PHYSICAL REVIEW A VOLUME 41, NUMBER 9 1 MAY 1990

Convergence properties of multireference many-body perturbation theory

S. Zarrabian
Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

W. D. Laidig
Miami Valley Laboratories, Procter & Gamble Company, P.O. Box 398707, Cincinnati, Ohio 45239-8707

Rodney J. Bartlett
Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611

(Received 18 October 1989)

The applicability of multireference many-body perturbation theory is considered by numerically investigating the practical convergence properties of a common variant. Perturbation energies through 20th order are reported for BeH_2 at geometries near the $Be \rightarrow H_2$ symmetric-insertion transition state and for BH in its equilibrium region. The recursive perturbation-theory equations are solved using a computationally intensive, but conceptually simple, configuration-based algorithm. In the study of diverse regions of molecular potential-energy surfaces, the difficulties involved in selecting appropriate zeroth-order models, which consist of the choice of reference functions, orbitals, and zeroth-order Hamiltonian, are addressed. We also consider convergence-acceleration techniques such as series resummation using Padé approximants.

INTRODUCTION

Many-body perturbation theory (MBPT) based on a single reference (SR) has proven to be a powerful tool in studying the electronic structure of molecules.[1,2] It has been applied with great success to a wide variety of problems. However, at practical levels of truncation it cannot be profitably used for quasidegenerate problems, or when there are important effects from several configurations. This frequently occurs in the calculation of energies for excited states and when treating the bond-breaking regions of potential-energy surfaces (PES's). Infinite-order coupled-cluster (CC) generalizations of single reference MBPT resolve some quasidegenerate problems but not all.[3]

A natural solution to the shortcomings of SR-MBPT has been the generalization to multireference (MR) MBPT. The fundamental idea is that of an effective Hamiltonian whose eigenvalues coincide with a subset of the eigenvalues of the exact Hamiltonian. Several different MR approaches have been proposed. The first complete linked diagram theory was formulated by Brandow.[4] This approach employs a complete reference space. This method has been applied by Stern and Kaldor[5] and by Freed and co-workers.[6] An incomplete reference MR-MBPT approach has been proposed and applied by Hose and Kaldor.[7] Numerical comparison of the various MR-MBPT approaches, however, has been limited since most previous molecular studies have been carried out to no more than third order[5-9] (see Ref. 10 for an exception). As a result, the *practical* convergence behavior of any of these methods (as opposed to mathematical convergence) beyond low order is largely unknown.

In this paper we discuss the convergence properties of a common MR variant of Rayleigh-Schrödinger perturbation theory (RSPT) that does not require a complete reference space.[7,8,10] Employing a MR generalization of our earlier configuration-based SR algorithm,[11] we can compute MR perturbation energies through arbitrarily high order for cases in which the corresponding complete configuration-interaction (CI) calculation can be performed. Though this MR-RSPT procedure is computationally expensive due to inclusion of mutually cancelling size-inextensive terms arising from different categories of excitation, provided that all possible excitations are included at any order, it should yield energies identical to its MR-MBPT counterpart containing only size-extensive terms.[2]

Specifically, we present MR-MBPT results for BeH_2 in its $Be \rightarrow H_2$ symmetric-insertion transition state region. This prototype multireference problem has been previously studied with single[12] and multireference CC (Refs. 13 and 14) methods, and with low-order MR MBPT.[15] We also consider BH near its equilibrium geometry, and we discuss divergent MR calculations on BH at several stretched geometries and H_2O along its symmetric O—H bond dissociation pathway. These BeH_2, BH, and H_2O results illustrate the difficulties in selecting a consistent zeroth-order model (reference space, orbitals, and zeroth-order Hamiltonian) that will lead to a rapidly convergent series over an entire PES. In the process we will investigate the nature of the so-called intruder state problem, and the use of convergence-acceleration techniques such as series resummation using Padé approximants.

THEORY

The MR-MBPT approach we adopt is a straightforward generalization of RSPT to multireference cases as given by Lindgren.[16] This yields an expansion based on the Bloch equation, which provides a clear order-by-order breakdown and is particularly suited to the algorithm we use.

We introduce two projectors, P for the reference space and Q for its orthogonal complement,[16]

$$\psi^0 = P\psi \ , \tag{1}$$

$$P = |\Phi^0\rangle\langle\Phi^0| , \quad \Phi^0 = \{\phi_i^0|, i=1,d\} \tag{2}$$

$$P = \sum_{i=1}^{d} p_i = \sum_{i=1}^{d} |\phi_i^0\rangle\langle\phi_i^0| , \quad Q = 1-P = |\mathbf{h}\rangle\langle\mathbf{h}| \tag{3}$$

where the ϕ_i^0 are the set of orthonormal reference functions, and the set of functions $|\mathbf{h}\rangle$ spans the orthogonal complement. In intermediate normalization, we introduce the wave operator Ω,[16] which takes a model function defined in terms of the model space $\{\phi_i^0\}$ into the exact wave function:

$$\psi = \Omega\psi^0 \ , \tag{4}$$

Inserting the above definitions into the Schrödinger equation and projecting by P, we have

$$PH\Omega\psi^0 = \mathcal{H}\psi^0 = E\psi^0 \ . \tag{5}$$

The effective Hamiltonian $\mathcal{H}$ will yield the exact energy E when acting upon the model function ψ^0. Elements of the effective Hamiltonian of any order can now be defined

$$\mathcal{H}_{ij}^{(n)} = \langle\phi_i^0|\mathcal{H}^{(n)}|\phi_j^0\rangle = \langle\phi_i^0|PH\Omega^{(n-1)}|\phi_j^0\rangle \tag{6}$$

$$= \langle\phi_i^0|PV\Omega^{(n-1)}|p_j|\phi_j^0\rangle \tag{7}$$

where we have used $H = H^0 + V$ and adopt the following Hamiltonian partitioning in the second-quantized formalism:

$$H^0 = \sum_p f_{pp} p^\dagger p , \quad f_{pq} = h_{pq} + \sum_t \langle pt\|qt\rangle = h_{pq} + u_{pq} \ , \tag{8}$$

$$V = \tfrac{1}{2} \sum_{p,q,r,s} \langle pq|rs\rangle p^\dagger q^\dagger rs + \sum_{p\neq q} f_{pq} p^\dagger q - \sum_{p,q} u_{pq} p^\dagger q \tag{9}$$

[when canonical self-consistent-field (SCF) orbitals are used the Fock operator f simplifies to $f_{pp} = \varepsilon_p$ and $f_{pq} = 0$]. Therefore, to obtain the elements of the effective Hamiltonian $\mathcal{H}$ at any order (n), we need expressions for $\Omega^{(n-1)}p_j$. To obtain such expressions we use the Bloch equation which can be derived from the Schrödinger equation[16]

$$[\Omega, H^0]P = V\Omega P - \Omega PV\Omega P \tag{10}$$

or, by introducing the excitation operator $\chi = \Omega - 1$,

$$[\Omega, H^0]P = QV\Omega P - \chi PV\Omega P \ . \tag{11}$$

We use this equation to obtain expressions for $\Omega^{(n)}p_j$. We can accomplish this by right-multiplying the above equation by any p_j and expanding order by order. This scheme essentially defines a different reference for each column of the effective Hamiltonian analogous to the Hose and Kaldor[7] treatment in MBPT and that of Jeziorski and Monkhorst in the CC framework.[17]

