints into account.

In this paper we extend the COEP methodology to highly excited (Rydberg) states. We achieve the effect of excitation electrons by using orthogonality constraints imposed on orbitals of the excited Kohn–Sham (KS) determinant. Specifically, local potentials are derived whose KS determinants minimize the total energies and are simultaneously orthogonal to the determinants of lower energies.

Basic tenets of TI-DFT for excited states are considered in Section 2 together with its COEP implementation. In Section 3, matrix Kohn–Sham-like equations for highly excited (including doubly excited) states are derived. Results of calculations for more than 20 highly excited states of the He and Li atoms are presented and discussed in Section 4, while Section 5 contains our conclusions.

2. Outline of TI-DFT and Its COEP Implementation

Over the years, a vast number of DFT papers devoted to excited states (ES) have been reported and only the scantiest of selections will be given here. We shall focus on TI-DFT-OEP based methods whose extension to excited states is neither unique nor straightforward. There exist the distinct formulations (see, e.g., [7–29] and references therein) and their number continues growing. Some of them rely

on a variational treatment focusing either on ensembles [7,18–22] or on an individual excited state approach [3,4,13–17]. Others use non-variational approaches (e.g., [25–29]).

An early rigorous DFT approach to treat excited states was given by Theophilou [7] and was reformulated as a subspace DFT [18] (later as equiensemble theory). It was later generalized into the theory of unequally weighted ensembles of excited states by Gross, Oliveria and Kohn [19–22]. An important step towards practical calculations within the ensemble theory was made by Nagy who generalized the OEP idea for ensemble of excited states [23]. Later, a ghost-interaction correction to this scheme [30] has showed on atoms that the ensemble Kohn–Sham theory with the exact ensemble-exchange potential can be as accurate as the ground state calculations [30,31]. However, practically no applications exist for highly excited states having the same spatial and spin symmetry.

For the universal variational excited-state functional of the kinetic and electron–electron repulsion energies, the second approach includes a “pure state” bifunctional formulation [3,4] or a “pure state” unifunctional formulation of Ayers, Levy, and Nagy [15,16] that utilizes special properties of the Coulomb potential. A useful analysis of the “pure state” approaches can be found in [13–16] and references within. An appeal of this pure-state approach is that it generates directly the desired individual excited-state energies and densities. This point was confirmed, to some extent, by excited state calculations based on the COEP method proposed in [1] and later developed in Refs. [32–34]. It was shown, that an excited state produced by excitation of electron, for example, from orbital φ_{0k} of the ground state KS determinant Φ_0 can be presented by imposition of some orthogonality constraints on the ES orbitals.

Let us consider a singly excited state to make clear the idea of this method. If the ground state orbitals are determined by a one-particle equation with an effective local potential $V_{0eff}(r)$

$$\left[-\frac{1}{2}\nabla^2 + V_{0eff}^\sigma(\vec{r}) \right] \phi_{0i}^\sigma(\vec{r}) = \varepsilon_{0i}^\sigma \phi_{0i}^\sigma(\vec{r}), \quad \sigma = \alpha, \beta, \quad i = 1, 2, \dots, n \quad (1)$$

then orbitals $\{\varphi_i\}$ of the excited state determinant Φ , generated by excitation of an electron from orbital ϕ_{0k}^α are determined by

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}^\sigma(\vec{r}) \right] \phi_i^\sigma(\vec{r}) = \varepsilon_i^\sigma \phi_i^\sigma(\vec{r}) \quad (2)$$

subject to constraints

$$\langle \phi_{0k}^\alpha | \phi_j^\alpha \rangle = 0, \quad j = 1, 2, \dots, n^\alpha \quad (3)$$

According to the asymptotic projection method constrained eigenvalue Problems (2) and (3) can be easily reduced to an equivalent unconstrained eigenvalue problem with the initial operator modified as follows (see [1] for more details):

$$\begin{aligned} \left[-\frac{1}{2}\nabla^2 + V_{eff}^\alpha(\vec{r}) + \lambda P_{0k}^\alpha \right] \phi_i^\alpha(\vec{r}) &= \varepsilon_i^\alpha \phi_i^\alpha(\vec{r}) \\ \lambda &\rightarrow \infty \\ \left[-\frac{1}{2}\nabla^2 + V_{eff}^\beta(\vec{r}) \right] \phi_i^\beta(\vec{r}) &= \varepsilon_i^\beta \phi_i^\beta(\vec{r}) \end{aligned} \quad (4)$$

where P_{0k}^α is the projection operator $P_{0k}^\alpha = |\phi_{0k}^\alpha\rangle\langle\phi_{0k}^\alpha|$.

