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RESEARCH ARTICLE

Role of triplet states in geminal-based perturbation theory

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We show that to obtain accurate potential curves by perturbing geminal-type wave functions it is insufficient to restrict the geminals to their singlet-coupled states. Including triplet excited geminals to form 4-electron singlets via Serber coupling is essential to describe processes involving simultaneous dissociation of two non-isolated single bonds.

Keywords: multi-reference theory; geminals; triplet states

1. Introduction

The choice of an appropriate reference state for subsequent perturbative treatment is a delicate question of current quantum chemistry. Many chemical processes require multi-reference states to form a qualitatively acceptable starting point. Multi-reference quantum chemistry is therefore an actual and important field, and it is our pleasure to highlight the work of Professor Sourav Pal in it (see e.g. Refs.[1–12]).

In cases where single-reference states are inappropriate, the theory of antisymmetrized product of strongly orthogonal geminals offers an interesting alternative[13–19]. This method is a generalization of the Hartree-Fock scheme in the sense that the antisymmetrized one-electron orbitals used in the latter are replaced by two-electron functions (geminals) :

$$|\Psi_{APSG}\rangle = \psi_1^\dagger \psi_2^\dagger \dots \psi_N^\dagger |vac\rangle \tag{1}$$

where the geminals ψ_i can be expanded in orthogonal and mutually exclusive subspaces of one-electron spin-orbitals μ, ν to ensure strong orthogonality:

$$\psi_i^\dagger = \sum_{\mu<\nu}^{(i)} C_{\mu\nu}^i \; a_\mu^\dagger a_\nu^\dagger. \tag{2}$$

Symbol (i) on the summation indicates the i-th subspace. In many applications one restricts oneself to the $S_z = 0$ case, where the geminal is written in terms of spatial orbitals as

$$\psi_i^{q\dagger} = \sum_{mn}^{(i)} C_{mn}^{iq} \; a_{m\alpha}^\dagger a_{n\beta}^\dagger \tag{3}$$

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where q labels the states of geminal i, and the expansion coefficients C^{iq}_{mn} are obtained variationally, which is equivalent to solving the local Schrödinger equation

$$\sum_{rs} (\hat{H}^{eff}_i)_{mn,rs}\ C^{iq}_{rs} \ = \ E^q_i\ C^{iq}_{mn} \tag{4}$$

(for more details, see Ref.[20]. It is customary to use *singlet coupled* geminals in which case coefficient matrices C^i are symmetric.

Geminals have been suggested for use already in the early days of quantum chemistry[21–27], and were kept in a dormant state for some time. Geminal theory is a special case of group function theory [28] and, as such it can be considered an early forerunner of the approach presented here.

The advantage of geminal based approaches is that the dissociation of two-electron bonds can be described correctly. The present renaissance of geminal theories[29–42] is perhaps a consequence of the need of simple but flexible and qualitatively correct reference states in multi-configuration theory.

2. Perturbing singlet geminals

We shall use the APSG wave function as a reference state, and aim to include dynamical correlation perturbatively. As known, the results of perturbation theory depend strongly on the partitioning applied. It was shown that the so-called optimal partitioning[43, 44] of Rayleigh-Schrödinger perturbation theory recovers the linearized coupled cluster method. For this reason, designation 'perturbation theory' and 'linearized coupled cluster' is used interchangeably. Since the APSG wave function constitutes a multi-configurational reference state, we work in the spirit of *Multireference* Linearized Coupled Cluster (MR-LCC) theory[45–47] to describe dynamical correlation.

We write the Schrödinger equation as

$$\hat{H}e^{\hat{T}}|\mathrm{APSG}\rangle = Ee^{\hat{T}}|\mathrm{APSG}\rangle. \tag{5}$$

An example for the cluster operator is

$$\hat{T} = \sum_{i<j}\sum_{p}^{n_i}\sum_{q}^{n_j} t^{pq}_{ij}\ \psi^+_{ip}\psi^+_{jq}\psi^-_{j0}\psi^-_{i0}, \tag{6}$$

where p and q run over the excited states of geminals i and j respectively (n_i is the number of excited states of geminal i), and ψ^+_{ip} and ψ^+_{jq} refer to the excited state creation operators of the corresponding geminal while ψ^-_{i0} and ψ^-_{j0} annihilate ground-state geminals). The energy formula is given by

$$\langle \mathrm{APSG}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\mathrm{APSG}\rangle = E \tag{7}$$

Restricting to linearized coupled cluster approximation means a truncation of the Baker-Campbell-Hausdorff expansion after the second term:

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} \approx \hat{H} + [\hat{H}, \hat{T}] \tag{8}$$

leading to the energy formula

$$E = \langle \mathrm{APSG}|\hat{H}|\mathrm{APSG}\rangle + \langle \mathrm{APSG}|[\hat{H},\hat{T}]|\mathrm{APSG}\rangle. \quad (9)$$

