

論文の内容の要旨

論文題目

Development and Applications of Multireference

Perturbation Theory

(多参照摂動論の開発と応用)

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Multireference perturbation theory (MRPT) is more and more widely used as a standard tool for quantum-chemical calculations. It ensures reliable results for ground and excited states of small and medium-size molecules. One of the biggest advantages of MRPT is that it can be used on the whole potential energy surface, including the bond-breaking and far-from-equilibrium regions, and therefore it can be applied for computations on chemical reactions. There are many different multireference perturbation theories, usually differing by employing different partitionings of Hamiltonian and different choices for a reference space. The most widely used one is the second-order Møller-Plesset MRPT based on a reference space spanned by a complete active space (CAS). Its most popular realizations are known as Multireference Møller-Plesset Perturbation Theory (MRMP), Multiconfigurational Quasidegenerated Perturbation Theory (MC-QDPT), and the second-order Complete Active Space Perturbation Theory (CASPT2).

The second-order Møller-Plesset MRPT method reproduces experimental results with high accuracy; usually the excitation energies are computed with accuracy within 0.3eV, bond lengths within 0.005Å, and the error for harmonic vibrational frequencies is not larger than 50 wavenumbers. However, sometimes the second-order energies calculated using MRPT possess a large error, even of order of tens of

electronvolts. The erroneous character of such results can be seen most clearly when computing potential energy surfaces. Some points deviate from calculated curves, either being shifted upward or downward; only removing these points from calculations yields smooth potentials. These numerical instabilities are related to quasidegeneracies in the spectrum of a zeroth-order Hamiltonian. The second-order energy for a reference state $|\alpha\rangle$ is given by

$$E_{\alpha}^{(2)} = -\sum_{q \in Q} \frac{|\langle q|\hat{H}|\alpha\rangle|^2}{E_q^{(0)} - E_{\alpha}^{(0)}}.$$

If, for any state $|q\rangle$ from the orthogonal space Q , its zeroth-order energy $E_q^{(0)}$ is quasidegenerated to the zeroth-order energy $E_{\alpha}^{(0)}$ of a reference state, and moreover the coupling element $\langle q|\hat{H}|\alpha\rangle$ is non-zero, then the contribution from $|q\rangle$ to $E_{\alpha}^{(2)}$ tends to infinity as $E_q^{(0)} - E_{\alpha}^{(0)}$ tends to zero. There can be two reasons for quasidegeneracies observed in the zeroth-order Hamiltonian's spectrum, related either to a poor choice of reference space, or to a poor choice of zeroth-order Hamiltonian. In the former case, the reference space does not contain some low-lying states important for proper description of nondynamical correlation in the reference state. The remedy for it is rather simple: quasidegeneracies vanish after moving these states to the reference space. This however, may be very difficult when CAS is used as a reference space. Moving some states into CAS corresponds to its enlarging – such enlarging can