The key moment of the asymptotic projection method is based on the following proposal [5,6,35]:

- The constraint vector $|\phi_{0k}^\alpha\rangle$ tends to an eigenvector of the modified operator

$$h_{\text{mod}} = \left[-\frac{1}{2}\nabla^2 + V_{eff}^\alpha(\vec{r}) + \lambda P_{0k}^\alpha \right], \quad \text{if and only if } \lambda \Rightarrow \pm\infty$$

Then, fulfillment of Equation (3) will follow automatically due to the orthogonality of the eigenvectors, which correspond to different eigenvalues of a self-conjugate operator. The only additional computation beyond that required for the ground state (see Equation (1)) is the evaluation of the overlap matrix element $\langle \phi_{0k}^\alpha | \phi_j^\alpha \rangle$. This remark is important, especially, when different optimized basis sets are used for different states.

3. Matrix Kohn–Sham-Like Equations for Highly Excited States

In this Section we shall show how this methodology can be easily extended to high excitations, including doubly, triply and so on excitations. For example, a doubly excited state Φ^{double} produced by excitation of electrons from ϕ_{0k}^α and ϕ_{0l}^β orbitals can be obtained by using the following orthogonality constraints imposed on orbitals $\{\varphi_j\}$ of the doubly excited state Slater determinant Φ^{double} :

$$\langle \phi_{0k}^\alpha | \phi_j^\alpha \rangle = 0, j = 1, 2, \dots, n^\alpha \tag{5}$$

and

$$\langle \phi_{0l}^\beta | \phi_j^\beta \rangle = 0, j = 1, 2, \dots, n^\beta \tag{6}$$

Then, using the asymptotic projection methodology, we have the corresponding KS-like equations in a form:

$$(h^\alpha + \lambda P_k^\alpha - \varepsilon_i^\alpha) | \phi_i^\alpha \rangle = 0 \tag{7}$$

$$\lambda \rightarrow \infty$$

$$(h^\beta + \lambda P_l^\beta - \varepsilon_i^\beta) | \phi_i^\beta \rangle = 0 \tag{8}$$

with the orthoprojectors: $P_k^\alpha = | \phi_{0k}^\alpha \rangle \langle \phi_{0k}^\alpha |$ and $P_l^\beta = | \phi_{0l}^\beta \rangle \langle \phi_{0l}^\beta |$, and the operator $h^\sigma = -\frac{1}{2} \nabla^2 + V_{eff}^\sigma(\vec{r})$ with an effective potential

$$V_{eff}^\sigma(\vec{r}) = V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}^\sigma(\vec{r}), \sigma = \alpha, \beta \tag{9}$$

where $V_{ext}(\vec{r})$, $V_H(\vec{r})$ are the external and the Hartree (classical Coulomb) potentials and $V_{xc}^\sigma(\vec{r})$ is a local exchange-correlation potential.

In order to obtain equations for second excited state we should substitute the operators P_k^α and P_l^β by the orthoprojectors

$$P_k^\alpha = | \phi_{0k}^\alpha \rangle \langle \phi_{0k}^\alpha | + | \phi_{1k}^\alpha \rangle \langle \phi_{1k}^\alpha |, \text{ etc.} \tag{10}$$

$$P_l^\beta = | \phi_{0l}^\beta \rangle \langle \phi_{0l}^\beta | + | \phi_{1l}^\beta \rangle \langle \phi_{1l}^\beta |, \text{ etc.} \tag{11}$$

where ϕ_{1k}^α and ϕ_{1l}^β are orbitals from the first ES determinant. In addition, in general, indices k or l for orbitals in different determinants may be different. It allows us to construct various classes of excited states in a unique approach. It is clear that for arbitrary N -th excited state, we have

$$P_k^\alpha = \sum_{m=0}^{N^\alpha-1} | \varphi_{mk}^\alpha \rangle \langle \varphi_{mk}^\alpha | \text{ and } P_l^\beta = \sum_{m=0}^{N^\beta-1} | \varphi_{ml}^\beta \rangle \langle \varphi_{ml}^\beta | \tag{12}$$

