PHYSICAL REVIEW A VOLUME 54, NUMBER 1 JULY 1996

Convergence behavior of multireference perturbation theory: Forced degeneracy and optimization partitioning applied to the beryllium atom

James P. Finley, Rajat K. Chaudhuri, and Karl F. Freed
The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

(Received 5 February 1996)

High-order multireference perturbation theory is applied to the ^1S states of the beryllium atom using a reference (model) space composed of the $|1s^22s^2\rangle$ and the $|1s^22p^2\rangle$ configuration-state functions (CSF's), a system that is known to yield divergent expansions using Mǿller-Plesset and Epstein-Nesbet partitioning methods. Computations of the eigenvalues are made through 40th order using forced degeneracy (FD) partitioning and the recently introduced optimization (OPT) partitioning. The former forces the $2s$ and $2p$ orbitals to be degenerate in zeroth order, while the latter chooses optimal zeroth-order energies of the (few) most important states. Our methodology employs simple models for understanding and suggesting remedies for unsuitable choices of reference spaces and partitioning methods. By examining a two-state model composed of only the $|1s^22p^2\rangle$ and $|1s^22s3s\rangle$ states of the beryllium atom, it is demonstrated that the full computation with 1323 CSF's can converge only if the zeroth-order energy of the $|1s^22s3s\rangle$ Rydberg state from the orthogonal space lies below the zeroth-order energy of the $|1s^22p^2\rangle$ CSF from the reference space. Thus convergence in this case requires a zeroth-order spectral overlap between the orthogonal and reference spaces. The FD partitioning is not capable of generating this type of spectral overlap and thus yields a divergent expansion. However, the expansion is actually asymptotically convergent, with divergent behavior not displayed until the 11th order because the $|1s^22s3s\rangle$ Rydberg state is only weakly coupled with the $|1s^22p^2\rangle$ CSF and because these states are energetically well separated in zeroth order. The OPT partitioning chooses the correct zeroth-order energy ordering and thus yields a convergent expansion that is also very accurate in low orders compared to the exact solution within the basis. [S1050-2947(96)02607-8]

PACS number(s): 31.15.−p

I. INTRODUCTION

The application of many-body perturbation theory for the computation of ground-state energies provides a very popular and powerful method when the zeroth-order state yields a reasonable representation for the state of interest (e.g., a closed-shell ground state). Systems possessing degeneracies or quasidegeneracies in zeroth order (e.g., open-shell systems and excited states) can be described by multireference perturbation theory with a degenerate reference space, where the quasidegenerate case is treated by introducing an additional perturbation that lifts the imposed degeneracy. This method computes an effective Hamiltonian H_{eff} that is employed to obtain the perturbed matrix elements between the degenerate states that comprise the multireference space. A final matrix diagonalization yields the eigenvalues of interest. The widely used nondegenerate perturbation theory emerges as the special limit with a single reference configuration-state function (CSF) and thus is often called single-reference perturbation theory.

Situations arise where a single, closed-shell, zeroth-order reference state is strongly coupled with one or more excited CSF's from the orthogonal space, rendering the single-reference perturbation series either divergent or slowly convergent. When one or more of these strongly coupled excited states is not quasidegenerate with the reference space state, it is natural to employ multireference perturbation theory with a nondegenerate reference space [1,2]. This treatment includes in the reference space the states that would otherwise disrupt the perturbative convergence if left in the orthogonal space. Unfortunately, applications of multireference perturbation theory to systems with nondegenerate reference space states usually yield divergent expansions from so-called intruder states. It is widely believed that these problems exist regardless of the choice of the zeroth-order Hamiltonian H_0 (the partitioning of the full Hamiltonian H into H_0 and the perturbation V). This belief can be traced to the theoretical work of Schucan and Weidenmüller [3,4]. Our recent application [5] of double-reference perturbation theory to the hydrogen rectangular system (four hydrogen atoms arranged in a rectangular geometry) contradicts this pessimistic conclusion. Otherwise divergent perturbative expansions can be rendered convergent by carefully choosing the eigenvalues of H_0 (the zeroth-order energies). This partitioning approach utilizes a completely general form of H_0 in which the zeroth-order energies are, in principle, arbitrary, and can, therefore, be chosen in a systematic fashion to enhance convergence.

Our recent work [5] on the hydrogen rectangular system (HRS) also demonstrates the underlying reasons why variants of Epstein-Nesbet (EN) and Mǿller-Plesset (MP) partitionings produce perturbative expansions that are prone to intruder-state divergence when employed for multireference spaces. These traditional partitioning methods are inadequate because they often place the zeroth-order energies for important pairs of interspace states too close together, where a pair of interspace states is defined as consisting of one state from the reference (P) space and one from the orthogonal (Q) space. Furthermore, two-state systems, constructed from the pair of interspace states responsible for the intruder-state behavior, accurately model the divergent behavior of the full computations. Also, in contrast to the traditional partitioning methods, the method of forcing the reference space to be degenerate [denoted as forced degeneracy (FD) partitioning] does not place interspace states too close for the HRS and thus yields a convergent expansion. These conclusions are drawn from a minimum-basis-set treatment of the HRS, raising some questions as to their applicability to more ''realistic'' systems with much higher CSF dimensionalities than the eight CSF's for the ^1A_g states of the HRS. It is also of interest to determine whether simple two- (or few-) level treatments can accurately describe the convergence behavior for large-dimensionality problems.

The present work examines another four-electron system, the beryllium atom, with a basis set of moderate size that generates 1323 CSF's of ^1S symmetry. The basis set includes diffuse functions and thus also describes Rydberg states. The lowest-lying orthogonal space state with a $|1s^2 2s 3s\rangle$ occupation ''naturally'' lies below the zeroth-order $|1s^2 2p^2\rangle$ reference space state. (The $|1s^2 2s^2\rangle$ CSF is also in the reference space.) Thus, unlike the minimum-basis-set HRS, the Be system has an inherent overlap in the zeroth-order energy spectra of the P and Q spaces. The spectra of the exact states also, in a sense, overlap, since the exact state dominated by the $|1s^2 2p^2\rangle$ CSF lies above the Rydberg state dominated by the $|1s^2 2s 3s\rangle$ CSF. Many previous workers, including Schucan and Weidenmüller, believe that these conditions of zeroth-order or ''exact'' spectral overlap, of necessity produce intruder-state-induced divergence for multireference perturbation expansions. Hence, not surprisingly, Solomonson, Lindgren, and Martensson [6] and Heully and Daudey [7] obtain divergent multireference perturbation expansions from the traditional partitioning methods for the beryllium atom when both the $|1s^2 2s^2\rangle$ and $|1s^2 2p^2\rangle$ CSF's are chosen as the reference space states. The FD partitioning method forces all the reference space states to be degenerate in zeroth order and thus removes the P-Q space spectral overlap that otherwise naturally occurs for other partitioning choices. The present work provides an examination of the convergence behavior of the forced degeneracy partitioning method [5] for systems in which there exists, prior to forcing degeneracy, a spectral overlap in the zeroth-order energies of the P and Q spaces.

We obtain converged perturbative expansions that are free of intruder states for the beryllium atom by employing the optimization (OPT) partitioning [5]. This method systematically optimizes the zeroth-order energies of *only* the (few) most important zeroth-order states by a simple and efficient iterative method. The OPT approach yields a rapidly convergent perturbation series for the two eigenvalues of the effective Hamiltonian $H_{\rm eff}$. In addition to providing the ground-state energy, the diagonalized $H_{\rm eff}$ also yields the *second* excited state of ^1S symmetry, and not the first. This behavior is explained by the one-to-one mapping between zeroth-order and exact states [3,4]. The shortcomings of the other partitioning methods are predicted and/or modeled by simple two-state systems constructed from pairs of interspace states. The overall success of these simple models in explaining the behavior of the full computations suggests that interspace two-state models, or other models using a small number of states, can be employed to evaluate partitioning methods and diagnose their potential problems.

The present paper is one in a series that analyzes the high-order perturbative behavior of multireference methods for small systems where full configuration-interaction (FCI) computations are possible. These analyses are designed to further our understanding of the multireference perturbative methods in order to develop new, systematic methods that are usefully convergent when truncated at low (second or third) orders, since these low orders represent the practical limits for large systems that are not amenable to FCI. The analyses are also pursued to devise simple diagnostics that are useful for evaluating the various degrees of freedom available in multireference perturbation computations, including reference spaces and partitioning methods. For example, previous high-order computations for the HRS [5] suggest that a minimum requirement, with few exceptions, for perturbative convergence is that *all* two-state models constructed from interspace states of the full computation have radii of convergence greater than unity. These two-state analyses can be performed rather rapidly and suggest the presence of, source of, and remedies for convergence problems.

