

# Multireference perturbation theory with optimized partitioning.

## I. Theoretical and computational aspects

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A multireference perturbation method is formulated, that uses an optimized partitioning. The zeroth-order energies are chosen in a way that guarantees vanishing the first neglected term in the perturbational ansatz for the wave function,  $\Psi^{(n)}=0$ . This procedure yields a family of zeroth-order Hamiltonians that allows for systematic control of errors arising from truncating the perturbative expansion of the wave function. The second-order version of the proposed method, denoted as MROPT(2), is shown to be (almost) size-consistent. The slight extensivity violation is shown numerically. The total energies obtained with MROPT(2) are similar to these obtained using the multireference configuration interaction method with Davidson-type corrections. We discuss connections of the MROPT(2) method to related approaches, the optimized partitioning introduced by Szabados and Surján and the linearized multireference coupled-cluster method. The MROPT(2) method requires using state-optimized orbitals; we show on example of  $N_2$  that using Hartree–Fock orbitals for some excited states may lead to nonphysical results. © 2003 American Institute of Physics. [DOI: 10.1063/1.1563618]

### I. INTRODUCTION

Partitioning the Hamiltonian  $\hat{H}$  into the zeroth-order Hamiltonian  $\hat{H}_0$  and the perturbation operator  $\hat{V}$  is one of the most crucial decisions for quantum-chemical calculation using perturbation theory (PT). The two most popular choices are Møller–Plesset (MP) partitioning<sup>1</sup> and Epstein–Nesbet (EN) partitioning.<sup>2,3</sup> These two partitionings were introduced relatively early (1930s) and since then they proved many advantages and disadvantages. Epstein–Nesbet partitioning is very simple conceptually and can be very easily applied for computations using both single- and multi-reference zeroth-order wave functions. Moreover, since  $E^{(1)}=0$ , it allows one to simplify considerably the wave function formulas in Rayleigh–Schrödinger perturbation theory (RSPT). Unfortunately, deviations from size-consistency in low-order EN-RSPT are rather large. EN-RSPT also lacks an efficient and easily computable sum-over-orbitals formula. Therefore, Rayleigh–Schrödinger perturbation theory using Epstein–Nesbet partitioning did not become very popular. Møller–Plesset partitioning uses a zeroth-order Hamiltonian that is a sum of one-electron operators. This allows for using fast, sum-over-orbitals computation formulas. Unfortunately, generalization of the MP partitioning for calculations using multiconfigurational wave function is not unique and may lead to nondiagonal resolvents. Usually, these problems are overcome by using a diagonal approximation to the zeroth-order Hamiltonian  $\hat{H}_0$  in the multideterminant basis after diagonalizing the density matrix by canonicalization of orbitals to define the orbital set. The MP partitioning used with low-order RSPT is the most popular perturbative method in quantum chemistry.

In the last few decades, many new partitionings have been proposed.<sup>4–20</sup> Usually, they are various modifications of the MP partitioning designed for some specific purposes. We would like to focus here on the formulations that were designed to enhance convergence of perturbation theory. Amos,<sup>4</sup> following Feenberg and Goldhammer,<sup>21,22</sup> used a single variational parameter in the definition of  $\hat{H}_0$  that was adjusted to make the third-order energy vanish,  $E^{(3)}=0$ . This procedure yielded better second-order energies than that one with nonoptimized zeroth-order Hamiltonian. A similar approach but using multiple variational parameters was suggested by Szabados and Surján.<sup>10,11</sup> The number of variational parameters—interpreted as a state-dependent shift of the zeroth-order energy—is equal to the number of Hilbert space states used in the first-order perturbational expansion of the wave function. These parameters are obtained by variational optimization of Rayleigh quotient taken with the first-order perturbational ansatz for the wave function. This optimized partitioning was shown to work in much more efficient way than the original EN and MP partitionings. Another way of optimizing the zeroth-order energies, employing a concept of maximum radius of convergence, was proposed by Finley.<sup>15</sup> He used a two-state model—consisting of the reference state and one excited state at each time—to obtain an approximate equation for the radius of convergence for every state used in the wave function perturbation expansion. Subsequently, the zeroth-order energies were chosen in such a way that they yield the maximum radius of convergence for every state. Another approach presented by Finley and co-workers<sup>12,23</sup> used a small subspace of the most important zeroth-order states to optimize the functional

$$|E - E^{[3]}| + |E - E^{[4]}|, \quad (1.1)$$

with respect to the zeroth-order energies. In Eq. (1.1),  $E$

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denotes the FCI energy and  $E^{[3]}$ , and  $E^{[4]}$  denote the perturbational energy through the third- and fourth-order, respectively; all quantities are determined within the chosen subspace.

In this paper we are going to develop a multireference perturbation method that is based on RSPT and uses optimized partitioning. This method is abbreviated as MROPT. The presented approach of optimizing the zeroth-order energies has an advantage that it can be systematically improved. The second-order version of our method, MROPT(2), can be considered as a multireference version of the perturbation technique presented by Szabados and Surján.<sup>10,11</sup> The equations defining MROPT(2) are also identical to those for the linearized multireference coupled cluster method proposed by Laidig, Saxe, and Bartlett.<sup>24,25</sup> The present paper gives a general theory of the MROPT method. We also give here discussion of theoretical and computational aspects of the second-order MROPT(2) method, such as size-consistency, orbital dependence, and a comparison of total MROPT(2) energies with those obtained using other related methods. Applications of MROPT(2) to molecular systems will be presented in a subsequent paper.<sup>26</sup>

## II. THEORY

### A. Multireference perturbation theory with optimized partitioning

The aim of this Section is to develop a perturbational technique, based on Rayleigh–Schrödinger perturbation theory and using a multideterminantal wave function  $|\alpha\rangle$  as the zeroth-order reference function, which is characterized by fast convergence of energy and wave function perturbation series. This is done by introducing a family of optimized zeroth-order Hamiltonians that allow for partial control of the errors arising from truncation of perturbational series.

Let  $|\alpha\rangle$  be a multideterminantal wave function, obtained by diagonalizing the Hamiltonian within a reference space spanned by a given set of configuration state functions (CSFs)  $\{\Phi_i\}$ , and corresponding to the ground or some excited state  $\alpha$  of a given molecular system. The wave function  $|\alpha\rangle$  is determined uniquely by specifying a set of one-electron orbitals, a set of configuration state functions  $\{\Phi_j\}$  constituting the reference space, and a set of CI coefficients of  $|\alpha\rangle$  in the basis of the functions  $\{\Phi_i\}$ . We solve perturbatively the Schrödinger equation for the state  $\alpha$

$$\hat{H}\Psi_\alpha = E_\alpha \Psi_\alpha, \quad (2.1)$$

using the multideterminantal wave function  $|\alpha\rangle$  as the zeroth-order reference function. We use a matrix representation  $H$  of the Hamiltonian operator  $\hat{H}$  in a space spanned by multi-configurational functions  $|\alpha\rangle, |k_1\rangle, |k_2\rangle, \dots$  and all the non-redundant single-configurational CSFs  $|q_1\rangle, |q_2\rangle, |q_3\rangle, \dots$  obtained by applying single, double, triple, and higher excitations to the set of reference space configuration state functions. (Excitations from reference space orbitals to reference space orbitals are not considered.) The multi-configurational functions  $|\alpha\rangle, |k_1\rangle, |k_2\rangle, \dots$  are obtained by diagonalizing the Hamiltonian within the reference space. It is convenient to distinguish here the set of all singly and doubly excited CSFs

with respect to the reference space single-configurational functions  $\{\Phi_i\}$ . For further use, we call this set a first-order interacting space (FOCI). Similarly, we distinguish the set of all triply and quadruply excited CSFs and call it a third-order interacting space (TOCI). The set of all multi-configurational functions  $|k_i\rangle$  different than  $|\alpha\rangle$  is denoted by REF.

