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Multi-Configuration Electron-Hole Potential Method for Excited States

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The recently proposed electron-hole potential (EHP) method for excited states is extended to the multi-configurational case. The variation equation is solved using the quadratic convergence method. The EHP methods are shown to be approximations to the complete singly excited configuration interaction (CSECI) in the variational sense. Extended Brillouin theorems are proved for the EHP methods. The excitation energies and wave functions obtained by one and two configurational EHP methods agree well with those of the CSECI method. The EHP methods have clear advantage in the computer time requirement over the CI method and are especially suited for a calculation of approximate excited states of large molecules. The EHP methods are applicable to excited states which belong to the same irreducible representation as the ground state.

Key words: Electron hole potential (EHP) method – Complete singly excited configuration interaction – Extended Brillouin theorems – Excited states

1. Introduction

In the past several years the *ab initio* SCF MO method based on the Roothaan Equation [1] has been extensively used to calculate the wave function, the energy and properties of closed shell molecules. These calculations have shown that the SCF MO method of the closed shell system is extremely powerful in predicting the geometry and many other physical properties of the ground state [2], though the method does not take the electronic correlation into account. Several methods have been proposed for calculation of wave functions of excited states of a closed shell molecule: the Hartree-Fock method for the open shell system [3, 4], the traditional and more elaborate, (iterative) configuration interaction (CI) [5], and still controversial equation of motion method [6]. The CI method is extremely time consuming especially for large molecules in the integral transformation step. The multiconfigurational wave function also makes the analysis more complicated. The straight Hartree-Fock method cannot be applied to excited states which belong to the same irreducible representation as the ground state.

Very recently we proposed an extended Hartree-Fock theory for excited states or the electron-hole potential (EHP) method [7]. This method is an extension of the transformation of virtual orbitals, which has been proposed by many [8], to the transformation of both occupied and virtual orbitals in order to minimize the energy of an excited state. The EHP method is equivalent to the method proposed independently by Davidson [8] based on a somewhat different consideration.

The EHP method gives a well defined single configuration wave function, which is very handy for calculation of molecular properties. The EHP single determinant wave function does not include the correlation energy, and can be compared almost directly with the ground state SCF wave function. The EHP wave function for an excited state is guaranteed to be orthogonal to the ground state. So the method can be applied to an excited state belonging to the same irreducible representation as the ground state. The computer time required for an EHP calculation is of the comparable order with a ground state SCF calculation and is much smaller than a CI calculation, especially for large molecules.

The EHP method has been successfully used to calculate the hydrogen bond energy of lower excited states for the formaldehyde-water system [10, 11], the acrolein-water system [12], and the stabilization energy and geometry of the charge transfer state of the cyanocarbonyl-ROR and tetracyanoethylene-ROR complexes [13].

For some excited states, however, the EHP wave function is not quite appropriate. One such example is excited state of a dimer, a complex between two identical molecules. Let us assume for simplicity that two molecules in the dimer is related to each other by a symmetry operation. Then occupied orbitals of the dimer will form a set of two which can be approximated by plus and minus linear combinations of monomer orbitals:

$$\psi_{\pm}^{HO} \sim \psi_1^{HO} \pm \psi_2^{HO} .$$

Similarly for vacant orbitals of the dimer:

$$\psi_{\pm}^{LV} \sim \psi_1^{LV} \pm \psi_2^{LV} .$$

If one takes a single configuration wave function in which one electron is excited from, say, ψ_{+}^{HO} to, say, ψ_{+}^{LV}:

$$\Psi(\psi_{+}^{HO} \rightarrow \psi_{+}^{LV}) \sim \Psi(\psi_1^{HO} \rightarrow \psi_1^{LV}) + \Psi(\psi_2^{HO} \rightarrow \psi_2^{LV}) + \Psi(\psi_1^{HO} \rightarrow \psi_2^{LV}) + \Psi(\psi_2^{HO} \rightarrow \psi_1^{LV}) ,$$

one finds this wave function includes with an equal weight the intramolecular excitation and the intermolecular charge-transfer excitation. Usually the energy of the intramolecular excited state is different from the intermolecular one. In order to allow the mixing of intra- and inter-molecular excitations in a correct weight, the wave function must be at the simplest a linear combination of two configurations, such as

$$C_1 \Psi(\psi_{+}^{HO} \rightarrow \psi_{+}^{LV}) + C_2 \Psi(\psi_{-}^{HO} \rightarrow \psi_{-}^{LV})$$

$$C_3 \Psi(\psi_{+}^{HO} \rightarrow \psi_{-}^{LV}) + C_4 \Psi(\psi_{-}^{HO} \rightarrow \psi_{+}^{LV}) .$$

Here a multiconfigurational wave function is needed even for a qualitative purpose.

Another example consists of some excited states of particular molecules such as the lowest π–π^* singlet state of formaldehyde and ethylene and the $B\,^3\Sigma_u^-$ state of oxygen [14]. In these cases the π–π^* configuration mixes strongly with σ–σ^* configurations. Therefore at least two configurations are required to describe these state semi-quantitatively.

Multiconfigurational (MC) SCF methods have been successfully used for such cases [15]. Considering the advantages of the EHP method for the single configurational case, we have developed the multiconfigurational EHP method. Even though the discussion is restricted to the two configurational (TC) EHP method in this paper, an extension to more than two configurations is straightforward.

2. Review of One Configuration Electron Hole Potential (EHP) Method

The starting point of the method is the canonical SCF molecular orbitals $\{\psi\}$ which diagonalize the Hartree-Fock operator F of the closed-shell ground state. The total wave function of the ground state in the SCF approximation is given by a single Slater determinant as,

$$\Psi_0 = \mathscr{A}\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\ldots\psi_N\bar{\psi}_N \equiv |G\rangle \tag{1}$$

whose total energy is called E_0. Here $\mathscr{A}$ is an antisymmetrizer operator.

Before developing the two-configurational (TC) EHP method, it is convenient to review the (one-configurational) EHP method. We will use the second quantization form for convenience.