Here

$$\hat{T} = \sum_{i<j}\sum_{p}^{n_i}\sum_{q}^{n_j} t_{ij}^{pq}\ \psi_{ip}^{+}\psi_{jq}^{+}\psi_{j0}^{-}\psi_{i0}^{-} = \sum_k t_k \hat{X}_k \quad (10)$$

with straightforward notations for the geminal excitations $\hat{X}_k = \psi_{ip}^{+}\psi_{jq}^{+}\psi_{j0}^{-}\psi_{i0}^{-}$ and their amplitudes $t_k = t_{ij}^{pq}$.

Similarly to the above written dispersive-like excitations[14], cluster operators for other types have to be considered, including those which transfer one or two electrons between geminals.

To obtain the amplitude equations, we write

$$e^{-\hat{T}}\hat{H}e^{\hat{T}}|\mathrm{APSG}\rangle = E|\mathrm{APSG}\rangle. \quad (11)$$

Projecting this equation with $\langle \mathrm{APSG}|\hat{X}_j^{\dagger}$ and linearizing again in the amplitudes we get

$$\langle \mathrm{APSG}|\hat{X}_j^{\dagger}[\hat{T},\hat{H}]|\mathrm{APSG}\rangle = \langle \mathrm{APSG}|\hat{X}_j^{\dagger}\hat{H}|\mathrm{APSG}\rangle. \quad (12)$$

Substituting the expansion of the cluster operator, we obtain

$$\sum_i \langle \mathrm{APSG}|\hat{X}_j^{\dagger}(\hat{X}_i\hat{H} - \hat{H}\hat{X}_i)|\mathrm{APSG}\rangle t_i = \langle \mathrm{APSG}|\hat{X}_j^{\dagger}\hat{H}|\mathrm{APSG}\rangle \quad (13)$$

which is a linear system of equations of the shape

$$\mathbf{A}\ \ \mathbf{t} = \mathbf{b} \quad (14)$$

for the amplitudes $\mathbf{t}$ with straightforward notations.

When more bonds are involved in a dissociation process (or in case of multiple-bond dissociation), the energy formula of Eq.(9) was found to perform well only around equilibrium[14]. As Fig. 1. illustrates, a failure occurs at moderately stretched geometry when elongating both OH bonds of H_2O, and the error of LCC corrected APSG is signifanctly increased in the dissociation limit.

3. Including triplet geminals in the reference

Instead of using merely singlet-coupled geminals with symmetric coefficients C applied in Eq.(3), we may also allow for more general two-electron wave functions

$$|^1S\rangle = \sum_{mn}^{(i)} {}^1C_{mn}^{i}\ a_{m\alpha}^{\dagger}a_{n\beta}^{\dagger} \quad (15)$$

$$|^3T^0\rangle = \sum_{mn}^{(i)} {}^3C^i_{mn}\ a^\dagger_{m\alpha}a^\dagger_{n\beta} \tag{16}$$

$$|^3T^\uparrow\rangle = \sum_{m<n}^{(i)} {}^\uparrow C^i_{mn}\ a^\dagger_{m\alpha}a^\dagger_{n\alpha} \tag{17}$$

$$|^3T^\downarrow\rangle = \sum_{m<n}^{(i)} {}^\downarrow C^i_{mn}\ a^\dagger_{m\beta}a^\dagger_{n\beta} \tag{18}$$

Here the matrix of singlet coefficients ${}^1C^i_{mn}$ is symmetric, that of $S_z = 0$ triplets ${}^3C^i_{mn}$ is antisymmetric, and those of $S_z \neq 0$ components are triangular to avoid double counting of configurations.

For two geminals a and b, the singlet-coupled APSG wave function is constructed with geminals of Eq.(15)

$$|\psi_I\rangle = |^1S^1_aS_b\rangle\ . \tag{19}$$

Triplet geminals of Eqs.(16)-(18) are coupled to a 4-electron singlet

$$|\psi_{II}\rangle = \frac{1}{\sqrt{3}}\ \Big(\ |^3T^0_a\ {}^3T^0_b\ \rangle\ -\ |^3T^\uparrow_a\ {}^3T^\downarrow_b\rangle\ -\ |^3T^\downarrow_a\ {}^3T^\uparrow_b\rangle\ \Big) \tag{20}$$

with the appropriate Clebshes (cf. Serber-coupling[48]). Functions ψ_I and ψ_{II} are considered to form a two-dimensional subspace. An improved reference state, denoted APSG-TT, is obtained as

$$|\text{APSG-TT}\rangle\ =\ c_I\ |\psi_I\rangle + c_{II}\ |\psi_{II}\rangle \tag{21}$$

with c_I and c_{II} determined by diagonalizing the matrix of H formed in the two-dimensional subspace, and using $c_I^2 + c_{II}^2 = 1$ for normalization. The MR-LCC procedure based on the reference function of Eq.(21) is carried out in the manner described in the previous section.

