

# Orthogonality-constrained Hartree–Fock and perturbation theory for high-spin open-shell excited states

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**Abstract** We present the orthogonality-constrained Hartree–Fock (HF) method for excited states in a combination with the Møller–Plesset-like perturbation theory for the correlation energy. This developed “HF + MP2” formalism for excited states allows for the treatment of both ground and excited states in a balanced manner. Unlike a previous work (Glushkov in *Chem Phys Lett* 287:189, 1998), our interest has shifted toward highly doubly excited states of atoms and doubly ionized core hole molecular states which are attractive from the experimental point of view. The accuracy of the method is demonstrated by calculations of more than 30 highly excited states of the He and Li atoms and about 10 doubly excited core hole states of some diatomic molecules (CO, NO and LiF).

**Keywords** Excited states · Constrained Hartree–Fock · Perturbation theory · Double core hole states · Frozen orbitals

## 1 Introduction

It is well known that Hartree–Fock (HF) theory not only has been proven to be quite suitable for calculations of ground state (GS) properties of electronic systems, but has also served as a starting point to develop many-particle approaches which deal with electronic correlation, like perturbation theory, configuration interaction methods and so on (see e.g., [1]). Therefore, a large number of sophisticated computational approaches have been developed for the description of the ground states based on the HF approximation. One of the most popular computational tools in quantum chemistry for GS calculations is based on the effectiveness of the HF approximation and the computational advantages of the widely used many-body Møller–Plesset perturbation theory (MPPT) for correlation effects. We designate this scheme as “HF + MPPT,” here after denoted “HF + MP2.”

There is far less reported experience for the HF studies of electronic excited states (ESs). Especially, highly, doubly and core hole excited (ionized) states are not often studied. It is clear that existing ground state self-consistent field (SCF) methods cannot be directly applied to excited states of the same symmetry or of the same spin multiplicity as a lower state because of the so-called variational collapse i.e., the optimization procedure will find only the lowest solution of a given symmetry or a given spin multiplicity. Therefore, such calculations for ES cannot be considered as routine. The most powerful scheme for accurate treatment of ESs is based on multireference methods [2–8]. They typically provide an accuracy of about 0.1 eV but require the expense of much computational cost. Thus, it can be quite difficult to carry out the corresponding calculations. Such methods are, however, indispensable to study systems where

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single-configuration methods cannot be applied. However, in cases where a multireference approach is necessary, it is clear that the orbitals of a single configuration, together with a basis set that has been specifically optimized for a given excited state, will prove more appropriate for the development of many-body correlation methods than orbitals expanded in a basis set constructed for the ground state. Furthermore, it would be very useful to have an analogue of the “HF + MP2” formalism for the description of excited states which can be adequately described by a single Slater determinant. In doing so, we should take into account that the basis functions that are used to construct molecular orbitals are typically optimized to describe the ground states of atoms. Remembering that the ground and excited states are often of quite different character, it is desirable to use different basis sets for different states. “The desirability of using different basis sets for different states” was already pointed out by Shull and Löwdin [9] in 1958. It is especially important for highly excited states. We shall show that our methodology allows a basis set to be optimized for the excited state under consideration with essentially the same computational efforts as for the ground state. Such an approach provides a compact and accurate representation of excited state wave functions. On the other hand, finding a method that offers a well-balanced treatment of both states is often problematic. Accounting for electron correlation in excited states is not as straightforward as in the ground state.

In this contribution, we further develop the “HF + MP2” formalism for excited states focusing our attention on calculations of the ground state and excited state energies in a balanced manner, i.e.,

1. Reference configurations are constructed by employing the same computational scheme. For example, the ground and excited SCF functions are constructed using the Hartree–Fock equations, whose solutions are approximated in one particle basis sets optimized specifically to the state under consideration.
2. Correlation effects are taken into account using comparable schemes for the ground and excited states using, for example, many-body Møller–Plesset-like perturbation theory.

Some preliminary results in this direction were reported in papers [10, 11]. Here, we extend the theory and practical calculations to highly doubly excited states and doubly ionized core hole states. A simple and easily implemented asymptotic projection (AP) method for taking orthogonality constraints into account, which has been proposed earlier [12–14], allows one to perform the “HF + MP2” scheme for the ground and excited states with essentially the same computational costs. The AP method is based on the properties of self-conjugate operators. It is general and

applicable to any problem that can be cast in the form of an eigenvalue equation with some orthogonality constraints imposed on the eigenvectors.

The present work is arranged as follows: in Sect. 2, orthogonality constraints for single determinantal wave functions and some existing methods to prevent “variational collapse” are briefly discussed. Our orthogonality-constrained HF method for excited states is presented in Sect. 3. Unlike existing self-consistent field (SCF) techniques based on the Roothaan open-shell theory [15], it does not involve off-diagonal Lagrange multipliers. Additionally, equations for basis set optimization are also derived. The well-defined Møller–Plesset-like perturbation theory based on optimal excited orbitals generated by the proposed HF method is the subject of Sect. 4. In addition single excitations do not contribute because the excited state orbitals, like the ground state orbitals, satisfy the generalized Brillouin theorem. In Sect. 5, we apply the formalism to highly doubly excited states of atoms as well as to doubly ionized core hole states of diatomic molecules.

