SINGLE-ROOT MULTIREFERENCE BRILLOUIN–WIGNER COUPLED-CLUSTER THEORY. ROTATIONAL BARRIER OF THE ETHYLENE MOLECULE

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Dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday.

Recently developed single-root multireference Brillouin–Wigner coupled cluster (MR BWCC) theory is applied to study the rotational barrier of the ethylene molecule. The method belongs to a broad family of state-selective coupled-cluster (CC) methods and may be considered as a bridge connecting the single-reference and multireference CC theories. In a highly nondegenerate case, it becomes identical with the standard single-reference CC method while in a quasi-degenerate case gives results very close to the Hilbert space MR CC method. The method switches between the two cases in a continuous way, providing thus smooth potential energy surfaces, not plagued by intruder states. The rotation about the double bond in ethylene represents a typical two-state problem. To demonstrate abilities of our approach, we study the rotation barrier using the single-root MR BWCC theory at the CCSD level of approximation and the results are compared with other CC methods.

Key words: State-selective; Multireference; Coupled cluster; Hilbert space; Brillouin–Wigner; Single-root; *Ab initio* calculations; Quantum chemistry.

In the past two decades, the single-reference coupled-cluster (CC) method, based on the exponential expansion of the wave function, has become one of the most efficient and reliable methods to account for electron correlation in the close-shell nondegenerate ground states of atoms and molecules[1–8]. Nevertheless, its extension to a multireference (MR) case, that is necessary when handling quasi-degenerate or general open-shell systems, has proven far from being an easy or straightforward task. Among them, two important classes can be distinguished: the Fock space[9–15] and Hilbert space[16–23] approaches.

The main reason why existing multireference coupled-cluster (MR CC) methods as well as related multireference Rayleigh–Schrödinger many-body perturbation theory

(MR MBPT) cannot be considered as standard or routine methods is the occurrence of intruder states or convergence problems. Needless to say, majority of existing MR CC/MBPT methods are based on the so-called Bloch theory[24], *i.e.* several states are treated simultaneously. However, such a treatment is not very suitable to explore global potential energy surfaces (PES) since it is hardly possible to construct such a model space that would be large enough to describe a manifold of states over the whole PES simultaneously. Moreover, in order to ensure size-extensivity, both theories prefer the complete model space formulations what makes the situation even worse.

Therefore, it is highly desirable to develop alternative methods which would focus on a single state while employing a multiconfigurational reference. These approaches are often denoted as one-state or state-selective (SS) or state-specific or single-root methods. From recent works, one should mention various MR CEPA (coupled electron pair approximation) approaches[25–32], the two-determinant Hilbert space MR CC approach for open-shell singlet states[22], SS MR CC method of Oliphant and Adamowicz[33,34], SS open-shell CC method based on the unitary group approach of Li and Paldus[35,36] and SS version of the Hilbert space MR CC method of Meller *et al*.[37]. In our recent articles[38,39] we have formulated the so-called single-root multireference Brillouin–Wigner coupled-cluster (MR BWCC) theory which deals with one state while employing a multiconfigurational reference. The method represents a brand-new CC approach to quasidegenerate problems which combines merits of two theories: the single-reference CC method in a nondegenerate case and the Hilbert space MR CC method[16] in quasidegenerate case. In this respect, more convenient name of the method should be the SS Hilbert space MR CC approach. The method has several advantages over the Hilbert space based MR CC approaches: (i) no coupling terms, (ii) equations for cluster amplitudes do not mix various sets of amplitudes, (iii) no redundancy problem, (iv) the method can be very easily implemented into existing CC codes, and (v) in a highly nondegenerate case the method reduces to the standard single-reference CC method. On the other hand, the method is not fully size-extensive due to the presence of disconnected terms.

