Introduction to SAC-CI method

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preface

Symmetry Adapted Cluster /Configuration Interaction

This method has been developed mainly by the **Nakatsuji** laboratory, both in theories and algorithms, and has been successfully applied to various chemical phenomena involving more then 150 molecules

preface

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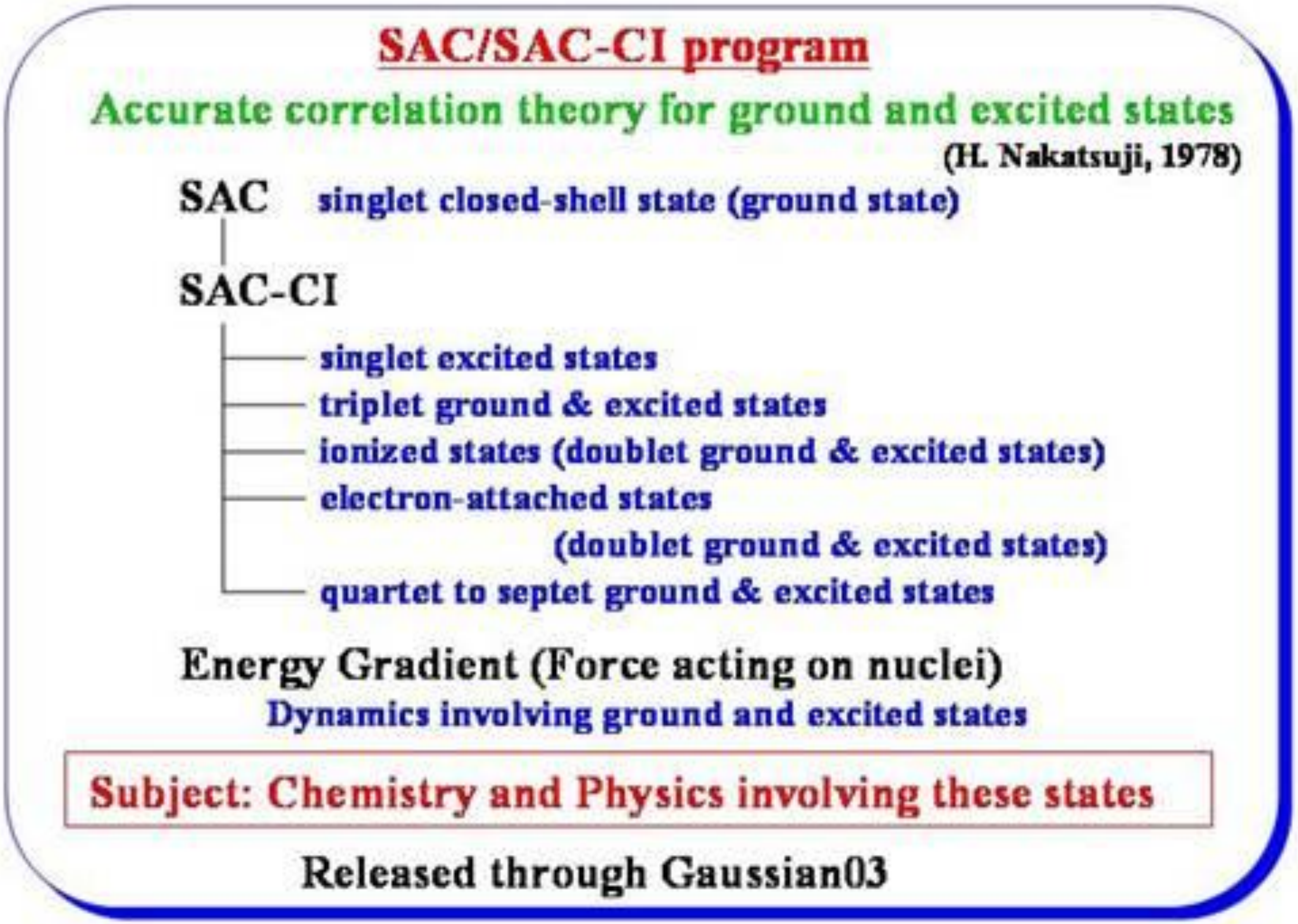
preface



SAC/SAC-CI program

Accurate correlation theory for ground and excited states

(H. Nakatsuji, 1978)

SAC singlet closed-shell state (ground state)