## 2 Specific features of SCF excited states calculations

Quantum mechanics requires *exact* wave functions to be orthogonal, but it makes no such demand on SCF functions. Indeed, consider the orthogonality condition for the *exact* many-electron wave functions describing the ground state,  $\Psi_0$ , and the first excited state  $\Psi_1$ , i.e., (see also [11])

$$\langle \Psi_0 | \Psi_1 \rangle = 0 \quad (1)$$

The exact ground state wave function,  $\Psi_0$ , can be written

$$\Psi_0 = \Phi_0 + \chi_0 \quad (2)$$

where  $\Phi_0$  is the many-electron ground state SCF wave function and  $\chi_0$  is the correlation correction. Without loss of generality, we can require

$$\langle \Phi_0 | \chi_0 \rangle = 0 \quad (3)$$

Similarly, the exact excited state wave function,  $\Psi_1$ , can be written

$$\Psi_1 = \Phi_1 + \chi_1 \quad (4)$$

where  $\Phi_1$  is the many-electron excited state SCF wave function and  $\chi_1$  is the corresponding correlation correction. Again, without loss of generality, we can require

$$\langle \Phi_1 | \chi_1 \rangle = 0 \quad (5)$$

Substituting (2) and (4) into (1), we have

$$\begin{aligned} \langle \Psi_0 | \Psi_1 \rangle &= \langle \Phi_0 | \Phi_1 \rangle + \langle \Phi_0 | \chi_1 \rangle \\ &\quad + \langle \chi_0 | \Phi_1 \rangle + \langle \chi_0 | \chi_1 \rangle = 0 \end{aligned} \quad (6)$$

or

$$\langle \Phi_0 | \Phi_1 \rangle = -[\langle \Phi_0 | \chi_1 \rangle + \langle \chi_0 | \Phi_1 \rangle + \langle \chi_0 | \chi_1 \rangle] \quad (7)$$

Thus we see that the SCF wave functions do not, in general, satisfy orthogonality constraints analogous to those obeyed by the exact wave functions.

It is worth also noting that the imposition of the orthogonality constraint on an approximate lower state wave function, such as the Hartree–Fock function, does not, in general, yield an excited state energy which is an upper bound to the exact excited state energy. An upper bound to the excited state energy is obtained if we impose the additional constraint

$$\langle \Phi_0 | H | \Phi_1 \rangle = 0$$

which is much more difficult to implement. In practice, if the lower state energy and the corresponding wave function are known accurately, then the coupling matrix element  $\langle \Phi_0 | H | \Phi_1 \rangle$  is expected to be small.

Several useful methods have been proposed to overcome the “variational collapse” problem, and a number of different schemes have been proposed for obtaining SCF wave functions for excited states [10, 16–26]. In recent years, there has been renewed interest in the orthogonality-constrained methods [14, 27] as well as in the SCF theory for excited states [28–32]. It is clear that an experience accumulated for the HF excited state calculations can be useful to develop similar methods within density functional theory [33–36]. Some of these approaches [10, 18, 19, 23, 24, 26, 30–35] explicitly introduce orthogonality constraints to lower states. Other methods [21, 22, 25] either use this restriction implicitly or locate excited states as higher solutions of nonlinear SCF equations [29]. In latter type of scheme, the excited state SCF wave functions of interest are not necessarily orthogonal to the best SCF functions for a lower state or states of the same symmetry.

In our methodology we impose a constraint upon the SCF excited state function so that

$$\langle \Phi_0 | \Phi_1 \rangle = 0, \quad (8)$$

i.e., we explicitly introduce the orthogonality constraint on  $\Phi_1$  to the best SCF ground state function  $\Phi_0$ . On the one hand, the restriction (8) limits slightly the variational degrees of freedom, but, on the other hand, the imposition of the constraint (8) has some advantages:

1. it preserves the important orthogonality property of exact eigenstates;
2. any lack of orthogonality of the SCF wave functions may lead to excited state energies lying below the corresponding exact energies (For example, Cohen and Kelly [37] found for the *He* atom the first singlet excited state energy  $E_1 = -2.16984$  hartree, whereas

the observed energy  $E_1^{\text{extract}} = -2.14598$  hartree (See also the work of Tatewaki et al. [38]).);

3. it allows the study of properties which depend on the wave functions of different states, e.g., in the evaluation of transition properties (see also [23, 24]);
4. it facilitates the development of a simple perturbation theory expansion for correlation effects in excited states [10] (see also Sect. 4).

We shall be concerned with ground and excited electronic states which can be adequately described by a single determinantal wave function. For simplicity, we consider singly excited states and show how our formalism can be applied to highly and doubly excited states.

Let  $\Phi_0$  be the ground state *unrestricted* Slater determinant constructed from a set of spin orbitals consisting of spatial part  $|\varphi_{0i}^\alpha\rangle$ , ( $i^\alpha = 1, 2, \dots, n^\alpha$ ) associated with  $\alpha$  spin functions and orbitals  $|\varphi_{0i}^\beta\rangle$ , ( $i^\beta = 1, 2, \dots, n^\beta$ ) associated with  $\beta$  spin functions, i.e.,

$$\Phi_0 = (N!)^{-1/2} \det \left| \varphi_{01}^\alpha \alpha, \dots, \varphi_{0n}^\alpha \alpha; \varphi_{01}^\beta \beta, \dots, \varphi_{0n}^\beta \beta \right| \quad (9)$$

without loss of generality, we define  $n^\alpha > n^\beta$ ,  $n^\alpha + n^\beta = N$ , where  $N$  is a number of electrons and  $S = S_z = (n^\alpha - n^\beta)/2$  is the total spin. Similarly,  $\Phi_1$  is a single *unrestricted* determinant wave function for the first excited state:

$$\Phi_1 = (N!)^{-1/2} \det \left| \varphi_{11}^\alpha \alpha, \dots, \varphi_{1n}^\alpha \alpha; \varphi_{11}^\beta \beta, \dots, \varphi_{1n}^\beta \beta \right| \quad (10)$$