4. Illustration

We illustrate the role of triplet geminal states on the example of the symmetric dissociation of water. The importance of triplets for this system was previously emphasized by Li et al[49]. We use a simple split-shell basis set (6-31G) with the oxygen core frozen and compare the results to full CI.

Fig. 1. shows absolute energy curves, while in Fig. 2. deviations from full-CI are presented. Both figures illustrate well the message: the reference states APSG and APSG-TT produce a potential curve with acceptable shapes, but lie rather far from full CI. When perturbing these states with the MR-LCC approach, APSG-LCC turns out to be useless the curve passing through a singularity, while the APSG-TT+LCC results form a well-shaped potential curve approaching full CI quite close.

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Figure 1. Potential curve for the symmetric dissociation of the water molecule. For notations, see text

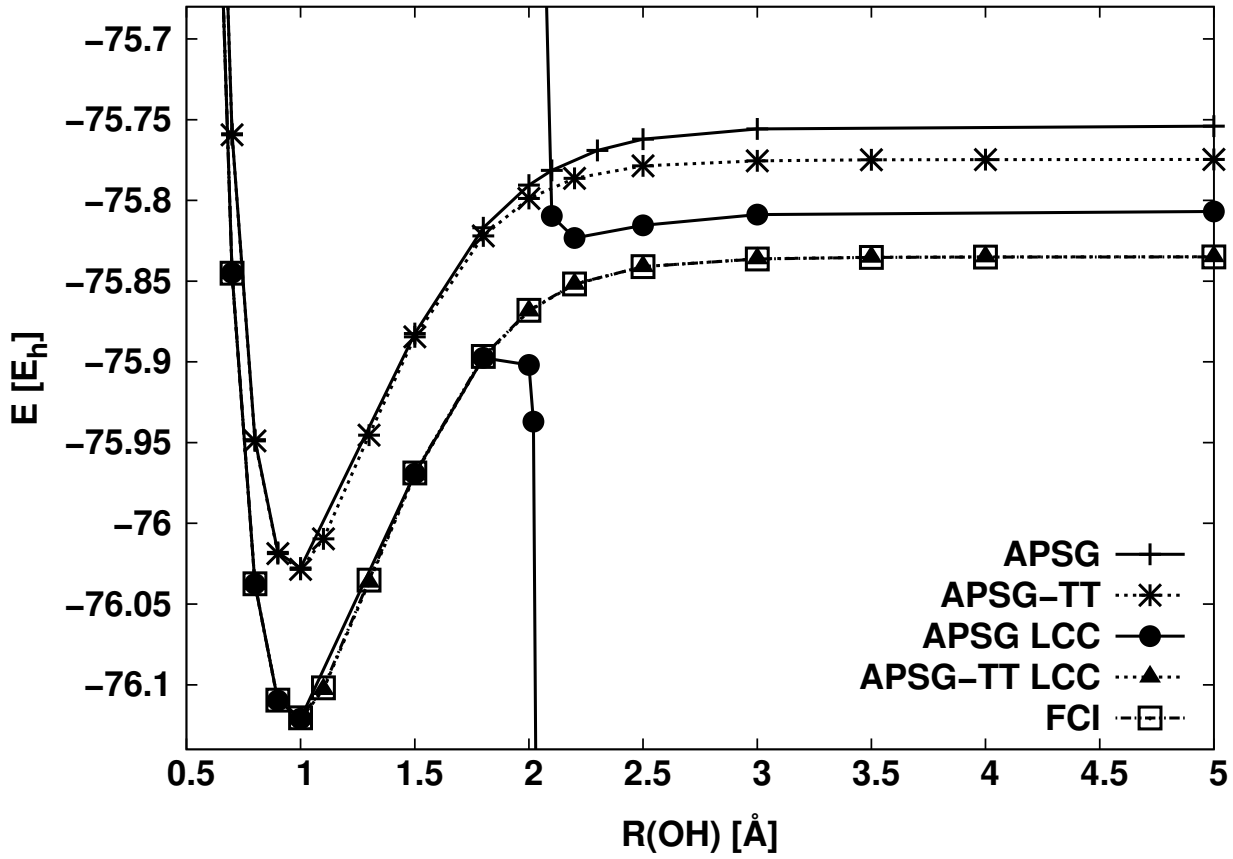

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Figure 2. Relative energy differences wrt full CI for the symmetric dissociation of the water molecule. For notations, see text