Upon expansion we have

$$[\Omega^{(1)}, H^0]p_j = QVp_j \ , \tag{12a}$$

$$\Omega^{(1)}p_j = R_j V p_j \ , \tag{12b}$$

$$[\Omega^{(2)}, H^0]p_j = QV\Omega^{(1)}p_j - \Omega^{(1)}PVp_j \ , \tag{13a}$$

$$\Omega^{(2)}p_j = R_j V\Omega^{(1)}p_j - R_j\Omega^{(1)}PVp_j \ , \tag{13b}$$

$$[\Omega^{(3)}, H^0]p_j = QV\Omega^{(2)}p_j - \Omega^{(1)}PV\Omega^{(1)}p_j - \Omega^{(2)}PVp_j \ , \tag{14a}$$

$$\Omega^{(3)}p_j = R_j V\Omega^{(2)}p_j - R_j\Omega^{(1)}PV\Omega^{(1)}p_j - R_j\Omega^{(2)}PVp_j \ , \tag{14b}$$

$$[\Omega^{(n)}, H^0]p_j = QV\Omega^{(n-1)}p_j - \left[\sum_{m=1}^{n-1} \Omega^{(m)}PV\Omega^{(n-m-1)}\right]p_j \ , \tag{15a}$$

$$\Omega^{(n)}p_j = R_j V\Omega^{(n-1)}p_j - R_j\left[\sum_{m=1}^{n-1}\sum_{l=1}^{d} \Omega^{(m)}p_l V\Omega^{(n-m-1)}\right]p_j \ , \tag{15b}$$

where $R_j = Q(E_j^0 - H^0Q)^{-1}$ is the resolvent operator[18] associated with the jth reference configuration. These equations can be evaluated diagrammatically,[9] and have been programmed and applied in some applications,[7,9] however, the enormous number of diagrams even in fourth order makes it difficult to evaluate high-order contributions. We thus choose to evaluate these equations in a configuration-based framework.[11,19,20]

We will use the inner-projected form of each resolvent operator R_j corresponding to a reference j,

$$R_j = |\mathbf{h}\rangle\mathbf{R}_j\langle\mathbf{h}| , \quad \mathbf{R}_j = \langle\mathbf{h}|E_j^0 - H^0|\mathbf{h}\rangle^{-1} \ , \tag{16}$$

and rewrite the expressions for the elements of the effective Hamiltonian $\mathcal{H}$ as

$$\mathcal{H}_{ij}^{(n)} = \langle\phi_i^0|PV\Omega^{(n-1)}p_j|\phi_j^0\rangle = \langle\phi_i^0|PVQ\Omega^{(n-1)}p_j|\phi_j^0\rangle \ , \tag{17}$$

$$\begin{gathered} \mathcal{H}_{ij}^{(n)} = \langle\phi_i^0|V|\mathbf{h}\rangle\langle\mathbf{h}|\Omega^{(n-1)}p_j|\phi_j^0\rangle , \quad Q = |\mathbf{h}\rangle\langle\mathbf{h}| \ , \\ \mathcal{H}_{ij}^{(n)} = \langle\phi_i^0|V|\mathbf{h}\rangle\alpha_j^{(n-1)} \ , \end{gathered} \tag{18}$$

where

$$\alpha_j^{(n-1)} = \langle\mathbf{h}|\Omega^{(n-1)}p_j|\phi_j^0\rangle \ . \tag{19}$$

For lower orders we will specifically have

$$\alpha_j^{(1)} = \langle\mathbf{h}|\Omega^{(1)}p_j|\phi_j^0\rangle = \langle\mathbf{h}|R_j V p_j|\phi_j^0\rangle \ , \tag{20}$$

$$\alpha_j^{(1)} = \mathbf{R}_j\langle\mathbf{h}|V|\phi_j^0\rangle \ , \tag{21}$$

where we used Eqs. (16) and (20) to obtain the last equation:

$$\mathcal{H}_{ij}^{(2)} = \langle\phi_i^0|V|\mathbf{h}\rangle\alpha_j^{(1)} \ . \tag{22}$$

Similarly for $\boldsymbol{\alpha}_j^{(2)}$ and $\mathcal{H}_{ij}^{(3)}$ we have

$$\begin{aligned} \boldsymbol{\alpha}_j^{(2)} &= \mathbf{R}_j \left[\mathbf{V}\boldsymbol{\alpha}_j^{(1)} - \sum_{k=1}^{d} \boldsymbol{\alpha}_k^{(1)} \mathcal{H}_{kj}^{(1)} \right], \quad \mathbf{V} = \langle \mathbf{h} | V | \mathbf{h} \rangle \\ \mathcal{H}_{ij}^{(3)} &= \langle \phi_i^0 | V | \mathbf{h} \rangle \boldsymbol{\alpha}_j^{(2)} . \end{aligned} \tag{23}$$

Following this scheme, a general expression for $\boldsymbol{\alpha}_j^{(n)}$ can be derived:

$$\boldsymbol{\alpha}_j^{(n)} = \mathbf{R}_j \left[\mathbf{V}\boldsymbol{\alpha}_j^{(n-1)} - \sum_{m=1}^{n-1} \sum_{k=1}^{d} \boldsymbol{\alpha}_k^{(m)} \mathcal{H}_{kj}^{(n-m)} \right] , \tag{24}$$

$$\mathcal{H}_{ij}^{(n)} = \langle \phi_i^0 | V | \mathbf{h} \rangle \boldsymbol{\alpha}_j^{(n-1)} . \tag{25}$$

In the expression for the $\boldsymbol{\alpha}$'s, the first term is what is usually referred to as the principle part and the rest are the renormalization parts. We can see from the above equations that any $\boldsymbol{\alpha}$ can be constructed from the previous ones in an iterative manner.[11,19,20] When $\boldsymbol{\alpha}_j^{(n)}$ is constructed for all $j = 1, 2, \ldots, d$, the effective Hamiltonian of the next order can be evaluated and diagonalized to obtain the contribution to the energy at that order.

The most time-consuming part of this algorithm is the construction of $\mathbf{V}\boldsymbol{\alpha}$ in each iteration, which is basically a matrix multiplication of the CI matrix times a vector. If this multiplication can be carried out for a given example, we can, in principle, construct the effective Hamiltonian up to any order.