Then, one can show [10, 11] that the orthogonality condition (8) is fulfilled if

$$\langle u | \varphi_{1j}^\alpha \rangle = 0, \quad j = 1, 2, \dots, n^\alpha \quad (11)$$

where  $|u\rangle = \sum_i^{n^\alpha} b_i |\varphi_{0i}^\alpha\rangle$ . Eq. (11) requires the orthogonality of all occupied excited state orbital associated with  $\alpha$  spin functions to the arbitrary vector  $|u\rangle$ , from the subspace of the occupied ground state orbitals associated with  $\alpha$  spin functions. In other words the vector  $|u\rangle$  is orthogonal to the subspace defined by occupied excited state  $\alpha$ -orbitals. A similar condition was also used in Refs. [23, 24, 35]. However, our practical implementation differs essentially from these works. In general, the coefficients  $b_i$  can be determined by minimizing the excited state Hartree–Fock energy, i.e., the complete variational space can be used instead of simply  $|u\rangle = |\varphi_{0n}^\alpha\rangle$ , where  $\varphi_{0n}^\alpha$  is the highest occupied molecular orbital. However, our computational experience showed that such a choice is a good approximation for  $|u\rangle$  and provides very simple implementation during SCF iteration procedure. Using an orthoprojector

$$P_u^\alpha = |\varphi_{0n}^\alpha\rangle \langle \varphi_{0n}^\alpha|$$

the requirement (11) can be rewritten in a symmetrical form, which is useful when deriving the excited state Hartree–Fock equations for orbitals, as follows:

$$\sum_j^{n^\alpha} \langle \varphi_{1j}^\alpha | P_u^\alpha | \varphi_{1j}^\alpha \rangle = 0, \quad (12)$$

This result can be easily extended to higher energy levels. For example, for the second excited state the operator  $P_u^\alpha$  should be substituted by the orthoprojector

$$P_u^\alpha = |\varphi_{0n}^\alpha\rangle\langle\varphi_{0n}^\alpha| + |\varphi_{1n}^\alpha\rangle\langle\varphi_{1n}^\alpha| \equiv P_{u,0}^\alpha + P_{u,1}^\alpha \text{ etc.}$$

It is clear, for arbitrary  $K^{\text{th}}$  singly excited state we have

$$P_u^\alpha = \sum_{k=0}^{K-1} P_{u,k}^\alpha, \quad \text{with } P_{u,k}^\alpha = |\varphi_{kn}^\alpha\rangle\langle\varphi_{kn}^\alpha|.$$

Furthermore, this idea can be extended to doubly, triply etc. excited states. In contrast to existing SCF methods for hole states, we achieve the effect of the excitation (or ionization) of electrons by using orthogonality constraints imposed on the orbitals of the doubly excited state's Slater determinant. For example, for description of excitations from  $\varphi_{0k}^\alpha$  and  $\varphi_{0l}^\beta$  ground state orbitals, we require a fulfillment of conditions

$$\sum_j^{n^\alpha} \langle \varphi_{1j}^\alpha | P_k^\alpha | \varphi_{1j}^\alpha \rangle = 0, \quad (13)$$

and

$$\sum_j^{n^\beta} \langle \varphi_{1j}^\beta | P_l^\beta | \varphi_{1j}^\beta \rangle = 0, \quad (14)$$

where  $P_k^\alpha = |\varphi_{0k}^\alpha\rangle\langle\varphi_{0k}^\alpha|$  and  $P_l^\beta = |\varphi_{0l}^\beta\rangle\langle\varphi_{0l}^\beta|$ .

At the HF level of theory, we call this method constrained self-consistent field (CSCF).

### 3 Hartree–Fock and basis set optimization equations for excited states

We shall follow the unrestricted Hartree–Fock (UHF) formalism for obtaining the restricted open-shell HF (ROHF) functions to derive the Hartree–Fock equations for excited states. For the sake of simplicity, we restrict our attention to the first excited state. The problem can be described as:

$$E_1^{\text{UHF}} = \min \langle \Phi_1 | H | \Phi_1 \rangle / \langle \Phi_1 | \Phi_1 \rangle \quad (15)$$

provided that

$$\langle \Phi_0 | \Phi_1 \rangle = 0, \quad (16)$$

$$\langle \Phi_1 | \{ \hat{S}^2 - S(S+1) \} | \Phi_1 \rangle = 0. \quad (17)$$

Equations (16) and (17) can be written in terms of one-particle orbitals:

1. Orbitals must satisfy the restrictions (12) which ensure the orthogonality of Slater determinants (16);
2. Equation (17) means that the excited Slater determinant must be an eigenvector of the  $S^2$  operator. As shown by Fock [39], the condition (17) is fulfilled if the set of orbitals associated with the  $\beta$  spin functions lies completely within the space defined by the set associated with the  $\alpha$  spin functions. This condition eliminates spin contamination and can be written as the orthogonality constraint [40]:

$$\sum_j^{n^\beta} \langle \varphi_{1j}^\beta | Q_1^\alpha | \varphi_{1j}^\beta \rangle = 0, \quad (18)$$

$Q_1^\alpha = I - P_1^\alpha$  is the orthoprojector on the subspace of the virtual  $\alpha$  spin orbitals and

$$P_1^\alpha = \sum_{i=1}^{n^\alpha} |\varphi_{1i}^\alpha\rangle\langle\varphi_{1i}^\alpha|$$

In order to obtain equations for optimal orbitals for the first excited state, we use the stationary condition

$$\delta L = \delta \left\{ E_1^{\text{UHF}} + \lambda_s \sum_{i=1}^{n^\beta} \langle \varphi_{1i}^\beta | Q_1^\alpha | \varphi_{1i}^\beta \rangle + \lambda_o \sum_{i=1}^{n^\alpha} \langle \varphi_{1i}^\alpha | P_u^\alpha | \varphi_{1i}^\alpha \rangle \right\} \quad (19)$$

Lagrange multipliers  $\lambda_o$  and  $\lambda_s$  are determined by the asymptotic projection methodology [10, 11, 40]. In practical applications, we invariably invoke the algebraic approximation by parameterizing the orbitals in a finite basis set. This approximation may be written

$$|\varphi_{1i}\rangle = P_1 |\varphi_{1i}\rangle \quad (20)$$

where  $P_1$  is an orthoprojector defined by a chosen basis set for the first excited state.