Section II reviews necessary background theory and definitions from multireference perturbation theory. The theory employs completely general definitions of the diagonal zeroth-order Hamiltonian H_0, definitions which are essential for producing multireference perturbation methods that are free from many of the convergence difficulties experienced by traditional partitioning methods. Section III describes the interspace two-state systems that provide a transparent modeling of the full computations, as described in Sec. V. The FD and OPT partitioning methods are delineated in Sec. IV. The perturbation expansions in Sec. V are carried to 40th order, and Padé approximants are tested as a means for improving the perturbative convergence. Two-state models are used in Sec. V to explain or predict the divergent character of the EN, MP, and FD perturbation expansions and the convergent nature of the OPT expansion. A discussion is provided in Secs. VII and VIII of various problems with applications of the FD and OPT partitioning methods.

II. THEORY

A. Basic formalism

Perturbative methods introduce a partitioning of the Hamiltonian H into a zeroth-order part H_0 and the perturbation V,

$$H = H_0 + V. \tag{2.1}$$

The eigenfunctions of H_0 provide a complete set of determinantal states which are partitioned into a model, or P, space with projector

$$P = \sum_i |p_i\rangle\langle p_i|, \tag{2.2}$$

and the orthogonal, or Q, space with projector

$$Q = \sum_j |q_j\rangle\langle q_j|, \tag{2.3}$$

where

$$P+Q=1. \tag{2.4}$$

The model functions $|\Psi_i^0\rangle$ are defined as the projections of the exact eigenfunctions $|\Psi_i\rangle$ onto the P space,

$$|\Psi_i^0\rangle=P|\Psi_i\rangle \quad (i=1,2,\ldots,d), \tag{2.5}$$

where d is the dimension of the model space. Conversely, the wave operator Ω transforms the model functions into their corresponding exact states,

$$|\Psi_i\rangle=\Omega|\Psi_i^0\rangle \quad (i=1,2,\ldots,d). \tag{2.6}$$

There is a one-to-one correspondence between the model functions and d exact states [3,4].

Various derivations exist for the Rayleigh-Schrödinger perturbation expansion appropriate to a complete model space [1,2,8,9]. Most derivations are based on obtaining the effective Hamiltonian H_{eff}. The simplest form is non-Hermitian and is given by

$$H_{\mathrm{eff}}=PH\Omega P. \tag{2.7}$$

An order-by-order perturbation expansion of Ω is obtained by solving the generalized Bloch equation [1,2,10]

$$[\Omega,H_0]P=[V\Omega-\Omega V\Omega]P, \tag{2.8}$$

which is applicable if the model space is either degenerate or nondegenerate. A perturbative expansion for the wave operator

$$\Omega=1+\Omega^{(1)}+\Omega^{(2)}\cdots \tag{2.9}$$

generates $\Omega^{(n)}$ as nth order in the perturbation V. Substituting Eq. (2.9) into Eq. (2.8) the nth-order expression for Ω can be written as

$$[\Omega^{(n)},H_0]P=\left[V\Omega^{(n-1)}-\sum_{m=1}^{n-1}\Omega^{(m)}V\Omega^{(n-m-1)}\right]P, \tag{2.10}$$

and the nth-order correction for the H_{eff} matrix elements involving the $|p_i\rangle$ and $|p_j\rangle$ kets is given by

$$\langle p_i|H_{\mathrm{eff}}^{(n)}|p_j\rangle=\langle p_i|PV\Omega^{(n-1)}P|p_j\rangle. \tag{2.11}$$

The explicit forms of Ω and H_{eff} depend on the ket upon which H_{eff} operates unless the reference space is degenerate and is a complete model space (a complete active space). A matrix-based iterative method has been developed by Zarrabian, Laidig, and Bartlett [11] to obtain the matrix elements of H_{eff} to arbitrarily high orders. This method is employed below and is convenient when the dimension of the Q space is not very large.

B. Zeroth-order Hamiltonian (H_0)

We consider all partitioning methods in which H_0 is written as the most general diagonal ''sum over orbitals'' form, given by

$$H_0=\sum_i \epsilon_i a_i^\dagger a_i, \tag{2.12}$$

as variants of Møller-Plesset partitioning, where the sum on i in Eq. (2.12) is over all orbitals, ϵ_i are the orbital energies, and $a_i^\dagger(a_i)$ are the creation (annihilation) operators. The orbitals for Eq. (2.12) are usually defined as eigenfunctions of Fock operators. The most natural choice for the orbital energies ϵ_i is the eigenvalue of the Fock operator defining the orbitals. However, since both the orbitals i and the energies ϵ_i in Eq. (2.12) are, in principle, arbitrary and independent, other choices may be employed to enhance convergence. The forced valence orbital degeneracy method (denoted FD) of Freed and co-workers, also called the H^v method, uses multiple Fock operators to obtain the spatial orbitals and then forces the valence orbital to be degenerate in zeroth order. Sawatzki and Cederbaum [12] and also Finley and Freed [13] employ fractional-occupancy Fock operators to enhance convergence.

The most general diagonal form of H_0 can be written as

$$H_0=\sum_i |i\rangle E_i^0\langle i|, \tag{2.13}$$

where the sum over i runs over all states, and E_i^0 is the ith-state zeroth-order energy, which is at our disposal. Usually, Epstein-Nesbet partitioning chooses the zeroth-order state energy as

$$E_i^0=\langle i|H|i\rangle, \tag{2.14}$$

which makes the diagonal elements of V vanish with either a determinantal or CSF basis. Since the H_0 differs for the latter two cases, the determinantal-based Epstein-Nesbet and CSF-based Epstein-Nesbet partitioning methods generate different perturbation expansions. (Note that a unitary transformation of the H_0 from a determinantal-based Epstein-Nesbet basis to a CSF basis leads to a nondiagonal H_0.) The computation below, denoted by EN, employs a hybrid of the determinantal- and CSF-based Epstein-Nesbet partitionings. This variant of Epstein-Nesbet partitioning defines the zeroth-order energies of each CSF by the barycentric expression [14]

$$E_i^0=\sum_d [C_d^i]^2\langle d|H|d\rangle, \tag{2.15}$$

where the CSF function $|i\rangle$ is given by a linear combination of determinantal states $|d\rangle$,

$$|i\rangle=\sum_d C_d^i|d\rangle. \tag{2.16}$$

Our previous investigation of the HRS [5] also employs this partitioning method. Except for single determinantal states $|i\rangle$, the diagonal matrix elements of the perturbation V no longer vanish for the H_0 of Eq. (2.15).

The OPT partitioning method presented below selects a small number of the zeroth-order energies E_i^0 in an optimal fashion using a CSF basis. The other states employ the above-defined barycentric EN definition for their zeroth-order energies. Note that any partitioning method that is represented in the form of Eq. (2.12) can also be expressed in the form of Eq. (2.13), but not vice versa.

III. TWO-STATE THEORY

The convergence properties for the beryllium atom computations in subsequent sections are transparently understood by the use of simple two-dimensional models that are constructed from a pair of interspace states taken from the full problem consisting of 1323 CSF's. The convergence behavior is investigated by considering the parametrized Hamiltonian H,

$$H(z)=H_0+zV, \tag{3.1}$$

where z is the complex perturbation parameter. The $z=1$ limit recovers the exact H, while $z=0$ produces the unperturbed system. Denote $|p\rangle$ and $|q\rangle$ as the P and Q space states of the two-dimensional system, and ϵ_p and ϵ_q are their zeroth-order energies, respectively. The exact eigenvalues of the two-dimensional Hamiltonian H can be expressed as

$$E_{\pm}(z)=\tfrac{1}{2}\mathrm{Tr}\mathbf{H}\pm\tfrac{1}{2}\{[\Delta\epsilon-(\Delta\epsilon-\Delta H)z]^2+4V_{pq}^2z^2\}^{1/2}, \tag{3.2}$$

where

$$V_{pq}=\langle p|V|q\rangle,$$

$$\Delta\epsilon=\epsilon_q-\epsilon_p,$$

$$\Delta H=\langle q|(H_0+V)|q\rangle-\langle p|(H_0+V)|p\rangle,$$

and the z-dependent trace of the Hamiltonian matrix $\mathbf{H}$ is given by

$$\mathrm{Tr}\mathbf{H}=\langle p|H(z)|p\rangle+\langle q|H(z)|q\rangle.$$

Both eigenvalues become degenerate in the complex z plane at the pair of branch points z_d and z_d^*, where use of Eq. (3.2) gives

$$z_d=\frac{\Delta\epsilon}{4V_{pq}^2+(\Delta\epsilon-\Delta H)^2}[(\Delta\epsilon-\Delta H)+2V_{pq}i]. \tag{3.3}$$

The radius of convergence R_c for the single-reference Rayleigh-Schrödinger perturbation expansion is $R_c=|z_d|=|z_d^*|$ and follows from Eq. (3.3) as

$$R_c=\frac{\Delta\epsilon}{\sqrt{(\Delta\epsilon-\Delta H)^2+4V_{pq}^2}}. \tag{3.4}$$

