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REGULAR ARTICLE

Exploration of Electronic Excited States via Variational Self-Consistent Field Methods

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Abstract: A new criterion that can be used to locate the lowest excited state in a variational self-consistent field framework has been proposed. Molecular orbital (MO) relaxation effects are included in our method. The excitation energies calculated using the present formula are in good agreement with experimental values. The MOs obtained from our formula appear to be the approximate natural orbitals of the corresponding configuration interaction singles (CIS) excited states. This approach can be used for the construction of a pure spin state. Several properties of the excited-state wave function have been investigated, and the utility of a single Slater determinant to describe excited states has been verified.

AMS subject classifications: 92E99, 70G75

Keywords: self-consistent field framework (SCF), excited states, electron occupation, spin-adapted, relaxation effects

1. Introduction

Exploration of electronic excited states via the variational self-consistent field (SCF) method is a fundamental problem in the domain of quantum chemistry. According to the Ritz variational principle [1]，for any trial wave function Ψ, the energy expectation value E is an upper bound to the exact ground state energy E_0:

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$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0 , \quad (1)$$

When one applies this theorem to excited states that have the same symmetry as the ground state, variational collapse always occurs and the upper bound to the excited-state energy is no longer valid. Bound excited states can be obtained, however, as higher roots of a secular equation such as the configuration interaction singles (CIS) [2] according to the Hylleraas-Undheim-MacDonald (HUM) theorem [3,4], which asserts that the approximate excited-state wave function is orthogonal and non-interacting with all approximate wave functions of lower-lying states and that the corresponding energy is higher than the exact excited-state energy. In other words, when the above two conditions (orthogonality and non-interaction with lower-lying wave functions) are satisfied, the wave functions of lower-lying states are not required to be exact. Many studies, however, require only orthogonality and hence, in principle, need exact lower-lying states as reference states to obey the HUM theorem. In practical calculations, however, only approximate lower-state wave functions can be determined (such as the Hartree-Fock-Slater determinants), and the orthogonal relation between approximate wave functions is not strictly met. Some explicit or implicit formulas have been proposed to take orthogonality into consideration [5-12], but the foundations of those methods need to be revisited. On the other hand, the orthogonal constraint is not convenient for practical calculations, especially when more than one excited state is explored [6]. Gilbert et al. proposed a criterion that requires maximum overlap between new and old molecular orbitals in each SCF iteration [13], so that the excited state is located in an SCF framework. In fact, the philosophy of the maximum overlap method (MOM) is similar to that of the delta-SCF (ΔSCF) method, which abandons the Aufbau principle and maintains a single electronic state throughout the SCF procedure.

The main objective of this report is to propose a new criterion that can be used to locate an excited state in a variational SCF framework. In this manner, we can obtain excited states and the ground state on an equal footing without variational collapse. We explore the difference between the ground state and excited states from the point of view of electron occupation in the orbital space. The excited state can be seen as promoting one electron from the occupied space of the ground state to the virtual space of a reference state; some proper constraint conditions may be imposed on the variational functional, and an effective single-electron equation can be obtained and solved to construct the determinant wave function of the excited state to calculate the corresponding energy. Finally, we explore the properties of the excited-state wave functions to validate the use of a single Slater determinant to describe the excited state. We have found that the spin-adapted excited-state configurations of a closed-shell system can be written as a linear combination of two-determinant wave functions obtained by the present method.

2. Method

If a single Slater determinant is used to describe an excited state, the electron density ρ_e can be written as

$$\rho_e = \sum_{i}^{N_{occ}} \psi_i^e \psi_i^e , \tag{2}$$

The molecular orbitals (MOs) Ψ_j^e of an excited state can be expanded as a linear combination of the MOs of the ground state

$$\psi_j^e = \sum_{i=1}^{N_{occ}} C_{ij} \psi_i^g + \sum_{a=N_{occ}+1}^{N_b} C_{aj} \psi_a^g , \tag{3}$$

where the superscripts e and g denote the excited and ground state, respectively; N_{occ} denotes the number of occupied orbitals; and N_b denotes the number of basis sets. As usual, the subscripts i (j, k) and a (b, c) are used to denote the occupied molecular orbitals and virtual orbitals, respectively. Integration of ρ_e will give the number of electrons N_e.

$$\int \rho_e \; dr_N = \sum_{j=1}^{N_{occ}} \left(\sum_{i=1}^{N_{occ}} C_{ij} C_{ij} + \sum_{a=N_{occ}+1}^{N_b} C_{aj} C_{aj} \right) = N_e , \tag{4}$$