Then the variations in orbitals can be divided into the following independent parts, e.g., for the  $\alpha$  set

$$|\delta\varphi_{1i}^\alpha\rangle = P_1^\alpha |\delta\varphi_{1i}^\alpha\rangle + (P_1 - P_1^\alpha) |\delta\varphi_{1i}^\alpha\rangle + \sum_a (\partial_a P_1) |\varphi_{1i}^\alpha\rangle \delta\mu_a, \quad (21)$$

where  $\mu_a$ ,  $a = 1, 2, \dots, A$ , represents the basis set parameters (i.e., the exponents and the positions) and  $\partial_a P_1 = \partial P_1 / \partial \mu_a$ . The first term in Eq. (21) does not lead to changes in the total energy because it is invariant to any orthogonal transformation of the orbitals of any spin among themselves. The energetically significant variations are described by the second and third terms. The second term corresponds to variations

within the finite-dimensional subspace spanned by the chosen basis set. The last term allows this subspace to be rotated within the Hilbert space of one-particle states to attain the deeper minimum with respect to the total energy.

Substituting Eq. (21) into Eq. (19) and taking into account the independence of the variations and their arbitrariness, we obtain the following equations for orbitals (see [10, 11] for more details):

$$P_1 \left( F^\alpha - \lambda_s P_1^\beta + \lambda_o P_u^\alpha - \epsilon_i^\alpha \right) P_1 |\varphi_{1i}^\alpha\rangle = 0, \quad \lambda_s, \lambda_o \rightarrow \infty$$

$$P_1 \left( F^\beta + \lambda_s Q_1^\alpha - \epsilon_i^\beta \right) P_1 |\varphi_{1i}^\beta\rangle = 0, \quad i = 1, 2, \dots, M \quad (22)$$

and equations for basis set optimization

$$\sum_i^{n^\alpha} \langle \varphi_{1i}^\alpha | (\partial_a P_1) F^\alpha | \varphi_{1i}^\alpha \rangle + \sum_i^{n^\beta} \langle \varphi_{1i}^\beta | (\partial_a P_1) F^\beta | \varphi_{1i}^\beta \rangle = 0, \quad a = 1, 2, \dots, A \quad (23)$$

If the  $K$ th excited state is considered then, as mentioned, the projector  $P_u^\alpha$  takes the following form  $P_u^\alpha = \sum_{k=0}^{K-1} |\varphi_{kn}^\alpha\rangle \langle \varphi_{kn}^\alpha|$ . Equations (22) represent the orthogonality-constrained HF method in its general form. According to the AP methodology, the orthogonality constraint of Eqs. (12) and (18) is satisfied in the limit  $\lambda_o \rightarrow \infty$  and  $\lambda_s \rightarrow \infty$ , respectively. By setting  $\lambda_s = 0$ , we can relax the spin-purity constraint (18) and go back from ROHF to UHF solutions. By setting  $\lambda_o = 0$ , we fall back to the ground state. The corresponding orbitals form an optimal set which satisfy the generalized Brillouin's theorem (see [40] for more details) and lead to the same total energy that the one obtained by the Roothaan procedure. In our method, the only additional computation required, beyond that arising in the standard UHF scheme, is the evaluation of the overlap matrix element  $\langle \varphi_{0n} | \varphi_{kn} \rangle$ .

Left side of Eq. (23) represent a gradient of the total energy with respect to nonlinear basis set parameters  $\{\mu_a\}$ . This expression allows these parameters to be determined *variationally* and can be also used to construct an algorithm for optimization based on the gradient-like methods.

Since neither  $\lambda_s$  nor  $\lambda_o$  can be infinity in practical calculations, one has to settle on some large finite values. The recommended values are  $\lambda_s = 100$  hartrees for the spin-purity constraint and  $\lambda_o = 1000$  hartrees for the orthogonality constraint. They provide target accuracy close to  $10^{-6}$ .

In concluding this section, it is also worth noting that in our method all excited configurations based on the excited Slater determinant  $\Phi_1$ , viz.,  $\Phi_i^\alpha$ ,  $\Phi_{ij}^{ab}$  etc., where  $i$  and  $j$  refer

to occupied orbitals and  $a$  and  $b$  to virtual ones, are orthogonal both to  $\Phi_0$  and among themselves. Therefore, these functions form the orthonormal basis set in the many-body space and can be used, unlike other SCF methods which do not satisfy the orthogonality of states in the explicit form, to develop many-body methods incorporating the correlation effects, in particular, a many-body Møller–Plesset-like perturbation theory (see next Section).

#### 4 Second-order correction to the energy for excited states

It is known that within the framework of the Roothaan coupling operator approach, there is no unique way of choosing a reference Hamiltonian,  $H^{(0)}$ , with respect to which a perturbation expansion for correlation effects can be developed. Several proposals have been made for open-shell many-body perturbation theory expansions based on a reference from the ROHF formalism [41, 42] or the unrestricted Hartree–Fock formalism [43, 44]. We follow our papers [10, 45] where an alternative technique for the open-shell systems has been developed. In our method, the second-order correction to the ground state energy can be presented by [45]:

$$E_0^{(2)} = \sum_{i>j}^{\text{occ}} \sum_{a>b}^{\text{virt}} \frac{(\varphi_{0a}\varphi_{0i}|\varphi_{0b}\varphi_{0j}) - (\varphi_{0a}\varphi_{0j}|\varphi_{0b}\varphi_{0i})^2}{\epsilon_{0i} + \epsilon_{0j} - \epsilon_{0a} - \epsilon_{0b}} \quad (24)$$

The summations are over spin-orbitals. Subscripts  $i, j$  and  $a, b$  correspond to occupied and virtual orbitals of the ground state determinant, respectively. Unlike the formalism developed in Refs. [43, 44], single excitations do not contribute because our orbitals satisfy the generalized Brillouin theorem.