To achieve a convergent perturbation series, it is necessary to have $R_c\geqslant 1$, which occurs only if the numerator in Eq. (3.4) exceeds the denominator. This condition for convergence implies that $\Delta\epsilon$ (the zeroth-order energy difference) must satisfy the requirements

$$\Delta\epsilon\begin{cases}\geqslant\dfrac{1}{2}\left[\Delta H+\dfrac{4V_{pq}^2}{\Delta H}\right] & \text{if } \Delta H>0,\\[2ex] \leqslant\dfrac{1}{2}\left[\Delta H+\dfrac{4V_{pq}^2}{\Delta H}\right] & \text{if } \Delta H<0.\end{cases} \tag{3.5}$$

Thus both $\Delta\epsilon$ and ΔH must have the same sign; otherwise the perturbation series diverges. Also, when $\Delta H\neq 0$, Eq. (3.5) indicates that $\Delta\epsilon$ can always be selected so that $R_c>1$. This last conclusion is also reached by examining the maximum radius of convergence R_c as a function of $\Delta\epsilon$ [15]. If either V_{pq} is modestly large or ΔH is modestly small, traditional partitioning methods, such as EN and MP, frequently yield divergent expansions, since $\Delta\epsilon$ is then often too small and leads to $R_c<1$. If either V_{pq} is very large or ΔH is very small while $\Delta\epsilon$ is large enough so that $R_c>1$, then the convergence is very slow. Qualitatively, the presence of large values of the parameter $V_{pq}/\Delta H$ seems to be most important in adversely influencing convergence. However, the quantitative dependence of the convergence rate on V_{pq} and ΔH has not been investigated.

Intruder states are defined as the orthogonal space states responsible for destroying the convergence of a perturbation expansion. The presence of intruder states is usually detected by observing the variation of the eigenvalues as a function of the perturbation parameter z for real z. An avoided crossing point z_{ac} occurs where the two eigenvalues are closest. The z_{ac} is computed in the two-state model by minimizing $[E_-(\mathrm{Re}\,z)-E_+(\mathrm{Re}\,z)]$ with respect to z,

$$z_{\mathrm{ac}}=\frac{\Delta\epsilon(\Delta\epsilon-\Delta H)}{4V_{pq}^2+(\Delta\epsilon-\Delta H)^2}. \tag{3.6}$$

Comparing this equation with Eq. (3.3) shows that z_{ac} is simply $\mathrm{Re}\,z_d$. [Note that the eigenvalues $E_-(z)$ and $E_+(z)$ cannot be degenerate for real z when $V_{pq}\neq 0$.] When the avoided crossing appears with $0<z_{\mathrm{ac}}<1$ and hence the perturbation expansion diverges ($R_c<1$), then the convergence is disrupted by what is termed a front-door intruder state. Similarly, an avoided crossing with $z_{\mathrm{ac}}<0$ is called a back-door intruder state [16,17] when $R_c<1$. Equation (3.6) implies that a back-door intruder state $z_{\mathrm{ac}}<0$ occurs whenever ΔH and $\Delta\epsilon$ have the same signs and satisfy $|\Delta H|>|\Delta\epsilon|$. On the other hand, if $\Delta\epsilon$ and ΔH are of opposite signs or if $|\Delta H|<|\Delta\epsilon|$, then the avoided crossing appears with $z_{\mathrm{ac}}>0$.

We define correct energy ordering as the relative ordering of the zeroth-order energies that is a necessary, but not a sufficient, condition for convergence ($R_c>1$). Since $\Delta\epsilon$ and ΔH must have the same sign for a convergent two-state system, when $\langle p|H(1)|p\rangle>\langle q|H(1)|q\rangle$, the correct energy ordering is $\epsilon_p>\epsilon_q$. Similarly, if $\langle p|H(1)|p\rangle<\langle q|H(1)|q\rangle$ then the correct ordering is $\epsilon_p<\epsilon_q$.

For incorrect energy ordering, the limit of $V_{pq}\to 0$ has z_d real and positive ($\mathrm{Im}\,z_d\to 0$) with

$$z_d\to\frac{\Delta\epsilon}{(\Delta\epsilon-\Delta H)}. \tag{3.7}$$

Equation (3.7) also emerges when the z-dependent diagonal elements of H are degenerate. In actual calculations involving a large number of states, if the incorrectly ordered interspace states are weakly coupled, both among themselves and to other states, then both z_d and z_{ac} are approximately equal to the value of z for which the diagonal elements of $H(z)$ are degenerate. Furthermore, such cases yield a very pronounced avoided crossing with the energies, and wave functions change abruptly in the vicinity of z_d. This situation is found in Sec. V for the computation involving the FD partitioning, where the $|1s^22s3s\rangle$ state (the intruder state) is incorrectly placed above the $|1s^22p^2\rangle$ reference state in zeroth order. By

TABLE I. Zeroth-order energies of the eight lowest-lying CSF's (in a.u.).

CSF	EN	MP	FD	OPT	preFD[a]	$\langle H\rangle$[b]
$\vert 1s^2 2s^2\rangle$	−14.571 90	−10.081 75	−10.019 26	−14.571 90	−10.081 75	−14.571 90
$\vert 1s^2 2s3s\rangle$	−14.317 82	−9.663 00	−9.631 76	−14.317 82	−9.663 00	−14.300 93
$\vert 1s^2 2p^2\rangle$	−14.197 05	−9.374 64	−10.019 26	−14.197 05	−9.956 78	−14.168 71
$\vert 1s^2 2s4s\rangle$	−14.041 55	−9.332 00	−9.300 76	−13.841 55	−9.332 00	−14.015 07
$\vert 1s^2 2p3p\rangle$	−14.079 66	−9.249 93	−9.572 24	−13.779 66	−9.541 00	−14.005 18
$\vert 1s^2 3s^2\rangle$	−13.934 86	−9.244 25	−9.244 25	−13.934 86	−9.244 25	−13.934 86
$\vert 1s^2 3p^2\rangle$	−13.954 95	−9.125 22	−9.125 22	−13.554 95	−9.125 22	−13.931 05

[a] Zeroth-order energies from FD partitioning prior to forcing the $2s$ and $2p$ orbitals to be degenerate.

[b] Expectation values of the Hamiltonian.

contrast, when a two-state system has the zeroth-order states correctly ordered, the limit of $V_{pq}\to 0$ then produces a convergent expansion with $R_c\to\infty$. In addition, the special case of $\Delta H=\Delta\epsilon$ (i.e., for Epstein-Nesbet partitioning) yields the avoided crossing point at $z_{\mathrm{ac}}=0$, since z_d is purely imaginary [see Eq. (3.3)]. A two-state system with barycentric EN partitioning does not produce a purely imaginary degeneracy point z_d, unless both states are determinantal states.

It should be emphasized that many formally divergent series are asymptotically convergent and are quite useful if they provide good approximations when truncated at low orders (e.g., Stirling's formula for the expansion of $\ln n!$). Thus, when divergent series are obtained from the full-scale calculations, these series are analyzed below to assess their useful asymptotic character and their behavior when resummed by Padé approximants.

IV. METHODS

We employ a $6s5p1d$ basis set for Be constructed from the 6-311 G set of Krishnan *et al.* [18] with two added diffuse s and p Gaussian functions (exponents 0.207 and 0.069) to describe the excited Rydberg states. The ^1S ground-state energy from a full configuration-interaction calculation is −14.636 853 45 a.u. The self-consistent-field (SCF) energy from the $|1s^2 2s^2\rangle$ CSF is −14.571 903 77 a.u. The $|1s^2 2s^2\rangle$ and $|1s^2 2p^2\rangle$ CSF's are taken as the reference functions (P space), a double reference space, and there are a total of 1323 CSF's of ^1S symmetry.

We have applied the configuration-based multireference perturbation theory algorithm [11,19,20] to evaluate the energy through 40th order using Epstein-Nesbet (EN), Mϕller-Plesset (MP), forced valence orbital degeneracy (denoted as FD), and optimized zeroth-order energy partitioning (denoted as OPT). Table I displays the zeroth-order energies for these partitioning schemes as well as the expectation values of H for the eight lowest CSF's. All the partitioning methods listed in Table I, except the FD partitioning, place the zeroth-order energy of the $|1s^2 2s3s\rangle$ Q space state below that of the $|1s^2 2p^2\rangle$ P space state. Hence a P-Q space overlap exists for the zeroth-order energy spectra. Diagonalization of the full 1323-dimensional CI matrix shows that the ground and the second excited states for beryllium are primarily described by the $|1s^2 2s^2\rangle$ and $|1s^2 2p^2\rangle$ CSF's from the reference space, whereas the first excited state is a Rydberg state dominated by the $|1s^2 2s3s\rangle$ CSF from the orthogonal space (Q). Thus, in a sense, the exact spectrum also has a P-Q space spectral overlap. The $|1s^2 2s^2\rangle$, $|1s^2 2s3s\rangle$, and $|1s^2 2p^2\rangle$ CSF's cumulatively contribute 91%, 89%, and 66% to the ground, first, and second excited states, respectively.