We define the zeroth-order Hamiltonian  $H_0$  as a diagonal matrix operator

$$(H_0)_{ij} = \delta_{ij} E_i^{(0)}, \quad (2.2)$$

where the zeroth-order energies  $E_i^{(0)}$  are defined by

$$E_i^{(0)} = \begin{cases} H_{\alpha\alpha} & \text{if } i = \alpha \\ H_{ii} + \Delta_i & \text{if } i = k_s, q_s. \end{cases} \quad (2.3)$$

Subsequently, the matrix  $V$  of the perturbation operator  $\hat{V}$  is given by

$$V_{ij} = H_{ij} - (H_0)_{ij} = \begin{cases} H_{ij} & \text{if } i \neq j \\ 0 & \text{if } i = j = \alpha \\ -\Delta_i & \text{if } i = j \neq \alpha. \end{cases} \quad (2.4)$$

The state-dependent zeroth-energy shift parameters  $\Delta_i$  are going to be determined below in a manner ensuring fast convergence of energy and wave function perturbation series.

In practical applications, the perturbational expansion of wave function  $\Psi_\alpha$  is usually cut in some low order producing an appropriate  $n$ th-order perturbational ansatz for the wave function

$$\Psi_\alpha^{[n]} = |\alpha\rangle + \Psi_\alpha^{(1)} + \dots + \Psi_\alpha^{(n)}. \quad (2.5)$$

This approximation generally works well, since the neglected terms are rather small. However, for slowly converging series, the neglected terms may introduce rather large error when calculating energy and other molecular properties. There is no standard way of estimating these errors, since the higher-order terms of the wave function perturbational expansion are usually not computed. The perturbational technique proposed in this Section allows for a partial control of these errors. The state-dependent zeroth-energy shift parameters  $\Delta_i$  in Eqs. (2.3) and (2.4) are chosen in such a way that the largest neglected term in Eq. (2.5), namely  $\Psi_\alpha^{(n+1)}$ , is identically equal to zero. The implicit equation used to determine  $\Delta_i$  is

$$\Psi_\alpha^{(n+1)} = 0. \quad (2.6)$$

Since

$$\Psi_\alpha^{(n+1)} = \sum_{j \neq \alpha} c_j^{(n+1)} |j\rangle \quad \text{for } |j\rangle = |q_i\rangle, |k_i\rangle. \quad (2.7)$$

Equation (2.6) can be written more explicitly as a set of equations

$$\forall j: c_j^{(n+1)} = 0 \quad \text{for } j = q_i, k_i, \quad (2.8)$$

where  $c_j^{(p)}$  are the usual wave function expansion coefficients in  $p$ th-order of RSPT. It is difficult to give an explicit and compact equation defining the shift parameters  $\Delta_i$  for a general case. However, after introducing a diagonally shifted Hamiltonian  $\tilde{H}$  given by

$$\tilde{H}_{ij} = H_{ij} - \delta_{ij} E_{\alpha}^{(0)}, \quad (2.9)$$

and a new variable  $\Lambda_i$  given by

$$\Lambda_i = \frac{1}{H_{ii} + \Delta_i - E_{\alpha}^{(0)}} = \frac{1}{\tilde{H}_{ii} + \Delta_i}, \quad (2.10)$$

it is possible to give appropriate equations for low-order PT. The explicit equations defining  $\Lambda_i$  for the second-, third-, and fourth-order perturbation theory are given below. (Note, that for calculating energy through the second-order, we use the wave function through the *first-order*. Therefore, the appropriate form of Eq. (2.6) for the second-order perturbational energy is not  $\Psi_{\alpha}^{(2+1)} = 0$ , but  $\Psi_{\alpha}^{(1+1)} = 0$ .) We have

$$\Psi_{\alpha}^{(2)} = 0 \Leftrightarrow \forall j: \sum_{s \neq \alpha} \tilde{H}_{\alpha s} \tilde{H}_{s j} \Lambda_s = \tilde{H}_{\alpha j}, \quad (2.11)$$

$$\Psi_{\alpha}^{(3)} = 0 \Leftrightarrow \forall j:$$

$$2 \sum_{s \neq \alpha} \tilde{H}_{\alpha s} \tilde{H}_{s j} \Lambda_s - \sum_{s \neq \alpha} \sum_{t \neq \alpha} \tilde{H}_{\alpha s} (\tilde{H}_{s t} \tilde{H}_{t j} - \tilde{H}_{\alpha t}^2 \delta_{s j}) \Lambda_s \Lambda_t = \tilde{H}_{\alpha j} \quad (2.12)$$

and

$$\Psi_{\alpha}^{(4)} = 0 \Leftrightarrow \forall j:$$

$$3 \sum_{s \neq \alpha} \tilde{H}_{\alpha s} \tilde{H}_{s j} \Lambda_s - 3 \sum_{s \neq \alpha} \sum_{t \neq \alpha} \tilde{H}_{\alpha s} (\tilde{H}_{s t} \tilde{H}_{t j} - \tilde{H}_{\alpha t}^2 \delta_{s j}) \Lambda_s \Lambda_t + \sum_{s \neq \alpha} \sum_{t \neq \alpha} \sum_{u \neq \alpha} \tilde{H}_{\alpha u} [\tilde{H}_{j s} (\tilde{H}_{s t} \tilde{H}_{t u} - \tilde{H}_{\alpha t}^2 \delta_{u s}) - (\tilde{H}_{\alpha t} \delta_{s j} + \tilde{H}_{\alpha s} \delta_{t j}) \tilde{H}_{\alpha s} \tilde{H}_{t u}] \Lambda_s \Lambda_t \Lambda_u = \tilde{H}_{\alpha j}, \quad (2.13)$$

where the index  $j$  runs over all FOCI states in Eq. (2.11) and over all FOCI, TOCI, and REF states in Eqs. (2.12) and (2.13). These equations do not define the shift parameters  $\Delta_i$  for other states; they can be set to zero, since anyway those states are not coupled to the reference state  $|\alpha\rangle$ . Note, that Eqs. (2.11)–(2.13) have a rather high symmetry: All terms appearing in lower order appear also in higher order, and the coefficients in front of every term are the binomial coefficients. Further analysis of these equations may lead to more general formulas.