An optimum set of MOs obtained by means of Eq. (22) allows us to construct a well-defined open-shell perturbation theory for excited states which is a natural extension of the popular closed-shell MP2. For example, the zeroth-order Hamiltonian for the first excited state is as follows:

$$H^{(0)} = \sum_{m=\text{electrons}}^{n^\alpha} F^\alpha(m) + \sum_{m=\text{electrons}}^{n^\beta} F^\beta(m)$$

with Fockians

$$F^\sigma = \sum_i^{M-1} |\varphi_i^\sigma\rangle \epsilon_i^\sigma \langle \varphi_i^\sigma|, \quad \sigma = \alpha, \beta$$

The summation up to  $M - 1$  means that the vector  $|\varphi_{0n}^\alpha\rangle$  is excluded from the subspace of virtual orbitals. Remind  $M$  is the dimension of the basis set for the first ES. We

**Table 1** Constrained self-consistent ( $E^{\text{CSCF}}$ ) Hartree–Fock energies (in hartrees) of triplet  $1s\ ns$  ( $n = 2, 3, \dots, 10$ ) states of the He atom and energy difference between the MOM method ( $E^{\text{MOM}}$ ) and the one proposed here ( $E$ ),  $\Delta^{\text{HF}} = E^{\text{CSCF}} - E^{\text{MOM}}$  ( $\mu$ hartrees)

State	$E^{\text{CSCF}}$ (this paper)	$E^{\text{MOM}}$ [46]	$\Delta^{\text{HF}}$
$1s2s\ ^3S$	-2.174 250 72	-2.174 250 78	0.06
$1s3s\ ^3S$	-2.068 484 88	-2.068 484 95	0.07
$1s4s\ ^3S$	-2.036 436 35	-2.036 436 42	0.07
$1s5s\ ^3S$	-2.022 582 55	-2.022 582 62	0.07
$1s6s\ ^3S$	-2.015 357 22	-2.015 357 34	0.12
$1s7s\ ^3S$	-2.011 117 33	-2.011 117 58	0.25
$1s8s\ ^3S$	-2.008 418 90	-2.008 419 01	0.11
$1s9s\ ^3S$	-2.006 595 66	-2.006 595 90	0.24
$1s10s\ ^3S$	-2.005 306 45	-2.005 306 75	0.30

shall also omit the subscript “1” for a given ES and  $\Phi_1 \equiv \Phi^{(0)}$ ,  $\Phi_0 \equiv \Phi_0^{(0)}$ .

In contrast to the ground state case, for the excited state it is necessary to take into consideration the orthogonality constraints. For the first-order correction to the excited state reference function,  $\Phi^{(1)}$ , these constraints have the form

$$\langle \Phi^{(0)} | \Phi^{(1)} \rangle = 0,$$

and the constraints determined by the orthogonality condition for the states in the first-order perturbation theory leads to equation

$$P_0^{(0)} | \Phi^{(0)} \rangle + P_0^{(1)} | \Phi^{(1)} \rangle = 0$$

where  $P_0^{(0)} = | \Phi_0^{(0)} \rangle \langle \Phi_0^{(0)} |$  and  $P_0^{(1)} = | \Phi_0^{(0)} \rangle \langle \Phi_0^{(1)} | + | \Phi_0^{(1)} \rangle \langle \Phi_0^{(0)} |$ . Then one can show that the Rayleigh–Schrödinger perturbation theory leads to the following expression for the second-order correction to the ES energy [10]:

$$E^{(2)} = \sum_{i>j}^{\text{occ}} \sum_{a>b}^{\text{virt}} \frac{|(\varphi_a \varphi_i | \varphi_b \varphi_j) - (\varphi_a \varphi_j | \varphi_b \varphi_i)|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} - \langle \Phi^{(0)} | H | \Phi_0^{(0)} \rangle \langle \Phi_0^{(1)} | \Phi^{(0)} \rangle \quad (25)$$

Here subscripts “ $i$ ” and “ $j$ ” are occupied and “ $a$ ,” “ $b$ ” are virtual orbitals in  $\Phi^{(0)}$ .

The first term in Eq. (25) is immediately recognized as the second-order perturbation theory expression for the ground state energy [*cf.* with (24)]. The second term in Eq. (25) appears because the Hartree–Fock ground and excited state functions are not eigenfunctions of the Hamiltonian  $H$ . In practice, if the ground state and excited state energies and the corresponding wave functions are known accurately then the coupling matrix element  $\langle \Phi^{(0)} | H | \Phi_0^{(0)} \rangle$

is expected to be small (see also [14], Sect. 3.1). Furthermore, as the overlap element  $\langle \Phi_0^{(1)} | \Phi^{(0)} \rangle < 1$ , the last term in Eq. (25) may be neglected during the first stage of calculations. We used this approximation here.

Thus, we obtain comparable perturbation schemes for the ground and excited state energies. Use of the asymptotic projection technique ensures that calculations for excited states require practically the same computational time as those for the ground state.

## 5 Results and discussion

At present, there are only very few published finite basis set calculations for excited states (especially for Rydberg states [46]) having the same symmetry as the ground state which are based on existing Hartree–Fock methods. In this section we demonstrate the potential of our methodology by means of the HF calculations for highly doubly excited  $^3S$  states of the He atom ( $2s\ ns$ ,  $n = 3, 4, \dots, 10$  and  $3s\ ns$ ,  $n = 4, 5, \dots, 11$ ), highly excited  $1s^2\ ns$  ( $n = 3, \dots, 9$ ) states of the Li atom and of the doubly ionized core hole states for some diatomic molecules (CO, NO, LiF) computed at the HF + MP2 level of theory.

### 5.1 Atoms

For atoms, basis sets of  $42s$ -gaussians were constructed according to the even-tempered prescription i.e., the exponents,  $\zeta_p$ , were defined by the geometric series:

$$\zeta_p = \alpha \beta^p, \quad p = 1, 2, \dots, M$$

The parameters  $\alpha$  and  $\beta$  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. [47]. More information for highly excited state basis sets is available from authors on request.