We write the wave function of an excited state, singly excited from the ground state, in the following form.

$$\Psi(\phi_\alpha \to \phi_\mu) = (1/\sqrt{2})\,[A^\dagger_{\bar{\mu}} A_{\bar{\alpha}} \pm A^\dagger_\mu A_\alpha]\,|G\rangle \tag{2}$$

where A_α and $A^\dagger_\mu$ are the annihilation operator for ϕ_α and the creation operator for ϕ_μ, respectively, with – referring to a β spin and no – to an α spin. The upper and lower signs in Eq. (2) and throughout the paper correspond to the singlet and triplet states, respectively. In the EHP method we assume that the operators A_α and $A^\dagger_\mu$ are expanded in terms of the annihilation and creation operators A_j and $A^\dagger_k$ of canonical SCF occupied MO's ψ_j and vacant MO's ψ_k.

$$A_\alpha = \sum_j^{\text{occ}} A_j b_{j\alpha}\,, \qquad A^\dagger_\mu = \sum_k^{\text{vac}} A^\dagger_k b_{k\mu}\,. \tag{3}$$

That is equivalent to saying that the MO ϕ_α and ϕ_μ are expanded in terms of ψ_j's and ψ_k's, respectively. The normalization of ϕ_α and ϕ_μ is equivalent to the anticommutation relations

$$[A^\dagger_\alpha, A_\alpha]_+ = 1\,, \qquad [A^\dagger_\mu, A_\mu]_+ = 1\,. \tag{4}$$

By using the Hartree-Fock operator F for the ground state, the energy $E(\alpha\to\mu)$ of the excited state $\Psi(\phi_\alpha\to\phi_\mu)$ is a function only of ϕ_α and ϕ_μ:

$$E(\alpha\to\mu) = E_0 + \langle\phi_\mu|F|\phi_\mu\rangle - \langle\phi_\alpha|F|\phi_\alpha\rangle - L^{\mu\mu}_{\alpha\alpha} \tag{5}$$

where

$$\begin{aligned} L^{\mu\nu}_{\beta\alpha} &= \langle\phi_\beta\phi_\alpha|\phi_\mu\phi_\nu\rangle - \langle\phi_\beta\phi_\nu|\phi_\mu\phi_\alpha\rangle \mp \langle\phi_\beta\phi_\nu|\phi_\mu\phi_\alpha\rangle \\ &\equiv \langle\phi_\beta|L_{\mu\nu}|\phi_\alpha\rangle \equiv \langle\phi_\mu|L_{\beta\alpha}|\phi_\nu\rangle \end{aligned} \tag{6}$$

$$\langle\phi_\delta\phi_\varepsilon|\phi_\zeta\phi_\eta\rangle = \int \phi^*_\delta(1)\,\phi_\varepsilon(1)\,\frac{1}{r_{12}}\,\phi^*_\zeta(2)\,\phi_\eta(2)\,d\tau_1\,d\tau_2\,. \tag{7}$$

MO's ϕ_α and ϕ_μ, i.e. the expansion coefficients $\{b_{j\alpha}\}$ and $\{b_{k\mu}\}$ of Eq. (3), are determined by the variation method such that the energy $E(\alpha \rightarrow \mu)$ is minimized. The coupled equations to be satisfied by ϕ_α and ϕ_μ are given by:

$$\begin{aligned} (F + L_{\mu\mu})|\phi_\alpha\rangle &= \lambda_\alpha|\phi_\alpha\rangle \\ (F - L_{\alpha\alpha})|\phi_\mu\rangle &= \lambda_\mu|\phi_\mu\rangle . \end{aligned} \tag{8}$$

By inserting Eq. (3) to Eq. (2), one can express the EHP wave function $\Psi(\phi_\alpha \rightarrow \phi_\mu)$ as a linear combination of singly excited configurations $\Psi(\psi_j \rightarrow \psi_k)$ based on the canonical SCF MO's.

$$\begin{aligned} \Psi(\phi_\alpha \rightarrow \phi_\mu) &= \sum_j^{\text{occ}} \sum_k^{\text{vac}} (b_{j\alpha} b_{k\mu}/\sqrt{2})\,[A_{\bar{k}}^{\dagger} A_{\bar{j}} \pm A_k^{\dagger} A_j]\,|G\rangle \\ &= \sum_j^{\text{occ}} \sum_k^{\text{vac}} b_{j\alpha} b_{k\mu} \Psi(\psi_j \rightarrow \psi_k) . \end{aligned} \tag{9}$$

In the configuration interaction method including only all the singly excited configurations (called C (complete) SECI), the wave function of the excited state is written as

$$\Psi^{\text{SECI}} = \sum_j^{\text{occ}} \sum_k^{\text{vac}} C_{jk} \Psi(\psi_j \rightarrow \psi_k) . \tag{10}$$

Comparing Eq. (9) with Eq. (10), one can see that the $m_\alpha \times m_\mu$ variation parameters C_{jk} in CSECI are decoupled into products $a_{j\alpha} \cdot b_{k\mu}$ in EHP, in which $(m_\alpha + m_\mu)$ coefficients, $a_{j\alpha}$ and $b_{k\mu}$, are determined variationally. Here m_α and m_μ are the numbers of the occupied and vacant MO's belonging to the same irreducible representations as ϕ_α and ϕ_μ, respectively.

3. Two-Configuration (TC) EHP Method

The starting point of the TCEHP method is the canonical SCF molecular orbitals as in the one configurational EHP method discussed in Section 2. The above formulation can then easily be extended to the two- (and multi-) configurational case. In the TCEHP method the wave function of the excited state is assumed to be written a linear combination of two excited configurations as

$$\Psi^{\text{TC}} = B_{\alpha\mu} \Psi(\phi_\alpha \rightarrow \phi_\mu) + B_{\beta\nu} \Psi(\phi_\beta \rightarrow \phi_\nu) \tag{11}$$

where $\Psi(\phi_\alpha \rightarrow \phi_\mu)$ and $\Psi(\phi_\beta \rightarrow \phi_\nu)$ are defined by Eq. (2) under the restrictions of Eq. (3). By using the variation method, the coefficients $B_{\alpha\mu}$ and $B_{\beta\nu}$, and new MO's ϕ_α, ϕ_μ, ϕ_β, and ϕ_ν are determined under the orthonormal conditions

$$\begin{aligned} &\langle\phi_\alpha|\phi_\alpha\rangle = \langle\phi_\beta|\phi_\beta\rangle = \langle\phi_\mu|\phi_\mu\rangle = \langle\phi_\nu|\phi_\nu\rangle = 1 , \\ &\langle\phi_\alpha|\phi_\beta\rangle = \langle\phi_\mu|\phi_\nu\rangle = 0 , \\ &\langle\Psi^{\text{TC}}|\Psi^{\text{TC}}\rangle = 1 . \end{aligned} \tag{12}$$