## B. Connection to optimized partitioning of Szabados and Surján

Surján and Szabados<sup>10,11</sup> proposed another way of derivation of Eq. (2.11). Similarly, their partitioning is defined by Eqs. (2.2) and (2.4). The shift parameters  $\Delta_i$  are determined by optimizing the Rayleigh quotient

$$\forall j: \frac{\partial}{\partial \Delta_j} \frac{\langle \Psi_{\alpha}^{[1]} | \hat{H} | \Psi_{\alpha}^{[1]} \rangle}{\langle \Psi_{\alpha}^{[1]} | \Psi_{\alpha}^{[1]} \rangle} = 0, \quad (2.14)$$

where  $\Psi_{\alpha}^{[1]}$  is the first-order perturbational ansatz for the wave function

$$\Psi_{\alpha}^{[1]} = |\alpha\rangle + \Psi_{\alpha}^{(1)}. \quad (2.15)$$

This leads exactly to Eq. (2.11), if all nonlinear terms are neglected. All  $\Delta_i$  not determined by this procedure are set to zero. Neglecting the nonlinear terms in  $\Lambda_j$  corresponds to neglecting all the unconnected terms in the CISD scheme; these terms violate size extensivity.

Surján and Szabados showed<sup>10,11</sup> that the partitioning defined by them exhibits many appealing features when applied to single-reference RSPT: (i) It is size-consistent, (ii) it is orbital invariant, (iii) third-order energy is identically equal zero, (iv) most fifth-order terms vanish, (v) low-order (2, 4) corrections are quite accurate, (vi) it has better convergence characteristic than the Møller–Plesset and Epstein–Nesbet partitioning RSPTs, (vii) the second-order single reference PT using the optimized partitioning is shown to be equivalent to the linearized coupled cluster method<sup>27</sup> and to CEPA-0 (coupled electron pair approximation) method.<sup>28</sup>

Recently, Szabados, Surján, and Szekeres<sup>20</sup> have applied their optimized partitioning for general nonsymmetrical multireference perturbation theory to correct the energies and wave functions obtained from limited CC calculations. Their results show that the optimized partitioning yields significantly better corrections than these ones obtained with the MP and Dyson-type<sup>29</sup> zeroth-order energies.

One may expect that optimizing the Rayleigh quotient using a higher-order perturbational ansatz would produce Eqs. (2.12) and (2.13). This is not, however, the case, even if the resulting formulas are somewhat similar.

## C. Connection to linearized multireference coupled cluster method (MR-LCCM)

Another way of deriving Eq. (2.11) was proposed by Laidig, Saxe, and Bartlett.<sup>24,25</sup> They start from the exponential ansatz for a CASSCF wave function

$$\Psi_{\alpha} = \exp(\hat{T}) |\alpha\rangle, \quad (2.16)$$

where the wave operator  $\hat{T}$  is a sum of one- and two-electron excitation operators with coefficients,  $t_r^u$  and  $t_{rs}^{uv}$ , to be determined. All active to active excitation were excluded, i.e., all  $t_b^a$  and  $t_{ab}^{cd}$  were set to zero, where  $a, b, c$ , and  $d$  denote active orbitals. The Schrödinger equation, Eq. (2.1), is then transformed to the following form:

$$\exp(-\hat{T}) \hat{H} \exp(\hat{T}) |\alpha\rangle = E_{\alpha} |\alpha\rangle. \quad (2.17)$$

Expanding the exponentials using the Baker–Campbell–Hausdorff commutator expansion and retaining only linear terms in  $\hat{T}$ , yields, after projection on  $|\alpha\rangle$ , the MR-LCCM equation for energy

$$E_{\alpha}^{\text{MR-LCCM}} = E_{\alpha}^{(0)} + \sum_{q \in \text{FOCI}} \tilde{H}_{\alpha q} T_{q\alpha}, \quad (2.18)$$

where  $T_{q\alpha}$  is given by

$$T_{q\alpha} = \langle q | \hat{T} | \alpha \rangle. \quad (2.19)$$

Similar projection on the states  $|j\rangle$  from first-order configuration interaction (FOCI) space, produces the set of equations

$$\forall j: \sum_{s \in \text{FOCI}} \tilde{H}_{j s} (-T_{s\alpha}) + \sum_{s \in \text{FOCI}} T_{s j} \tilde{H}_{\alpha s} = \tilde{H}_{\alpha j}, \quad (2.20)$$

which defines the coefficients  $T_{s\alpha}$ . The second term,  $\sum T_{sj}\tilde{H}_{\alpha s}$ , is shown to be rather small, and it is neglected yielding the set of linear equations

$$\forall j: \sum_{s \in \text{FOCI}} \tilde{H}_{js}(-T_{s\alpha}) = \tilde{H}_{\alpha j}, \quad (2.21)$$

defining the MR-LCCM  $T_{s\alpha}$  amplitudes. Note, that Eq. (2.21) is formally identical to Eq. (2.11), what allows for an identification of the MR-LCCM cluster amplitudes  $T_{s\alpha}$  as the components of the first-order perturbational wave function with optimized partitioning

$$T_{s\alpha} = -\tilde{H}_{\alpha s}\Lambda_s. \quad (2.22)$$

#### D. Second-order multireference perturbation theory with optimized partitioning

Multireference second-order Rayleigh–Schrödinger perturbation theory using the optimized partitioning is derived from Eqs. (2.2), (2.4), and (2.11). Energy of state  $\alpha$  is given by

$$E_\alpha = \langle \alpha | \hat{H} | \Psi_\alpha^{[1]} \rangle = E_\alpha^{(0)} - \sum_{q \in \text{FOCI}} H_{\alpha q}^2 \Lambda_q, \quad (2.23)$$

where the parameters  $\Lambda_i$  are obtained by solving a set of linear equations given by Eq. (2.11). The third-order energy  $E_\alpha^{(3)}$  is identically equal to zero. The higher-order energy corrections are believed to be small. Therefore, Eq. (2.23) should give a good approximation of the exact energy of the state  $\alpha$ . For further use, this approach is referred to as the MROPT(2) method.

#### E. Iterative convergence of the MROPT(2) method

Using the MROPT(2) method requires solving a set of linear equations for the state-dependent shift parameters given by Eq. (2.11). Even for small size of a reference space and a basis set, the dimension of this set of equations can be very large; in our largest calculations it is close to 40 millions. Such huge sets of linear equations cannot be solved directly, they require using some iterative methods. We have used various iterative approaches: (i) Jacobi method, (ii) a modified Jacobi method, (iii) a modified Jacobi method with least-square fitting. In this section, we analyze the iterative convergence of these approaches.

In order to solve Eq. (2.11) iteratively, we rearrange it to a following form:

$$\forall j: \Lambda_j = \frac{1}{H_{jj} - H_{\alpha\alpha}} - \sum_{s \neq j} \frac{H_{\alpha s} H_{sj}}{H_{\alpha j} (H_{jj} - H_{\alpha\alpha})} \Lambda_s. \quad (2.24)$$

This form of Eq. (2.11) allows us to use iterative techniques. Introducing new symbols,  $b_j$  and  $A_{js}$ , we write Eq. (2.24) as

$$\forall j: \Lambda_j^{(k+1)} = b_j - \sum_{s \neq j} A_{js} \Lambda_s^{(k)}. \quad (2.25)$$

Equations (2.24) and (2.25) are not well defined for states for which  $H_{\alpha j} = 0$ ; for these states, we set  $\Delta_j = 0$ . Note, that since  $H_{\alpha j} = 0$ , such a choice anyway satisfies the condition  $\Psi_\alpha^{(2)} = 0$ .