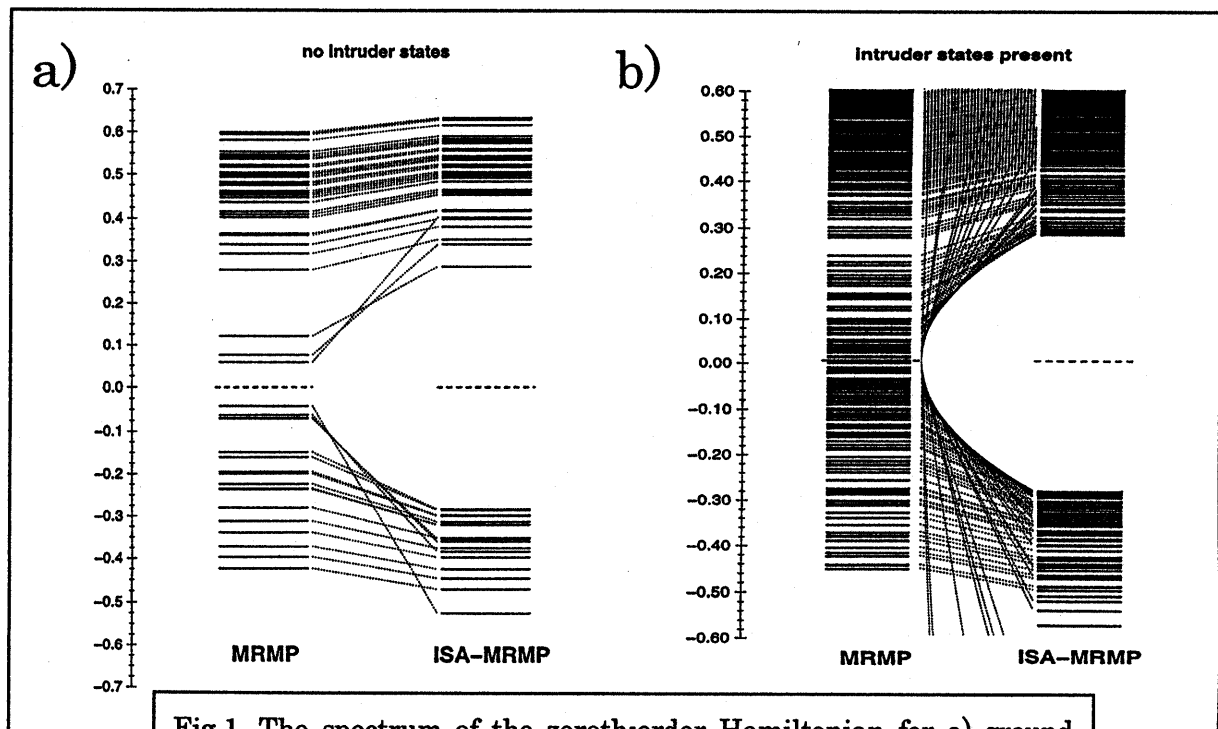
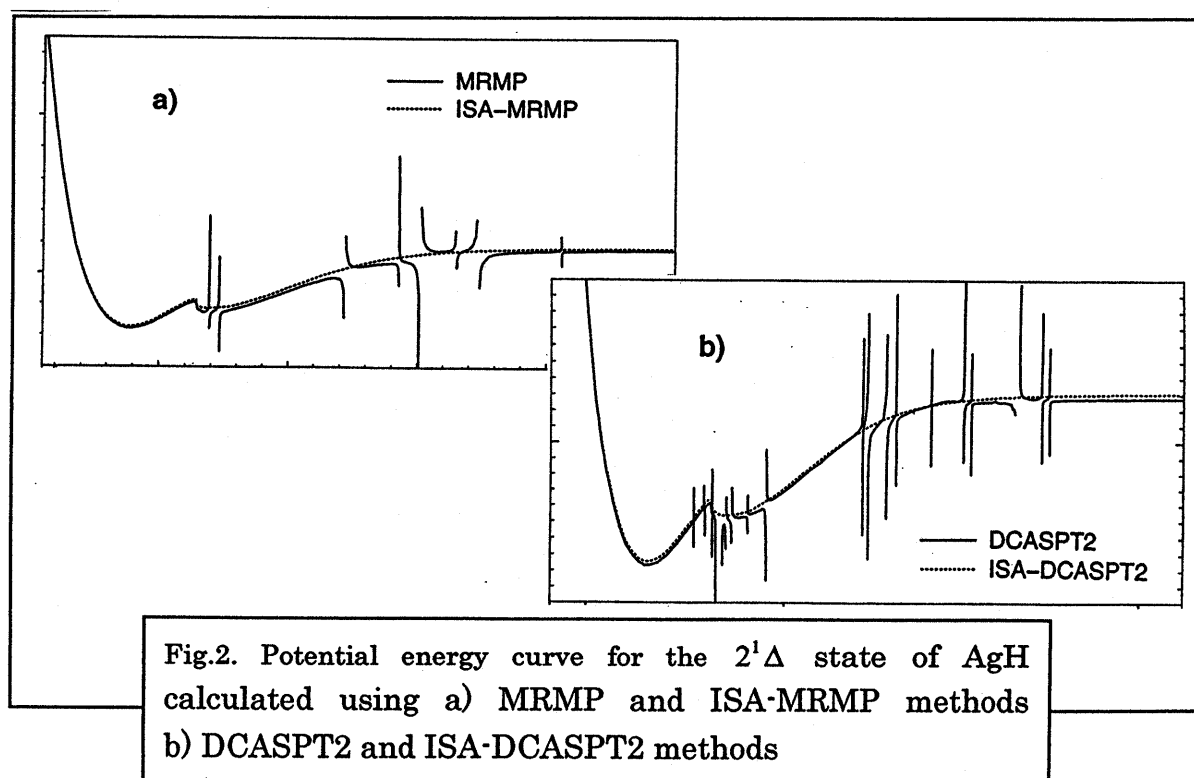