A. Forced valence orbital degeneracy (FD) partitioning

The molecular orbitals and zeroth-order energies for the MP partitioning are taken as the eigenfunctions and eigenvalues of the closed-shell ground-state Fock operator. The FD partitioning defines all orbitals and their energies the same way as in MP partitioning, except that the $2p$ valence orbital energy ϵ_{2p} *before averaging* is defined as the expectation value of an ($N-1$)-electron Fock operator $\hat{f}^{(N-1)}$ with respect to one of the $2p_\alpha$ spin orbitals. (The orbitals for both α and β spins are degenerate.) This $\hat{f}^{(N-1)}$ operator has an occupation of $1s_\alpha 1s_\beta 2s_\alpha$, and its spin-independent form when operating on an α-spin orbital is given by [13]

$$\hat{f}^{(N-1)}=h(1)+2J_{1s}-K_{1s}+J_{2s}-K_{2s}, \tag{4.1}$$

where J and K are the spin-independent Coulomb and exchange operators, respectively. Equation (4.1) is the same as the ground-state, closed-shell N-electron Fock operator $\hat{f}^N$, except for the absence of a single $2s$ Coulomb operator J_{2s}. For FD partitioning, the orbital energies for the $2s$ and $2p$ valence orbital are then replaced by their average value $\epsilon_{\bar{v}} = \frac{1}{4}(\epsilon_{2s}+3\epsilon_{2p})$. Virtually all multireference perturbative computations performed by Freed and co-workers employ the H^v method [13,21–25]. These computations use reference spaces that are defined by a complete active space (CAS) and forced degenerate valence orbitals that are eigenfunctions of V^{N-1} potentials.

B. Zeroth-order energy optimization (OPT) partitioning

We now consider the recently introduced optimization partitioning method [5] in which some of the zeroth-order state energies E_i^0 in Eq. (2.13) are determined in an optimal manner from calculations using a small subset of zeroth-order states. Any criterion for defining the optimized zeroth-order energies depends on the type of convergence required. For example, a criterion producing the most favorable convergence in high orders may be unsatisfactory in low orders where practical computations are often truncated. Our goal is to optimize the performance of the OPT method in third order, which represents the practical limit of large-scale multireference perturbation calculations. Therefore we begin by

TABLE II. The ground-state energy (in a.u.) as computed by multireference perturbation theory through 40th order (N) using a double-reference space. Various partitioning methods are employed, and $[N,M]$ Padé approximants are constructed from the asymptotic FD expansion. All entries are the differences from the FCI energy. (Negative entries imply energies higher than FCI.) The FCI energy is −14.636 853 45 a.u., and the first-order deviation from the FCI is 0.054 174 62 a.u. for all partitioning methods considered, since all methods use the same ket basis.

N	EN	MP	FD	$[N,M]$	Padé	OPT
2	−0.020 845 86	−0.005 531 58	0.000 927 70			0.005 310 94
3	0.005 324 80	0.002 967 53	0.002 326 80	[1,0]	0.000 732 56	−0.000 019 79
4	0.013 243 79	0.008 915 70	0.000 767 89	[1,1]	0.002 290 98	−0.000 703 27
5	−0.020 401 36	−0.017 034 53	0.000 128 27	[2,1]	0.001 541 14	−0.000 724 95
6	−0.011 011 47	0.006 034 78	0.000 167 22	[2,2]	0.000 606 69	−0.000 037 54
7	0.029 905 70	0.011 687 56	0.000 088 08	[3,2]	0.000 271 07	0.000 456 22
8	−0.007 976 40	−0.293 065 66	0.000 055 00	[3,3]	0.000 086 87	0.000 340 11
9	−0.305 410 59	0.020 472 84	0.000 044 31	[4,3]	0.000 048 91	0.000 175 36
10	0.071 595 60	−0.002 617 96	0.000 034 73	[4,4]	0.000 028 86	0.000 017 05
11	0.067 518 48	−3.557 520 86	0.000 036 64	[5,4]	0.000 022 87	−0.000 067 42
12	−2.127 698 40	−0.008 348 56	0.000 047 29	[5,5]	0.000 027 95	−0.000 039 47
13	−0.081 428 72	−0.583 217 34	0.000 064 34	[6,5]	0.000 048 70	0.000 013 75
14	0.171 957 23	−25.771 912 6	0.000 086 70	[6,6]	0.000 008 49	0.000 048 01
15	−5.080 526 01	61.523 473 0	0.000 113 39	[7,6]	0.000 610 51	0.000 052 07
16	−16.306 531 55	−46.377 925 7	0.000 144 96	[7,7]	−0.000 036 79	0.000 026 76
17	34.051 798 78	−158.470 675	0.000 183 31	[8,7]	0.000 088 95	−0.000 003 13
18	5.312 036 56	613.359 055 0	0.000 231 39	[8,8]	0.000 021 37	−0.000 019 64
19	−122.943 336 16	−887.322 692	0.000 293 10	[9,8]	0.000 010 09	−0.000 020 08
20	53.247 251 15	−669.434 155	0.000 373 22	[9,9]	0.000 010 66	−0.000 009 27
21			0.000 477 88	[10,9]	0.000 010 04	0.000 002 68
22			0.000 615 46	[10,10]	0.000 001 70	0.000 008 37
26			0.001 867 44	[12,12]	−0.000 004 46	−0.000 004 55
30			0.010 627 49	[14,14]	−0.000 005 12	0.000 002 16
35			−0.357 729 24	[17,16]	−0.000 005 80	−0.000 000 40
40			−1.890 965 11	[19,19]	−0.000 001 78	0.000 000 20

considering a sum S consisting of the absolute deviations for the third- and fourth-order energies from the FCI. Explicitly, this sum is written as

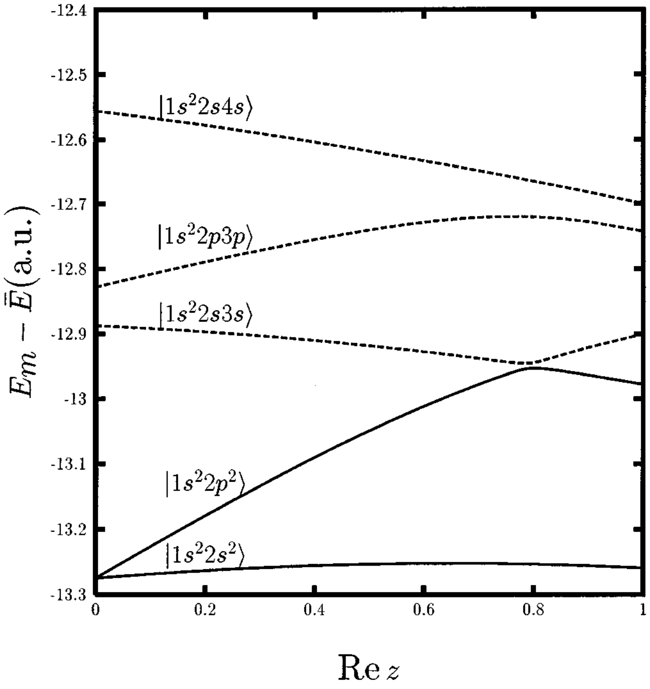
$$S=|E_{\mathrm{FCI}}-E_3|+|E_{\mathrm{FCI}}-E_4|, \tag{4.2}$$

where E_3 and E_4 are the third- and fourth-order approximations to the FCI energy E_{FCI}. Our goal of obtaining the most accurate possible third-order energies explains why the first term in expression (4.2) is present. Inclusion of the second term involving E_4 appears to be useful for generating a unique solution for the optimized zeroth-order energies. We have tried other combinations containing the second- and third-order deviations that are less satisfactory for third-order computations, probably because the second-order deviation is normally much larger than that from third order.

Since large-scale calculations of interest cannot, of course, obtain E_{FCI}, some approximations are necessary in order to minimize S. Fortunately, only a small number of states are responsible either for ‘‘driving’’ the convergence or for producing a divergent series. Therefore, to obtain accurate results, we only need to minimize S with respect to the zeroth-order energies of the important states for describing the state of interest. For the OPT computation presented below, E_{FCI} in expression (4.2) is taken as the ground-state eigenvalue from a small CI computation containing only the eight lowest-lying states. These eight zeroth-order states include the dominant states for representing both the ground and second excited states. Also, E_3 and E_4 in Eq. (4.2) are the perturbative energies from a perturbative expansion computed with just these eight states—two P space and six Q space states. The optimization method is achieved iteratively and, except for a constant shift, defines these eight zeroth-order energies. Therefore we uniquely specify the zeroth-order energies of these eight states by selecting the zeroth-order energy of the (single determinantal) $|1s^2 2s^2\rangle$ state as its Epstein-Nesbet partitioning value (its expectation value of H). Similarly, the zeroth-order energies E_i^0 for the (unoptimized) remaining higher-lying states are chosen to be their values from the Epstein-Nesbet variant defined by Eq. (2.15). Computations for other systems may require the consideration of more or less than eight states, but the present example serves to illustrate the excellent convergence produced by optimizing the zeroth-order energies for a very small subset of all states.