SAC-CI

- singlet excited states
- triplet ground & excited states
- ionized states (doublet ground & excited states)
- electron-attached states (doublet ground & excited states)
- quartet to septet ground & excited states

Energy Gradient (Force acting on nuclei)

Dynamics involving ground and excited states

Subject: Chemistry and Physics involving these states

Released through Gaussian03

SAC theory

For the totally symmetric singlet closed-shell state, we define symmetry adapted cluster (SAC) expansion as:

$$\left|\Psi_g\right\rangle = \exp\left(\sum_I C_I S_I\right)\left|0\right\rangle$$

$$= \left(1 + \sum_I C_I S_I + \tfrac{1}{2}\sum_I C_I C_J S_I S_J + \ldots\right)\left|0\right\rangle$$

Where |***0***> is Hartree-Fock and $\boldsymbol{S_I}$ is symmetry adapted excitation operator.

SAC theory

In the SAC expansion the unknown variables ***C*$_I$** are associated to ***S*$_I$**, so that we require the Schrödinger equation is satisfied within the space of the linked configurations as:

$$\langle 0 | H - E_g | \Psi_g^{SAC} \rangle = 0$$

$$\langle 0 | S_I (H - E_g) | \Psi_g^{SAC} \rangle = 0$$

This solution is called as non-variational solution.

SAC theory

As in the original paper, the variational solution is obtained by applying the variational principle to the SAC wave function and the equations are:

$$\left\langle \Psi_g^{SAC} \middle| H - E_g \middle| \Psi_g^{SAC} \right\rangle = 0$$

$$\left\langle \Psi_g^{SAC} \middle| S_I (H - E_g) S_I^+ \middle| \Psi_g^{SAC} \right\rangle = 0$$

SAC-CI theory

The SAC theory defines not only the SAC wave function for the ground state, but also the excited functions which span the basis of high quality for the excited states. We define the excited functions ($\boldsymbol{\Phi}_K$) by using the SAC wave function as

$$\Phi_K = PS_K^+ \left| \Psi_g^{SAC} \right\rangle$$

where P is an operator which projects out the ground state

$$P = 1 - \left| \Psi_g^{SAC} \right\rangle \left\langle \Psi_g^{SAC} \right|$$

SAC-CI theory

It is easily shown that the functions satisfy the important relation of the basis for excited states:

$$\left\langle \Phi_K \middle| \Psi_g^{SAC} \right\rangle = 0, \left\langle \Phi_K \middle| H \middle| \Psi_g^{SAC} \right\rangle = 0$$

We therefore describe the excited state by a linear conbination of the functions

$$\Psi_e^{SAC-CI} = \sum_K d_K \Phi_K$$

$$= (\sum_K d_K R_K + \sum_{K,I} d_K C_I R_K S_I + \ldots) \left|0\right\rangle - \sum_K d_K S_{gK} \left|\psi_g\right\rangle$$

SAC-CI theory

Applying the variational principle for solving the unknown variables ($\boldsymbol{d}_K$), we obtain

$$\left\langle \Phi_K \middle| H - E_e \middle| \Psi_e^{SAC-CI} \right\rangle = 0$$

The SAC-CI wave function automatically satisfies the orthogonality and Hamiltonian orthogonality with the ground state and also with different excited states.

SAC-CI theory

The SAC-CI wave function is also defined for the excited states having different symmetries, and for ionized and electron attached states. We generalize as

$$\Phi_K = P R_K^{+} \left| \Psi_g^{SAC} \right\rangle$$

where ($\boldsymbol{R}_K$) represent a set of excitation, ionization, and/or electron attachment operators.

SAC-CI theory

Though the formulation of the SAC-CI theory is variational, non-variational formulation is also possible. The non-variational SAC-CI solution is obtained by projecting the Schrödinger equation onto the space of the linked configurations

$$\left\langle 0 \middle| R_K (H - E_e) \middle| \Psi_e^{SAC-CI} \right\rangle = 0$$

SAC-CI theory

In the case of totally symmetric singlet excited states, equation of the non-variational SAC-CI solution with Hartree-Fock configuration is also written as in more explicit form as

$$\begin{pmatrix} \langle 0|(H-E_e)e^S|0\rangle & \langle 0|(H-E_e)R_K^+e^S|0\rangle \\ \langle 0|R_K(H-E_e)e^S|0\rangle & \langle 0|R_K(H-E_e)R_K^+e^S|0\rangle \end{pmatrix} = 0$$