We consider only single-electron excitations throughout this report. If one electron is excited from the occupied space to the virtual space of the ground state, that is, if

$$\sum_{j=1}^{N_{occ}} \sum_{i=1}^{N_{occ}} C_{ij} C_{ij} = N_e - 1 \text{ and } \sum_{j}^{N_{occ}} \sum_{a=N_{occ}+1}^{N_b} C_{aj} C_{aj} = 1 , \tag{5}$$

then an excited state may be obtained. We define the operator Π_g

$$\Pi_g = \sum_{j}^{N_{occ}} \left| \psi_j^g \right\rangle \left\langle \psi_j^g \right| , \tag{6}$$

where the conditions in eq. (5) can be rewritten as

$$\begin{aligned} \sum_{i}^{N_{occ}} \left\langle \psi_i^e \middle| \Pi_g \middle| \psi_i^e \right\rangle &= N_e - 1 \\ \sum_{i}^{N_{occ}} \left\langle \psi_i^e \middle| 1\text{-}\Pi_g \middle| \psi_i^e \right\rangle &= 1 \end{aligned} , \tag{7}$$

The "1" on the left side of the above equation represents the unit operator in the limited basis set, while the "1" on the right side is simply a number. If only the spin-up (↑) electron is excited, eq. (7) can be rewritten as

$$\sum_{i}^{N_\alpha} \left\langle \psi_{i\uparrow}^{e} \middle| \Pi_{g\uparrow} \middle| \psi_{i\uparrow}^{e} \right\rangle = N_\alpha - 1, \tag{8a}$$

$$\sum_{i}^{N_\alpha} \left\langle \psi_{i\uparrow}^{e} \middle| 1 - \Pi_{g\uparrow} \middle| \psi_{i\uparrow}^{e} \right\rangle = 1, \tag{8b}$$

for spin-up electrons and

$$\sum_{j}^{N_\beta} \left\langle \psi_{j\downarrow}^{e} \middle| \Pi_{g\downarrow} \middle| \psi_{j\downarrow}^{e} \right\rangle = N_\beta, \tag{9a}$$

$$\sum_{j}^{N_\beta} \left\langle \psi_{j\downarrow}^{e} \middle| 1 - \Pi_{g\downarrow} \middle| \psi_{j\downarrow}^{e} \right\rangle = 0, \tag{9b}$$

for spin-down electrons (↓). In the above equations, $N_\alpha (N_\beta)$ refers to the number of spin-up (spin-down) electrons. Eq. (9) restricts the β-orbitals in the excited-state rotation to be within the occupied space of the ground state. At this stage, a functional $\Xi[\{\Psi_{i\uparrow}^{e}\}\{\Psi_{i\downarrow}^{e}\}]$ can be defined using eqs. (8) and (9) as constraints:

$$\begin{aligned} \Xi[\{\psi_{i\uparrow}^{e}\}\{\psi_{i\downarrow}^{e}\}] = E^{UHF} &+ \lambda[\sum_{i}^{N_\alpha} \left\langle \psi_{i\uparrow}^{e} \middle| \Pi_{g\uparrow} \middle| \psi_{i\uparrow}^{e} \right\rangle - N_\alpha + 1] + \gamma \sum_{k}^{N_\beta} \left\langle \psi_{i\downarrow}^{e} \middle| 1 - \Pi_{g\downarrow} \middle| \psi_{i\downarrow}^{e} \right\rangle \\ -\sum_{m,n} \xi_{mn} (\left\langle \psi_{m\uparrow}^{e} \middle| \psi_{n\uparrow}^{e} \right\rangle - \delta_{mn}) &- \sum_{p,q} \xi_{\mathrm{pq}} (\left\langle \psi_{p\downarrow}^{e} \middle| \psi_{q\downarrow}^{e} \right\rangle - \delta_{pq}) \end{aligned}, \tag{10}$$

where E^{UHF} is the energy functional of the system, and λ and γ are the Lagrange multipliers corresponding to constraints (8a) and (9b), respectively. In should be noted that condition (8a) projects an electron out of the occupied space and (8b) ensures that a single electron goes into the virtual space. The two conditions in eqs. (8a) and (8b) are equivalent if the number of electrons is conserved, and then only one needs to be applied to E^{UHF} as a constraint.

The effective single-electron equation for excited-state molecular orbitals takes the form

$$(\mathrm{f}^{\uparrow} + \lambda \Pi_{g\uparrow}) \left| \psi_{k\uparrow} \right\rangle = \xi_{k\uparrow} \left| \psi_{k\uparrow} \right\rangle, \tag{11a}$$

$$(\mathrm{f}^{\downarrow} + \gamma (1 - \Pi_{g\downarrow})) \left| \psi_{k\downarrow} \right\rangle = \xi_{k\downarrow} \left| \psi_{k\downarrow} \right\rangle, \tag{11b}$$

where $f^{\downarrow}$and $f^{\uparrow}$are Fock operators similar to those of the ground state. In this paper, we wish to explore the lowest nondegenerate excited state. If the HOMO-LUMO transition or any one-to-one or one-to-many transition from the occupied space to the virtual space of the ground state is the main contribution to the lowest excited state, condition (8a) may be rewritten as (for the HOMO-virtual orbital transition case):

$$\sum_{i}^{N_\alpha}\left\langle \psi_{i\uparrow}^{e} \middle| \psi_{g\uparrow}^{h} \right\rangle \left\langle \psi_{g\uparrow}^{h} \middle| \psi_{i\uparrow}^{e} \right\rangle = 0, \tag{12}$$

where $\Psi_{g\uparrow}^{h}$ is the HOMO for spin-up electrons in the ground state. Defined as

$$\Pi_{g\uparrow}^{h} = \left|\psi_{g\uparrow}^{h}\right\rangle\left\langle\psi_{g\uparrow}^{h}\right|, \tag{13}$$