In practical applications, we invariably invoke the algebraic approximation by parameterizing the orbitals in a finite one-particle basis set. This approximation may be written

$$| \phi_i^\sigma \rangle = \sum_{p=1}^M c_{pi}^\sigma | \chi_p \rangle, \sigma = \alpha, \beta \tag{13}$$

It should be stressed that, in general, the basis set for the excited state, is distinct from that for the ground state. This is because calculations on excited states can be meaningless without including sufficiently diffuse basis functions.

Once the basis set $\{\chi_p\}$ is introduced, the integro-differential Equations (7) and (8) become generalized matrix eigenvalue problems:

$$\sum_{q=1}^M \tilde{h}_{pq}^{\sigma} c_{qi}^{\sigma} = \epsilon_i \sum_{q=1}^M S_{pq} c_{qi}^{\sigma} \tag{14}$$

with $S_{pq} = \langle \chi_p | \chi_q \rangle$ is the overlap matrix and \tilde{h}_{pq}^{σ} are modified h matrices with the elements

$$\tilde{h}_{pq}^{\alpha} = \langle \chi_p | h^{\alpha} | \chi_q \rangle + \lambda \sum_{m=0}^{N^{\alpha}-1} \langle \chi_p | \phi_{mk}^{\alpha} \rangle \langle \phi_{mk}^{\alpha} | \chi_q \rangle \tag{15}$$

$$\tilde{h}_{pq}^{\beta} = \langle \chi_p | h^{\beta} | \chi_q \rangle + \lambda \sum_{m=0}^{N^{\beta}-1} \langle \chi_p | \phi_{ml}^{\beta} \rangle \langle \phi_{ml}^{\beta} | \chi_q \rangle \tag{16}$$

Since λ cannot be infinity in practical calculations, one has to settle on some large finite values. Reasonable compromise is achieved if λ is of order of 10^3 – 10^4 hartrees. This value provides a target accuracy for $\langle \phi_{0k}^{\alpha} | \phi_j^{\alpha} \rangle$ and $\langle \phi_{0l}^{\beta} | \phi_j^{\beta} \rangle \sim 10^{-5}$ [35] and leads to orthogonality of the KS determinants which describe excited states.

After solving Equation (14) with Matrices (15) and (16) the excited state energy is determined by

$$E\{\phi\} = \sum_{\sigma} \sum_{i=1}^{n^{\sigma}} \langle \phi_i^{\sigma} | -\frac{1}{2} \nabla^2 | \phi_i^{\sigma} \rangle + \int \rho(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + \frac{1}{2} \int \rho(\vec{r}) V_H(\vec{r}) d\vec{r} + E_{xc}\{\phi\} \tag{17}$$

where ρ is the electron density and $E_{xc}\{\phi\}$ is the exchange-correlation energy functional. If we use an exchange-only approximation then $E_{xc}\{\phi\}$ should be replaced by the exchange energy functional $E_x\{\phi\}$ expressed in terms of orbitals from Equations (7) and (8):

$$E_x\{\phi\} = -\frac{1}{2} \sum_{\sigma} \sum_{i,j}^{n^{\sigma}} \int d\vec{r} \int \frac{\phi_i^{\sigma*}(\vec{r}) \phi_j^{\sigma*}(\vec{r}') \phi_i^{\sigma}(\vec{r}') \phi_j^{\sigma}(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' \tag{18}$$

In concluding this section, it is worth also noting that the imposition of the orthogonality constraint on an approximate lower state wave function, such as the Kohn–Sham reference function, does not, in general, yield an excited state energy which is an upper bound to the exact excited state energy.

4. Results of Calculations and Their Discussion

In this section we demonstrate the potential of our exchange-only COEP (x-COEP) implementation for highly excited 3S states of the He atom ($1sns, n = 2, 3, \dots, 7; 2sns, n = 3, 4, \dots, 8; 3sns, n = 4, 5, \dots, 8$; and $4sns, n = 5, \dots, 8$) and highly excited $1s^2ns$ ($n = 3, \dots, 7$) doublet states of the Li atom.