MR-MBPT CONVERGENCE CONSIDERATIONS

Clearly, there is a certain neighborhood of convergence associated with the series of wave operators in Eq. (15), and this radius is critically associated with the choice of H^0 and E_j^0. If our zeroth-order approximations to the energy and the wave function are outside this neighborhood the series will diverge. Fortunately, in most cases treated by SR-MBPT, the ground state is dominated by a single configuration, i.e., the zeroth-order approximation is adequate and one obtains reasonable results (the series, however, is still likely to be only asymptotically convergent). But when the ground state is populated by more than a single configuration, then the above expansion can diverge or converge only conditionally. Some of these convergence problems can be overcome by using an unrestricted Hartree-Fock (UHF) reference especially for molecules in their bond-breaking regions. However, in such cases even high-order perturbed wave functions can still be severely spin contaminated.[20,21] What one intends to do by using a MR approach is to construct a zeroth-order approximation of the correct spin symmetry which is within the neighborhood of convergence for its associated series. However, there are various difficulties involved.

If we are to use finite-order MBPT (single or multireference) to construct PES's, then the rate of convergence of the energy series should be comparable at all geometries. Otherwise, for truncated series, different fractions of the correlation energy will be recovered at different geometries and, as a consequence, valid order-by-order energy comparisons between points on the PES cannot be made. (Infinite-order coupled-cluster methods have less such difficulty.[3]) Therefore, since the SR-MBPT series is generally either poorly convergent or divergent outside the equilibrium region, its use for constructing meaningful PES's is quite limited.

One problem with developing a perturbation series which is rapidly convergent everywhere on the PES is the difficulty in selecting one zeroth-order model for use at all geometries. While it is possible to pick a reference space and orbitals which lead to a convergent series at virtually every geometry, it is generally accepted that the same reference space must be used for the entire PES to yield consistent results (allowing the reference space to vary as we move around the PES would lead to a bumpy surface, and would hardly be acceptable for a rigorous theory). Unfortunately, adopting a fixed P- and Q-space partitioning nearly always leads to the so-called intruder state problem in at least some PES regions.

The intruder state problem arises whenever the eigenspectrum of the exact effective Hamiltonian $\mathcal{H}$ does not smoothly evolve from the zeroth-order eigenspectrum $\mathcal{H}^{(0)}$ as the perturbation λ is varied from $0 \rightarrow 1$ where $\mathcal{H} = \mathcal{H}^{(0)} + \lambda \mathcal{H}^{(1)} + \frac{1}{2}\lambda^2 \mathcal{H}^{(2)} + \cdots$. In such cases, Schucan and Weidenmüller[22] demonstrated that an order-by-order expansion of the perturbation series will diverge due to the overlap of the P and Q eigenspectrums. What this implies for the construction of an everywhere convergent MR-MBPT PES is that the eigenvalues of $\mathcal{H}^{(0)}$ must map into the lowest n_P eigenvalues of H for every point on the potential surface. In addition, if the perturbation series is to be rapidly convergent over the entire PES then the P and Q eigenspectrums should everywhere be well separated. In practice, such a situation is very difficult to achieve, because a particular reference that is important at one geometry might not be very significant at another and vice versa. Not surprisingly, this problem becomes much worse as the size of the P space grows.

In addition to choosing the reference space, one also has to select a set of orbitals, and as long as we insist upon a diagonal resolvent operator, the choice of orbitals is tied to the choice of H^0. If the matrix series for $\mathcal{H}$ is to converge, then every matrix element in the series also has to converge (since each element of the effective Hamiltonian is a function of all the elements of the lower-order matrices [Eqs. (22) and (23)] divergence in one element will eventually lead to divergence of the whole matrix). Consequently, every element of $\mathcal{H}^{(0)}$ must be a good approximation to the corresponding element of $\mathcal{H}$. In the present framework, each column of $\mathcal{H}$ is constructed using a different reference function. Therefore, if we employ Hartree-Fock orbitals for a specific configuration, these orbitals will typically form a good zeroth-order approximation for that configuration's column of $\mathcal{H}$. However, the remaining columns will not necessarily be good zeroth-order approximations and this may lead to series divergence.

A better choice would be some sort of average orbitals simultaneously optimized for all P-space configurations. As we will demonstrate in the next section, orbitals obtained from ionized SCF calculations where all active electrons are removed appear to often be a more reasonable choice since a larger orbital energy gap is typically found between the occupied and virtual orbitals leading to a better separation of the *P*- and *Q*-space eigenspectrums. Other promising orbital choices might be single-state or state-averaged multiconfiguration self-consistent-field (MCSCF) orbitals. The use of MCSCF orbitals in a MR-MBPT framework necessitates the use of a nondiagonal resolvent which typically requires separation into a diagonal and off-diagonal part and is followed by some infinite summation of the nondiagonal terms. Such summations are routinely made in single reference CC theory when non-Hartree-Fock reference functions are chosen, e.g.[23] Others use similar techniques.[24]

RESULTS AND DISCUSSION

As our first numerical test of MR-MBPT convergence we investigate the C_{2v} insertion pathway of Be into H_2. This system has been previously studied using SR-MBPT,[12] low-order MR-MBPT,[15] CC methods with both SR (Ref. 12) and MR variants,[13,14] and full CI.[12] Be has a quasidegeneracy between its 2*s* and 2*p* orbitals. This, together with the near degeneracy of the $1\sigma_g^2$ and $1\sigma_u^2$ configurations of H_2 in its bond-breaking region, makes this an interesting example. A 3*s*, 1*p* basis set on Be and 2*s* on H is used.[12] The calculations are performed at the three geometries previously considered:[12]

Geometry	r (Be-H_2)	r (H-H)
A	2.50	2.78
B	2.75	2.55
C	3.00	2.32

The lowest-energy state in all three geometries is the $^3B_2$ state with electron configuration $(1a_1^2,2a_1^2,3a_1,1b_2)$. The next two lowest states are the $^1A_1$ configurations $(1a_1^2,2a_1^2,3a_1^2)$ and $(1a_1^2,2a_1^2,1b_2^2)$ which we refer to as states I and II, respectively. The SCF energy curves for these two states cross near geometry *B* (Fig. 1).

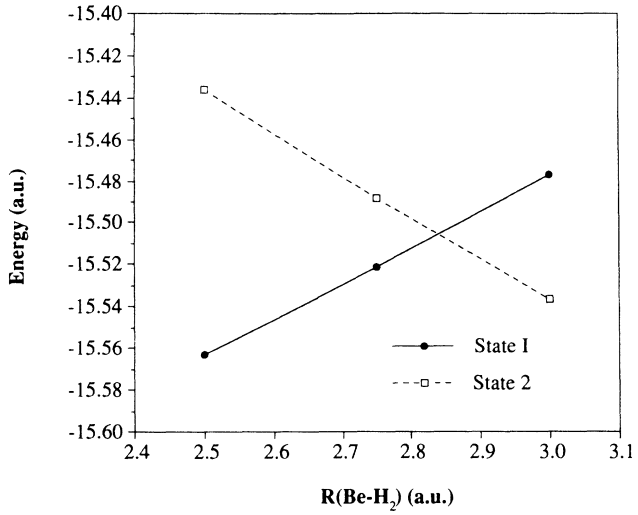

FIG. 1. SCF energies for the lowest $^1A_1$ states of BeH_2.