Then, eq. (11a) can be rewritten as

$$(\mathrm{f}^{\uparrow} + \lambda\Pi_{g\uparrow}^{h})\left|\psi_{k\uparrow}\right\rangle = \xi_{k\uparrow}\left|\psi_{k\uparrow}\right\rangle, \tag{14}$$

Combining (14) with (11b)

$$(\mathrm{f}^{\downarrow} + \gamma(1-\Pi_{g\downarrow}))\left|\psi_{k\downarrow}\right\rangle = \xi_{k\downarrow}\left|\psi_{k\downarrow}\right\rangle, \tag{15}$$

we get the working equations that can be solved self-consistently to locate the first excited state. For high-spin open-shell systems, there is a possibility that the lowest excitation comes from a closed shell. It is easy to find examples of this behavior, such as in oxygen atoms or high-spin transition metal complexes. In this case, the operator (13) should be defined for the β-electron (if the unpaired electrons are α-electrons).

Based on the works of Glushkov [12] and Zhao and Parr [14], the conditions in eqs. (9b) and (12) will be met if and only if the Lagrange multipliers λ and γ approach infinity. In practical calculations, however, constraints (9b) and (12) will be satisfied when the values of λ and γ are sufficiently large [15]. In the Results section, we show that $\lambda = \gamma \approx 5000$a.u. is sufficient for most atoms and molecules to obtain convergent results.

In practical calculations, atomic central basis sets are used to expand the molecule orbitals of excited states:

$$\psi_{j}^{e} = \sum_{u} c_{uj}\chi_{u}, \tag{16}$$

Substituting this into eqs. (14) and (15), we have, for α-electrons,

$$\begin{aligned} \sum_{v}(\mathrm{F}_{uv}^{\uparrow} + \lambda\Pi_{uv})c_{vm} &= \varepsilon_{m}\sum_{v}S_{uv}c_{vm} \\ \Pi_{uv} = \left\langle\chi_{u}\middle|\Pi_{g\uparrow}\middle|\chi_{v}\right\rangle &= \sum_{\tau\sigma}S_{u\tau}P_{\tau\sigma}^{g\uparrow}S_{\sigma v} \end{aligned}, \tag{17}$$

where S is the overlap matrix and $P^{g\uparrow}$denotes the density matrix constructed from the HOMO orbital of the ground state. Similar equations can be obtained for spin-down electrons.

The formula presented above has been implemented along with Pulay's direct inversion of the iterative subspace (DIIS) method [16] to improve the convergence speed. The 6-311G(3+, 3+) basis sets are used for all calculations, except for helium atoms and the molecular ion HeH^+, where the Dunning correlation-consistent basis sets aug-cc-pVDZ and 6-31g(d,p) were used, respectively. The calculations for H_2, N_2, H_2O, and H_2O_2 were carried out in the experimental gas phase geometries given in [6]. For CO, R(CO) = 1.128 Å [17]. For ethylene and formaldehyde, we used the optimal geometries calculated at the MP2/6-311G(3+, 3+) level.

3. Benchmark Testing and Discussion

3.1 Convergence properties of working equations (14) and (15)

The energies of the lowest excited states corresponding to different λ have been calculated, and the results are listed in **Table 1**. As the value of λ increases, the energy approaches a stable value; when the value of λ exceeds 1000 a.u., convergence is usually achieved. In practical calculations, we set λ = 5000 a.u., which is sufficient to achieve convergence. The time requirement for convergence is similar to ground state SCF calculations and only a few iteration steps are needed to locate the excited states.

Table 1 Convergent properties of the energy of the lowest excited state related to the Lagrange multiplier for some atoms and a molecule

System	λ	E (a.u.)
He	50	–2.06776365
	100	–2.06776365
	1000	–2.06776365
	5000	–2.06776365
Li	50	–7.36429264
	100	–7.36429205
	1000	–7.36429144
	5000	–7.36429138
H_2O	50	–75.75275651
	100	–75.75275651
	1000	–75.75275651
	5000	–75.75275651

3.2 Excitation energies for atoms and small molecules

Excitation energies for a few of the atoms have been calculated, and the results are listed in **Table 2**. The abbreviations "eHF" and "eDFT" in the following sections refer to the ground state wave function as a Hartree-Fock Slater determinant and Kohn-Sham determinant, respectively.

Table 2 Excitation energies for various atoms in eV. Exp denotes the experimental values. The values in parentheses represent the absolute deviation of the calculated value from the experimental value. MOM/HF refers to the results obtained from MOM method at HF levels and $<S^2>$ denotes the expected value of the spin square operator.