SAC-CI theory

The SAC-CI theory is based on the correlated basis function, whose concept has been now widely adopted in other methods for excited states. Omitting the projector, or including the identity operator into , we can write the SAC-CI wave function as

$$\Psi_e^{SAC-CI} = \Re \Psi_g^{SAC}$$

where the excitator $\Re$ (a kind of reaction operator) is defined as

$$\Re = \sum_K d_K R_K^+$$

Analytical energy gradients of the SAC-CI method

The expression of the energy gradient can be written in a general form as

$$\frac{\partial E_{corr}}{\partial \alpha} = \sum_{pq} \gamma_{pq} F^{\alpha}_{pq} + \Gamma_{pq,rs}(pq\,|\,rs)^{\alpha}$$

$$- \sum_{pq} X_{pq} S^{\alpha}_{pq} + \sum_{p>q} (X_{pq} - X_{qp}) T^{\alpha}_{pq}$$

where γ_{pq} and $\Gamma_{pq,rs}$ are one and two electron reduced density matrices, respectively. The F^{α}_{pq} ,$(pq|rs)^{\alpha}$, and S^{α}_{pq} are the skeleton Fock, two-electron, and overlap derivative integrals, respectively.

Analytical energy gradients of the SAC-CI method

This equation explicitly includes the anti-symmetric part of the CPHF coefficient T^{α}_{pq}. This entity can be obtained from the coupled-perturbed (CP)-MOD equations.

$$\frac{\partial}{\partial \alpha}\left(M^{x_0} - (M^{x_0})^T\right) = 0$$

which is due to the condition of minimum-orbital deformation described below.

Minimum-orbital deformation method

This method minimizes the deformation of the MO’s induced by the perturbation at the neighborhood of the geometry under consideration. The perturbation dependence of the unitary transformation among MO's is attributed to ***T***^{x}, the anti-symmetric part of the CPHF coefficients. Therefore, it is required that the matrix elements between any real occupied [unoccupied] MOs ***T***$^{x}_{ij}$[***T***$^{x}_{ab}$] vanish.

$$T_{ij}^{x} = U_{ij}^{x} - U_{ji}^{x} = 0$$

Minimum-orbital deformation method

The matrix $\boldsymbol{U}^x$ is the so-called CPHF coefficients at the given geometry x and satisfies

$$U^x = C^T S \tfrac{dC}{dx} \, or \, \tfrac{dC}{dx} = CU^x$$

The matrices C and S denote the MO coefficient and overlap, respectively. Next we introduce “displaced” overlap matrix defined by

$$M^{x_0} = C^{x_0 T} S^{x_0} C$$

where x_0 denotes the reference geometry.

Minimum-orbital deformation method

During the geometry optimization, we assume that the coordinate *x* is restricted within the neighborhood of the reference coordinate and the Taylor series of the MO coefficient *C* converges well to the first-order in the nuclear displacement, x-x_0. This would lead to an approximate equation

$$M^{x_0} = 1 + (x - x_0) U^x$$

and

$$0 = T^x = U^x - (U^x)^T = (x - x_0)^{-1} (M^{x_0} - (M^{x_0})^T)$$

Minimum-orbital deformation method

Hance, a condition

$$(M^{x_0} - (M^{x_0})^T = 0$$

diminishes the unphysical orbital rotations. The MO $\boldsymbol{\Psi}$ is obtained by the orthogonal transformations of the canonical MOs $\{\boldsymbol{\Psi}_i\}$ as

$$\Psi_j = \sum_i \tilde{\Psi}_i W_{ij}^{x_0}$$

where the transformation W^{x_0} leading to a minimum orbital-deformation (MOD) is given by

Minimum-orbital deformation method

$$W^{x_0} = \{(\tilde{M}^{x_0})^T \tilde{M}^{x_0}\}^{-1/2} (\tilde{M}^{x_0})^T$$

and

$$\tilde{M}^{x_0} = (C^{x_0})^T S^{x_0} \tilde{C}$$

where $\tilde{C}$ stands for the orbital coefficient matrix for the canonical MOs. The displaced overlap matrix $\tilde{M}^{x_0}$ is asymmetric and the transformation rotates the canonical orbitals $\tilde{\Psi}_i$ so as to make one-to-one correspondence to the reference MOs.

The END

Thank You
for
Your Attention