The two $^1A_1$ configurations are chosen as reference functions and three sets of MR-MBPT calculations are performed employing SCF orbitals from the $^3B_2$ and two $^1A_1$ states, respectively. Of the six $^1A_1$ MR-MBPT calculations (three geometries, two orbital choices), only one is found to be convergent (state I at geometry *A*). The $^3B_2$ orbital choice and associated $H^0=\sum_i \varepsilon_i |i\rangle\langle i|$ for $\{i\}$, the occupied restricted open-shell Hartree-Fock (ROHF) $^3B_2$ orbitals, and $\{\varepsilon_i\}$, the associated orbital energies, which was previously used,[15] leads to a convergent series at all three geometries. This is consistent with our argument for employing an unbiased orbital set (with respect to any of the reference functions) presented in the preceding section. However, at the separated limit (Be+H_2), this two reference *P* space will lead to divergence, regardless of the orbital choice. This is because at the separated limit, the exact eigenvalue corresponding to the *P*-space configuration $(1a_1^2,2a_1^2,1b_2^2)$ lies in the *Q*-space eigenspectrum. This illustrates our contention, that, in general, no fixed *P*- and *Q*-space partitioning will lead to a PES which is everywhere convergent. This is an inherent problem with using MR MBPT built upon effective Hamiltonians. A single but multiconfigurational reference method, one form of which has been considered in an approximate CC method,[13,25] does not have this problem since there can be no intruder states. MR-CI methods also use a single but multiconfigurational reference, so convergence is generally not hurt by enlarging the reference space.

The convergence behavior of the $^3B_2$ orbital calculations is detailed in Tables I–III where the order-by-order MR perturbation energies and their corresponding "staircase" Padé approximants are listed for states I and II at geometries *A*, *B*, and *C*, respectively. All three calculations converge at comparable rates. The resummed series constructed from Padé approximants to each eigenvalue series do not converge appreciably faster except for state II at geometry *A*. Though a reasonable MR-MBPT PES cannot be constructed using this zeroth-order model these BeH_2 calculations demonstrate that within a local region MR-MBPT can be used to compute ground- and excited-state energies which are not amenable to SR treatments.

Next we consider double ζ plus polarization[26] (DZP) BH at several different geometries ($R=2.329$ a.u., 1.5*R*, 2.0*R*, and 5.0*R*). Although a number of different orbital choices and configuration-space partitionings were tried, we were unable to find a unique reference space and orbital choice (i.e., the same zeroth-order model) which leads to a convergent MR-MBPT series at all four geometries. We were able, however, to find a different zeroth-order model at each geometry for which the perturbation series would converge.

To illustrate the importance of choosing the proper orbitals, we report MR-MBPT calculations on BH at its equilibrium geometry (1.0*R*) using two different sets of orbitals: ground-state SCF orbitals for neutral BH and for BH^{2+} where all active orbitals are unoccupied. The reference space consists of the three configurations I$[a_1^2,a_1^2,a_1^2]$, II$[a_1^2,a_1^2,b_1^2]$, and III$[a_1^2,a_1^2,b_2^2]$ (note that C_{2v} symmetry group is used) with the highest weight in

TABLE I. MR-MBPT results for states I and II of BeH_2 at geometry *A*.

Order	State I $E^n - E^{\text{Full CI}}$	 $E^{\text{Padé}(n)} - E^{\text{Full CI}}$	State II $E^n - E^{\text{Full CI}}$	 $E^{\text{Padé}(n)} - E^{\text{Full CI}}$
1	0.127 375[a]		0.102 692	
2	0.026 022	[1,0]=0.025 350	0.019 761	[1,0]=0.019 316
3	0.021 263	[1,1]=0.021 028	0.000 863	[1,1]=−0.004 714
4	0.009 112	[2,1]=0.027 470	−0.000 660	[2,1]=−0.000 805
5	0.003 619	[2,2]=−0.004 680	0.000 989	[2,2]=0.003 714
6	0.003 685	[3,2]=0.005 547	0.001 043	[3,2]=0.000 910
7	0.001 951	[3,3]=0.001 739	−0.000 097	[3,3]=−0.000 177
8	0.001 097	[4,3]=0.000 818	−0.000 561	[4,3]=0.000 046
9	0.000 695	[4,4]=−0.001 200	−0.000 131	[4,4]=0.000 008
10	0.000 096	[5,4]=−0.003 552	0.000 307	[5,4]=0.000 025
11	0.000 132	[5,5]=−0.001 391	0.000 250	[5,5]=0.000 062
12	0.000 204	[6,5]=−0.000 025	−0.000 084	[6,5]=0.000 031
13	0.000 029	[6,6]=−0.000 048	−0.000 227	[6,6]=0.000 022
14	−0.000 062	[7,6]=−0.000 122	−0.000 066	[7,6]=0.000 228
15	−0.000 082	[7,7]=0.000 110[b]	0.000 116	[7,7]=−0.000 002[b]
16	−0.000 041	[8,7]=−0.000 135	0.000 101	[8,7]=−0.000 004
17	0.000 025	[8,8]=−0.000 063	−0.000 031	[8,8]=−0.000 009
18	0.000 009	[9,8]=−0.000 053	−0.000 091	[9,8]=−0.000 005
19	−0.000 037	[9,9]=0.000 016	−0.000 028	[9,9]=−0.000 004
20	−0.000 038	[10,9]=−0.000 011	0.000 052	[10,9]=0.000 000

[a] All energy differences in a.u.

[b] Order-by-order energies used in the Padé approximant calculations were assumed to be accurate to eight decimal places. However, energy variances by up to 1×10^{-8} led to Padé approximant standard deviations greater than 1×10^{-6} for two values and both varied in the sixth decimal place.

TABLE II. MR-MBPT results for states I and II of BeH_2 at geometry *B*.

Order	State I $E^n - E^{\text{Full CI}}$	 $E^{\text{Padé}(n)} - E^{\text{Full CI}}$	State II $E^n - E^{\text{Full CI}}$	 $E^{\text{Padé}(n)} - E^{\text{Full CI}}$
1	0.114 223[a]		0.119 489	
2	0.028 961	[1,0]=0.028 487	0.025 225	[1,0]=0.024 647
3	0.016 192	[1,1]=+0.013 944	0.004 219	[1,1]=−0.001 804
4	0.007 971	[2,1]=−0.007 877	−0.000 060	[2,1]=−0.001 155
5	0.004 673	[2,2]=0.002 071	0.000 808	[2,2]=−0.002 004
6	0.002 340	[3,2]=0.000 264	0.000 716	[3,2]=0.000 718
7	0.001 079	[3,3]=−0.000 888	0.000 180	[3,3]=0.000 373
8	0.000 526	[4,3]=−0.000 319	−0.000 086	[4,3]=−0.000 257
9	0.000 253	[4,4]=−0.000 077	−0.000 028	[4,4]=0.000 049
10	0.000 120	[5,4]=+0.000 010	0.000 076	[5,4]=0.000 062
11	0.000 026	[5,5]=−0.000 045	0.000 043	[5,5]=0.000 051
12	−0.000 022	[6,5]=−0.000 065	−0.000 032	[6,5]=+0.000 000
13	−0.000 033	[6,6]=−0.000 058	−0.000 052	[6,6]=−0.000 052
14	−0.000 029	[7,6]=−0.000 148[b(1)]	−0.000 023	[7,6]=−0.000 025
15	−0.000 022	[7,7]=0.000 330[b(2)]	0.000 004	[7,7]=−0.000 005
16	−0.000 017	[8,7]=−0.000 064[b(1)]	0.000 005	[8,7]=−0.000 008
17	−0.000 013	[8,8]=0.000 011	−0.000 004	[8,8]=−0.000 006
18	−0.000 009	[9,8]=+0.000 005	−0.000 007	[9,8]=+0.000 000
19	−0.000 005	[9,9]=0.000 056[b(3)]	−0.000 002	[9,9]=+0.000 000
20	−0.000 002	[10,9]=−0.000 004	0.000 002	[10,9]=−0.000 002[b(2)]