V. RESULTS

The computed order-by-order perturbative energies for the ground and the *second* excited states of the beryllium



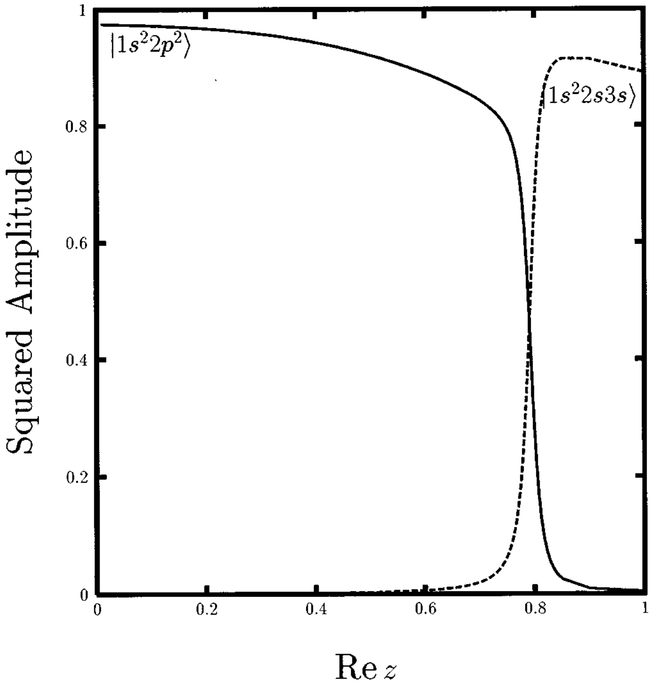


FIG. 1. The five lowest ^1S state FCI energies for the beryllium atom using FD energy partitioning and presented as a function of the real perturbation parameter z with H given by Eq. (3.1). The states are labeled by their unperturbed limit for $z\rightarrow 0$. States which become (correspond to) P space state for $z\rightarrow 0$ are presented by a solid line, and dashed lines are used for states that become Q space states.

FIG. 2. The squared probability amplitudes of the two dominant CSF's for the beryllium atom first excited ^1S state using FD partitioning as a function of real z.

atom are displayed through 40th order in Tables II and III, respectively, for both the FD and OPT partitioning schemes. The divergent MP and EN partitioning series are also presented. The first excited state is not obtained by the perturbation expansions, since this is a Rydberg state that is dominated by the $|1s^22s3s\rangle$ CSF from the Q space and it is, therefore, not described by the reference space. The perturbative expansions for the ground- and second-excited-state eigenvalues are either both divergent or both convergent, because both eigenvalues depend on the same effective Hamiltonian $H_{\rm eff}$. Furthermore, the radii of convergence are equivalent for both the ground- and the second-excited-state energies. Tables II and III indicate that the FD partitioning perturbation expansions diverge for both eigenvalues, but they are well behaved in low orders. The series are asymptotically convergent. The low orders are of particular interest, since a low-order truncation is almost always required for actual computations involving more than a very small number of electrons. The OPT partitioning expansions, on the other hand, are convergent and extremely accurate in low orders, especially for the ground state. The third- and fourth-order ground-state eigenvalues from the OPT partitioning deviate only by 0.012 and 0.44 kcal/mol from the FCI, respectively, compared to 1.46 and 0.48 kcal/mol for the FD partitioning. The second-excited-state eigenvalues are somewhat less accurate. The OPT-partitioning, third- and fourth-order second-excited-state eigenvalues are 1.41 and 5.0 kcal/mol from the FCI, respectively, compared to 13.7 and 2.2 kcal/mol for the FD partitioning.

Tables II and III also display the $[N,N-1]$ and the $[N,N]$ Padé resummations [26] of the order-by-order FD partitioning eigenvalues through 40th order. The resummed Padé approximants for each eigenvalue series yield slightly worse agreement with the FCI in low orders, but the high orders are better behaved. Note that it is most appropriate to compare a given $[N,N-1]$ or $[N,N]$ Padé approximant with the highest perturbative order needed to obtain that approximant. For example, perturbative orders through $N=3$ are needed to generate the [1,0] approximant. Therefore the eigenvalue computed perturbatively through third order is on the same line in Tables II and III with the [1,0] approximant.

A. Analysis of why FD partitioning yields a divergent expansion: Incorrect energy ordering

The following examines the FD partitioning eigenvalues and eigenfunctions, obtained from the z-dependent FCI, as a function of the perturbation parameter z for the complex $H(z)$ given by Eq. (3.1). This analysis yields the radius of convergence R_c as defined by $|z_d|$, where z_d is the closest degeneracy point to the origin involving two states that become an interspace pair of states as $z\rightarrow 0$. One of the two degenerate states at $z=z_d$ evolves into a P space state as $z\rightarrow 0$ (called a P-corresponding state) and the other to a Q space state (called a Q-corresponding state). All partitioning methods considered below have one of the degenerate states at z_d evolve into the $|1s^22p^2\rangle$ (P space) CSF when $z\rightarrow 0$. The intruder state is defined as the *zeroth-order state* from the Q space state that contributes most to the P-corresponding state in the vicinity of z_d. Other slightly different definitions of intruder states have also been used. Schucan and Weidenmüller [3,4] identify problematic "collective states," composed predominantly of Q space states, that near $z=1$ describe low-lying exact states.

TABLE III. Same as Table II except that the entries are for the second excited state. The FCI energy is −14.277 595 96 a.u., and the first-order deviation from the FCI is 0.119 661 97 a.u.

N	EN	MP	FD	$[N,M]$	Padé	OPT
2	−0.046 035 90	−0.044 418 06	0.056 037 70			0.003 960 69
3	−0.009 743 71	0.013 174 40	0.021 938 98	[1,0]	0.055 750 49	0.002 253 27
4	0.068 799 98	0.050 226 37	0.003 495 35	[1,1]	−0.017 441 23	−0.008 445 26
5	−0.051 747 88	−0.099 861 68	−0.004 649 63	[2,1]	−0.018 233 55	−0.007 054 38
6	−0.075 018 65	0.046 676 37	−0.006 442 30	[2,2]	−0.017 507 46	−0.002 940 43
7	0.198 170 29	0.215 579 56	−0.005 098 67	[3,2]	0.019 314 24	0.000 671 22
8	0.006 031 94	−0.304 006 56	−0.003 023 61	[3,3]	0.000 406 27	0.001 712 13
9	−0.262 290 93	0.483 252 91	−0.001 558 99	[4,3]	−0.004 301 33	0.001 055 42
10	0.467 985 72	0.930 086 23	−0.001 179 62	[4,4]	−0.002 554 80	0.000 112 02
11	0.945 779 37	−0.333 050 49	−0.001 794 65	[5,4]	−0.003 262 04	−0.000 539 23
12	−0.327 364 42	5.720 397 67	−0.003 059 83	[5,5]	0.002 788 72	−0.000 641 42
13	−0.440 686 21	1.777 240 51	−0.004 629 46	[6,5]	−0.018 564 24	−0.000 362 22
14	7.438 533 54	−0.185 009 03	−0.006 298 40	[6,6]	0.018 548 97	−0.000 027 68
15	−0.760 565 59	−0.718 034 69	−0.008 040 60	[7,6]	−0.002 021 94	0.000 189 05
16	−0.772 534 15	2.153 977 77	−0.009 977 06	[7,7]	−0.001 419 26	0.000 225 41
17	0.394 733 44	2.788 430 93	−0.012 313 93	[8,7]	−0.006 026 45	0.000 126 10
18	13.187 880 99	−4.452 653 48	−0.015 285 68	[8,8]	0.000 770 51	−0.000 002 94
19	−2.095 364 49	13.629 471 09	−0.019 123 68	[9,8]	0.000 072 67	−0.000 084 67
20	12.797 282 81	84.976 719 41	−0.024 054 46	[9,9]	0.000 131 8	−0.000 091 45
21			−0.030 321 49	[10,9]	0.000 089 87	−0.000 042 62
22			−0.038 219 27	[10,10]	−0.000 098 62	0.000 015 7
26			−0.095 796 12	[12,12]	−0.000 003 85	−0.000 013 39
30			−0.244 261 21	[14,14]	−0.000 006 14	−0.000 009 44
35			−0.369 848 35	[17,16]	−0.000 005 66	−0.000 006 04
40			−0.365 415 34	[19,19]	−0.000 038 46	0.000 000 77

Figure 1 presents the variation of the FCI energies as a function of real z for the ground state ($m=0$) and the four lowest excited states ($m=1$, 2, 3, and 4) from FD partitioning computations, where $H(z)$ is given by Eq. (3.1). (Only the lower-lying states in Fig. 1 are discussed). The eigenvalues in Fig. 1 are presented as $(E_m-\overline{E})$, instead of simply as E_m, since the former yields a much smaller ordinate range, where $\overline{E}$ is the z-dependent average energy of the eight lowest-lying states. (Note that the FCI eigenvalues are independent of the perturbative partitioning only for $z=1$.) For clarity, an avoided crossing point involving the first- and second-excited-state energies is denoted as $z_{\mathrm{ac}}^{(1,2)}$, while the degeneracy point defining R_c is written as $z_d^{(1,2)}$. Figure 1 exhibits an avoided crossing between the first- and second-excited-state energies for $z_{\mathrm{ac}}^{(1,2)}=0.79$. Since the first and second excited states are nearly degenerate at $z_{\mathrm{ac}}^{(1,2)}$, we anticipate that $z_d^{(1,2)}\approx z_{\mathrm{ac}}^{(1,2)}$ and that the imaginary component of $z_d^{(1,2)}$ is small.