Direct use of Eq. (2.25) leads to Jacobi method.<sup>30</sup> Unfortunately, convergence of this method is rather poor. In our calculations it has converged only for around 20% of cases. Much better convergence characteristics is obtained if we modify Jacobi method in a following way. We split the set of linear equation in Eq. (2.25) into two halves, denoted by FOCI1 and FOCI2. The choice of these subspaces of FOCI can be done in principle in any way. In our calculations, FOCI1 consists of states  $j$  for which  $H_{\alpha j} > 0$ , and FOCI2, of states  $j$  for which  $H_{\alpha j} < 0$ . (Note, that it is not a good choice in a general case, since the sign of  $H_{\alpha j}$  can be easily modified by changing the phase of  $|j\rangle$ .) Subsequently a four-step algorithm is used which is repeated until convergence. The four steps are given by the following equations:

$$1. \quad \Lambda_j^{(k+1)} = b_j - \sum_{s \neq j} A_{js} \Lambda_s^{(k)} \quad \text{if } j \in \text{FOCI}, \quad (2.26)$$

$$2. \quad \Lambda_j^{(k+2)} = \begin{cases} b_j - \sum_{s \neq j} A_{js} \Lambda_s^{(k+1)} & \text{if } j \in \text{FOCI1} \\ \Lambda_j^{(k+1)} & \text{if } j \in \text{FOCI2}, \end{cases} \quad (2.27)$$

$$3. \quad \Lambda_j^{(k+3)} = b_j - \sum_{s \neq j} A_{js} \Lambda_s^{(k+2)} \quad \text{if } j \in \text{FOCI}, \quad (2.28)$$

$$4. \quad \Lambda_j^{(k+4)} = \begin{cases} \Lambda_j^{(k+3)} & \text{if } j \in \text{FOCI1} \\ b_j - \sum_{s \neq j} A_{js} \Lambda_s^{(k+3)} & \text{if } j \in \text{FOCI2}. \end{cases} \quad (2.29)$$

This modified Jacobi method works significantly better than the original Jacobi method. We have been able to obtain a solution of Eq. (2.11) with it in more than 80% of cases. Still, in about 20% of cases this method has produced a diverging iterative sequence, especially for large dimension of FOCI.

The most successful approach has proved to be the modified Jacobi method combined with the least-squares fitting of the iterative sequence to the final solution. The fitting has been performed in a spirit similar to Refs. 31 and 32. The iterative sequence,  $\Lambda^{(1)}, \Lambda^{(2)}, \dots, \Lambda^{(M)}$ , is used to construct the best approximation to the unknown vector  $\Lambda^\dagger$

$$\Lambda^\dagger = \beta_1 \Lambda^{(1)} + \beta_2 \Lambda^{(2)} + \dots + \beta_M \Lambda^{(M)}. \quad (2.30)$$

The parameters  $\beta_1, \beta_2, \dots, \beta_M$  are obtained by minimizing the 2-norm  $\|\cdot\|_2$  (defined as a square-root of a sum of squares of vector's coordinates) of the residual vector derived from Eq. (2.11) and given by

$$\|\mathbf{B}\Lambda^\dagger - \mathbf{H}_\alpha\|_2, \quad (2.31)$$

where

$$\mathbf{B}_{ij} = H_{\alpha j} (H_{ij} - \delta_{ij} H_{\alpha\alpha}) \quad (2.32)$$

and

$$(\mathbf{H}_\alpha)_i = H_{\alpha i}. \quad (2.33)$$

This approach yields a solution very fast; usually from 20 to 40 expansion vectors is needed to obtain the vector  $\Lambda$  for all the calculated molecular states. In our calculations, no solu-

TABLE I. Total energies (hartree) for the ground state and the two lowest excited states of ethylene, butadiene, benzene,  $N_2$ , and  $O_2$  calculated using various methods. MRCI+Q denotes the MRCI energies with the renormalized Davidson correction.

Ground state					
Method	Ethylene ( ${}^1A_g$ )	Butadiene ( ${}^1A_g$ )	Benzene ( ${}^1A_{1g}$ )	$N_2$ ( ${}^1\Sigma_g^+$ )	$O_2$ ( ${}^3\Sigma_g^-$ )
CASSCF	-78.092 447	-155.029 010	-230.852 983	-109.118 337	-149.767 682
MRCI	-0.327 976	-0.556 500	-0.590 521	-0.204 220	-0.352 464
MRCI+Q	-0.360 959	-0.646 059	-0.705 446	-0.217 539	-0.380 728
MREN(2)	-0.381 799	-0.668 080	-0.728 801	-0.207 107	-0.397 444
MREN(3)	-0.349 358	-0.633 677	-0.692 039	-0.200 325	-0.356 657
MRMP(2)	-0.334 299	-0.607 738	-0.672 865	-0.183 352	-0.365 566
MRMP(3)	-0.350 793	-0.633 684	-0.691 085	-0.198 246	-0.357 682
MROPT(2)	-0.365 149	-0.665 552	-0.733 773	-0.217 746	-0.381 312
First excited state					
Method	Ethylene ( ${}^3B_{1u}$ )	Butadiene ( ${}^3B_u$ )	Benzene ( ${}^3B_{1u}$ )	$N_2$ ( ${}^3\Sigma_u^+$ )	$O_2$ ( ${}^1\Delta_g$ )
CASSCF	-77.934 492	-154.903 559	-230.710 847	-108.882 612	-149.732 733
MRCI	-0.320 801	-0.555 026	-0.581 885	-0.218 137	-0.350 832
MRCI+Q	-0.352 579	-0.644 452	-0.693 976	-0.235 033	-0.378 098
MREN(2)	-0.370 857	-0.669 357	-0.701 804	-0.227 167	-0.391 673
MREN(3)	-0.345 585	-0.633 939	-0.684 894	-0.215 108	-0.356 640
MRMP(2)	-0.329 159	-0.615 689	-0.670 721	-0.214 378	-0.363 026
MRMP(3)	-0.345 716	-0.634 578	-0.681 841	-0.210 119	-0.357 262
MROPT(2)	-0.356 576	-0.663 806	-0.721 779	-0.233 529	-0.379 231
Second excited state					
Method	Ethylene ( ${}^1B_{1u}$ )	Butadiene ( ${}^3A_g$ )	Benzene ( ${}^3E_{1u}$ )	$N_2$ ( ${}^3\Pi_g$ )	$O_2$ ( ${}^1\Sigma_g^+$ )
CASSCF	-77.752 001	-154.840 959	-230.669 142	-108.771 292	-149.713 722
MRCI	-0.351 324	-0.552 637	-0.592 251	-0.274 115	-0.346 537
MRCI+Q	-0.396 822	-0.641 087	-0.709 362	-0.307 732	-0.372 895
MREN(2)	-0.436 258	-0.653 294	-0.728 431	-0.327 963	-0.384 126
MREN(3)	-0.368 609	-0.635 157	-0.695 870	-0.244 002	-0.353 246
MRMP(2)	-0.372 029	-0.613 711	-0.693 730	-0.284 540	-0.357 817
MRMP(3)	-0.379 414	-0.634 405	-0.690 304	-0.258 511	-0.351 914
MROPT(2)	-0.422 609	-0.660 604	-0.737 537	-0.306 926	-0.374 366