[a] All energy differences in a.u.

[b] Order-by-order energies used in the Padé approximant calculations were assumed to be accurate to eight decimal places. However, energy variances by up to 1×10^{-8} led to Padé approximant standard deviations greater than 1×10^{-6} for five values: those labeled (1), (2), and (3) varied in the sixth, fifth, and fourth decimal places, respectively.

TABLE III. MR-MBPT results for states I and II of BeH_2 at geometry *C*.

	State I		State II	
Order	$E^n - E^{\text{Full CI}}$	$E^{\text{Padé}(n)} - E^{\text{Full CI}}$	$E^n - E^{\text{Full CI}}$	$E^{\text{Padé}(n)} - E^{\text{Full CI}}$
1	0.122 419[a]		0.104 101	
2	0.034 680	[1,0]=0.034 181	0.021 167	[1,0]=0.020 719
3	0.013 626	[1,1]=0.006 978	0.006 136	[1,1]=0.002 809
4	0.004 238	[2,1]=−0.003 388	0.004 208	[2,1]=0.003 922
5	0.002 377	[2,2]=0.001 047	0.003 458	[2,2]=0.003 509
6	0.000 605	[3,2]=0.000 375	0.001 731	[3,2]=0.004 225
7	0.000 358	[3,3]=−0.000 399	0.000 492	[3,3]=0.002 316
8	−0.000 028	[4,3]=−0.000 159	0.000 140	[4,3]=−0.000 011
9	0.000 027	[4,4]=0.000 132	0.000 155	[4,4]=0.000 078
10	−0.000 023	[5,4]=0.000 008	0.000 133	[5,4]=0.000 032
11	−0.000 011	[5,5]=−0.000 331[b(1)]	0.000 024	[5,5]=0.013 883[b(2)]
12	−0.000 032	[6,5]=−0.000 031	−0.000 032	[6,5]=−0.000 010
13	−0.000 023	[6,6]=−0.000 026	−0.000 028	[6,6]=−0.000 039
14	−0.000 015	[7,6]=−0.000 040	−0.000 005	[7,6]=−0.000 029
15	−0.000 007	[7,7]=0.000 028	−0.000 003	[7,7]=−0.000 010
16	−0.000 005	[8,7]=0.000 012	−0.000 008	[8,7]=−0.000 008
17	−0.000 004	[8,8]=−0.000 018[b(1)]	−0.000 009	[8,8]=−0.000 013
18	−0.000 002	[9,8]=−0.000 004[b(1)]	−0.000 004	[9,8]=0.000 010
19	0.000 000	[9,9]=0.000 009[b(3)]	0.000 000	[9,9]=+0.000 002
20	0.000 000	[10,9]=−0.000 001	0.000 000	[10,9]=+0.000 001

[a] All energy differences in a.u.

[b] Order-by-order energies used in the Padé approximant calculations were assumed to be accurate to eight decimal places. However, energy variances by up to 1×10^{-8} led to Padé approximant standard deviations greater than 1×10^{-6} for five values: those labeled (1), (2), and (3) varied in the sixth, third, and fifth decimal places, respectively.

TABLE IV. Cumulative order-by-order MBPT results for the lowest three eigenvalues of BH.

	1 reference	3 references					
	Root 1	Root 1		Root 2		Root 3	
Order	BH orbitals	BH orbitals	BH^{2+} orbitals	BH orbitals	BH^{2+} orbitals	BH orbitals	BH^{2+} orbitals
1	−25.125 260[a]	−25.132 441	−25.053 718	−24.839 052	−24.823 503	−24.799 838	−24.755 780
2	−25.198 988	−25.238 917	−25.226 773	−25.021 810	−24.994 624	−25.138 268	−24.951 013
3	−25.216 566	−25.211 613	−25.227 123	−25.016 295	−25.009 917	−2.532 309[b]	−24.973 125
4	−25.222 567	−25.216 543	−25.224 705	−24.987 981	−25.002 883		−24.962 035
5	−25.225 101	−25.223 101[b]	−25.227 382	−25.001 902[b]	−25.001 289		−24.956 349
6	−25.226 322		−25.227 651		−25.004 032		−24.960 322
7	−25.226 952		−25.227 407		−25.005 525		−24.964 326
8	−25.227 284		−25.227 784		−25.004 990		−24.963 825
9	−25.227 459		−25.227 760		−25.004 333		−24.961 863
10	−25.227 549		−25.227 466		−25.004 433		−24.961 636
11	−25.227 593		−25.227 505		−25.004 763		−24.962 680
12	−25.227 615		−25.227 706		−25.004 815		−24.963 172
13	−25.227 624		−25.227 712		−25.004 685		−24.962 760
14	−25.227 627		−25.227 597		−25.004 635		−24.962 352
15	−25.227 628		−25.227 568		−25.004 687		−24.962 470
16	−25.227 628		−25.227 629		−25.004 726		−24.962 761
17	−25.227 628		−25.227 664		−25.004 712		−24.962 787
18	−25.227 628		−25.227 638		−25.004 689		−24.962 614
19	−25.227 627		−25.227 606		−25.004 691		−24.962 540
20	−25.227 627		−25.227 613		−25.004 703		−24.962 625
Full CI	−25.227 627	−25.227 627	−25.227 627	−25.004 700	−25.004 700	−24.962 641	−24.962 641

[a] All energies in a.u.

[b] Energies beyond fifth order (third order for root 3) are divergent and are not reported.