Since the energy of the excited state is written as

$$\begin{aligned} E^{\mathrm{TC}} = E_0 &+ (B_{\alpha\mu})^2 [\langle\phi_\mu|F|\phi_\mu\rangle - \langle\phi_\alpha|F|\phi_\alpha\rangle - L^{\mu\mu}_{\alpha\alpha}] \\ &+ (B_{\beta\nu})^2 [\langle\phi_\nu|F|\phi_\nu\rangle - \langle\phi_\beta|F|\phi_\beta\rangle - L^{\nu\nu}_{\beta\beta}] \\ &- B_{\alpha\mu}B_{\beta\nu}[L^{\mu\nu}_{\beta\alpha} + L^{\nu\mu}_{\alpha\beta}] \end{aligned} \tag{13}$$

the coupled equations to be solved are derived as follows:

$$(B_{\alpha\mu})^2 (F + L_{\mu\mu})|\phi_\alpha\rangle + B_{\alpha\mu}B_{\beta\nu}L_{\nu\mu}|\phi_\beta\rangle = |\phi_\alpha\rangle\lambda_{\alpha\alpha} + |\phi_\beta\rangle\lambda_{\beta\alpha} \tag{14a}$$

$$B_{\alpha\mu}B_{\beta\nu}L_{\mu\nu}|\phi_\alpha\rangle + (B_{\beta\nu})^2 (F + L_{\nu\nu})|\phi_\beta\rangle = |\phi_\alpha\rangle\lambda_{\alpha\beta} + |\phi_\beta\rangle\lambda_{\beta\beta} \tag{14b}$$

$$(B_{\alpha\mu})^2 (F - L_{\alpha\alpha})|\phi_\mu\rangle - B_{\alpha\mu}B_{\beta\nu}L_{\beta\alpha}|\phi_\nu\rangle = |\phi_\mu\rangle\lambda_{\mu\mu} + |\phi_\nu\rangle\lambda_{\nu\mu} \tag{15a}$$

$$-B_{\alpha\mu}B_{\beta\nu}L_{\alpha\beta}|\phi_\mu\rangle + (B_{\beta\nu})^2 (F - L_{\beta\beta})|\phi_\nu\rangle = |\phi_\mu\rangle\lambda_{\mu\nu} + |\phi_\nu\rangle\lambda_{\nu\nu} \tag{15b}$$

where λ's are the Lagrange multipliers and the L operators are defined by Eq. (6). By using the expansion Eq. (3), Eqs. (14) and (15) can be written in a matrix form as

$$\boldsymbol{G}_{\alpha\alpha}\boldsymbol{b}_\alpha + \boldsymbol{G}_{\alpha\beta}\boldsymbol{b}_\beta = \boldsymbol{b}_\alpha\lambda_{\alpha\alpha} + \boldsymbol{b}_\beta\lambda_{\beta\alpha} \tag{16a}$$

$$\boldsymbol{G}_{\beta\alpha}\boldsymbol{b}_\alpha + \boldsymbol{G}_{\beta\beta}\boldsymbol{b}_\beta = \boldsymbol{b}_\alpha\lambda_{\alpha\beta} + \boldsymbol{b}_\beta\lambda_{\beta\beta} \tag{16b}$$

$$\boldsymbol{G}_{\mu\mu}\boldsymbol{b}_\mu + \boldsymbol{G}_{\mu\nu}\boldsymbol{b}_\nu = \boldsymbol{b}_\mu\lambda_{\mu\mu} + \boldsymbol{b}_\nu\lambda_{\nu\mu} \tag{17a}$$

$$\boldsymbol{G}_{\nu\mu}\boldsymbol{b}_\mu + \boldsymbol{G}_{\nu\nu}\boldsymbol{b}_\nu = \boldsymbol{b}_\mu\lambda_{\nu\mu} + \boldsymbol{b}_\nu\lambda_{\nu\nu} \tag{17b}$$

where, for instance,

$$(\boldsymbol{G}_{\alpha\alpha})_{jj'} = (B_{\alpha\mu})^2 \langle\psi_j|F + L_{\mu\mu}|\psi_{j'}\rangle \qquad j \text{ and } j'\text{: occ. orbitals}$$

$$(\boldsymbol{G}_{\nu\nu})_{kk'} = (B_{\beta\nu})^2 \langle\psi_k|F - L_{\beta\beta}|\psi_{k'}\rangle \qquad k \text{ and } k'\text{: vac. orbitals}$$

and $\boldsymbol{b}_\alpha$ is a column vector whose elements are $b_{j\alpha}$.

In addition there is a 2-by-2 CI secular equation to be satisfied by $B_{\alpha\mu}$ and $B_{\beta\nu}$. From here one we assume for simplicity the coefficients, B's and $\boldsymbol{b}$'s and the $\boldsymbol{G}$ matrices are all real.

The coupled Eqs. (16) and (17) do not constitute a diagonalizable pseudo-eigenvalue problem but can be solved by the use of so-called quadratic convergence method. As an example, we show how to solve the set of Eq. (16). An approximation to $B_{\alpha\mu}$, $B_{\beta\nu}$, ϕ_μ, and ϕ_ν is assumed to be known and is used to calculate $\boldsymbol{G}$ matrices. It is also assumed that approximate values (zero-order solutions) of coefficients, $\boldsymbol{b}^0_\alpha$ and $\boldsymbol{b}^0_\beta$, which are orthonormal, are known. Applying the Newton-Raphson method, one can obtain the following set of simultaneous equations to the first order in the changes $\delta\boldsymbol{b}_\alpha$ and $\delta\boldsymbol{b}_\beta$:

$$\begin{aligned} (\boldsymbol{G}_{\alpha\alpha} - \lambda^0_{\alpha\alpha})\,\delta\boldsymbol{b}_\alpha + (\boldsymbol{G}_{\alpha\beta} - \lambda_{\beta\alpha})\,\delta\boldsymbol{b}_\beta - \boldsymbol{b}^0_\alpha\,\delta\lambda_{\alpha\alpha} - \boldsymbol{b}^0_\beta\,\delta\lambda_{\beta\alpha} \\ = -[(\boldsymbol{G}_{\alpha\alpha} - \lambda^0_{\alpha\alpha})\,\boldsymbol{b}^0_\alpha + (\boldsymbol{G}_{\alpha\beta} - \lambda^0_{\beta\alpha})\,\boldsymbol{b}^0_\beta] \end{aligned} \tag{18a}$$