As a first test for orthogonality-constrained HF method, hereafter denoted CSCF for constrained self-consistent field, the energies of triplet singly excited  $1s\ ns$  ( $n = 2, 3, \dots, 10$ ) states of the He atom were computed and compared with the HF energies obtained with the maximum overlap method (MOM) [46] which does not use orthogonality restrictions. The calculations in [46] were carried out using  $70s$  even-tempered Slater-type basis functions. The results of [46] can be considered as benchmark data. These authors used the extended precision in the Mathematica package to avoid problems with almost linearly dependent basis set. Unlike Ref. [46], our calculations were restricted to nine states (up to  $1s\ 10s$ ) because for  $n > 10$  we observed that the corresponding basis sets present some linear dependencies and the iterative SCF procedure does not converge. We used double precision. The corresponding results are listed

**Table 2** Doubly excited energies (hartrees) computed at the constrained self-consistent Hartree–Fock level (method proposed in this paper) and their comparison with “exact” values for the  $2s\ ns$  ( $n = 3, 4, \dots, 10$ ) states of He

State	$E^{\text{CSCF}}$ (this work)	$E^{\text{exact}}$ [48] <sup>a</sup>	$E^{\text{CSCF}} - E^{\text{exact}}$
$2s3s\ ^3S$	−0.584 843 21	−0.602 577 51	0.017 734 30
$2s4s\ ^3S$	−0.541 993 88	−0.548 840 86	0.006 846 98
$2s5s\ ^3S$	−0.525 150 96	−0.528 413 97	0.003 263 01
$2s6s\ ^3S$	−0.516 757 01	−0.518 546 37	0.001 789 36
$2s7s\ ^3S$	−0.511 964 04	−0.513 046 50	0.001 789 36
$2s8s\ ^3S$	−0.508 969 03	−0.509 672 80	0.001 082 46
$2s9s\ ^3S$	−0.506 966 91	−0.507 456 06	0.000 489 15
$2s10s\ ^3S$	−0.505 538 99	−0.505 922 15	0.000 383 16

<sup>a</sup> Configuration interaction method with the Hylleraas basis set functions

**Table 3** Doubly excited energies (hartrees) computed at the constrained self-consistent Hartree–Fock level and their comparison with “exact” values for the  $3s\ ns$  ( $n = 4, 5, \dots, 11$ ) states of He

State	$E^{\text{CSCF}}$ (this work)	$E^{\text{exact}}$ [48] <sup>a</sup>	$E^{\text{CSCF}} - E^{\text{exact}}$
$3s4s\ ^3S$	−0.272 245 05	−0.287 277 14	0.015 032 09
$3s5s\ ^3S$	−0.250 554 08	−0.258 133 98	0.007 579 90
$3s6s\ ^3S$	−0.240 598 58	−0.244 807 49	0.004 208 91
$3s7s\ ^3S$	−0.235 129 72	−0.237 672 21	0.002 542 49
$3s8s\ ^3S$	−0.231 791 54	−0.233 433 33	0.001 641 79
$3s9s\ ^3S$	−0.229 600 06	−0.230 719 09	0.001 119 03
$3s10s\ ^3S$	−0.228 079 97	−0.228 880 00	0.000 800 03
$3s11s\ ^3S$	−0.226 915 03	−0.227 577 80	0.000 662 77

<sup>a</sup> Configuration interaction method with the Hylleraas basis set functions

in Table 1. One can see that the largest deviation from benchmark results is only 0.30  $\mu$ hartrees.

In Tables 2 and 3, triplet doubly excited energies of  $2s\ ns$  ( $n = 3, 4, \dots, 10$ ) states and  $3s\ ns$  ( $n = 4, 5, \dots, 11$ ) states of He, computed at the CSCF level, are presented. Calculations of Ref. [46] were restricted to only singly excited states. Therefore, we compare our CSCF calculations with accurate theoretical calculations based on a configuration interaction approach with the explicitly correlated Hylleraas basis set functions [48]. One can see that the accuracy of the CSCF calculations is improved when  $n$  increases. This observation is in agreement with Ref. [46], 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 Hartree–Fock method, which neglects such effects, may be an excellent approximation.”

In Table 4, we compare our CSCF excited doublet  $1s^2\ ns$  ( $n = 3, \dots, 9$ ) energies and excitation energies of the

**Table 4** Excited doublet  $1s^2\ ns$  ( $n = 3, 4, \dots, 9$ ) energies (hartrees) and excitation energies  $\Delta E$  (eV) computed at the constrained self-consistent Hartree–Fock level with respect to the  $1s^2\ 3s$  state and their comparison to “exact” [49] values for Li atom

State	$E^{\text{CSCF}}$ (this work)	$E^{\text{exact}}$ [49] <sup>a</sup>	$\Delta E$ (eV)	
			CSCF	«Exact» [49] <sup>a</sup>
$1s^2\ 3s\ ^2S$	−7.310 207 76	−7.354 098 42	0	0
$1s^2\ 4s\ ^2S$	−7.274 883 90	−7.318 530 85	0.961	0.968
$1s^2\ 5s\ ^2S$	−7.259 978 78	−7.303 551 58	1.367	1.375
$1s^2\ 6s\ ^2S$	−7.252 316 91	−7.295 859 51	1.575	1.585
$1s^2\ 7s\ ^2S$	−7.247 864 34	−7.291 392 27	1.696	1.706
$1s^2\ 8s\ ^2S$	−7.245 049 87	−7.288 569 83	1.773	1.783
$1s^2\ 9s\ ^2S$	−7.243 155 19	−7.286 673 59	1.825	1.835

<sup>a</sup> Configuration interaction method with the Hylleraas basis set functions

