

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.

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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symmetry as the ground state, variational collapse always occurs and the upper bound to the excited-state energy is no longer valid.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 (Δ SCF) 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