Figures 2 and 3 depict the composition of the first and second excited ^1S state wave functions for the FD partitioning by presenting the squared CSF (probability) amplitudes (the squared expansion coefficients) as a function of real z. The first- and second-excited-state wave functions undergo a ‘‘transition’’ at $z_{\mathrm{ac}}^{(1,2)}$. The first excited state is dominated by the $|1s^2 2p^2\rangle$ state for $z<z_{\mathrm{ac}}^{(1,2)}$, while the $|1s^2 2s3s\rangle$ Rydberg state dominates for $z>z_{\mathrm{ac}}^{(1,2)}$, and vice versa for the second excited state. Thus the intruder state is clearly the zeroth-order $|1s^2 2s3s\rangle$ state. The zeroth-order $|1s^2 2p^2\rangle$ state is what we have termed the ‘‘departing’’ state, since, in a sense, it exits the reference space. The $|1s^2 2s3s\rangle$ and $|2s^2 2p^2\rangle$ states are the dominant CSF's for describing the first- and second-excited-state wave functions in the vicinity of $z_d^{(1,2)}$ (and to some extent in the region beyond $z_d^{(1,2)}$). Thus a two-state system composed exclusively of the $|2s^2 2p^2\rangle(\equiv|p\rangle)$ and $|1s^2 2s3s\rangle(\equiv|q\rangle)$ states provides a model for interpreting the divergence of the full computation involving all 1323 states. This model uses the same zeroth-order energies as defined by FD partitioning for the full computation involving all 1323 states. Also, the two states are weakly coupled with $V_{pq}=0.022\,09$ a.u. (See Sec. III for the two-state theory and notation.) The degeneracy points for this model occur at $z_d^m=0.74+i0.06$ and also, of course, at $(z_d^m)^*$. The avoided crossing point z_{ac}^m is just Re z_d^m. Thus we have $z_{\mathrm{ac}}^m=0.74$, which agrees reasonably well with $z_{\mathrm{ac}}^{(1,2)}=0.79$ for the full computations. The modest difference of 0.05 between $z_{\mathrm{ac}}^{(1,2)}$ and z_{ac}^m probably occurs because the $|1s^2 2s^2\rangle$ and $|1s^2 2p3p\rangle$ states provide non-negligible contributions to the second excited state (see Fig. 3) and thus apparently influence the precise location of $z_{\mathrm{ac}}^{(1,2)}$.

The perturbative divergence ($R_c<1$) for this two-state model occurs for FD partitioning because of incorrect energy ordering. Since $\langle p|H|p\rangle>\langle q|H|q\rangle$ ($z=1$), we must then have $\langle p|H_0|p\rangle>\langle q|H_0|q\rangle$ ($\epsilon_p>\epsilon_q$) or the two-state model series diverges ($R_c<1$). Unfortunately, the FD partitioning forces $\epsilon_p<\epsilon_q$, which results from defining the $2p$ orbital energy from a potential generated by only $(N-1)$ electrons (also called a V^{N-1} potential [13,27]), while using a V^N po-

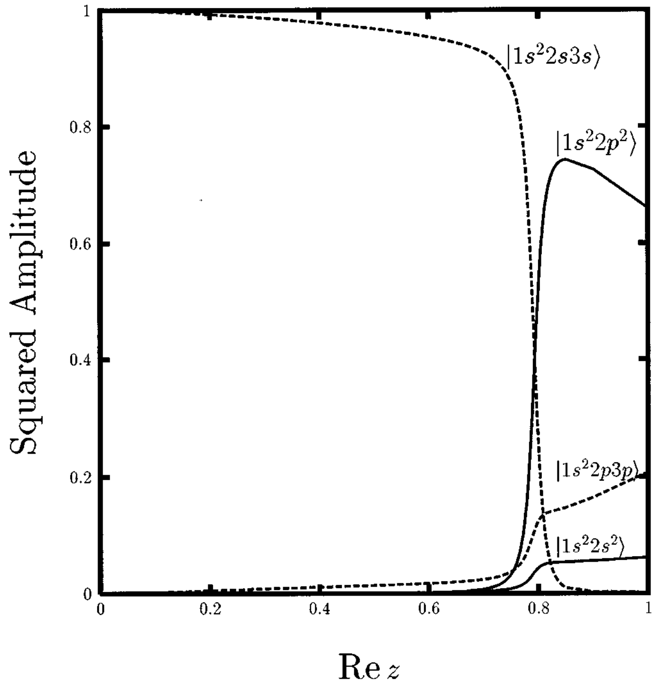


FIG. 3. Same as in Fig. 2, but for the second excited state.

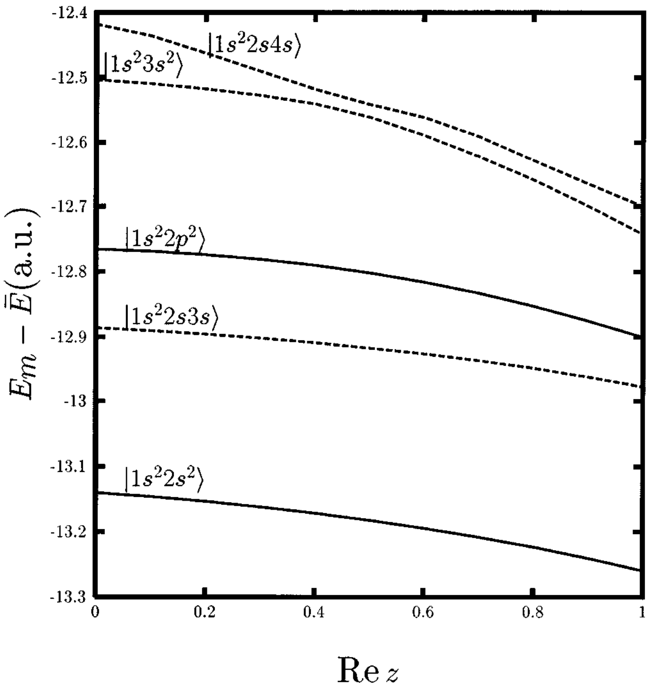


FIG. 4. Same as in Fig. 1, but for OPT partitioning.

tential for the singlet 3s orbital. (See Table I, column labeled preFD, for the zeroth-order state energies prior to forcing degeneracy.) The forcing of the 2s and 2p orbitals to be degenerate moves the $|1s^22s3s\rangle$ and $|2s^22p^2\rangle$ states slightly farther apart in zeroth order than they would otherwise be if no forced degeneracy were imposed. (Other states are, of course, also affected by forcing degeneracy.) Since this two-state system adequately models the convergence properties of the full computation, it is clear that the full FD computation also diverges from incorrect energy ordering. In addition, as is observed for other two-state systems [28], the weak coupling between the $|1s^22s3s\rangle$ and $|2s^22p^2\rangle$ states leads to the expectation that the wave functions and energies for these states exhibit an abrupt change in the region of their avoided crossing. This ‘‘transition’’ behavior is precisely what is observed in Figs. 2 and 3 for $z\approx z_{\mathrm{ac}}^{(1,2)}$. In contrast, when the pair of interstate space states is strongly coupled, the wave functions and energies change gradually in the vicinity of the degeneracy point (see Ref. [5] for examples).

Consider the two-state model discussed in the previous paragraph, with V_{pq} made arbitrarily small, but not with $V_{pq}=0$. Then we get

$$\lim_{V_{pq}\to 0} z_d^m = z_d^0, \tag{5.1}$$

where $z_d^0=0.74+i0$. Hence this degeneracy point occurs where the diagonal matrix elements $H(z)$ of the two states cross (see Sec. III). In contrast, a partitioning method with the correct energy ordering does not have its diagonal matrix elements of $H(z)$ cross as a function of z for pairs of interspace states. Since z_d^0 is close to z_d^m for the two-state model with $V_{pq}=0.022\,09$ a.u., the coupling between these states plays a rather minor role in understanding the divergence for the full computation involving all 1323 states.