**Table 5** Total energies (hartree) for the ground (GS) and doubly ionized states (DIS) calculated at different levels of approximation, namely at the constrained self-consistent Hartree–Fock level and at the HF + MP2 level

Molecule	Core level <sup>a</sup>	CSCF	HF + MP2
CO	GS	−112.776 750	−113.103 104
	DIS		
	$C1s^{-2}$	−88.253 476	−88.694 091
	$O1s^{-2}$	−69.636 053	−69.866 416
	$C1s^{-1} O1s^{-1}, S$	−81.367 221	−81.666 059
NO	$C1s^{-1} O1s^{-1}, T$	−81.367 167	−81.665 687
	GS	−129.264 594	−129.623 929
	DIS		
	$O1s^{-2}, D$	−86.091 825	−86.341 259
LiF	$N1s^{-2}, D$	−96.024 538	−96.399 098
	GS	−106.988 804	−107.245 424
	DIS		
	$F1s^{-2}$	−52.645 367	−52.816 963
	$Li1s^{-1} F1s^{-1}, S$	−79.049 260	−79.232 405
$Li1s^{-1} F1s^{-1}, T$	−79.049 465	−79.232 198	

T, D and S refer to triplet, doublet and singlet of two holes created on different atomic sites, respectively

<sup>a</sup> Core level notations of Ref. [51] are used, for example, core level  $C1s^{-1} O1s^{-1}$  means double core hole state obtained by removing electrons from the  $1s$  carbon core orbital and from the  $1s$  oxygen core orbital

Li atom to the “exact” energies obtained with the most accurate configuration interaction wave function using the Hylleraas basis set [49]. The calculations show that the correlation energies  $E^{\text{exact}} - E^{\text{CSCF}}$  for different excited states are very similar, since they mainly arise from the  $1s$ – $1s$  correlation. As a result, excitation energies based on the

**Table 6** Double core hole ionization potentials (eV) calculated at different levels of approximation

Molecule	Core level	CSCF (this work)	SCF [51]	HF + MP2 (this work)	CASSCF [51]
CO <sup>a</sup>	C1s <sup>-2</sup> , S	667.32	667.90	664.22	664.42
	O1s <sup>-2</sup> , S	1173.93	1175.38	1176.55	1176.56
	C1s <sup>-1</sup> O1s <sup>-1</sup> , S	854.71	857.07	855.47	854.74
	C1s <sup>-1</sup> O1s <sup>-1</sup> , T	854.71	857.07	855.48	855.20
NO <sup>b</sup>	O1s <sup>-2</sup> , D	1174.80	1176.43	1177.79	1177.70
	N1s <sup>-2</sup> , D	904.51	904.85	904.10	902.95
LiF	F1s <sup>-2</sup> , S	1478.77	1480.42	1481.09	1481.49
	Li1s <sup>-1</sup> F1s <sup>-1</sup> , S	760.28	763.45	762.28	763.21
	Li1s <sup>-1</sup> F1s <sup>-1</sup> , T	760.28	763.44	762.28	763.28

T, D and S refer, respectively, to triplet, doublet and singlet spin couplings of two holes created on different atomic sites

<sup>a</sup> Experimental values Ref. [53]: C1s<sup>-2</sup>: 667.9 eV; C1s<sup>-1</sup> O1s<sup>-1</sup>: 855.3 eV

<sup>b</sup> SCF and CASSCF values are taken from Ref. [52]

CSCF method are in good agreement with those computed with highly correlated methods.

## 5.2 Molecules

In this subsection, we apply our HF + MP2 methodology on doubly ionized core hole states. It is known that double core ionization potentials are more sensitive to changes in the molecular environment [50]. It is worth also noting that there exist very few reported applications for double core hole (DCH) states, especially of open-shell molecules [51, 52]. For molecules under consideration (CO, NO, LiF), basis sets consisting of 30s9p distributed Gaussians were used. The exponents and positions of functions were determined by minimizing the HF energy for each individual state. Each *p*-functions were presented as a linear combination of two *s*-functions (so-called lobe representation). In Table 5, we present total energies for the ground (GS) and doubly ionized states (DIS) calculated at different levels of approximation (CSCF and HF + MP2). Using these data, double core hole ionization potentials were calculated (see Table 6) and compared for the NO molecule with results of Ref. [52] and for closed-shell molecules with results of Ref. [51] and available experiment [53]. In Refs. [51, 52], the corresponding calculations were carried out at the self-consistent field (SCF) level of theory and using the complete active space self-consistent field (CASSCF) method. It is worth noting that the SCF and CASSCF calculations in these works were performed using a large cc-pVTZ basis set.

One can see that our results at the CSCF and HF + MP2 level of approximation are in acceptable agreement with experiment and other calculations performed at the corresponding level of approximation.

We conclude that the developed constrained HF + MP2 formalism can be applied to both atoms and molecules

and to a wide class of physically different states, including highly excited states and core excited states, with a reasonable accuracy. However, it is also worth noting that the proposed approach cannot be directly applied to important class of singlet excited states which are usually described in terms of two open-shell determinants. Preliminary applications of our modified methodology to this problem can be found in Ref. [54] where a partially restricted Hartree–Fock wave function for singlet excited states is introduced.