tion could be obtained for one of the computed states, the  ${}^1E_{1u}$  state of benzene. (For results of calculations on benzene, see the subsequent paper.<sup>26</sup>) The reason for it is probably the quasi-singularity of the matrix  $\mathbf{B}$  for  ${}^1E_{1u}$ . Note, that if the matrix  $\mathbf{B}$  is singular, no solution of Eq. (2.11) exists, and if some of eigenvalues of  $\mathbf{B}$  are close to zero, the iterative techniques are not stable any more.

### III. NUMERICAL AND COMPUTATIONAL ASPECTS OF THE MROPT(2) METHOD

Second-order multireference perturbation theory with optimized partitioning, abbreviated as MROPT(2), defined by Eqs. (2.2), (2.4), (2.11), and (2.23), is applied for calculating various molecular properties of ground and excited states for a set of small and medium-size molecules. The results are given in the subsequent paper;<sup>26</sup> here, we focus on various numerical and computational issues concerning the MROPT(2) method.

#### A. Total energies

We perform a comparison of total MROPT(2) energies with the total energies obtained by other methods. Table I gives energies of the ground and two lowest excited states of  $N_2$ ,  $O_2$ , ethylene, butadiene, and benzene, calculated using eight different methods. For the complete active space self-

consistent field (CASSCF) method, total energies are given. For other methods, the entries are different to the CASSCF energy. We compare following methods: CASSCF, the multireference configuration interaction (MRCI) method, MRCI with the renormalized Davidson correction [MRCI+Q], second- [MREN(2)] and third-order [MREN(3)] multireference Rayleigh–Schrödinger perturbation theory with Epstein–Nesbet partitioning, second- [MRMP(2)] and third-order [MRMP(3)] multireference Rayleigh–Schrödinger perturbation theory with Møller–Plesset partitioning, and the MROPT(2) method. Table II gives average differences of total energies for MROPT(2) and other methods. These results have been obtained by performing several single point calculations for low-lying states using different basis sets or geometries; for details, see below. Here, MRCI+Q1 denotes MRCI with the original Davidson correction,<sup>33</sup> and MRCI+Q2, MRCI with the renormalized Davidson correction.<sup>34</sup>

The MROPT(2) total energies are most similar to the energies obtained using MRCI with the renormalized Davidson correction. Since MROPT(2) is an (almost) size-consistent method and corrected MRCI approaches are size-consistent only in an approximate manner—for comparison see Table III—we believe that the MROPT(2) energies would be very similar to the MRCI energies calculated with an “ideal” Davidson correction. Among the perturbative

TABLE II. Average differences of total energies (millihartree) between MROPT(2) and other methods. Numbers in parentheses denote the number of single-point calculations performed for every molecule. (For details, see text.) Q1 stands for the original Davidson correction and Q2 for the renormalized Davidson correction.

Method	Ethylene (9)	Butadiene (10)	Benzene (7)	N <sub>2</sub> (56)	O <sub>2</sub> (60)
MRCI	42.0	104.6	151.2	24.6	29.7
MRCI+Q1	11.6	31.5	52.0	3.2	3.9
MRCI+Q2	8.3	19.5	32.3	1.7	1.8
MREN(2)	18.8	16.7	27.5	8.0	9.7
MREN(3)	24.5	35.2	45.0	34.2	21.0
MRMP(2)	36.2	52.6	50.0	26.9	18.0
MRMP(3)	19.6	41.8	55.0	33.0	21.4

methods, we observe rather large discrepancy with methods using the Møller–Plesset partitioning. As anticipated, the MROPT(2) and MREN(2) energies are rather similar, since the state-dependent shift parameters  $\Delta_i$  used in the optimized partitioning are expected to be rather small. Note, that if  $\Delta_i = 0$  for all FOCI states, the MROPT(2) and MREN(2) energies are identical.

The results given in Table I are obtained using the following basis sets, geometries and active spaces: (i) ethylene: The basis set is cc-pVQZ (the acronym cc-pVnZ stands for correlation-consistent polarized Valence  $n$  Zeta basis set of Dunning,<sup>35</sup> where  $n$  is double, triple, etc.); the geometry is taken from experiment<sup>36</sup> ( $r_{CC} = 1.337$  Å,  $r_{CH} = 1.086$  Å, and  $\angle CCH = 117.6^\circ$ ); the active space consists of two orbitals ( $\pi$  and  $\pi^*$ ) and two electrons; (ii) butadiene: The basis set is cc-pVTZ;<sup>35</sup> the geometry is taken from experiment<sup>37</sup> ( $r_{C_1C_2} = 1.467$  Å,  $r_{C_2C_3} = 1.343$  Å,  $r_{CH} = 1.094$  Å,  $\angle CCC = 122.8^\circ$ , and  $\angle CCH = 119.5^\circ$ ); the active space consists of four orbitals ( $\pi_1, \pi_2, \pi_1^*, \pi_2^*$ ) and four electrons; (iii) benzene: The basis sets are of the ANO (atomic natural orbitals) type<sup>38</sup> with  $(14s9p4d)/[4s3p2d]$  contraction scheme for carbon and  $(8s4p)/[3s2p]$  for hydrogen; the geometry is very close to the experimental one<sup>36</sup> ( $r_{CC} = 1.395$  Å,  $r_{CH} = 1.084$  Å); the active space consists of six orbitals ( $a_{2u}, e_{1g}, e_{2u}, b_{2g}$ ) and six electrons; (iv) N<sub>2</sub>: the basis set is an ANO-type<sup>39</sup>  $(10s6p3d)/[4s3p2d]$  contraction scheme; the internuclear distances correspond to the minima of potential energy curves ( $r_{NN} = 1.100$  Å for  $X^1\Sigma_g^+$ ,  $r_{NN}$