Fig.1. The spectrum of the zeroth-order Hamiltonian for a) ground state of N₂ b) the ³Π_u state of N₂

be unfeasible if the CAS is originally big. Such situation occurs in calculations for the chromium dimer, where the proper description of the sextuple bond would require using 18 active orbitals, whereas practical limitations allow only 12 of them

The quasidegeneracies caused by a poor choice of zeroth-order Hamiltonian are much more difficult to deal with. Usually, the zeroth-order Hamiltonian is chosen in such a way that it provides an easy way to obtain the zeroth-order energies and eigenfunctions. The physical significance of obtained zeroth-order energies is rather limited. For example, the diagonal Møller-Plesset zeroth-order Hamiltonian corresponds to a system of non-interacting electrons and the diagonal Epstein-Nesbet zeroth-order Hamiltonian to a system of non-interacting states. Therefore, the quasidegeneracies present in the spectrum of the zeroth-order Hamiltonian can be described as accidental. The states from the Q space responsible for creating these quasidegeneracies are called intruder states, and the phenomena of divergent behavior of low-order MRPT energies due to intruder states is called the intruder state problem.

To solve the intruder state problem in MRPT, we propose a new method called intruder state avoidance (ISA) technique. It is based on the redefinition of the zeroth-order Hamiltonian by adding a state-dependent shift to zeroth-order energy of every singly and doubly excited state. The shift is reciprocally proportional to the difference in the zeroth-order energy between the given state and the reference state. This assures us that the modified zeroth-order energies are never quasidegenerated with the zeroth-order energy of the reference state.



To investigate the quality of the ISA technique we use it together with the MRMP method. We apply ISA-MRMP to the calculations on potential energy curves that are otherwise plagued by singularities when treated with MRMP; calculations are performed on the $1^3\Sigma_u^-$ state of O_2 ; and on the $2^1\Delta$, $3^1\Delta$, $2^3\Delta$ and $3^3\Delta$ states of AgH. The states of AgH are also calculated using the ISA-DCASPT2 (second-order diagrammatic complete active space perturbation theory) method; the curves obtained by both methods for the $2^1\Delta$ state are shown in Fig.2. ISA-MRMP is also applied to other calculations where MRMP is influenced by intruder states; calculations are performed on the $^3\Pi_u$ state of N_2 , the $^3\Pi$ state of CO, and the $2^1A'$ state of formamide. A number of calculations are also performed to illustrate that this approach has little or no effect on MRMP when intruder states are not present in perturbative calculations. Vertical excitation energies are calculated for the low-lying states of N_2 , C_2 , CO, and benzene; the adiabatic $^1A_1 \rightarrow ^3B_1$ energy separation in CH_2 and the spectroscopic parameters of O_2 are also calculated. Calculations on vertical excitation energies are also performed on the Q and B bands states of free-base, chlorin, and zinc-chlorin porphyrin.