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## References

- Gidopoulos NI, Papaconstantinou PG, Gross EKV (2002) Phys Rev Lett 88:33003
- Chattopadhyay S, Mahapatra US, Chaudhuri RK (2012) Theor Chem Acc 131:1213
- Roos BO (2005) In: Dykstra CE, Frenking G, Kim KS, Scuseria GE (eds) Theory and applications of computational chemistry: the first 40 years. Elsevier, Amsterdam, pp 725–764
- Pahari D, Chattopadhyay S, Das S, Mukherjee D, Mahapatra US (2005) In: Dykstra CE, Frenking G, Kim KS, Scuseria GE (eds) Theory and applications of computational chemistry: the first 40 years. Elsevier, Amsterdam, pp 581–633
- Piecuch P, Kowalski K (2002) Int J Mol Sci 3:676
- Lyakh DI, Musial M, Lotrich VF, Bartlett RJ (2012) Chem Rev 112:182
- Hoffmann MR, Datta D, Das S, Mukherjee D, Szabados A, Rolik Z, Surjan PR (2009) J Chem Phys 131:204104
- Kobayashi M, Szabados A, Nakai H, Surjan PR (2010) J Chem Theory Comput 6:2024
- Shull H, Löwdin P-O (1958) Phys Rev 110:1466
- Glushkov VN (1998) Chem Phys Lett 1998(287):189
- Glushkov VN, Gidopoulos N, Wilson S (2008) In: Wilson S, Grout PJ, Delgado-Barrio G, Maruani J, Piecuch P (eds) Frontiers in quantum systems in chemistry and physics. Progress in



- theoretical chemistry and physics, Pt. 2. Springer, Dordrecht, p 451
12. Glushkov VN (2002) *J Math Chem* 31:91
  13. Glushkov VN (2002) *Opt Spectrosc* 93:11
  14. Glushkov VN, Gidopoulos N, Wilson S (2008) In: Wilson S, Grout PJ, Delgado-Barrio G, Maruani J, Piecuch P (eds) *Frontiers in quantum systems in chemistry and physics. Progress in theoretical chemistry and physics, Pt. I*. Springer, Dordrecht, p 429
  15. Roothaan CCJ (1960) *Rev Mod Phys* 32:179
  16. Hunt WJ, Goddard WA (1969) *Chem Phys Lett* 3:414
  17. Huzinaga S, Arnau C (1971) *J Chem Phys* 54:1948
  18. Morokuma K, Iwata S (1972) *Chem Phys Lett* 16:192
  19. Mrozek J, Golebiewski A (1977) *Int J Quantum Chem* 12:207
  20. Firsht D, McWeeny R (1976) *Mol Phys* 32:1637
  21. Davidson ER, Stenkamp LZ (1976) *Int J Quantum Chem Symp* 10:21
  22. Davidson ER, McMurchie EL (1985) *Excit States* 5:1
  23. Colle R, Fortunelli A, Salvetti O (1987) *Theor Chim Acta* 71:467
  24. Colle R, Fortunelli A, Salvetti O (1989) *Theor Chim Acta* 75:323
  25. Gidopoulos N, Theophilou A (1994) *Phil Mag* 69:1067
  26. Assfeld X, Rivaill J-L (1996) *Chem Phys Lett* 263:100
  27. Surjan PR (2000) *Chem Phys Lett* 325:120
  28. Ferre N, Assfeld X (2002) *J Chem Phys* 117:4119
  29. Gilbert ATB, Besley NA, Gill PMW (2008) *J Phys Chem A* 112:13164
  30. Tassi M, Theophilou I, Thanos S (2013) *Int J Quantum Chem* 113:690
  31. Richings GW, Karadakov PB (2007) *Mol Phys* 105:2363
  32. Richings GW, Karadakov PB (2013) *Theor Chem Acc* 132:1400
  33. Glushkov VN, Levy M (2007) *J Chem Phys* 126:174106
  34. Staroverov VN, Glushkov VN (2010) *J Chem Phys* 133:244104
  35. Evangelista FA, Shushkov R, Tully JC (2013) *J Phys Chem A* 113:690
  36. Cullen J, Krykunov M, Ziegler T (2011) *Chem Phys* 391:11
  37. Cohen M, Kelly PS (1965) *Can J Phys* 43:1867
  38. Tatewaki H, Koga T, Sakai Y, Thakkar AJ (1994) *J Chem Phys* 101:4945
  39. Fock VA (1940) *Z Exp Teor Fiz* 10:961
  40. Glushkov VN (1997) *Chem Phys Lett* 273:122
  41. Lauderdale WJ, Stanton JF, Gauss J, Watts JD, Bartlett RJ (1991) *Chem Phys Lett* 187:21
  42. Murray C, Davidson ER (1991) *Chem Phys Lett* 187:451
  43. Andrews JS, Jayatilaka D, Bone RGA, Handy NC, Amos RD (1991) *Chem Phys Lett* 183:423
  44. Knowles PJ, Andrews JS, Amos RD, Handy NC, Pople JA (1991) *Chem Phys Lett* 186:130
  45. Glushkov VN (2004) *Int J Quantum Chem* 99:236
  46. Deng J, Gilbert ATB, Gill PMW (2009) *Int J Quantum Chem* 109:1915
  47. Glushkov VN, Wilson S (2006) In: Julien J-P, Maruani J, Mayou D, Wilson S, Delgado-Barrio G (eds) *Progress in theoretical chemistry and physics. Recent advances in the theory of chemical and physical systems*. Springer, Dordrecht, p 107
  48. Burgers A, Wintgen D, Rost J-M (1995) *J Phys B: At Mol Opt Phys* 28:3163
  49. Puchalski M, Kedziera D, Pachucki K (2010) *Phys Rev A* 82:062509
  50. Cederbaum LS, Tarantelli F, Sgamellotti A, Schrimmer J (1986) *J Chem Phys* 85:6513
  51. Tashiro M, Ehara M, Fukuzawa H, Ueda K, Buth C, Kryzhevoi NV, Cederbaum LS (2010) *J Chem Phys* 132:184302
  52. Tashiro M, Ehara M, Ueda K (2010) *Chem Phys Lett* 496:217
  53. Berrah N, Fang L, Murphy B, Osipov T, Ueda K, Kukuk E, Feifel R, van der Meulen P, Salen P, Schmidt HT, Thomas RD, Larsson M, Richter R, Prince KC, Bozek JD, Bostedt C, Wada S, Piancastelli MN, Tashiro M, Ehara M (2011) *Proc Natl Acad Sci* 108:16912
  54. Glushkov VN (2007) *Comput Lett* 3:65