$= 1.275$  Å for  $A^3\Sigma_u^+$ , and  $r_{NN} = 1.225$  Å for  $B^3\Pi_g$ ); the active space consists of eight orbitals ( $\sigma_{2p_z}, \pi_{2p_x}, \pi_{2p_y}, \pi_{2p_x}^*, \pi_{2p_y}^*, \sigma_{2p_z}^*, \sigma_{3s},$  and  $\sigma_{3s}^*$ ) and six electrons; (v) O<sub>2</sub>: The basis set is an ANO-type<sup>38</sup>  $(14s9p4d3f)/[4s3p2d1f]$  contraction scheme; the internuclear distances correspond to the minima of potential energy curves ( $r_{OO} = 1.20752$  Å for  $X^3\Sigma_g^-, r_{OO} = 1.225$  Å for  $a^1\Delta_g$ , and  $r_{OO} = 1.225$  Å for  $b^1\Sigma_g^+$ ); the active space consists of eight orbitals ( $\sigma_{2s}, \sigma_{2s}^*, \sigma_{2p_z}, \pi_{2p_x}, \pi_{2p_y}, \pi_{2p_x}^*, \pi_{2p_y}^*$ , and  $\sigma_{2p_z}^*$ ) and 12 electrons. The results in Table II have been obtained using the same active spaces as above; also, the geometries for ethylene, butadiene and benzene are identical to these described above. In the averaging, we have considered three electronic states of ethylene ( $X^1A_g, 1^1B_{1u}$ , and  $1^3B_{1u}$ ) in three different basis sets (cc-pVDZ, cc-pVTZ, and cc-pVQZ<sup>35</sup>), five states of butadiene ( $X^1A_g, 2^1A_g, 1^1B_u, 1^3B_u$ , and  $1^3A_g$ ) in two basis sets (cc-pVDZ and cc-pVTZ), and seven states of benzene ( $X^1A_g, 1^1E_{2g}, 1^1B_{1u}, 1^1B_{2u}, 3^1B_{1u}, 3^1B_{2u}$ , and  $3^1E_{1u}$ ) in the ANO-type basis set described above. For N<sub>2</sub>, we have considered eight electronic states ( $X^1\Sigma_g^+, w^1\Delta_u, W^3\Delta_u, A^3\Sigma_u^+, a'^1\Sigma_u^-, a^1\Pi_g, B'^3\Sigma_u^-,$  and  $B^3\Pi_g$ ) at seven different geometries in range  $[r_e - 0.1 \text{ Å}, r_e + 0.1 \text{ Å}]$ , where  $r_e$  is the equilibrium geometry of a given state. For O<sub>2</sub>, we have considered six states ( $b^1\Sigma_g^+, c^1\Sigma_u^-, a^1\Delta_g, A'^3\Delta_u, X^3\Sigma_g^-,$  and  $A^3\Sigma_u^+$ ) at ten intermolecular distances. The basis sets used for calculations on O<sub>2</sub> and N<sub>2</sub> are the same as described above.

TABLE III. Size-consistency check for the MROPT(2) method. Entries (kcal/mol) are the differences between the energy of the Ne<sub>2</sub> molecule at nuclear separation  $r = 100$  Å and the energy of two Ne atoms. For comparison, we give also deviations from size-consistency for other methods. Two different active spaces have been used; for details look text. The basis sets cc-pVDZ, cc-pVTZ, and cc-pVQZ denoted, respectively, as DZ, TZ, and QZ, are taken from Dunning (Ref. 35). Q1 stands for the original Davidson correction and Q2 for the renormalized Davidson correction.

Method	RHF orbitals					CASSCF orbitals				
	Active space 1			Active space 2		Active space 1			Active space 2	
	DZ	TZ	QZ	DZ	TZ	DZ	TZ	QZ	DZ	TZ
CASCI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MRCI	5.39	9.05	10.62	5.28	9.54	5.39	9.02	10.51	5.28	9.55
MRCI+Q1	0.71	1.55	2.05	0.62	1.78	0.71	1.54	1.98	0.62	1.80
MRCI+Q2	0.35	0.85	1.20	0.26	1.05	0.35	0.84	1.14	0.26	1.06
MREN(2)	30.74	33.30	32.48	30.21	33.30	30.74	34.11	33.49	30.12	28.35
MREN(3)	-8.28	-7.75	-6.80	-8.07	-7.63	-8.28	-9.28	-8.84	-8.07	-5.41
MRMP(2)	-0.05	-0.04	-0.02	-0.09	-0.08	-0.05	-0.06	-0.07	-0.09	-0.15
MRMP(3)	0.04	0.04	0.02	0.09	0.08	0.04	0.06	0.07	0.09	0.14
MROPT(2)	0.02	-0.02	-0.05	-0.17	-0.08	0.02	-0.01	-0.02	-0.18	0.00

TABLE IV. Comparison of the MROPT(2) rotational barrier (kcal/mol) and excitation energies (eV) of ethylene calculated using two sets of orbitals, the ground-state RHF orbitals and the state-specific CASSCF orbitals.

Method	Excitation energies					
	Rotational barrier		$1^1B_{1u}$		$1^3B_{1u}$	
	RHF orb.	CAS orb.	RHF orb.	CAS orb.	RHF orb.	CAS orb.
CASSCF	81.6	67.5	9.34	9.26	5.01	4.30
MRCI	75.1	67.9	8.55	8.63	4.84	4.49
MRCI+Q1	68.2	67.2	8.27	8.35	4.59	4.52
MRCI+Q2	66.3	67.0	8.21	8.29	4.52	4.53
MREN(2)	74.4	72.4	7.41	7.78	4.77	4.60
MREN(3)	70.9	65.5	8.64	8.74	4.38	4.40
MRMP(2)	67.1	65.0	7.93	8.24	4.65	4.44
MRMP(3)	70.8	65.8	8.28	8.48	4.46	4.44
MROPT(2)	49.2	65.6	7.89	7.70	4.09	4.53
Exp.	$\approx 65^a$		$\approx 8.0^b$		4.36 <sup>c</sup>	

<sup>a</sup>References 44 and 45.<sup>b</sup>Estimated vertical excitation energy from earlier theoretical work (Refs. 46–49).<sup>c</sup>References 50 and 51.

## B. Size-consistency test

Size consistency test has been performed using two neon atoms placed at the distance of 100 Å. We have used three different basis sets<sup>35</sup> (cc-pVDZ, cc-pVTZ, and cc-pVQZ) and two different complete active spaces. The active space denoted by 1 consisted of atomic  $2p$  and  $3s$  orbitals. The  $2s$  orbital has been correlated in the MRCI and perturbational calculations, while the  $1s$  orbital has been kept frozen. The active space denoted by 2 consisted of atomic  $2s$ ,  $2p$ , and  $3s$  orbitals. The  $1s$  orbital has been correlated in the MRCI and perturbational calculations. We have also used two different sets of orbitals, the ground-state RHF and CASSCF orbitals.

Results are given in Table III. Entries are the differences between the energy of the molecule and doubled atomic energy. The MROPT(2) method, similarly to MRMP(2) and MRMP(3), is almost size-consistent; the largest deviation from size-consistency is 0.18 kcal/mol. Very large deviations from size-consistency are observed for the MRCI method and the perturbative methods using Epstein–Nesbet partitioning. Davidson-type corrections improve the MRCI results significantly, the renormalized correction of Siegbahn doing noticeably better than the original correction of Langhoff and Davidson.