$$\begin{aligned} (\boldsymbol{G}_{\beta\alpha} - \lambda^0_{\alpha\beta})\,\delta\boldsymbol{b}_\alpha + (\boldsymbol{G}_{\beta\beta} - \lambda^0_{\beta\beta})\,\delta\boldsymbol{b}_\beta - \boldsymbol{b}^0_\alpha\,\delta\lambda_{\alpha\beta} - \boldsymbol{b}^0_\beta\,\delta\lambda_{\beta\beta} \\ = -[(\boldsymbol{G}_{\beta\alpha} - \lambda^0_{\alpha\beta})\,\boldsymbol{b}^0_\alpha + (\boldsymbol{G}_{\beta\beta} - \lambda^0_{\beta\beta})\,\boldsymbol{b}^0_\beta] \end{aligned} \tag{18b}$$

where λ^0's are defined as

$$\lambda^0_{\gamma\delta} = \tilde{\boldsymbol{b}}^0_\gamma \boldsymbol{G}_{\delta\alpha}\boldsymbol{b}^0_\alpha + \tilde{\boldsymbol{b}}^0_\gamma \boldsymbol{G}_{\delta\beta}\boldsymbol{b}^0_\beta\,, \qquad \gamma, \delta = \alpha \text{ or } \beta\,.$$

The changes of the Lagrange multipliers are functions of $\delta\boldsymbol{b}_\alpha$ and $\delta\boldsymbol{b}_\beta$ and can be obtained by multiplying $\tilde{\boldsymbol{b}}_\alpha^0$ and $\tilde{\boldsymbol{b}}_\beta^0$ on Eq. (18) as follows:

$$\delta\lambda_{\alpha\alpha}=\tilde{\boldsymbol{b}}_\alpha^0(\boldsymbol{G}_{\alpha\alpha}-\lambda_{\alpha\alpha}^0)\,\delta\boldsymbol{b}_\alpha+\tilde{\boldsymbol{b}}_\alpha^0(\boldsymbol{G}_{\alpha\beta}-\lambda_{\beta\alpha}^0)\,\delta\boldsymbol{b}_\beta \tag{19a}$$

$$\delta\lambda_{\beta\alpha}=\tilde{\boldsymbol{b}}_\beta^0(\boldsymbol{G}_{\alpha\alpha}-\lambda_{\alpha\alpha}^0)\,\delta\boldsymbol{b}_\alpha+\tilde{\boldsymbol{b}}_\beta^0(\boldsymbol{G}_{\alpha\beta}-\lambda_{\beta\alpha}^0)\,\delta\boldsymbol{b}_\beta \tag{19b}$$

$$\delta\lambda_{\alpha\beta}=\tilde{\boldsymbol{b}}_\alpha^0(\boldsymbol{G}_{\beta\alpha}-\lambda_{\alpha\beta}^0)\,\delta\boldsymbol{b}_\alpha+\tilde{\boldsymbol{b}}_\alpha^0(\boldsymbol{G}_{\beta\beta}-\lambda_{\beta\beta}^0)\,\delta\boldsymbol{b}_\beta \tag{19c}$$

$$\delta\lambda_{\beta\beta}=\tilde{\boldsymbol{b}}_\beta^0(\boldsymbol{G}_{\beta\alpha}-\lambda_{\alpha\beta}^0)\,\delta\boldsymbol{b}_\alpha+\tilde{\boldsymbol{b}}_\beta^0(\boldsymbol{G}_{\beta\beta}-\lambda_{\beta\beta}^0)\,\delta\boldsymbol{b}_\beta\,. \tag{19d}$$

For the variation equation to be meaningful, the off-diagonal Lagrange multipliers must be equal to each other.

$$\lambda_{\beta\alpha}=\lambda_{\alpha\beta}\,. \tag{20}$$

In order to force the solution of Eq. (16) to satisfy the relationship (20), only one of two off-diagonal multipliers, for instance, $\lambda_{\alpha\beta}$ should be used in Eq. (18) [4b]. By inserting Eqs. (19a), (19c), and (19d) into Eqs. (18a) and (18b), the simultaneous linear equations to be solved are obtained.

$$\begin{aligned}&[(1-\boldsymbol{b}_\alpha^0\tilde{\boldsymbol{b}}_\alpha^0)(\boldsymbol{G}_{\alpha\alpha}-\lambda_{\alpha\alpha}^0)-\boldsymbol{b}_\beta^0\tilde{\boldsymbol{b}}_\alpha^0(\boldsymbol{G}_{\beta\alpha}-\lambda_{\alpha\beta}^0)]\,\delta\boldsymbol{b}_\alpha\\&+[(1-\boldsymbol{b}_\alpha^0\tilde{\boldsymbol{b}}_\alpha^0)(\boldsymbol{G}_{\alpha\beta}-\lambda_{\alpha\beta}^0)-\boldsymbol{b}_\beta^0\tilde{\boldsymbol{b}}_\alpha^0(\boldsymbol{G}_{\beta\beta}-\lambda_{\beta\beta}^0)]\,\delta\boldsymbol{b}_\beta\\&=-[(\boldsymbol{G}_{\alpha\alpha}-\lambda_{\alpha\alpha}^0)\,\boldsymbol{b}_\alpha^0+(\boldsymbol{G}_{\alpha\beta}-\lambda_{\alpha\beta}^0)\,\boldsymbol{b}_\beta^0]\end{aligned} \tag{21a}$$

$$\begin{aligned}&(1-\boldsymbol{b}_\alpha^0\tilde{\boldsymbol{b}}_\alpha^0-\boldsymbol{b}_\beta^0\tilde{\boldsymbol{b}}_\beta^0)(\boldsymbol{G}_{\beta\alpha}-\lambda_{\alpha\beta}^0)\,\delta\boldsymbol{b}_\alpha\\&+(1-\boldsymbol{b}_\alpha^0\tilde{\boldsymbol{b}}_\alpha^0-\boldsymbol{b}_\beta^0\tilde{\boldsymbol{b}}_\beta^0)(\boldsymbol{G}_{\beta\beta}-\lambda_{\beta\beta}^0)\,\delta\boldsymbol{b}_\beta\\&=-[(\boldsymbol{G}_{\beta\alpha}-\lambda_{\alpha\beta}^0)\,\boldsymbol{b}_\alpha^0+(\boldsymbol{G}_{\beta\beta}-\lambda_{\beta\beta}^0)\,\boldsymbol{b}_\beta^0]\,.\end{aligned} \tag{21b}$$

By multiplying $\tilde{\boldsymbol{b}}_\beta^0$ from the left of Eq. (21a), one can show the relationship:

$$\lambda_{\alpha\beta}^0+\delta\lambda_{\alpha\beta}=\lambda_{\beta\alpha}^0+\delta\lambda_{\beta\alpha}\,, \tag{22}$$

that is, the Hermiticity of Lagrange multipliers, Eq. (20), is satisfied by the solution of Eq. (21) within the first order of the changes of coefficients. And this Hermiticity assures the orthogonality of the orbitals ϕ_α and ϕ_β within the first order [18].