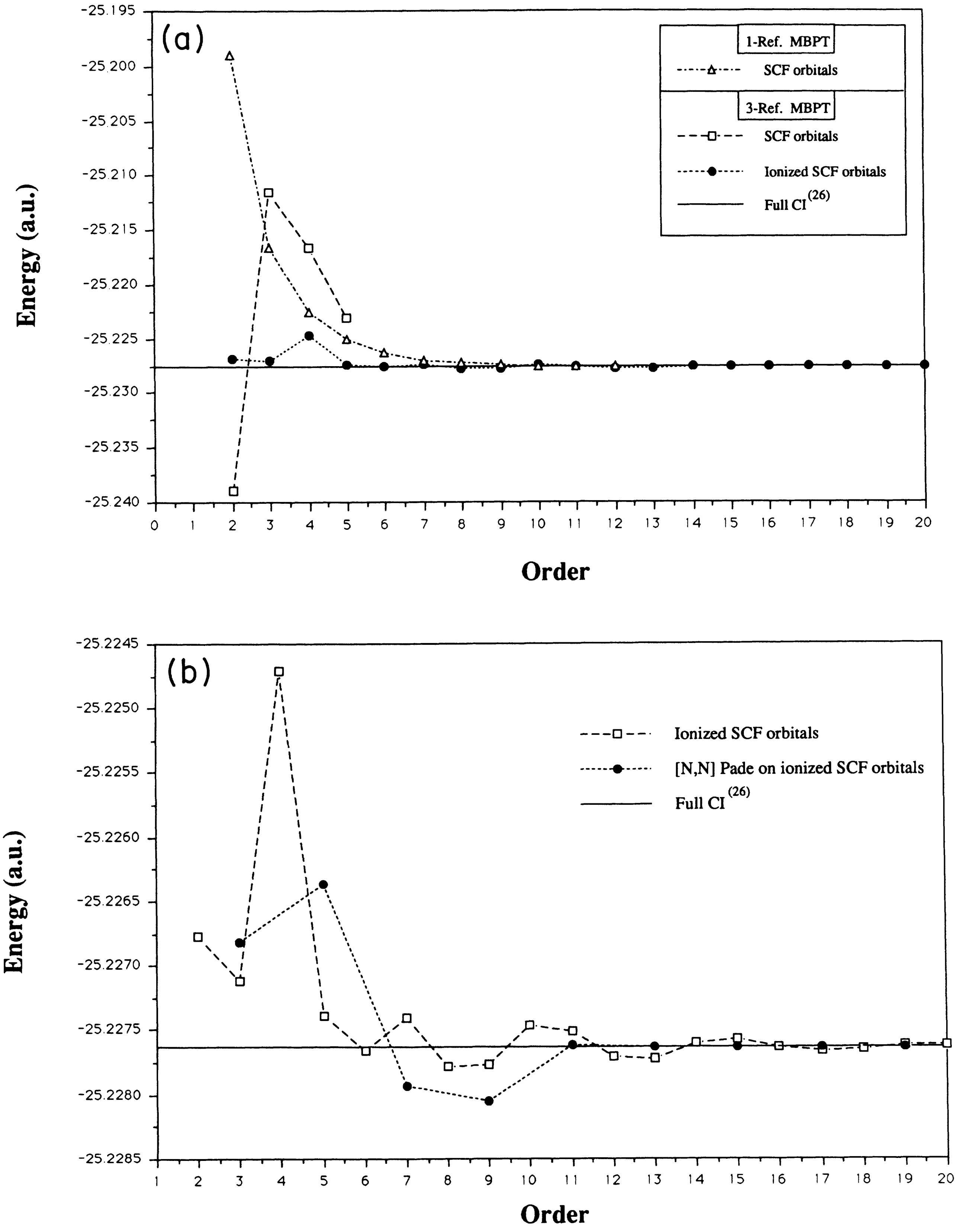

FIG. 2. (a) SR- and MR-MBPT convergence behavior for the lowest eigenvalue of the effective Hamiltonian for BH. SCF orbital results are not plotted beyond fifth order due to series divergence. (b) Comparison of MR-MBPT and Padé resummed MR-MPBT convergence behavior for the lowest eigenvalue of the effective Hamiltonian for BH using ionized SCF orbitals.

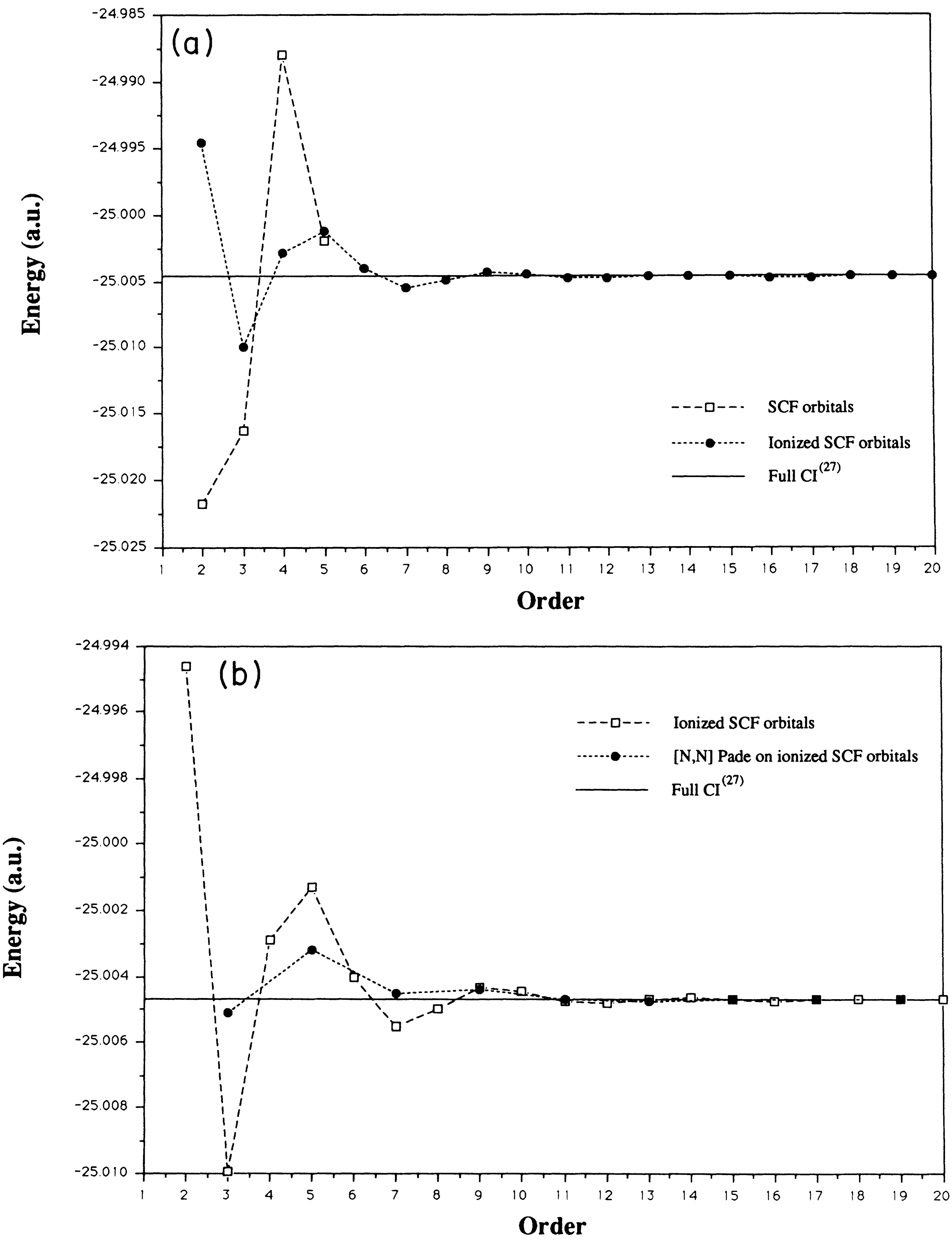

FIG. 3. (a) MR-MBPT convergence behavior for the second eigenvalue of the effective Hamiltonian for BH. SCF orbital results are not plotted beyond fifth order due to series divergence. (b) Comparison of MR-MBPT and Padé resummed MR-MBPT convergence behavior for the second lowest eigenvalue of the effective Hamiltonian for BH using ionized SCF orbitals.

the ground-state full CI wave function. Configurations II and III are degenerate in energy.