So far, the single-root MR BWCC method has been successfully applied to several small systems, such as the trapezoidal H4 model system[38,39], dissociation of the F_2 molecule[40] and rotational barrier of the N_2H_2 molecule[41] at the CCSD level of approximation (*i.e.* CC method truncated at the single and double excitation level) using a two-determinant model space. The model space was spanned by two closed-shell type configurations: the ground state configuration and biexcited configuration $\mathrm{HOMO}^2 \rightarrow \mathrm{LUMO}^2$ where HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital.

The main goal of this article is to study the rotational barrier of the ethylene molecule and focuses on the performance of the MR BWCCSD method in comparison to other *ab initio* approaches. The rotation of the C_2H_4 molecule around the double bond represents a typical two-state problem in which the weights of reference configurations can change from 0 to 1 in a continuous way (for a twisted geometry we observe full configurational degeneracy); however, in contrast to the diimine molecule, the relaxation effects play much more important role here.

THEORY

In this section we give a brief review of the single-root MR BWCC approach; more details can be found in our articles[38,39]. To this end, let us assume that we are interested in one state, say, for simplicity, the ground state ψ_0 and our task is to solve the Schrodinger equation

$$H\Psi_0 = \varepsilon_0 \Psi_0 \ . \tag{1}$$

Let us further assume that we are able to split the exact Hamiltonian H into two parts

$$H = H_0 + V \ , \tag{2}$$

where H_0 is a zeroth-order Hamiltonian and V is a perturbation and we know the solution of the characteristic problem of H_0

$$H_0 \Phi_\mu = E_\mu \Phi_\mu \ . \tag{3}$$

If the most important contributions to the ground state are provided by d configurations Φ_μ represented by Slater determinants (in a spin-orbital form), within the multireference Brillouin–Wigner perturbation theory[42] the exact wave function ψ_0 can be expressed as follows

$$\Psi_0 = (1 + B_0 V + B_0 V B_0 V + \ldots)\Psi_0^P \ , \tag{4}$$

where B_0 is the Brillouin–Wigner-like propagator

$$B_0 = \sum_{q \in \mathrm{Q}} \frac{|\Phi_q\rangle \langle\Phi_q|}{\varepsilon_0 - E_q} \tag{5}$$

and Ψ_0^{P} is a projection of the exact wave function onto the model space. The model or reference space P is spanned by *d* dominant configuration Φ_μ; its orthogonal complement is denoted as a Q space.

Now, one can introduce a state-specific wave operator $\tilde{\Omega}$, acting on states from the model space, in the following way

$$\tilde{\Omega} = 1 + B_0 V + B_0 V B_0 V + \ldots \ . \tag{6}$$

The wave operator $\tilde{\Omega}$ obeys the operator equation

$$\tilde{\Omega} = 1 + B_0 V \tilde{\Omega} \tag{7}$$

that can be viewed as an analogue of the Bloch equation for the state-specific wave operator. We recall that the wave operator $\tilde{\Omega}$ converts just one projected wave function into the corresponding exact wave function and should not be confused with the so-called Bloch wave operator that transforms several projected wave functions Ψ_α^{P} into corresponding exact states; therefore we prefer the use of a tilde. The "effective" hamiltonian $\tilde{H}_{\mathrm{eff}}$ is defined in the same way as in the Bloch theory, *i*.e.

$$\tilde{H}_{\mathrm{eff}} = \mathrm{P} H \tilde{\Omega} \mathrm{P} \tag{8}$$

which implies that the exact energy of the ground state $\mathcal{E}_0$ is obtained as one of its eigenvalues. Remaining eigenvalues do not represent any physical meaningful solution.