B. Analysis of why EN and MP partitioning yield divergent expansions

The divergent behavior of EN and MP expansions is anticipated because both series possess interspace states that produce $R_c<1$ from two-state models. For EN partitioning, the two-state model, composed of the $|1s^22p^2\rangle(\equiv|p\rangle)$ and $|1s^22p3p\rangle(\equiv|q\rangle)$ states, has $z_d^m=-0.08\pm0.46i$ with $R_c=0.46$. The same model yields $R_c=0.49$ and $z_d^m=-0.07\pm0.48i$ for MP partitioning. In addition, MP partitioning provides the two-state model of the $|1s^22p^2\rangle$ and $|1s^22s4s\rangle(\equiv|q\rangle)$ states that yields $z_d^m=-0.37\pm0.08i$ with $R_c=0.38$. The divergence of these EN and MP partitioning models arises from the zeroth-order energy differences being too small, but correctly ordered. However, the zeroth-order P space energies are not quasidegenerate. (A detailed account of the inadequacies of the MP and EN partitionings is given elsewhere [5].) Since there are *two* different two-state models that produce $R_c<1$ for MP partitioning, we anticipate that quantitative agreement between $z_d^{(1,2)}$ and z_d requires using the three-state model composed of the $|1s^22p^2\rangle(\equiv|p\rangle)$, $|1s^22p3p\rangle(\equiv|q\rangle)$, and $|1s^22s4s\rangle(\equiv|q'\rangle)$ states. (A preliminary investigation supports this hypothesis.)

C. Analysis of the convergent OPT partitioning method

Figure 4 displays the z-dependent energies from the FCI for the five lowest states as computed with OPT partitioning. No avoided crossings are present for Re z between -1 and $+1$, indicating that probably $R_c>1$, in agreement with the order-by-order computations. Unlike the case with FD partitioning, the zeroth-order energy of the $|1s^22p^2\rangle$ P space state exceeds that of the $|1s^22s3s\rangle$ Rydberg state. This energy ordering generates the correct one-to-one mapping between these zeroth-order states and their corresponding exact states for $z=1$. The $|1s^22s3s\rangle$ state evolves into the (exact) first excited state when Re z adiabatically changes from zero to unity, while the $|1s^22p^2\rangle$ CSF evolves into the second excited state. Thus, besides converging to the ground-state energy, the perturbation expansion yields the *second* excited state, and not the first.

VI. DISCUSSION

Schucan and Weidenmüller hypothesize that multireference perturbation expansions must diverge whenever an exact state, which is predominantly composed of configurations outside the reference space, appears within the energy spectrum of the exact states that are predominantly represented by reference space states [3,4]. This conjecture emerges from using a zeroth-order Hamiltonian in which the zeroth-order P and Q space states are not permitted to overlap in energy. We have demonstrated that this pessimistic conclusion is *not* valid if the restriction is lifted to allow energy overlap between the zeroth-order P and Q spaces. Perturbative computations with overlapping P-Q space energy spectra can have the zeroth-order energies of their interspace states correctly ordered and, therefore, produce convergent expansions. For example, the OPT computation for the beryllium atom places the P space $|1s^22s^2\rangle$ CSF above the Q space $|1s^22s3s\rangle$ (Rydberg) CSF. Besides converging to the ground-state energy, the perturbative computation of two reference states converges to the *second* excited state, and not the first.

We have examined the radii of convergence for the multireference perturbation expansion of the beryllium atom energies using MP, EN, FD, and OPT partitioning with a double-reference space composed of the $|1s^22p^2\rangle$ and $|1s^22s^2\rangle$ CSF's. Consider now the single-reference computation with a P space consisting of only the $|1s^22p^2\rangle$ CSF and with the $|1s^22s^2\rangle$ CSF now placed into the Q space. The radius of convergence for the single-reference space computation must be identical to that for the double-reference space if the $|1s^22p^2\rangle$ and $|1s^22s^2\rangle$ states are well separated in zeroth order so that the $|1s^22s^2\rangle$ state does not act as an intruder state. Furthermore, since these two states are only weakly coupled ($V_{pq}=0.02$ a.u.), we anticipate that a single-reference treatment to high orders with the $|1s^22p^2\rangle$ CSF should give similar order-by-order excited-state energies as those from the double-reference space. Further improvement in the perturbative convergence is expected if the $2p$ orbitals are defined from a $|1s^22p^2\rangle$ SCF computation, as opposed to the present computations which use SCF orbitals based on a $|1s^22s^2\rangle$ configuration, used here only to conform with previous multireference perturbation theory treatments of the Be atom. The present choice introduces strong coupling ($V_{pq}=0.13$ a.u.) between the $|1s^22p^2\rangle$ and $|1s^22p3p\rangle$ CSF's and yields $V_{pq}/\Delta H=1.29$, where ΔH is the difference in the expectation values of the Hamiltonian for the $|1s^22p^2\rangle$ and $|1s^22p3p\rangle$ CSF's. Such a large $V_{pq}/\Delta H$ ratio slows the convergence [5].

Traditional perturbative partitionings, such as variants of Møller-Plesset and Epstein-Nesbet partitionings, select H_0 without regard to the the couplings between the zeroth-order states. These approaches often produce convergence difficulties in situations where the ratio $V_{pq}/\Delta H$ is large for one or more pairs of interspace states, where a pair of interspace states is defined as consisting of one state from the reference (P) space and one from the orthogonal (Q) space. When two interspace states have a large $V_{pq}/\Delta H$ ratio, intruder states often plague the convergence of the perturbation expansion for traditional partitionings because certain energy denominator factors are frequently too small. This small-denominator situation typically leads to backdoor intruder states (see Ref. [5]), with the avoided crossings occurring for $z_{\mathrm{ac}}<0$ when the interspace states are correctly ordered. [On the other hand, ‘‘true’’ Epstein-Nesbet partitioning (with vanishing diagonal elements of V) is predicted to have a purely imaginary z_d, at least for two-state systems. Our investigations for Be and the HRS [5] employ the variant of Epstein-Nesbet given by Eq. (2.15), where the diagonal elements of V are nonzero and two-state systems do not yield a purely imaginary z_d.]

In contrast, when important zeroth-order states are incorrectly energy ordered, the avoided crossing can appear for $z_{\mathrm{ac}}>0$, a ‘‘front-door’’ intruder state. This type of divergence is characterized by the presence of a high-lying reference (P) space state, which, in a sense, ‘‘departs’’ from the ‘‘reference’’ space (the departing state), and of a Q space state which simultaneously ‘‘intrudes’’ into the ‘‘reference’’ space. In other words, the departing state is a zeroth-order state that describes a P-corresponding state for Re $z<z_{\mathrm{ac}}$ and a Q-corresponding state for Re $z>z_{\mathrm{ac}}$, and vice versa for the intruder state, where a P- (Q)-corresponding state is defined as one that evolves into a zeroth-order P (Q) space state for Re$z\rightarrow 0$. Furthermore, the intruder and departing states have their zeroth-order energies in the opposite ordering from that given by their expectation values of H. In contrast to backdoor intruder states, perturbative divergences induced by front-door intruder states (or departer states) may have rather small ratios $V_{pq}/\Delta H$ for the incorrectly ordered states. In such cases, when $V_{pq}/\Delta H$ is small or when both incorrectly ordered states produce insignificant contributions to the state(s) of interest, the perturbative convergence can be usefully asymptotic. An exception arises when the unimportant incorrectly ordered states are quasidegenerate in zeroth order because a large $V_{pq}/\Delta\epsilon$ ratio can generate divergent behavior in low orders, where $\Delta\epsilon$ is the zeroth-order energy difference between the two interspace space states. The double-reference treatment of the beryllium atom using FD partitioning encounters perturbative divergence because of incorrect energy ordering. The interspace states inducing this divergence are the $|1s^22p^2\rangle$ (departer) state and the $|1s^22s^23s^2\rangle$ (intruder) state. Since these states are only weakly coupled (V_{pq} is small) and have well-separated expectation values of H, a usefully asymptotically convergent expansion is produced.

The simplest model to explain the influence of incorrect energy ordering consists of two states that are incorrectly ordered and that have their off-diagonal matrix element given by V_{pq}. The crudest model takes V_{pq} as arbitrarily small ($V_{pq}\rightarrow 0$) but nonzero. For this model, the near degeneracy occurs at $z_d^0\rightarrow\Delta\epsilon/(\Delta\epsilon-\Delta H)$, where the expectation values of $H(z)$ (the diagonal matrix elements) for the two states become equal. Because of the noncrossing rule, the two states cannot cross at z_d^0 for V_{pq} arbitrarily small, but they do cross when $V_{pq}=0$. This model works reasonable well to describe the FD series divergence for the beryllium atom.