Effective Hamiltonian matrices up to the 20th order were computed in both calculations. The corresponding eigenvalues are listed in Table IV together with ground-state SCF SR-MBPT energies. The MR-MBPT calculations using regular SCF orbitals were divergent beyond fifth order for all three eigenvalues. However, when truncated at low order, the $\mathcal{H}^{(n)}$ eigenvalues for the lowest-energy state were sufficiently close to the full CI results to be misleading. The calculation using ionized SCF orbitals was convergent for all roots. It should be noted that there is some potential ambiguity in assigning eigenvalues to states in MR-MBPT since the energy ordering of such states can interchange in different perturbation-theory orders. To avoid a detailed consideration of the wave function in this initial study, the eigenvalue ordering was not changed from that produced by the matrix diagonalization routines.

In Fig. 2(a) the convergence behavior of the lowest-energy eigenvalue of both the neutral and ionized SCF orbital MR-MBPT calculations is displayed along with the ground-state SR-MBPT energies [the neutral SCF orbital MR-MBPT series are truncated at fifth order in Figs. 2(a) and 3(a) due to series divergence]. It is interesting to note that while the SR series converges rapidly and its MR counterpart diverges, the MR energies are better through second order. The MR perturbation series using ionized orbitals, in contrast, converges more rapidly than the neutral orbital SR series albeit in a more erratic fashion. Resumming the ionized orbital MR perturbation series using $[N,N]$ Padé approximants causes the series to converge more slowly in low orders, but much more rapidly beyond ninth order [Fig. 2(b)]. Figures 3 and 4 show the analogous MR results for the second and third lowest-energy eigenvalues. Both ionized orbital MR perturbation series show oscillatory convergence and the convergence rate of both series is generally improved via Padé resummation. These results and our previous high-order MR-MBPT study on Be excited states[10] suggest that MR-MBPT using an appropriate zeroth-order model can be used to calculate excited-state energies for isolated single points on PES's.

We also investigated the convergence of MR MBPT along the symmetric O—H bond-stretching pathway of DZ water. As for BH, we attempted to find a zeroth-order model which would be convergent everywhere along the entire bond-breaking path, but were unable to find one. In fact, we were only able to converge the MR-MBPT series at one point (located in the equilibrium region) and for one zeroth-order model [four-electron complete active space (CAS) reference space among the four orbitals required for bond breaking using quadruply ionized SCF orbitals computed with the CAS space empty].

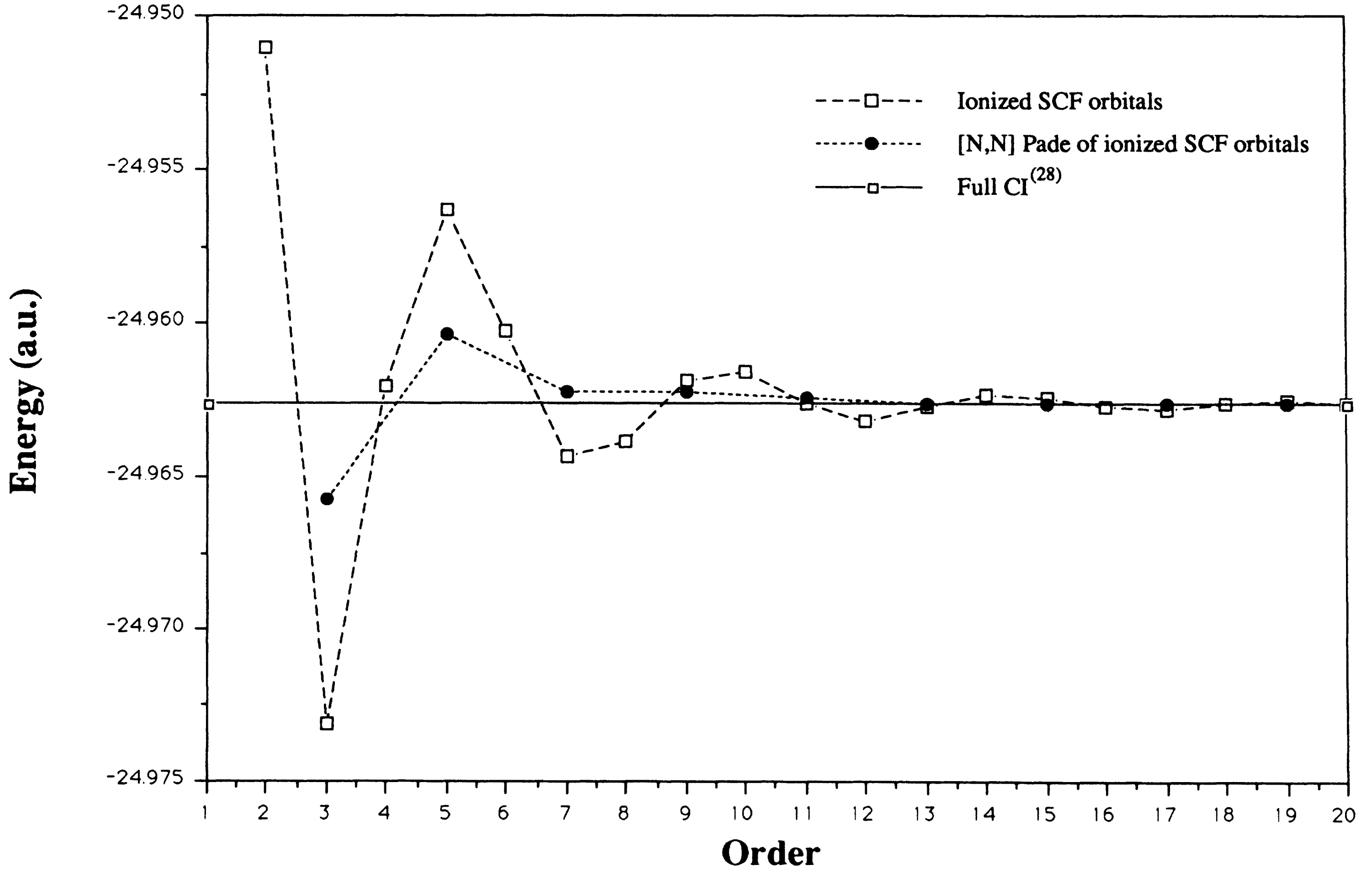

FIG. 4. Comparison of MR-MBPT and Padé resummed MR-MBPT convergence behavior for the third lowest eigenvalue of the effective Hamiltonian for BH using ionized SCF orbitals.