If we adopt an exponential expansion for the wave operator $\tilde{\Omega}$, we speak about the single-root MR BWCC method. The simplest way is to exploit the Hilbert space exponential ansatz of Jeziorski and Monkhorst[16]

$$\tilde{\Omega} = \sum_{\mu \in \mathrm{P}} \mathrm{e}^{T^\mu} |\Phi_\mu\rangle\langle\Phi_\mu| \ , \tag{9}$$

where T^μ is a cluster operator defined with respect to the μ-th configuration. In this sence, the method can be considered as a state-selective Hilbert space MR CC method, however, in contrast to other SS MR CC approaches, there is no redundancy problem. Substituting the exponential Ansatz (*9*) into Eq. (*7*) and projecting against the configurations from the Q and P subspaces, we get a system of equations

$$(\mathcal{E}_0 - H_{\mu\mu})\langle \Phi_q | e^{T^\mu} | \Phi_\mu \rangle = \langle \Phi_q | H_N(\mu)\, e^{T^\mu} | \Phi_\mu \rangle \qquad (10)$$

that can be used for the calculation of cluster amplitudes in the single-root MR BWCC theory. The symbol $H_N(\mu)$ denotes the normal-ordered Hamiltonian with respect to the μ-th configuration

$$H_N(\mu) = H - \langle \Phi_\mu | H | \Phi_\mu \rangle = H - H_{\mu\mu} \quad . \qquad (11)$$

In contrast to approaches based on the Bloch theory, the system of equations (*10*) is dependent on the exact energy of our interest and must be solved simultaneously with the eigenvalue problem for the effective Hamiltonian.

If the confine ourselves to a complete model space formulation at the CCSD level of approximation, the singly excited amplitudes are given by

$$(\mathcal{E}_0 - \tilde{H}^{\text{eff}}_{\mu\mu})\, t_I^A(\mu) = \langle \Phi_I^A(\mu) | H_N(\mu)\, e^{T^\mu} | \Phi_\mu \rangle_{\text{C}} \ , \qquad (12)$$

where the subscript C denotes a connected part. In a special case of a two-determinant model space, correpsonding to two active orbitals of different symmetry, the doubly excited amplitudes are given by

$$(\mathcal{E}_0 - \tilde{H}^{\text{eff}}_{\mu\mu})\, t_{IJ}^{AB}(\mu) = \langle \Phi_{IJ}^{AB}(\mu) | H_N(\mu)\, e^{T^\mu} | \Phi_\mu \rangle_{\text{C}} + (\mathcal{E}_0 - \tilde{H}^{\text{eff}}_{\mu\mu})(t_I^A\, t_J^B - t_J^A\, t_I^B)_\mu \ . \qquad (13)$$

RESULTS AND DISCUSSION

In order to better judge performance of the single-root MR BWCC method, we study the rotational barrier of the ethylene molecule at the CCSD level and the results are compared with other single-reference and MR CCSD methods. The 6-31G** basis set[43] has been used. As already spoken, the rotation around the double bond represents a typical two-state problem in which the weights of reference configurations can change from 0 to 1 in a continuous way. In order to obtain a qualitatively correct potential energy curve, two closed-shell-type configurations have to be included in the reference space: the ground state configuration and biexcited configuration HOMO^2 $\rightarrow$ LUMO^2. Such a model space corresponds to the active orbital space spanned by two orbitals: HOMO and LUMO. For a twisted conformation (dihedral angle about 90°) we observe full configurational degeneracy.

In constrast to our previous work on the N_2H_2 molecule, the relaxation effects in the $CH_2{=}CH_2$ molecule are much more important, therefore the geometry of the molecule was optimized at the CASSCF level (two electrons in two orbitals) for each point. For dihedral angle 0° (*i.e.* equilibrium geometry) the reamining internal coordinates are: r_{CC} = 2.528 bohr, r_{CH} = 2.034 bohr and Θ_{HCC} = 121.7° and for dihedral angle 90°: r_{CC} = 2.776 bohr, r_{CH} = 2.033 bohr and Θ_{HCC} = 121.3°. Molecular orbitals to be used in the MR BWCCSD calculations are taken from the restricted Hartree–Fock (RHF) calculations for the ground state. In view of a different spacial symmetry of active orbitals, the model space is complete and one can take advantage of Eq. (*13*) for doubly excited cluster amplitudes. We recall that the orbital HOMO-LUMO degeneracy is not observed in this case, even though the orbital degeneracy alone is of less concern in the CC approaches.