Before discussing results of calculations, we should point out that our x-COEP implementation employs a parameterized form of V_{eff} proposed in [36] and further developed in [37,38] where an effective potential is a direct mapping of the external potential V_{ext} and for N -electron atoms takes the form:

$$V_{eff}(r) = -\frac{Z}{r} + (N-1)C \frac{1 - \exp(-dr)}{r} \tag{19}$$

In the spirit of the OEP method, variational parameters C and d are determined by minimizing the energy $E\{\phi\} = \langle \Phi | H | \Phi \rangle$ for each individual state. The potential preserves symmetry properties

of the exact eigenstates and has proven to be successful for the ground state calculations of different characteristic atoms and molecules [34,37,38] and for low-lying excited states [1,2]. Therefore it is natural to try this potential for highly excited state calculations.

Our results are compared with the Hartree-Fock (HF) energies computed in Ref. [39] and high precision data obtained by the configuration interaction method in the basis set of Hylleraas functions that explicitly depend on interelectron separations [40,41]. Calculations were carried out using 42s-gaussians.

$$\chi_p(x, y, z) = \exp \left[-\zeta_p (x^2 + y^2 + z^2) \right], \quad p = 1, 2, \dots, M \tag{20}$$

which were constructed according to the even-tempered prescription, i.e., the exponents, ζ_p , were defined by the geometric series:

$$\zeta_p = \alpha \beta^{p-1}, \quad p = 1, 2, \dots, M \tag{21}$$

The parameters α and β were optimized for each atom and a given excited state. Information of the even-tempered basis sets for low-lying states of the He and Li atom can be found in Ref. [42].

We performed excited state calculations for the He atom using the different schemes:

- (i) Common basis set adjusted to the ground state and the potential parameters optimized for a given excited state were employed (x-COEP-bgs column in Table 1). We restricted parameters to 3 excited states to show some tendencies.
- (ii) Excited states were obtained from the ground state Hamiltonian but basis sets were optimized for each individual excited state (x-COEP-Vgs column in Tables 1 and 2).
- (iii) Both orbital basis sets and the potential parameters were optimized for a given excited state (x-COEP column in these tables).

Table 1. x-COEP energies (hartrees) of triplet $1sns$ ($n = 2, 3, \dots, 7$) states of He and their comparison with MOM method (basis set consists of 42s functions).

State	x-COEP-bgs *	x-COEP-Vgs **	x-COEP	MOM [43]	Δ ***
1s2s 3S	-2.171687	-2.171687	-2.171687	-2.174251	2.564
1s3s 3S	-2.000406	-2.067214	-2.067464	-2.068485	1.021
1s4s 3S	-0.525465	-2.034747	-2.035195	-2.036436	1.241
1s5s 3S	3.256538	-2.020897	-2.021524	-2.022583	1.059
1s6s 3S	-	-2.013670	-2.01424	-2.015357	1.114
1s7s 3S	-	-2.006859	-2.009609	-2.011118	1.509

* Ground state basis set and optimized V_{eff} for each individual state are used; ** ground state V_{eff} and optimized basis set adjusted to a given excited state are used; *** $\Delta = E(xCOEP) - E(MOM)$ (mhartrees).

The corresponding results are listed for triplet singly excited $1sns$ ($n = 2, 3, \dots, 7$) states (Table 1) and triplet doubly excited state energies of $2sns$ ($n = 3, 4, \dots, 8$) states (Table 2). x-COEP energies of triplet singly excited energies were compared with the HF energies obtained with the maximum overlap method (MOM) [43] which does not use orthogonality restrictions. The calculations in [43] were carried out using 70s even-tempered Slater-type basis functions. The results of [43] can be considered as benchmark HF data. These authors used the extended precision in the “Mathematica” package to avoid problems with almost linearly dependent basis set. Unlike Ref. [43] our calculations were restricted to 6 states (up to 1s7s) because for $n > 7$ we observed that the corresponding optimal basis sets present some linear dependencies. We used double precision and controlled the conditionality of the overlap matrix by calculating its eigenvalues in order to avoid the appearance of computational linear dependence. Calculations of Ref. [43] were restricted to only singly excited states. Therefore we compare doubly excited energies with our HF calculations [39] and accurate theoretical calculations (named in Tables 2–4 as E^{exact}) based on a configuration interaction approach with the explicitly correlated Hylleraas basis set functions [40]. A comparison of excited state energies presented in