## C. Orbital dependence of the MROPT(2) method

In order to investigate the orbital dependence of the MROPT(2) method, simultaneous calculations using different sets of orbitals have been performed for a few molecular systems. We have tested performance of the state-specific CASSCF orbitals versus ground-state restricted Hartree–Fock (RHF) orbitals for calculations of internal rotation barrier of ethylene, valence excitation energies of ethylene, potential energy curves of eight states of  $N_2$ , and size-consistency check employing the  $Ne_2$  molecule. We have also performed calculations of potential energy curves of six states of  $O_2$  using two sets of orbitals, the state-specific CASSCF and ground state ROHF orbitals. For calculations on the rotational barrier in ethylene, we have used an active

space consisting of two electrons and two orbitals ( $\pi$  and  $\pi^*$ ) and ANO-type basis sets<sup>39</sup> with  $(10s6p3d)/[7s6p3d]$  contraction scheme for C and  $(7s3p)/[6s3p]$  for H. The geometries have been fully optimized for every value of the dihedral angle  $\phi$  on the B3LYP/6-31++G(2d,2p) level of theory. The basis set used for calculations on excitation energies of ethylene is cc-pVQZ,<sup>35</sup> the geometry and active

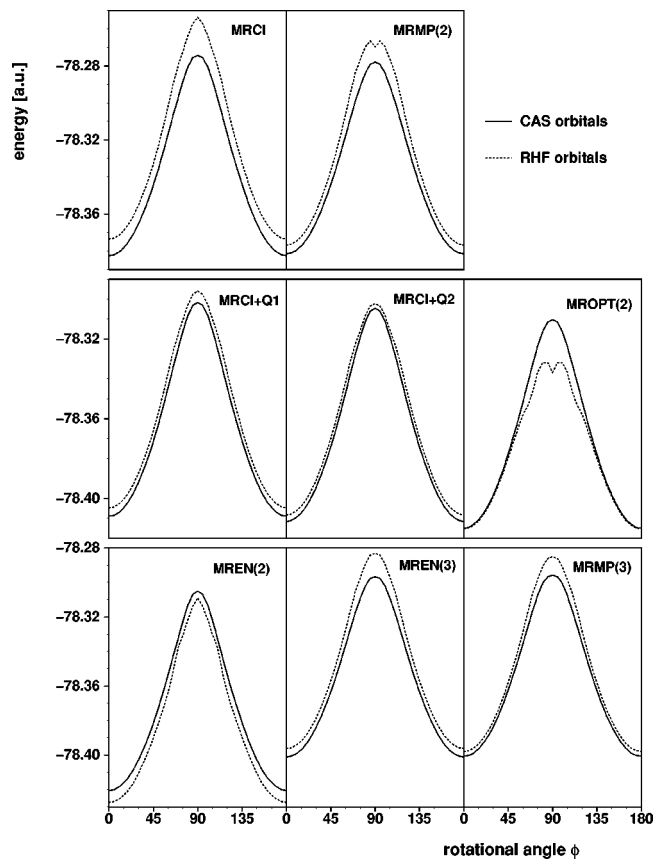


FIG. 1. Potential energy curve for the internal rotation barrier in ethylene calculated using various methods.

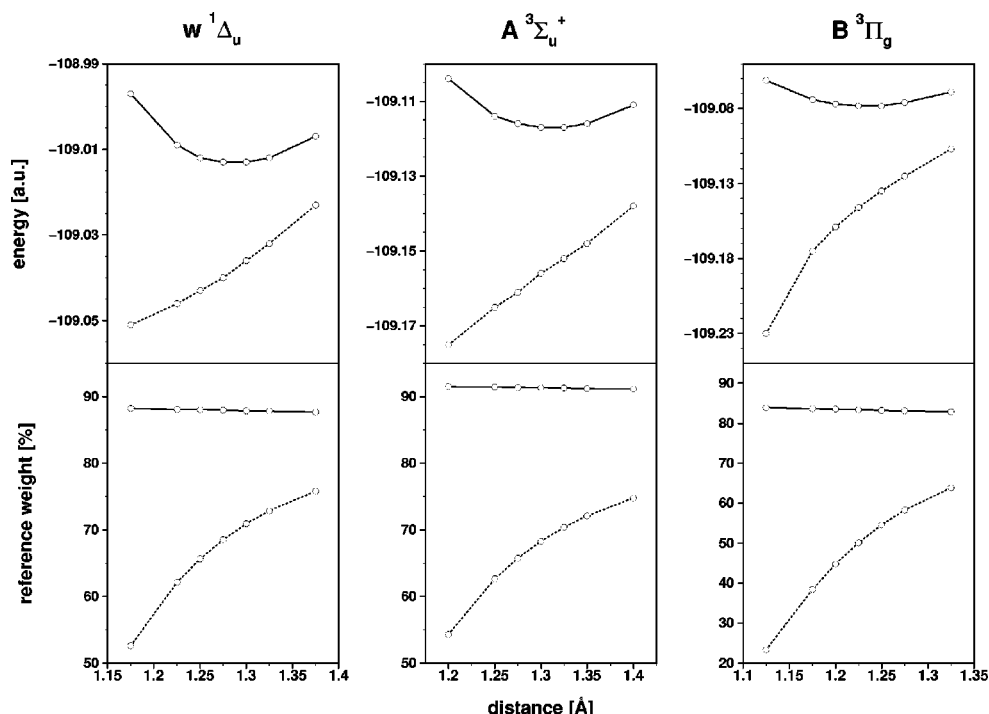


FIG. 2. Potential energy curves and reference weights in the equilibrium region for three excited states of  $N_2$  calculated using the MROPT(2) method with the state-specific CASSCF orbitals (solid line) and the ground-state RHF orbitals (dotted line).

space are the same as described in Sec. III A. The active space and basis sets used in the calculations on dimers have been given above.

The results for  $Ne_2$  are given in Table III. The ground state of  $Ne_2$  has a closed-shell character and the difference between the CASSCF and RHF orbitals is believed to be rather small. As expected, also the difference between the

results calculated with the two sets of orbitals is found to be small for all used methods. Similar situation happens for the ground state of other calculated molecules: The MROPT(2) ground-state energy depends rather weakly on the set of orbitals used for calculations.

The internal rotation barrier of ethylene and vertical excitation energies of two excited states of this molecule cal-