For the sake of comparison, we also carried out the Hilbert space MR CCSD and MC-QDPT2 (multiconfigurational quasi-degenerate perturbation theory up to the second-order of Nakano[44]) calculations within the same reference space as well as two single-reference calculations: RHF based CCSD (RHF-CCSD) and unrestricted Hartree–Fock based CCSD (UHF-CCSD) calculations. In the case of the Hilbert space MR CCSD method, we employ the RHF molecular orbitals and full expansion of the so-called coupling (renormalization) terms. In the case of the MC-QDPT2 calculations, the CASSCF orbitals are used. Two 1s core orbitals were frozen throughout the calculations.

In Fig. 1, we present a total view of potential energy curves for the ground state and first biexcited state. A detailed view of the ground state is shown in Fig. 2. As may be expected, the RHF-CCSD method provides a reliable description of the ground state in the nondegenerate region (*i.e.* for dihedral angles from 0° up to 70°) but completely fails in the region where the ground state configuration is no more a dominant configuration. Moreover, the convergence in that region is very slow.

The UHF-CCSD method remedies the failure of the RHF-CCSD approach in the quasi-degenerate region and gives a correct shape of the potential energy barrier, but the method is spin-contaminated. For dihedral angles less than 2° the UHF and RHF solutions coincide. Somewhat erroneous curvature of the UHF-CCSD potential energy curve in the region between 50 and 70° (it deviates more than its RHF counterpart) is attributed mainly to the spin contamination; it is worth mentioning that a similar behaviour of the UHF-CCSD curve was also found in the case of the fluorine molecule at geometries somewhat beyond the equilibrium distance[45].

The Hilbert space MR CCSD method gives a correct shape of the potential energy barrier almost over the whole range of dihedral angles, but fails in a highly nondegenerate region; *i.e.* in the region between 0 and 10°. Likewise, the convergence in this region is extremely bad and the use of convergence accelerators (such as DIIS) is necessary. As a by-product (besides the ground state) we also get the biexcited state that is depicted in Fig. 1. The Hilbert space MR CCSD potential energy curves show a sharp jump at point 4.96°. In the case of the excited state it is directly visible in Fig. 1 while in the case of the ground state in Fig. 2 it has been magnified for a better distinction.

The existence of the jump is probably related to the existence of multiple solutions of the MR CCSD equations, see refs[19,23,46]. As it is well known, the MR CCSD equations possess multiple solutions capable of describing not only the lowest states but also other various manifolds of states as long as they contain a significant contribution from the model space (depending on the starting approximation the Newton–Raphson iterative procedure converges to different solutions). On the other hand, other reasons could be the model space deficiency or occurrence of intruder states. Due to the curvature of the excited state in the region between 0 and 5° there is a suspicion of another solution (the curve seems to be a part of the higher excited state), but it is interesting that we were not able to obtain both solutions in any small region simultaneously. Even though we have used the method of an "analytic continuation" of solutions with a fine step of 0.01°, we were not able to follow a particular solution beyond the point 4.96°. A full understanding of this problem would require more investigation and numerical experience. Nevertheless, such a failure of the Hilbert space MR CC method appears to be typical and demonstrates why the Hilbert space MR CC methods are scarcely employed to study global potential energy surfaces.

The single-root MR BWCCSD and QDPT2 methods provide us with smooth and almost parallel potential energy barriers of a correct shape for all dihedral angles.