Though we feel it is likely that with more effort convergent MR perturbation series can be constructed for other points on the PES, we believe that it is extremely difficult to define a zeroth-order model which would result in a MR-MBPT PES which is everywhere convergent.

What can be done to improve the convergence properties of MR MBPT to allow construction of meaningful PES's? One possible remedy is the resummation of the perturbation series to improve its convergence. In this study, we have already tried with mixed results one variant of this technique (using $[N,N-1]$ and $[N,N]$ Padé approximants to resum the individual eigenvalue series). We[29] also tried two similar MR-MBPT convergence-acceleration techniques: using Padé approximants to resum each element of the matrix series separately before diagonalization and using matrix Padé approximants[30] to directly resum the matrix series. Both techniques were found to be less effective than applying Padé approximants directly to the eigenvalue series,[29] (though the difficulties involved in assigning the order-by-order eigenvalues to specific series are absent from these two techniques). One potentially better way to overcome these convergence difficulties is to add a constant to shift the zeroth-order energy of one or all references. Such shifts define an unperturbed Hamiltonian that is still diagonal but that gives rise to a series expansion about a different point within the series' neighborhood of convergence. In an upcoming paper[31] the nature of such shifts and their effect on series convergence will be presented. Similar shifts to force degeneracy in the zeroth-order P space have been used by Freed and co-workers[32] in their low-order MR-MBPT approach with good success. We will report similar high-order results in a forthcoming paper which does improve convergence.

Although some progress can doubtless be made using categories of infinite summation to improve convergence, for PES the fundamental problem with MR-MBPT or MR-CC methods,[13,14,33,34] for that matter, is the use of an effective Hamiltonian. If even one state suffers from an intruder, then other eigenvalues cannot necessarily be obtained. For an individual state theory, *single* but multiconfigurational approaches, by virtue of leading to a single element for the energy, would be preferred, but no rigorous size-extensive theory of this type is yet available. Other approaches to the intruder state problem are also worthy of attention.[33,34]

ACKNOWLEDGMENTS

This work has been supported by the U.S. Office Of Naval Research. The authors appreciate useful discussion with Professor J. Paldus.

---

[1] H. P. Kelly, Adv. Chem. Phys. **14**, 129 (1969).

[2] R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981); R. J. Bartlett and D. M. Silver, J. Chem. Phys. **62**, 3258 (1975).

[3] R. J. Bartlett, J. Phys. Chem. **93**, 1697 (1989).

[4] B. H. Brandow, Rev. Mod. Phys. **39**, 771 (1967).

[5] P. S. Stern and U. Kaldor, J. Chem. Phys. **63**, 2199 (1975); **64**, 2022 (1976).

[6] For a review, see K. F. Freed, in *Many-Body Methods in Quantum Chemistry,* Vol. 52 of *Lecture Notes in Chemistry,* edited by U. Kaldor (Springer, Berlin, 1989), p. 1.

[7] G. Hose and U. Kaldor, Phys. Scr. **21**, 357 (1980); J. Phys. B **12**, 3827 (1979); J. Chem. Phys. **81**, 2401 (1987).

[8] G. Hose, in *Many-Body Methods in Quantum Chemistry,* Vol. 52 of *Lecture Notes in Chemistry,* edited by U. Kaldor (Springer, Berlin, 1989), p. 43.

[9] S. A. Kucharski and R. J. Bartlett, Int. J. Quantum Chem. **S22**, 383 (1988).

[10] S. Zarrabian and R. J. Bartlett, Chem. Phys. Lett. **153**, 133 (1988).

[11] W. D. Laidig, G. B. Fitzgerald, and R. J. Bartlett, Chem. Phys. Lett. **113**, 51 (1985).

[12] G. D. Purvis III, R. Sheppard, F. B. Brown, and R. J. Bartlett, Int. J. Quantum Chem. **23**, 835 (1983).

[13] W. D. Laidig and R. J. Bartlett, Chem. Phys. Lett. **104**, 424 (1984).

[14] L. Meissner, K. Jankowski, and J. Wasilewski, Int. J. Quantum Chem. **34**, 535 (1988).

[15] Y. S. Lee and R. J. Bartlett, Int. J. Quantum Chem. **S17**, 347 (1983).

[16] I. Lindgren, Int. J. Quantum Chem. **12**, 33 (1978).

[17] B. Jeziorski and H. Monkhorst, Phys. Rev. A **24**, 1668 (1981).

[18] P.-O. Löwdin, J. Mol. Spectrosc. **10**, 12 (1963); **13**, 326 (1964).

[19] R. J. Bartlett and E. J. Brändas, J. Chem. Phys. **56**, 5467 (1972); **59**, 2032 (1973).

[20] N. C. Handy, P. J. Knowles, and K. Somasudram, Theor. Chim. Acta **68**, 87 (1985).

[21] R. J. Bartlett and G. D. Purvis III, Int. J. Quantum Chem. **14**, 561 (1978); Phys. Scr. **21**, 255 (1980).

[22] T. H. Schucan and H. A. Weidenmüller, Ann. Phys. (N.Y.) **73**, 108 (1972).

[23] W. D. Laidig, G. D. Purvis III, and R. J. Bartlett, J. Phys. Chem. **89**, 2161 (1985).

[24] K. Wolinski and P. Pulay, J. Chem. Phys. **90**, 3647 (1989).

[25] W. D. Laidig, P. Saxe, and R. J. Bartlett, J. Chem. Phys. **86**, 887 (1987).

[26] R. J. Harrison and N. C. Handy, Chem. Phys. Lett. **85**, 386 (1983).

[27] Our full CI energy for this excited state is $-25.004\,700$ a.u.

[28] Our full CI energy for this excited state is $-24.962\,641$ a.u.

[29] S. Zarrabian, Ph.D. thesis, University of Florida, 1987.

[30] J. R. Baker, Jr. and P. R. Graves-Morris, *Encyclopedia of Mathematics and Applications; (13,14) Padé Approximants* (Addison-Wesley, Reading, MA, 1981).

[31] S. Zarrabian and J. Paldus (unpublished).

[32] X. C. Wang and K. F. Freed, J. Chem. Phys. **91**, 1142 (1989); **91**, 3002 (1989).

[33] J. P. Malrieu, Ph. Durand, and J. P. Daudey, J. Phys. A **18**, 809 (1985).

[34] L. Meissner, S. A. Kucharski, and R. J. Bartlett, J. Chem. Phys. **91**, 6187 (1989).