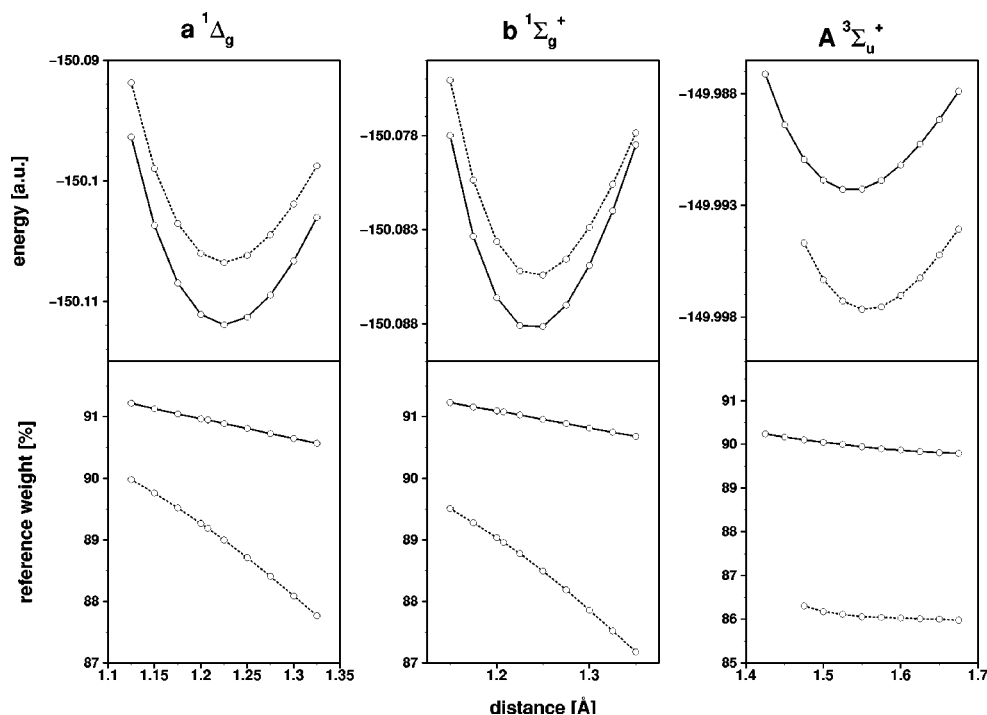


FIG. 3. Potential energy curves and reference weights in the equilibrium region for three excited states of  $O_2$  calculated using the MROPT(2) method with the state-specific CASSCF orbitals (solid line) and the ground-state ROHF orbitals (dotted line).



culated using the RHF and CASSCF sets of orbitals are given in Table IV. These results clearly show that the orbital dependence of the MROPT(2) method is rather strong; it is largest among the perturbative methods. The corrected MRCI results almost does not depend on the set of orbitals used for calculations. The difference between the MROPT(2)/RHF and MROPT(2)/CASSCF results is especially large for the rotational barrier of ethylene. This is caused by the erroneous shape of the MROPT(2)/RHF potential energy curve shown in Fig. 1. For the geometries close to planar, the MROPT(2)/RHF and MROPT(2)/CASSCF curves almost coincide. For the twisted geometry, where the RHF orbitals rather poorly describe the electronic structure of ethylene, the MROPT(2)/RHF potential energy curve displays some nonphysical features. Similar features—however, in much smaller degree—can be observed for the other second-order perturbative methods, MRMP/RHF and MREN/RHF.

The equilibrium regions of the MROPT(2) potential energy curves for three excited states of the  $N_2$  molecule,  $w^1\Delta_u$ ,  $A^3\Sigma_u^+$ , and  $B^3\Pi_g$ , are shown in Fig. 2. The curves obtained using the state-specific CASSCF orbitals correspond to experiment very well. (For comparison of calculated spectroscopic parameters with experiment, see the subsequent paper.<sup>26</sup>) However, the curves obtained using the RHF orbitals are not bounded; a closer inspection shows that for every state the weight of the reference function in the MROPT(2)/RHF wave function is very small. Such a situation indicates an occurrence of intruder states in the perturbation calculations, associated with quasidegeneracies in the spectrum of the zeroth-order Hamiltonian. These quasidegeneracies occur for seven of eight calculated states of  $N_2$ . Only for the ground state, for which the RHF orbitals have been obtained, there is no intruder states. The reason for this situation can be the character of the RHF orbitals: They are obtained for the  $X^1\Sigma_g^+$  state that corresponds in the equilibrium region to the  $1\pi_u^4 3\sigma_g^2$  electronic configuration, while the lowest excited states originate mostly from the  $1\pi_u^3 3\sigma_g^2 1\pi_g^{*1}$  and  $1\pi_u^3 3\sigma_g^2 3\sigma_u^{*1}$  electronic configurations. A poor description of the  $1\pi_g^*$  and  $3\sigma_u^*$  molecular orbitals in the set of RHF orbitals can cause divergencies. This example shows how important is using state-specific CASSCF orbitals for the MROPT(2) calculations. Note, that potential energy curves obtained using the RHF orbitals with other perturbative methods do not suffer from quasidegeneracies, even if the resultant curves differ noticeably from those obtained using the state-specific CASSCF orbitals.

Figure 3 displays the MROPT(2) potential energy curves in their equilibrium regions for three excited states of the  $O_2$  molecule,  $a^1\Delta_g$ ,  $b^1\Sigma_g^+$ , and  $A^1\Sigma_u^+$ , obtained using the state-specific CASSCF and ground-state ROHF orbitals. Similarly to  $N_2$ , we give also the reference weights. The MROPT(2)/CASSCF and MROPT(2)/ROHF curves are similar. We observe no intruder states in the perturbation calculations; the reference state weights are larger than 80% for all six calculated states. The essential difference between the ground-state RHF orbitals of  $N_2$  and the ground-state ROHF orbitals of  $O_2$  is a good description of the oxygen  $\pi^*$  molecular orbitals. We believe that the poor description of

these orbitals for  $N_2$  is the main source of differences between the MROPT(2) results for these two molecules.

## IV. CONCLUSIONS

We have presented a multireference perturbation method that is based on Rayleigh–Schrödinger perturbation theory and uses an optimized partitioning. We abbreviate this method as MROPT. The optimization of the zeroth-order energies for the  $n$ th-order MROPT method is performed by putting a condition  $\Psi^{(n)}=0$  on the first neglected term in the perturbative expansion of the wave function. This allows for cancellation of a large part of errors arising from truncating the wave function. We give explicit equations that enable determining the optimized zeroth-order energies for the second-, third-, and fourth-order perturbation theory.

The second-order multireference perturbation method with the optimized partitioning is derived from the condition  $\Psi^{(2)}=0$ . The resulting partitioning is shown to be identical to the partitioning derived by Surján and Szabados by minimizing the Rayleigh quotient with respect to a set of the zeroth-order energies. The MROPT energy formula is also clearly the same as the energy formula for the linearized multireference coupled cluster method.

We analyze various numerical and computational issues concerning the MROPT(2) method. We show on example of  $Ne_2$  that the MROPT(2) method is (almost) size-consistent. The averaged deviations of total energies of MROPT(2) to some related methods are shown in Table II for a set of five molecules. The MROPT(2) energies show close resemblance to those computed using MRCI with Davidson-type corrections. We notice also relatively small deviations for the second-order multireference PT with the EN partitioning. It clearly shows that the state-dependent shifts in Eq. (2.2) are not large.

We have noticed large dependence of the MROPT(2) energies on a set of one-electron orbitals used for calculations. The RHF orbitals used for calculations on excited states produce some nonphysical results. The potential energy curve for barrier of internal rotation in ethylene does not depend on the set of orbitals for the geometries close to planar. However, for the distorted geometries, the curve obtained using the RHF orbitals deviates strongly from the analogous curve obtained with CASSCF orbitals, showing an artificial minimum. The situation is even more severe when the RHF orbitals are used for calculations on potential energy curves of low-lying excited states of  $N_2$ ; none of the calculated curves is bounded. At the same time, the MROPT(2) curves obtained with the state-specific CASSCF orbitals show very good agreement with the experimental data. This example stresses the importance of using state-optimized orbitals for calculations with the MROPT(2) method.

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