Atom	Term	eHF	Exp[18]	MOM/HF[13]	$<S^2>$
H	^2S	10.20(0.00)	10.20	10.20(0.00)	0.7500 (G) 0.7500 (E)
He	^1S	21.43(0.82)	20.61	19.29(1.32)	0.0000 (G) 1.0000 (E)
Li	^2P	1.84 (0.01)	1.85	1.84 (0.01)	0.7500 (G) 0.7500 (E)
Be	^1P	3.53(1.75)	5.28	3.51(1.77)	0.0000 (G) 1.0000 (E)

G: ground state, E: excited state

The values calculated by our method are in good agreement with experimental values. For open-shell atoms, such as hydrogen and lithium, the calculated results are highly consistent with experimental values. For those atoms, the first excited state is a spin-adapted configuration that can be seen from the expectation value of the spin-square operator. When the ground state of the atom is a closed shell, such as in He and Be, spin contamination occurs.

Excitation energies for several small molecules are listed in **Table 3**. The excitation energies calculated using the present method is in good agreement with experimental values. In this table, we also list the excitation energies calculated using eq. (17) in the density functional theory (DFT) framework [23] where the B3LYP hybrid functional was used for the exchange-correlation potential. From the results in **Table 3**, the excitation energies found using the Hartree-Fock method are superior to the corresponding DFT energies. This may arise from a fortuitous cancellation of errors in the Hartree-Fock method and lack of a suitable exchange-correlation functional for excited states in the time-independent DFT [24]. The results obtained from the MOM at the Hartree-Fock level are also listed in the last columns of **Tables 2** and **Table 3** [13]. For atoms, our method yields similar results as obtained using the MOM. For molecules, however, our method is superior to the MOM.

Table 3 Excitation energies for various molecules in eV units. Exp denotes the experimental values. The values in parentheses represent the absolute deviation of the calculated value from the experimental value. MOM/HF refers to the results obtained from MOM method at HF levels. The transitions type of those molecules are: H_2: $\bar{X}^1\Sigma_g^+ \rightarrow \bar{A}^1\Sigma_u^+$; CO: $^1\Sigma\rightarrow{}^1\Pi$; N_2: $\tilde{X}^1\Sigma_g^+ \rightarrow \tilde{A}^1\Pi_g$; H_2O: $^1A_1\rightarrow{}^1B_1$, H_2O_2: $\tilde{X}^1A_1 \rightarrow \tilde{A}^1A_A$; Formaldehyde: $n \rightarrow \pi^*$; Ethylene: π → 3s.

	Exp	eHF	eDFT/B3LYP	MOM/HF[13]
H_2	11.19	11.76 (0.57)	11.82 (0.63)	
CO	8.51	7.17 (1.34)	6.99 (1.52)	
N_2	9.31[19]	9.01 (0.30)	8.92 (0.39)	
H_2O	7.40	7.19 (0.21)	7.74 (0.34)	
H_2O_2	5.16[20]	5.43 (0.27)	4.87 (0.29)	
Formaldehyde	4.07[21]	3.78 (0.29)	3.72 (0.35)	2.56(1.51)
Ethylene	7.11[22]	6.64 (0.47)	6.04 (1.07)	5.94(1.17)

Table 4 Excitation energies for polymer blends TFB/F8BT in two different stacking orientations. E(g) is the total energy of the ground state. E(e) is the energy of the excited state calculated by the present formula. Those two values are in a.u units, eDFT is the excitation energy in eV units

	E(g)	E(e)	eDFT	TDDFT[26]	Exp(FBT*)
Eclipsed	-7262.74930	-7262.66560	2.277	2.40	2.3
Staggered	-7262.75079	-7262.66512	2.33	2.36	2.3

3.3 Excitation energies for fluorene-based polymer blends TFB/F8BT

Polyfluorene-based polymer blends have been utilized in the development of optoelectronic devices. The constituent copolymers are chemically designed to facilitate more efficient electron/hole mobility. Poly[9,9-dioctylfluorene-*co*-*N*-(4-butylphenyl) diphenylamine] (TFB/ F8BT) is an example of such polymer blend. Semiempirical models have been used to examine these systems [25]. TDDFT has also been applied to this system in [26], but the extent of the computational effort and availability of required computational resources are bottlenecks for this type of calculation. The present formula has been utilized for this polymer using the 6-31g(d) basis sets, and the results are listed in **Table 4**. The calculations were carried out in the geometries given in [26]. For our calculation, only the SCF iterative process is needed, meaning the required computational resources are similar to the ground state SCF calculation.

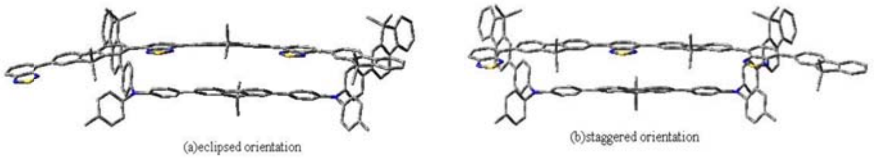
(a)eclipsed orientation
(b)staggered orientation

Figure 1: TFB/F8BT structures showing two different stacking orientations of the polymer constituents. (**a**) eclipsed orientation (**b**)staggered orientation.