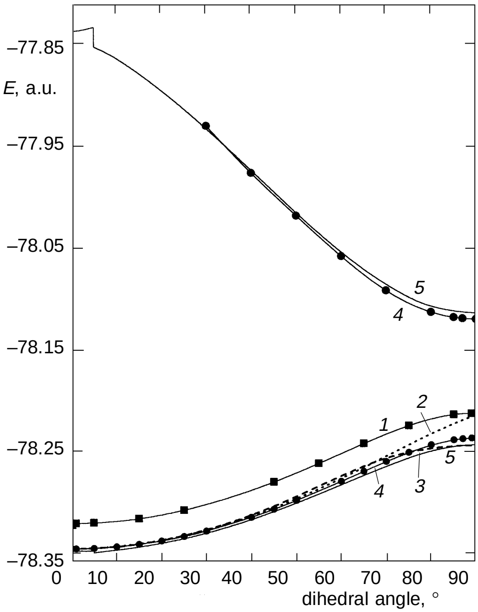

FIG. 1

Potential energy curves for the ground and first biexcited states of the ethylene molecule obtained by various *ab initio* methods for the rotation around the double bond. The 6-31G** basis set used; geometry optimized using the CASSCF (two electrons in two orbitals) method. Methods: *1* MC-QDPT2, *2* RHF-CCSD, *3* UHF-CCSD, *4* single-root MR BWCCSD, *5* Hilbert space MR CCSD

No intruder states were encountered. The potential energy barrier predicted by the MR BWCCSD is about 2.966 eV and differs from the QDPT2 one only by 0.017 eV. In the nondegenerate region, the single-root MR BWCCSD potential energy curve becomes identical with the RHF-CCSD one (with a negligible difference being 0.004 eV at 0°), while in the quasi-degenerate region approaches the Hilbert space MR CCSD curve. The single-root MR BWCCSD and Hilbert space MR CCSD approximations do not become identical even in the case of full configuration degeneracy since they work with different wave operators. The size-extensivity error of the MR BWCC method can be roughly assessed from the calculated potential barriers; the overall error is not worse than that for the QDPT2 method (at least in this case, of course).

Finally, let us mention the excited state. For completeness, we also performed the single-root MR BWCCSD calculations for the excited state (see Fig. 1) in the region between 30 and 90°. For dihedral angles less than 30° the method did not seem to converge or it converged to a higher state in the vicinity of 0°. It is remarkable, that the deviations from the Hilbert space MR CCSD method in the quasi-degenerate region are comparable to those observed for the ground state; so the single-root MR BWCC method can also be successfully applied to excited states; even though, in general, we are not able to exclude convergence difficulties in view of the Brillouin–Wigner-like denominators $\mathcal{E}_i - E_q$. One can thus conclude that the single-root MR BWCC method appears as a viable and promising approach for the calculation of the ground state potential energy surfaces and should deserve future attention, in particular using more reference configurations.

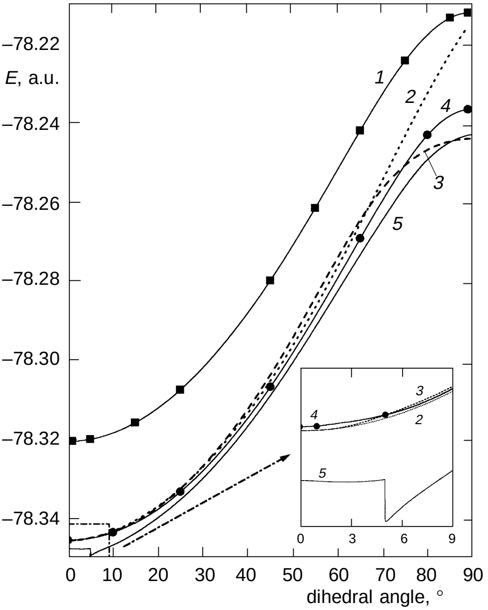

FIG. 2
Closeup view of the rotational barrier for the ethylene molecule obtained by the QDPT2 and various coupled-cluster methods. The 6-31G** basis set used; geometry optimized using the CASSCF (two electrons in two orbitals) method. Methods: *1* MC-QDPT2, *2* RHF-CCSD, *3* UHF-CCSD, *4* single-root MR BWCCSD, *5* Hilbert space MR CCSD

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