If the orbitals ϕ_α and ϕ_β belong to the different irreducible representations, the off-diagonal multiplier, $\lambda_{\alpha\beta}=\lambda_{\beta\alpha}$, is zero, so that Eq. (21) can be simplified as

$$\begin{aligned}&(1-\boldsymbol{b}_\alpha^0\tilde{\boldsymbol{b}}_\alpha^0)(\boldsymbol{G}_{\alpha\alpha}-\lambda_{\alpha\alpha}^0)\,\delta\boldsymbol{b}_\alpha+(1-\boldsymbol{b}_\alpha^0\tilde{\boldsymbol{b}}_\alpha^0)\,\boldsymbol{G}_{\alpha\beta}\delta\boldsymbol{b}_\beta\\&\qquad=-[(\boldsymbol{G}_{\alpha\alpha}-\lambda_{\alpha\alpha}^0)\,\boldsymbol{b}_\alpha^0+\boldsymbol{G}_{\alpha\beta}\boldsymbol{b}_\beta^0]\end{aligned} \tag{21a$'$}$$

$$\begin{aligned}&(1-\boldsymbol{b}_\beta^0\tilde{\boldsymbol{b}}_\beta^0)\,\boldsymbol{G}_{\beta\alpha}\delta\boldsymbol{b}_\alpha+(1-\boldsymbol{b}_\beta^0\tilde{\boldsymbol{b}}_\beta^0)(\boldsymbol{G}_{\beta\beta}-\lambda_{\beta\beta}^0)\,\delta\boldsymbol{b}_\beta\\&\qquad=-[\boldsymbol{G}_{\beta\alpha}\boldsymbol{b}_\alpha^0+(\boldsymbol{G}_{\beta\beta}-\lambda_{\beta\beta})\,\boldsymbol{b}_\beta^0]\,.\end{aligned} \tag{21b$'$}$$

Once the solutions $\delta\boldsymbol{b}_\alpha$ and $\delta\boldsymbol{b}_\beta$ of Eq. (21) are obtained, the new approximations for $\boldsymbol{b}_\alpha$ and $\boldsymbol{b}_\beta$ are calculated by replacing $\boldsymbol{b}_\alpha^0$ and $\boldsymbol{b}_\beta^0$ by $\boldsymbol{b}_\alpha^0+\delta\boldsymbol{b}_\alpha$ and $\boldsymbol{b}_\beta^0+\delta\boldsymbol{b}_\beta$, respectively. This process is repeated until $\delta\boldsymbol{b}_\alpha$ and $\delta\boldsymbol{b}_\beta$ become less than a predetermined threshold. This method is much faster than solving the eigenvalue problem. The vectors $\boldsymbol{b}_\alpha$ and $\boldsymbol{b}_\beta$ thus obtained are the solutions of Eq. (16) for a given set of $B_{\alpha\mu}$, $B_{\beta\nu}$, ϕ_μ, and ϕ_ν.

Practical procedures for completely solving the TCEHP problem are as follows;

(i) In the two-configurational wave function, Eq. (11), assume that MO's ϕ_α, ϕ_β, ϕ_ν, and ϕ_μ are SCF occupied and virtual MO's of the ground state. Namely, $\boldsymbol{b}_\alpha$, $\boldsymbol{b}_\beta$, $\boldsymbol{b}_\mu$, and $\boldsymbol{b}_\nu$ are assumed, as an initial guess, as unit vectors. By solving a 2-by-2 CI matrix, determine coefficients $B_{\alpha\mu}$ and $B_{\beta\nu}$.

(ii) By using B's, $\boldsymbol{b}_\alpha$ and $\boldsymbol{b}_\beta$ determined above, set up Eq. (17). New vectors $\boldsymbol{b}'_\mu$ and $\boldsymbol{b}'_\nu$ are calculated by solving iteratively the simultaneous equation similar to Eq. (21). Using $\boldsymbol{b}_\alpha$, $\boldsymbol{b}_\beta$, $\boldsymbol{b}'_\mu$, and $\boldsymbol{b}'_\nu$, determine new coefficients B's from the 2-by-2 CI matrix.

(iii) By the use of B's, $\boldsymbol{b}'_\mu$ and $\boldsymbol{b}'_\nu$ determined in (ii), set up Eq. (16). New vector $\boldsymbol{b}'_\alpha$ and $\boldsymbol{b}'_\beta$ are obtained by solving iteratively Eq. (21). Using $\boldsymbol{b}'_\alpha$, $\boldsymbol{b}'_\beta$, $\boldsymbol{b}'_\mu$ and $\boldsymbol{b}'_\nu$, one again determines new CI coefficients B's. The process (ii) and (iii) are repeated until the convergence of the energy or the vectors is achieved, which usually requires less than five cycles of (ii) and (iii).

Now we discuss some important properties of the TCEHP wave function ψ^{TC}. Analogous to Eq. (9), ψ^{TC} can be expressed as

$$\psi^{\mathrm{TC}} = [(B_{\alpha\mu}/\sqrt{2})(A^\dagger_{\bar{\mu}} A_{\bar{\alpha}} \pm A^\dagger_\mu A_\alpha) + (B_{\beta\nu}/\sqrt{2})(A^\dagger_{\bar{\nu}} A_{\bar{\beta}} \pm A^\dagger_\nu A_\beta)]\,|G\rangle\,. \tag{23a}$$

The orthogonalities of ϕ_α and ϕ_β, and ϕ_μ and ϕ_ν, respectively, are equivalent to the anticommutation relationships:

$$[A^\dagger_\alpha, A_\beta]_+ = [A^\dagger_\mu, A_\nu]_+ = 0\,.$$

By using the expansion Eq. (3), ψ^{TC} can be expanded into the sum of virtual singlet excited configurations:

$$\psi^{\mathrm{TC}} = \sum_j^{\mathrm{occ}} \sum_k^{\mathrm{vac}} (B_{\alpha\mu} b_{j\alpha} b_{k\mu} + B_{\beta\nu} b_{j\beta} b_{k\nu})\,\Psi(\psi_j \to \psi_k) \tag{23b}$$

which will be compared in Sec. III with the CSECI wave function, Eq. (10).