Two different stacking orientations of TFB/F8BT were constructed, as shown in **Figure 1**. The total energies of the ground state indicate that the staggered orientation is more stable than the eclipsed orientation by 40.3 meV. For excited states, however, the eclipsed orientation is more stable than the staggered orientation by 12.98 meV. The excitation energies of the staggered and eclipsed orientations are 2.33 eV and 2.28 eV, respectively. For both cases, the excitation energies are in general agreement with the experimental F8BT emission at 2.3 eV. This indicates that the excited state obtained by our method is the localized excited state TFB/F8BT*, which can be characterized as the excitonic state given in [26].

3.4 Potential energy curves of the molecular ion HeH$^+$

The present formula has been used to calculate the potential energy curves of the lowest electronic excited state of the molecular ion HeH$^+$; the results are shown in **Figure 2**. For comparison, we also calculate the potential energy curve of HeH$^+$ using the CIS method. The curve for the $^1\Sigma$ ground state comes from the unrestricted Hartree-Fock (UHF) calculation in which HeH$^+$ dissociates to He(1s^2) and H$^+$.

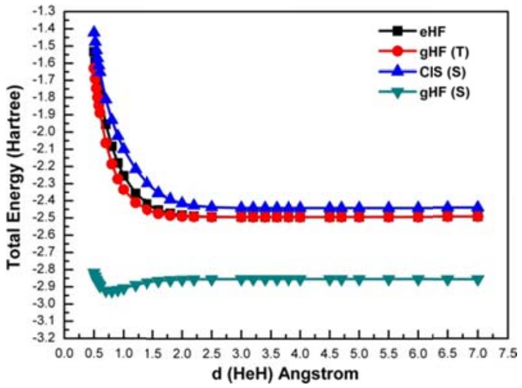

Figure 2: Potential energy curves for the ground and first excited state of HeH$^+$ with different method.

For the lowest excited state, our method describes the system correctly as He$^+$(1s) and

H(1s) at large internuclear distances with an energy *ca.* −2.492 Ha, which is almost equal to the exact value of −2.5 Ha [27]. The curve denoted "gHF(T)" that refers to the high-spin UHF wave function, used for the lowest triplet state $^3\Sigma$, also dissociates HeH^+ to He^+ and H, with an energy *ca.* −2.492 Ha. The first excited state (eHF) potential energy curve obtained using our approach and the lowest triplet state (gHF(T)) potential energy curve found with UHF method are virtually indistinguishable for He–H separations over 2.5 Å. The CIS first excited-state energy is higher than those produced by the other two methods, and leads to a dissociation limit of *ca.* −2.439 Ha. Throughout the studied range of He–H separations, our method predicts that the first excited-state energy is lower than the CIS value and higher than that of the UHF triplet state.

3.5 Wave function: Spin-adapted or not ?

As shown above, for open-shell atoms such as hydrogen and lithium, the first excited state has a spin-adapted configuration. Although some authors have proposed that an additional constraint should be added to the variational functional to arrive at a spin-adapted solution [28], this is not necessary for open-shell atoms or molecules. Considering the electron occupation, the additional constraint in [28] corresponds to a double-electron excitation for closed-shell systems; this is not suitable for single-electron excited states with single-determinant wave functions (see appendix A for more details). Of course, the spin-adapted excited state can be obtained using a linear combination of Slater determinants as in the case of the CIS wave function. It is interesting to note that the expectation values of the spin square operators for closed-shell atoms and molecules are exactly equal to one (see **Table 2**). This stems from mixing with higher multiplicity components. Imposing orthogonal constraints to obtain excited states shows similar spin features [6]. Thus, rather than obtaining a pure singlet or triplet state we obtain broken-symmetry solutions for closed-shell atoms and molecules. However, the spin-adapted wave function of the excited state for a closed-shell system can be obtained from the present formula. The expectation values of the spin square operators for those systems are equal to one, indicating the wave function obtained from eHF or eDFT calculations is a linear combination of singlet and triplet states with equal weighting. Consider a two-electron system with a double-occupied molecular orbital and virtual orbital for the ground state, which we denote a and b, respectively. The excited-state single-determinant solutions for closed-shell systems using the present formula are

$$\begin{aligned} \psi_{eHF(1)} &= | a(\uparrow) b(\downarrow) | \\ \psi_{eHF(2)} &= | a(\downarrow) b(\uparrow) | \end{aligned}, \tag{18}$$

which correspond to two degenerate states with an excited α- or β-electron, respectively. The correct singlet (s) and triplet (t) wave functions of the excited state can be written as a linear combinations of the above two determinants

$$\begin{aligned}\Phi_s &= 1/\sqrt{2}\,(|\,a(\uparrow)b(\downarrow)\,| - |\,a(\downarrow)b(\uparrow)\,|)\\ \Phi_t &= 1/\sqrt{2}\,(|\,a(\uparrow)b(\downarrow)\,| + |\,a(\downarrow)b(\uparrow)\,|)\end{aligned}, \tag{19}$$

where the energies of the above two states are

$$\begin{aligned}E_s &= \langle\psi_{eHF}|H|\psi_{eHF}\rangle - \langle\psi_{eHF(1)}|H|\psi_{eHF(2)}\rangle\\ E_t &= \langle\psi_{eHF}|H|\psi_{eHF}\rangle + \langle\psi_{eHF(1)}|H|\psi_{eHF(2)}\rangle\end{aligned}, \tag{20}$$