x-COEP-bgs and x-COEP-Vgs columns of Table 1 with the fully optimized results (x-COEP column) shows that basis set optimization plays a crucial role for a correct description of excited states with respect to optimization of potential parameters. We observed that potential parameters for the ground state differ from those for excited states. However, we did not notice any trends in their behavior. In the case of helium the dependence of the results on the values of the parameters is relatively weak and the same effective potential correctly describes both the ground state and the excited states. The columns x-COEP-Vgs in Tables 1 and 2 demonstrate that the ground state potential with parameters $C = 3.982687$ and $d = 0.248872$ and the optimization of the orbital basis for a given excited state can support a reasonable accuracy of excited energies.

Table 2. Doubly excited energies (hartrees) computed at the xCOEP level and their comparison with the Hartree-Fock and “exact” values for the $2sns$ ($n = 3, 4, \dots, 8$) states of He; (basis set consists of 42s functions).

State	x-COEP-Vgs *	x-COEP	HF [39]	E^{exact} [40]	Δ^{**}
2s3s 3S	−0.583918	−0.584750	−0.584843	−0.602578	17.828
2s4s 3S	−0.540931	−0.541915	−0.541994	−0.548841	6.926
2s5s 3S	−0.524047	−0.525104	−0.525151	−0.528414	3.310
2s6s 3S	−0.515899	−0.516738	−0.516757	−0.518546	1.808
2s7s 3S	−0.503937	−0.511622	−0.511964	−0.513046	1.424
2s8s 3S	−0.485457	−0.508428	−0.508969	−0.509673	1.245

* Ground state V_{off} and optimized basis set adjusted to a given excited state are used; ** $\Delta = E(\text{x-COEP}) - E^{\text{exact}}(\text{mhartrees})$.

In Tables 3 and 4 triplet doubly excited energies of $3sns$ ($n = 4, 5, \dots, 8$) states and $4sns$ ($n = 5, \dots, 8$) of He, computed at the x-COEP level, are given. One can see that the accuracy of the x-COEP calculations is improved when n increases. This observation is in agreement with Ref. [43] whose authors pointed out that “In those states where $n \gg 1$, the electrons are spatially well separated and one might anticipate intuitively that they will be weakly correlated and that the x-COEP and Hartree-Fock methods, which neglects such effects, may be an excellent approximation”.

Table 3. Doubly excited triplet energies (hartrees) computed at the xCOEP level and their comparison with the Hartree-Fock and “exact” values for the $3sns$ ($n = 4, \dots, 8$) states of He; (basis set consists of 42s functions).

State	x-COEP	HF	E^{exact} [40]	Δ^* (mhartrees)
3s4s	−0.272284	−0.272245	−0.287277	14.993
3s5s	−0.250622	−0.250554	−0.258134	7.512
3s6s	−0.240454	−0.240598	−0.244807	4.353
3s7s	−0.234329	−0.235129	−0.237672	3.343
3s8s	−0.231937	−0.231791	−0.233433	1.496

* $\Delta = E(\text{x-COEP}) - E^{\text{exact}}$.

Table 4. Doubly excited triplet energies (hartrees) computed at the xCOEP level and their comparison with the Hartree-Fock and “exact” values for the $4sns$ ($n = 5, 6, 7, 8$) states of He; (basis set consists of 42s functions).

State	x-COEP	HF	E^{exact} [40]	Δ^* (mhartrees)
4s5s	−0.157968	−0.157982	−0.169307	11.339
4s6s	−0.145387	−0.145402	−0.152122	6.735
4s7s	−0.138015	−0.138020	−0.143176	5.161
4s8s	−0.134051	−0.134134	−0.137961	3.91

* $\Delta = E(\text{x-COEP}) - E^{\text{exact}}$.

Our observations of Tables 2–4 show that energy differences $E^{\text{COEP}} - E^{\text{exact}}$ for different excited states are similar. As a result, excitation energies based on the x-COEP method are in good agreement with those computed with highly correlated methods (see Table 5).