Since Ψ^{TC} is written as Eq. (23), the one particle density matrix is simply calculated as follows.

$$\begin{aligned}\varrho^{\mathrm{TC}}(1,1') = \varrho^{G}(1,1') &+ (B_{\alpha\mu})^2\,(\phi^*_\mu(1)\,\phi_\mu(1') - \phi^*_\alpha(1)\,\phi_\alpha(1')) \\ &+ (B_{\beta\nu})^2\,(\phi^*_\nu(1)\,\phi_\nu(1') - \phi^*_\beta(1)\,\phi_\beta(1'))\,.\end{aligned}$$

where $\varrho^G(1,1')$ is the density matrix of the ground state. From this matrix one-electron properties of the state can be easily calculated.

The following Brillouin theorems are valid in TCEHP. Assume that the orbital ϕ_γ is known, which belongs to the occupied orbital subspace $\{\psi_i\}$ and is orthogonal to ϕ_α and ϕ_β. By multiplying ϕ^*_γ on Eq. (14a), one obtains

$$\begin{aligned}0 &= (B_{\alpha\mu})^2\,\langle\phi_\gamma|F|\phi_\alpha\rangle + (B_{\alpha\mu})^2\,L^{\gamma\alpha}_{\mu\mu} + B_{\alpha\mu}B_{\beta\nu}L^{\gamma\beta}_{\nu\mu} \\ &= -B_{\alpha\mu}\langle\{B_{\alpha\mu}\Psi(\phi_\alpha\to\phi_\mu) + B_{\beta\nu}\Psi(\phi_\beta\to\phi_\nu)\}\,|\mathscr{H}|\,\Psi(\phi_\gamma\to\phi_\mu)\rangle\,.\end{aligned}$$

that is,

$$\langle\Psi(\phi_\gamma\to\phi_\mu)|\mathscr{H}|\Psi^{\mathrm{TC}}\rangle = 0\,. \tag{24a}$$

Also, from Eq. (14b)

$$\langle\Psi(\phi_\gamma\to\phi_\nu)|\mathscr{H}|\Psi^{\mathrm{TC}}\rangle = 0\,. \tag{24b}$$

Similarly one can show that

$$\langle \Psi(\phi_\alpha \to \phi_\lambda) | \mathscr{H} | \Psi^{\mathrm{TC}} \rangle = 0 \tag{24c}$$

$$\langle \Psi(\phi_\beta \to \phi_\lambda) | \mathscr{H} | \Psi^{\mathrm{TC}} \rangle = 0 \tag{24d}$$

when ϕ_λ is a vacant orbital orthogonal to ϕ_μ and ϕ_ν.

The use of the Hermiticity of Lagrange multipliers [19] leads to additional theorems. Eqs. (14) and (15) and $\lambda_{\alpha\beta} = \lambda^*_{\beta\alpha}$ give:

$$\begin{aligned} &B_{\alpha\mu} B_{\beta\nu} L^{\alpha\alpha}_{\mu\nu} + (B_{\beta\nu})^2 \langle \phi_\alpha | F | \phi_\beta \rangle + (B_{\beta\nu})^2 L^{\alpha\beta}_{\nu\nu} \\ &= (B_{\alpha\mu})^2 \langle \phi_\alpha | F | \phi_\beta \rangle + (B_{\alpha\mu})^2 L^{\alpha\beta}_{\mu\mu} + B_{\alpha\mu} B_{\beta\nu} L^{\beta\beta}_{\mu\nu} \,. \end{aligned}$$

By subtracting $B_{\alpha\mu} B_{\beta\nu} \langle \phi_\mu | F | \phi_\nu \rangle$ from both sides, one can show

$$\begin{aligned} &- B_{\beta\nu} \langle \{ B_{\alpha\mu} \Psi(\phi_\alpha \to \phi_\mu) + B_{\beta\nu} \Psi(\phi_\beta \to \phi_\nu) \} | \mathscr{H} | \Psi(\phi_\alpha \to \phi_\nu) \rangle \\ &= - B_{\alpha\mu} \langle \Psi(\phi_\beta \to \phi_\mu) | \mathscr{H} | \{ B_{\alpha\mu} \Psi(\phi_\alpha \to \phi_\mu) + B_{\beta\nu} \Psi(\phi_\beta \to \phi_\nu) \} \rangle \,. \end{aligned} \tag{25a}$$

Also, from the relationships $\lambda_{\mu\nu} = \lambda^*_{\nu\mu}$,

$$\begin{aligned} &- B_{\alpha\mu} B_{\beta\nu} L^{\mu\mu}_{\alpha\beta} + (B_{\beta\nu})^2 \langle \phi_\mu | F | \phi_\nu \rangle - (B_{\beta\nu})^2 L^{\mu\nu}_{\beta\beta} \\ &= (B_{\alpha\mu})^2 \langle \phi_\mu | F | \phi_\nu \rangle - (B_{\alpha\mu})^2 L^{\mu\nu}_{\alpha\alpha} - B_{\alpha\mu} B_{\beta\nu} L^{\nu\nu}_{\beta\alpha} \,. \end{aligned}$$

By subtracting $B_{\alpha\mu} B_{\beta\nu} \langle \phi_\alpha | F | \phi_\beta \rangle$ from both sides one obtains

$$\begin{aligned} &B_{\beta\nu} \langle \Psi(\phi_\beta \to \phi_\mu) | \mathscr{H} | \{ B_{\alpha\mu} \Psi(\phi_\alpha \to \phi_\mu) + B_{\beta\nu} \Psi(\phi_\beta \to \phi_\nu) \} \rangle \\ &= B_{\alpha\mu} \langle \{ B_{\alpha\mu} \Psi(\phi_\alpha \to \phi_\mu) + B_{\beta\nu} \Psi(\phi_\beta \to \phi_\nu) \} | \mathscr{H} | \Psi(\phi_\alpha \to \phi_\nu) \rangle \end{aligned} \tag{25b}$$

By combining (25a) and (25b), the relationships

$$\langle \Psi(\phi_\alpha \to \phi_\nu) | \mathscr{H} | \Psi^{\mathrm{TC}} \rangle = 0 \tag{26a}$$

$$\langle \Psi(\phi_\beta \to \phi_\mu) | \mathscr{H} | \Psi^{\mathrm{TC}} \rangle = 0 \tag{26b}$$

are proved, unless

$$|B_{\alpha\mu}| = |B_{\beta\nu}| \,. \tag{27}$$

If the equality occurs, by an appropriate linear transformations of ϕ_α and ϕ_β, and of ϕ_μ and ϕ_ν, a new set of wave functions can be defined which satisfy Eq. (26).