The excited-state energy calculated by the present method is the first term in the right side of the above equation. From eq. (20), we obtain

$$\begin{aligned}E_t + E_s &= 2\langle\psi_{eHF}|H|\psi_{eHF}\rangle = 2E_{eHF}\\ E_t - E_s &= 2\langle\psi_{eHF(1)}|H|\psi_{eHF(2)}\rangle\\ E_s &= 2E_{eHF} - E_t\end{aligned}, \tag{21}$$

where E_t can be easily calculated using normal HF or DFT methods by noticing that the following three triplet states are degenerate:

$$\begin{aligned}\Phi_t^1 &= 1/\sqrt{2}\,(|\,a(\uparrow)b(\downarrow)\,| + |\,a(\downarrow)b(\uparrow)\,|)\\ \Phi_t^2 &= |\,a(\uparrow)b(\uparrow)\,|\\ \Phi_t^3 &= |\,a(\downarrow)b(\downarrow)\,|\end{aligned}, \tag{22}$$

The energy of the singlet excited state can be readily obtained from the eq. (21), which leads to the purification formula $eHF(\mathrm{c}) = eHF \times 2 - E_{CIS(T)}$, and the results are listed in **Table 5**.

From the above discussion, the spin-adapted process for excited states can be represented by the following generalized eigenvalue equation

$$\begin{pmatrix} E_{eHF} & \langle\psi_{eHF(1)}|H|\psi_{eHF(2)}\rangle \\ \langle\psi_{eHF(2)}|H|\psi_{eHF(1)}\rangle & E_{eHF}\end{pmatrix}\begin{pmatrix}1/\sqrt{2}\\ \pm 1/\sqrt{2}\end{pmatrix} = \begin{pmatrix}E_t & 0\\ 0 & E_s\end{pmatrix}\begin{pmatrix}1/\sqrt{2}\\ \pm 1/\sqrt{2}\end{pmatrix}, \tag{23}$$

3.6 Reference state: Slater determinant of the excited state

Molecular orbital relaxation effects have been taken into account in our formula, which is different from the CIS method where the orbital spaces are frozen. Mayer has demonstrated that a CIS wave function can be decomposed into several linear combinations of Slater determinants and usually only one main contribution term (see appendix B) [32]. The single-determinant wave function obtained from our method mainly resembles the lead term of Mayer's CIS wave function. For open-shell atoms such as H and Li, the molecular orbitals obtained using the present SCF scheme may be viewed as approximate natural orbitals of the CIS lowest excited state [33]. Of course, this does not mean that our method is merely a different form of the CIS wave function; the two methods are fundamentally different in nature. To shed further light on this issue, we used the single-determinant wave function of the lowest excited state of the Li atom as a reference state; then, we performed a CIS calculation on the excited-state wave function. The results are listed in **Table 6**. The single-determinant wave function is suitable for representing the first excited state. Using this state as the reference determinant and performing a CIS calculation, we arrive at the same excitation energy for the higher excited state as found using the CIS model. In addition, from the CIS calculation, we notice that the CIS lowest excited state mainly comes from four pairs of orbital transitions: s(1) ⟶ v(6), amplitude = 0.2859; s(1) ⟶ v(10), amplitude = 0.6897; s(1) ⟶ v(13), amplitude = − 0.6155; and s(1) ⟶ v(17), amplitude = 0.2423. A singly occupied orbital is denoted by "s" and a virtual orbital by "v". The numbers in parentheses represent the serial numbers of the molecular orbitals, and the amplitude is the square of the combination coefficients in the CIS wave function. This means that more than four Slater determinants are needed to construct the first excited state in the CIS model. In our formula, however, only a single determinant is used to represent the same excited states, which is a direct outcome of molecular orbital relaxation effects that are neglected in CIS but taken into account in our present formula. On the other hand, if we obtain the determinant wave function of the excited state and corresponding MOs, we can perform an electron correlation

Table 5: Excitation energies for various atoms and molecules calculated using the present method and CIS method. $eHF(c) = eHF \times 2 - E_{CIS(T)}$ accounting for the presence of a triplet component in the wave function. All values are in eV. The transitions type of those molecules are: H_2:$X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$, CO: $^1\Sigma \rightarrow {}^1\Pi$, H_2O: $^1A_1 \rightarrow {}^1B_1$

System	eHF	E_{CIS}	eHF(c)	Exp
He (1s2s)^{1}S	21.43	20.14(T) 22.43(S)	22.72	20.61
Be (2s2p)^{1}P	3.53	1.70(T) 5.05(S)	5.36	5.28
H_2	11.76	9.95(T) 12.69(S)	13.57	11.19[29]
CO	7.17	5.70(T) 8.69(S)	8.64	8.51[30]
H_2O	7.19	7.88(T) 8.56(S)	6.50	7.40[31]

T:triplet S:singlet

calculation using configuration interaction, couple-cluster, or many-body perturbation methods similar to those used in treatment of the ground state [1]. This could be a direct method for evaluating electron correlation effects of excited states.