Table 5. Doubly excitation energies (eV) from triplet state of He computed at the x-COEP level of approximation.

Excitation	x-COEP	“Exact” [40]
2s3s → 3s4s	8.5	8.58
2s4s → 3s5s	7.93	7.91
2s5s → 3s6s	7.75	7.72
2s6s → 3s7s	7.68	7.64
2s7s → 3s8s	7.61	7.6
3s4s → 4s5s	3.11	3.21
3s5s → 4s6s	2.86	2.88
3s6s → 4s7s	2.79	2.77
3s7s → 4s8s	2.73	2.71

In Table 6 we compare x-COEP excited doublet $1s^2ns$ ($n = 3, \dots, 7$) energies and excitation energies of the Li atom to the HF [38] and “exact” energies obtained with the most accurate configuration interaction wave function using the Hylleraas basis set [41]. It is known that high accuracy of calculation of the transition frequencies for Rydberg states of alkali metal atoms, in particular lithium, is a topical problem of theoretical methods for studying the electronic structure [44]. Such calculations for highly excited states have been carried out only recently [41]. Comparison of the calculated energies of excitation from the $1s^23s$ state with the high precision results [39] shows that the proposed implementation for ESs yields excellent agreement with the precision excitation energies (compare columns 5 and 6 of Table 6). Our calculation of the x-COEP ground state ($1s^22s$) energy yields $E = -7.431724$ hartrees. Comparison with the precision result $E^{\text{exact}} = -7.478060$ hartrees gives $E(\text{xCOEP}) - E^{\text{exact}} = 0.046336$ hartrees, which is in agreement with the accuracy of ES energy determination. For example, for the $1s^26s$ state $E(\text{xCOEP}) - E^{\text{exact}} = 0.046655$ hartrees. For the Li atom we collected also the optimum values of parameters “C” and “d” defining the effective potential (see Table 7). We can see that, unlike He, there are some trends in their behavior: the “C” parameter increases for higher excited states whereas the “d” parameter decreases.

Table 6. Excited doublet $1s^2ns$ ($n = 3, 4, \dots, 7$) energies (hartrees) and excitation energies ΔE (eV) computed at the x-COEP level with respect to the $1s^23s$ state and their comparison to “exact” values for the Li atom (basis set consists of 42s functions).

State	x-COEP	HF [39]	Exact * [41]	ΔE (eV)	
				x-COEP	«exact»
$1s^23s$	−7.307322	−7.310208	−7.354098	0	0
$1s^24s$	−7.273149	−7.274884	−7.318531	0.93	0.97
$1s^25s$	−7.257268	−7.259979	−7.303552	1.36	1.38
$1s^26s$	−7.249194	−7.252317	−7.295859	1.58	1.59
$1s^27s$	−7.242843	−7.247864	−7.291392	1.75	1.71

* Configuration interaction method with the Hylleraas basis set functions.

Table 7. The optimum values of parameters of the effective potential for the different doublet states of Li.

State	<i>C</i>	<i>d</i>
1s ² 2s	1.094723	1.661917
1s ² 3s	1.691346	1.204497
1s ² 4s	4.151071	0.694042
1s ² 5s	9.623142	0.431399
1s ² 6s	18.66719	0.301418
1s ² 7s	65.39487	0.157559

Thus, results show that the x-COEP implementation of TI-DFT can ensure the accuracy of energy determination for highly excited states comparable in accuracy to the ground state and can be considered to be the starting point for the development of many-body methods of calculation of correlation effects for such states. The computational cost of the method for highly excited states requires virtually the same computational efforts as for the ground state.

5. Concluding Remarks

In this paper we have briefly discussed time-independent DFT for excited states in its COEP implementation, which explicitly introduces orthogonality of the Kohn–Sham excited detrimental function to the lower states of the same symmetry. It was shown that our preliminary results (see [1]) for singly low-lying excited states can be easily extended to highly excited states having the same spatial and spin symmetry so that practical calculations of various classes of excited states can be done within a unified approach.

Excited state energies and excitation energies (for about 20 states) computed at the x-COEP level for the He and Li atoms are in a good agreement with the corresponding results obtained by the HF method and accurate theoretical calculations based on a configuration interaction approach with the explicitly correlated Hylleraas basis set functions.

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