In addition, since Ψ^{TC} is equivalent to a linear combination of singly excited configurations [Eq. (23a)] the usual Brillouin theorem between the ground state is still valid.

$$\langle \Psi_G | \mathscr{H} | \Psi^{\mathrm{TC}} \rangle = 0 \,. \tag{28}$$

One of the features of EHP method is that the wave function and energy in this method are approximations to the complete SECI in the sense of the variation method; that is, the energy gives an upper bound of that of the complete SECI.

4. Numerical Results and Discussion

Two-configurational EHP method was programmed for a modified version of GAUSS 70 *ab initio* program [16]. A few examples of numerical results are given in Tables 1–3. The second and third columns in Tables 1 and 2 show the

Table 1. Comparison of the vertical excitation energies of H_2–H_2[a] and HNO[b]

Molecules	SCF MO		EHP		CSECI
state	One conf.[c] eV	Two conf.[c] eV	One conf. eV	Two conf. eV	eV
H_2–H_2					
Singlet	8.568	8.565	8.531 (6)[c]	8.515 (11)	8.515 (11)[c]
Triplet	6.105	5.961	5.131 (6)	4.872 (11)	4.872 (11)
HNO					
$^3A''$	0.806	0.806	0.471 (8)	0.469 (17)	0.312 (29)
$^1A''$[d]	2.049	2.049	1.756 (8)	1.754 (17)	1.653 (29)
$^3A'$	3.941	3.941	3.586 (2)	3.533 (17)	3.515 (65)
$^1A'$	10.115	10.078	9.997 (2)	9.958 (17)	9.901 (65)

[a] No symmetry. Four atoms are placed at $(\pm 0.5, 0)$, $(+0.2916, 1.1818)$, and $(+0.2916, 2.1818)$ Å in a plane. Basis set: 4-31 G.

[b] The experimental geometry for the ground state [20]. (R(CH) = 1.063 Å, R(CN) = 1.212 Å, $\sphericalangle$HCN = 108.6°). Basis set: 4-31G. Ground state configuration: $\ldots(3a')^2(4a')^2(5a')^2(6a')^2(1a'')^2(7a')^2$. Total energy of the ground state: −129.57778 Hartree.

[c] N_F: Degree of freedom of variation parameters. For SCF MO (one configuration), $N_F = 0$; for SCF MO (2 configuration), $N_F = 1$.

[d] The experimental adiabatic excitation energy: 1.63 eV [20].

Table 2. Comparison of the vertical excitation energies of H_2CO

Geometry	SCF MO		EHP		CSECI
states	One conf. eV	Two conf. eV	One conf. eV	Two conf. eV	eV
Planar[a]					
$^3A_2\,(n\text{–}\pi^*)$	5.801	5.801	3.611 (3)[d]	3.608 (6)	3.555 (8)
$^1A_2\,(n\text{–}\pi^*)$	6.245	6.245	4.420 (3)	4.419 (6)	4.377 (8)
$^3A_1\,(\pi\text{–}\pi^*)$	7.854	7.854[c]	4.879 (2)	4.872 (6)[c]	4.779 (28)
$^1A_1\,(\pi\text{–}\pi^*)$	12.087	10.784[c]	12.079 (2)	10.607 (6)[c]	10.411 (28)
$^1B_1\,(\sigma\text{–}\pi^*)$	11.518	11.517	9.358 (6)	9.353 (10)	9.321 (18)
$^1B_2\,(n\text{–}\sigma^*)$	10.261	10.259	10.182 (4)	10.172 (11)	10.142 (22)
Bent[b]					
$^3A''\,(n\text{–}\pi^*)$	4.380	4.380	2.654 (9)	2.654 (17)	2.601 (35)
$^1A''\,(n\text{–}\pi^*)$	4.974	4.974	3.525 (9)	3.525 (17)	3.492 (35)
$^3A'\,(\pi\text{–}\pi^*)$	4.772	4.772	2.721 (13)	2.717 (17)	2.670 (59)
$^1A'\,(\sigma\text{–}\pi^*)$	10.481	10.475	7.534 (13)	7.517 (17)	7.505 (59)

[a] R(CH) = 1.120 Å, $\sphericalangle$HCH = 118°, R(CO) = 1.210 Å [11]. Basis set: STO3G plus one p (the exponents: 0.106 (O) and 0.06 (C)). Ground state: $\ldots(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^2$. Total energy −112.46157 Hartree.

[b] The experimental geometry for the $^1(n\text{–}\pi^*)$ state $^1A_2$ [20]. (R(CH) = 1.093 Å, $\sphericalangle$HCH = 119°, R(CO) = 1.323 Å, the out of plane angle = 31°). Basis set: STO-3G plus one p (the exponents: 0.106 (O) and 0.06 (C)). Ground state: $\ldots(3a')^2(4a')^2(1a'')^2(5a')^2(6a')^2(2a'')^2$. Total energy: −112.47460. The difference of the total energy between two geometry is 0.355 eV, which should be added to calculate the adiabatic excitation energies.

[c] Approximated by $B_1(1b_1 \rightarrow 2b_1) + B_2(2b_2 \rightarrow 4b_2)$. When $B_1'(1b_1 \rightarrow 2b_2) + B_2'(5a_1 \rightarrow 6a_1)$ is used, 7.854 (SCF) and 4.811 (TCEHP) for the triplet state, and 12.082 (SCF) and 11.152 (TCEHP) for the singlet state, respectively.

[d] N_F: see c) of Table 1.