3.7 Difference and connection between the present and previous formulas

Two steps, carried out sequentially, describe the present formula: (a) promoting one electron from the occupied space of the ground state to the virtual space of the reference state through the constraints in eqs. (8) and (9) and (b) allowing orbital relaxation to achieve self-consistency. This may seem similar to the ΔSCF technique, but we argue that in the ΔSCF method one would need, after abandoning the occupancy rule for the ground state, to maintain this electronic state throughout the SCF procedure; this is also the case for the MOM formula [13]. Some disagreement exists in those methods, mainly depending on primitive guesses. Indeed, the first process is out of the domain of the iterative process of the self-consistent field in the ΔSCF technique or MOM. On the other hand, ΔSCF assumes implicitly that a transition can be represented by an excitation involving only two orbitals, which generally seems not to be satisfied. However, in our method, this drawback is avoided. Davidson et al. have proposed a method [34-36] that produces the correct singlet excited state that is both orthogonal and non-interacting with the ground state, but their method can be applied only to smaller atoms and molecules.

In another class of methods, which more closely relate to the present one, the orthogonality condition between the ground and excited states is considered explicitly. As mentioned in the Introduction, those methods are conceptually misleading; for practical applications, our method is more straightforward and conceptually clear. The Huzinaga equation for excited states [9，10] also uses the projection operator technique, but in their method the occupancy of virtual orbitals varies independently in order to fulfill the orthogonality condition. This is quite different from our formula where both occupancy and virtual orbitals are variable in one SCF process. Glushkov et al. [28] have proposed a method that also considers the orthogonality condition. The reader may find that condition (12) is similar to the orthogonality constraint in Glushkov's method, but the starting points are obviously different.

Finally, a popular alternative to the study of excited-state properties is time-dependent DFT (TDDFT) in its adiabatic formulation [37, 38], which has been used as a compromise between accuracy and computational cost in many applications. However, TDDFT using popular exchange-correlation functionals fails for charge transfer excitation. It has been noted that the failure of TDDFT for charge transfer excitation is related to the orbital response parameter, which is kept at second order in the TDDFT energy expression [39, 40].

In contrast, our method takes into account the higher order response terms through orbital relaxation, which we expect is suitable for charge transfer excitation. We will revisit this point in future studies. Additionally, it is difficult for TDDFT to consider double electron transitions, which is easily achieved using our formula (see the following section for more details).

Table 6 Excitation energies in eV units of lithium atoms (^{2}P) using the lowest excited state as the reference state and calculated by the CIS method. Exp denotes the experimental values. The values of third column correspond to the addition of the lowest excitation energy, 1.84 eV, to the value in the second column. Because the 3*p* configuration is triply degenerate, we label this as *x*, *y*, and *z*

Li	eHF-CIS	eHF	CIS	Exp[18]
1s3*s*	1.49	3.33	3.34	3.37
1s3p_x	1.95	3.79	3.80	3.83
1s3p_y	1.95	3.79	3.80	3.83
1s3p_z	1.95	3.79	3.80	3.83

4. Concluding Remarks

In this report, we proposed a new criterion to locate the lowest excited state of atoms and molecules without variational collapse. Molecular orbital relaxation effects are included in our method. The excitation energies calculated using the present formula are in good agreement with experimental values. This approach can be used for the construction of a pure spin state. The wave function of the corresponding excited state is a proper reference state, which is suitable for the calculation of electron correlation energy, similar to the Hartree-Fock wave function for the ground state. The MOs obtained from our formula appear to be the approximate natural orbitals of the corresponding CIS excited states.

The present formula can be easily extended to calculate other types of excited states, such as two-electron excitations, core-electron excited states and so on. For example, if two-electron excited states are needed, the operator Π_g in eq. (11) can be defined as

$$\Pi_g = \sum_{i=1}^{2} |\psi_i\rangle\langle\psi_i|, \tag{24}$$

where the orbitals in this summation are those that are occupied in the ground state but virtual in the excited state. If more than one excited state is needed, excluding the first excited state, we can define a new operator

$$\Pi_g = |\psi_g^h\rangle\langle\psi_g^h| + |\psi_e^h\rangle\langle\psi_e^h|, \tag{25}$$

where the first orbital is the HOMO of the ground state and the second orbital is the HOMO of the first excited state. Of course, if the HOMO-LUMO transition is not the main contribution to the lowest excited state, more general equations (eqs. (8) and (9)) should be used. In this situation, the Zhao-Parr scheme [14] fails and an iterative scheme is needed to optimize the value of the Lagrange multipliers λ and γ. This issue also occurs in the constrained-DFT method developed by Wu et al. [41]. We will revisit this problem in future studies.