Table 3. Comparison of coefficients of configurations for bent H_2CO[a]

$^3A''$			$^1A''$			$^3A'$			$^1A'$		
Conf.	TCEHP[b]	CSECI[c]	Conf.	TCEHP[b]	CSECI[c]	Conf.	TCEHP[d]	CSECI[e]	Conf.	TCEHP[d]	CSECI[e]
8– 9	0.9111	0.9124	8– 9	0.9199	0.9208	7– 9	0.9004	0.8991	7– 9	−0.3188	−0.3013
8–13	0.3163	0.3189	8–13	0.3114	0.3123	7–13	0.3849	0.3850	7–13	−0.1231	−0.0728
8–16	−0.2228	−0.2186	8–16	−0.1981	−0.1948	7–16	−0.1910	−0.1932	6– 9	0.8526	0.8618
8–18	0.0349	0.0300	8–18	0.0381	0.0384	6– 9	0.0286	0.0215	6–13	0.3291	0.3407
5– 9	0.1195	0.0974	5– 9	0.1120	0.0965	6–13	0.0122	0.0148	6–16	−0.1545	−0.1626
5–13	0.0415	0.0211	5–13	0.0379	0.0258	6–16	−0.0061	−0.0029	6–18	0.0451	0.0427
5–16	−0.0292	−0.0687	5–16	−0.0241	−0.0599	8–15	0.0109	0.0178	3– 9	−0.0716	−0.0634
5–18	0.0046	0.0190	5–18	0.0046	0.0051	5–15	0.0099	0.0085	3–13	−0.0277	−0.0442
									8–15	0.0378	0.0409

[a] The order of the orbitals; 1*a*′, 2*a*′, 3*a*′, 4*a*′, 1*a*″, 5*a*′, 6*a*′, 2*a*″ for the occupied orbitals, and 7*a*′, 8*a*′, 9*a*′, 3*a*″, 10*a*′, 11*a*′, 4*a*″, 12*a*′, 13*a*′, 14*a*′, 5*a*″, 15*a*′ for the vacant orbitals. Eight or nine of the largest coefficients are given.

[b] Degree of freedom of the variation parameter, $N_F = 17$.

[c] $N_F = 35$.

[d] $N_F = 17$.

[e] $N_F = 59$.

energies of an electronic configuration and of the 2 × 2 configuration interaction wave function, respectively, both based on the canonical SCF MO of the ground state. The fourth and fifth columns are the energies obtained by the one- and two-configurational EHP method. In the last column results of the configuration interaction including completely all singly excited configurations (CSECI) are given.

One can see in the Tables that both EHP methods give very good approximation to the CSECI, even though a degree of freedom N_F in variation parameters in EHP methods is much smaller than in the CSECI. In the CI, N_F^{CI} is a number of configurations included -1 (because of the normalization). In the one-configurational EHP, N_F is written as

$$N_F^{\mathrm{OCEHP}} = n_\alpha + m_\mu - 2$$

where n_α is a number of occupied orbitals which belong to the same irreducible representation as the orbital ϕ_α, and m_μ is a number of vacant orbitals which belong to the same irreducible representation as the orbital ϕ_μ. Because of the normalization requirement of two orbitals, two has to be subtracted. The degree of freedom in two-configurational EHP is expressed as

$$N_F^{\mathrm{TCEHP}} = n_\alpha + n_\beta + m_\mu + m_\nu - N_s + 1$$

where N_s is 4 usually, but is 6 when ϕ_α and ϕ_β belong to the same irreducible representation, because the orthogonality in addition to the normalization is required between ϕ_α and ϕ_β and also between ϕ_μ and ϕ_ν. The (2 × 2) CI coefficients give an additional degree of freedom. In Tables N_F is shown in parentheses.

In the H_2–H_2 system, N_F of TCEHP is equal to that of CSECI. Therefore, in spite of the fact that equations solved are very different in the two methods, both variation methods should, and in fact do, give identical results.

Differences between the energies of the TCEHP and the CSECI methods are usually less than 0.06 eV (0.002 Hartree) with a few exceptions. Large differences are observed in the A'' states of HNO and in the A_1 states of the planar H_2CO, but still they are less than 0.2 eV (0.0007 Hartree). In the case of the H_2CO A_1 state, a linear combination of at least three configurations ($a_1 \to a_1^*$, $b_1 \to b_1^*$, and $b_2 \to b_2^*$) might be required to describe the wave functions appropriately.

As was shwon in Eq. (23b), the TCEHP wave function can be expanded as a linear combination of singly excited configurations based on canonical SCF MO's. The expansion coefficients for leading configurations for bent H_2CO are shown in Table 3 as well as coefficients in the CSECI calculation. As anticipated from the agreement of energies, two sets of coefficients agree quite well.

One of the most important advantages of the EHP method over the CI method is the saving of the computer time. For instance, in the bent H_2CO with STO $3\,G+p$ basis set (20 basis functions) the calculation of the ground state canonical SCF MO took 20 cycles and 1.34 CPU min on an IBM 360/65. The one configurational EHP method took 2–2.5 cycles and 0.23–0.40 CPU min per state, and the TCEHP method required 2.5–10 cycles and 0.63–2.40 min per state. On the other hand the CSECI calculation including integral transformation took

12 min. The difference of time needed between the CI method and the EHP methods increased drastically with a number of basis functions. Since the TCEHP method is a variational approximation to the CSECI method, the major advantage of the former will be for large molecules. Actually we have performed one and two configurational EHP calculations for many geometries and many excited states of formic acid dimer with 52 basis functions, hydrogen maleate ion with 43 basis functions and the tetracyanoethylene-water molecular complex with 57 basis functions [17]. For these systems a CI calculation would be extremely expensive.

5. Conclusion

(1) At first, the (one configurational) EHP method is reviewed. It is shown that the EHP wave function, which is a single determinant variational wave function, is an approximation to the wave function of the complete singly excited configuration interaction.

(2) The two configurational EHP method is developed. The variational equation is solved iteratively by using the quadratic convergence method. Extensions of the Broullioun theorem are proved. This method is also an approximation to the complete singly excited configuration interaction.

(3) The agreement of EHP results with CI results is excellent.

(4) The EHP methods have clear advantage in the computer time requirement over the CI method and especially suited for a calculation of approximate wave functions and energies of excited states of large molecules.

(5) The EHP methods can be applied to excited states which belong to the same irreducible representation as the ground state. Straight SCF methods for excited states fail to do so.

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