Finally, When the HOMO-LUMO transition is the main contribution to the lowest excited state, eqs. (14) and (15) can be written in a different form. If we act on both sides of eq. (14) with $1-\Pi_{g\uparrow}^{h}$ and consider that $\Pi_g(1-\Pi_g)\equiv 0$, the following equation is produced:

$$(1-\Pi_{g\uparrow}^{h})f^{\uparrow}(1-\Pi_{g\uparrow}^{h})\left|\psi_{k\uparrow}\right\rangle=\xi_{k\uparrow}(1-\Pi_{g\uparrow}^{h})\left|\psi_{k\uparrow}\right\rangle, \tag{26}$$

Note that

$$(1-\Pi_{g\uparrow}^{h})\left|\psi_{k\uparrow}\right\rangle\equiv\left|\psi_{k\uparrow}\right\rangle, \tag{27}$$

Eq. (26) is similar to the Huzinaga equation [9，10] and equivalent to eq. (14) in practical calculations. Similar equations can be obtained for spin-down electrons.

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Appendix A: Spin-adapted single-determinant wave function of an electronic excited state for a closed-shell system

Using a single-determinant wave function, the expectation values of the spin square operator can be written as

$$\left\langle S^2 \right\rangle = s(s-1) + N_\beta - Trace(S^{\alpha\beta}), \tag{A1}$$

where $s = (N_\alpha - N_\beta)/2$ and $N_\alpha(N_\beta)$ refers to the number of spin-up (spin-down) electrons. $S^{\alpha\beta}$ is the overlap matrix of the spin-up and spin-down spatial orbital with elements

$$S_{ij}^{\alpha\beta} = \left\langle \varphi_i^\alpha \mid \varphi_j^\beta \right\rangle, \tag{A2}$$

A spin-adapted configuration means that

$$\left\langle S^2 \right\rangle = s(s-1), \tag{A3}$$

which leads to

$$Tr(S^{\alpha\beta}) = N_\beta, \tag{A4}$$

This means that the spatial orbitals of β-electrons lie completely in the space extended by the spatial orbitals of α-electrons and that the β-spatial orbital can at most differ from the α-spatial orbital by a unitary transformation. If an α-electron is excited from an occupied orbital to a virtual orbital, in order to obtain the spin-adapted single-determinant wave function, the β-electron should also be excited to a virtual orbital in a similar manner. If an additional constraint corresponding to eq. (A4) is added to the variational functional to arrive at a spin-adapted solution [28], the double-electron excited state will be obtained.

Appendix B: Mayer's CIS wave function and the natural orbitals of the corresponding excited-state wave function

In terms of canonical HF orbitals, the CIS wave function can be written as

$$\Psi_{CIS} = \sum_{i\in occ} \sum_{p\in virt} C_i^p \varphi_p^+ \varphi_i^- \left| HF \right\rangle, \tag{B1}$$

where φ_p^+ and φ_i^- refer to the creation and annihilation operators corresponding to canonical HF orbitals and $|HF\rangle$ is the Hartree-Fock ground state. Mayer has noted that by considering the singular-value decomposition (SVD) of the CIS coefficient matrix, the CIS wave function is simplified to contain only N determinants, where N is the number of electrons [32].

$$\Lambda = U^T C V = \begin{pmatrix} \lambda_1 & \cdots & 0 \\ \vdots & \ddots & \vdots\ 0 \\ 0 & \cdots & \lambda_N \end{pmatrix}, \tag{B2}$$

Where U and V are appropriate $N_{occ} \times N_{occ}$ and $N_{virt} \times N_{virt}$ orthogonal matrices, respectively, and C refers to the $N_{occ} \times N_{virt}$ CIS coefficient matrix.

In terms of the new orbitals

$$\begin{aligned} \psi_r^v &= \sum_{p=1}^{virt} V_{pr} \varphi_p \\ \psi_k^o &= \sum_{i=1}^{occ} U_{ik} \varphi_i \end{aligned}, \tag{B3}$$

the CIS wave function will be transformed into the form

$$\Psi_{CIS} = \sum_{k=1}^{N} \lambda_k \psi_k^{v+} \psi_k^{o+} \left| HF \right\rangle, \tag{B4}$$

One may expect one or a few of the $\lambda_k$values to differ significantly from zero, and thus these excited configurations dominate the CIS wave function. The first-order reduced-density matrix, using the wave function (B4), can be written as [33]

$$P_{ab} = \delta_{ab} n_a - \lambda_a^2 \delta_{ab} n_a + \lambda_a^2 \delta_{ab} (1 - n_a), \tag{B5}$$

where $n_\alpha = 1,0$ indicates whether the orbital Ψ_a is occupied or virtual in the ground state. Thus, the first-order density matrix in the basis set of eq. (B3) is diagonal; that is, the associated orbitals are the natural orbitals of the system.