We define correct energy ordering as the energy ordering of the zeroth-order states that makes a convergent expansion possible. Therefore, if a perturbation expansion correctly orders the zeroth-order energies of interspace states and has them sufficiently separated, then $R_c > 1$. For two-state systems, correct energy ordering requires $\Delta\epsilon$ and ΔH to have the same sign for the interspace states. Perturbative computations with more than two states may sometimes require a different type of energy ordering to produce $R_c > 1$, especially when interspace states have quasidegeneracies in their expectation values of H. In such circumstances, a convergent series is only obtained when two interspace states have $\Delta\epsilon$ and ΔH with *differing* signs. For example, consider a three-state system with an interspace pair of states that are weakly coupled with $V_{pq} = -0.02$ a.u. The P space state from the pair is placed below the Q space state in zeroth order $\epsilon_p < \epsilon_q$, where $\epsilon_p = -10.0$ a.u. and $\epsilon_q = -9.6$ a.u. This ordering is opposite to the ordering of expectation values of H, $\langle q|H|q\rangle < \langle p|H|p\rangle$, where $\langle q|H|q\rangle = -14.3$ a.u. and $\langle p|H|p\rangle = -14.2$ a.u. Therefore the perturbation expansion for these two states *alone* has $R_c < 1$. A third state, denoted as $|q'\rangle$, is now added to the Q space with $\langle q'|H|q'\rangle = -13.0$ a.u. and $\epsilon_{q'} = -8.1$ a.u. Also, $|q'\rangle$ is coupled strongly to the P space state by $V_{p,q'} = 0.5$ a.u. but is only coupled weakly to the other Q space state by $V_{q,q'} = -0.03$ a.u. The computed radius of convergence (R_c) for this three-state system (with opposite signs of $\Delta\epsilon$ and ΔH for $|p\rangle$ and $|q\rangle$) is ≈ 1.3. Whereas the two-state model ($|p\rangle$ and $|q\rangle$) has incorrect energy ordering, the addition of the strongly coupled state $|q'\rangle$ state yields a three-state system with the correct energy ordering of the exact states, permitting the perturbative series to converge. In addition, if the two-state model ($|p\rangle$ and $|q\rangle$) is constructed such that $\Delta\epsilon$ and ΔH have the same signs, then the addition of the third state $|q'\rangle$ produces a divergent series with $R_c < 1$. In order to determine the correct ordering of interspace states, for general N-state systems, it may sometimes be necessary to consider a z-dependent model for the interspace states in question along with the other states that are strongly coupled to one or both of the interspace states. Alternatively, an examination of the (approximate) wave functions at $z = 1$ may be used to predict the ‘‘appropriate’’ one-to-one mapping between the zeroth-order and exact states and thereby establish the correct energy ordering. For example, consider the case with an interspace pair of states $|p\rangle$ and $|q\rangle$, where $|p\rangle(|q\rangle)$ dominates the FCI state $|p_d\rangle(|q_d\rangle)$ at $z = 1$. If the energy of the $|p_d\rangle$ state is greater than the $|q_d\rangle$ state energy, then it is reasonable to conclude that correct energy ordering requires the zeroth-order energy of the $|p\rangle$ state be greater than that of the $|q\rangle$ state. Nevertheless, the interspace two-state models provide the point of departure for analyzing and effecting perturbative convergence.

Epstein-Nesbet partitioning is not, in general, size extensive. Similarly, since the OPT method, as presently implemented, is also based on a sum-over-states formulation, it is, in general, not size consistent. However, size extensivity can be imposed by employing a sum-over-orbitals form of H_0 and by optimizing the orbital energies rather than the state energies. This type of OPT computation has been performed for BeH_2 [29].

The OPT method can also be applied for an incomplete reference space. The use of an incomplete reference space is an important tool for removing certain intruder states and for generating rapid perturbative convergence, especially if employed with the OPT method. The incomplete reference space method of Hose and Kaldor (HK) [30–32] selects the most important zeroth-order states to span the reference space. While the original HK method uses nonaveraged Hartree-Fock orbital energies, subsequent computations by Hose [32,33] also found it useful to force the reference space states to be degenerate in zeroth order. The HK approach removes intruder states from low orders of perturbation theory. However, because the choice of reference space in the Hose-Kaldor method often leads to interspace states with incorrect energy ordering, these types of computations are probably divergent, with the onset of divergent behavior usually occurring at high orders. Therefore, like the FD method, this method can produce asymptotically convergent series. Incorrect energy ordering with the HK method is a consequence of forcing degeneracy upon the P space and of leaving some low-lying weakly coupled states (such as Rydberg states) in the orthogonal space. As applied most recently by Hose [32,33], the HK method is actually quite similar to the FD method, except that the HK technique uses an incomplete reference space and that the zeroth-order energies of the reference space are rendered degenerate by setting the zeroth-order energy of all the reference space states to a single energy, instead of forcing the valence orbitals to be degenerate. The latter approach shifts the zeroth-order energies of all states that depend on the valence orbital energies, including the Q space states. Not surprisingly, poor results emerge from computations using the HK method and forcing the reference space to be degenerate with the energy of an excited reference state [33]. The latter behavior is probably due to energy denominators that are too small. Similarly, forced valence orbital degeneracy may lead to convergence problems of small-energy-denominator type [13]. The following two sections address some problems that may be encountered in employing FD and OPT partitioning.

VII. PROBLEMS WITH FD PARTITIONING

The FD partitioning method permits considerable latitude in choosing the orbitals and the orbital energies, except with the restriction that the valence orbital energies are forced to be degenerate. Thus the important degrees of freedom influencing convergence for FD partitioning are the reference space, the spatial orbitals, and the orbital energies. Because valence orbitals are forced to be degenerate, these variables are interwined in a very complicated way for FD partitioning, making it very difficult to determine *a priori* which combination of these variables yields accurate results, except for cases with very small reference spaces. Therefore, it is not surprising that problems may arise in applying FD partitioning methods, especially as the reference space becomes larger and less quasidegenerate. Because of this complexity, the present form of this method is not recommended for the same widespread usage, as is, for example, single-reference perturbation theory. However, prior experience provides some rough rules of thumb that enable generating satisfactory results for most systems, perhaps with some trial-and-error approaches and/or with detailed analysis. We now explore the complexities involved in choosing the degrees of freedom available in multireference perturbation computations with the constraint that the valence orbitals are forced to be degenerate.

A trade-off exists when choosing a reference space for the FD method. A larger reference space yields a better first-order approximation, but at the expense of introducing a larger diagonal perturbation V. In order to understand the origin of this trade-off, first consider the composition of the reference space for FD partitioning. The FD method uses a complete active space to specify the reference space. Therefore the reference spaces are defined through the specification of a set of valence (active) and core (inactive) orbitals as well as the excited orbitals. (Actually, the word ‘‘valence’’ is a misnomer, since ‘‘nonvalence’’ orbitals can also be active, e.g., Rydberg orbitals [21,22,34].) As the reference space is enlarged by the addition of more active orbitals (with fixed core), the variational theorem implies that the enlarged reference space produces better first-order energies, since its first-order eigenvalues are lower lying and are closer to the FCI energies. Thus less ‘‘dynamical’’ correlation energy has to be recovered perturbatively for the larger reference space. However, application of the FD method to the larger reference space requires the forced degeneracy of more valence orbitals, a procedure which usually produces larger diagonal elements of the perturbation V. These diagonal elements can be quite significant for large reference spaces if zeroth-order states that are very high lying are forced to be degenerate with much lower bound states. In addition, many diagonal elements involving Q (orthogonal) space states are also affected by forcing degeneracy since they also depend on the valence orbital energies. All things being equal, an increased perturbation V induces diminished perturbative performance. Thus a trade-off exists. A larger reference space yields a better first-order approximation at the expense of a larger diagonal perturbation. This trade-off may complicate the choice of the reference space for FD partitioning computations.

Forcing degeneracy can make certain classes of energy denominator factors very small, leading to convergence problems [13] in low orders. The choice of the reference space is further complicated by the need to keep these energy denominator factors from being too small. Consider, for example, how the energy denominator factors are affected by enlarging a particular reference space. Both the smaller and larger reference spaces have some energy denominators factors that shrink when orbital energies are forced to be degenerate, but the larger reference space generally has valence orbital energies that, prior to forcing degeneracy, span a wider energy range. Therefore the larger reference space has more shrunken energy denominators, and the degree of shrinkage is also more severe than for the smaller reference space. Hence, based on the energy denominator factors alone, the smaller reference space selects better energy denominator factors, but the situation is more complicated. The smaller reference space has Q space CSF's that are more strongly coupled to *important P* space CSF's, where the important P space CSF's are those dominating the description of the exact states of interest (e.g., the ground and low-lying states). Because of this stronger coupling involving *important* states, the smaller reference space has a greater dependence on the energy denominator factors and is, therefore, more sensitive to the presence of small energy denominator factors. In other words, while the larger reference space has a greater shrinkage in certain energy denominator factors from forcing degeneracy, it can afford increased shrinkage. This problem of energy denominator factors becoming too small can often be removed by redefining H_0 in a fashion that corresponds to performing orbital energy shifts [13], with the constraint that the valence orbitals remain degenerate. However, without some trial-and-error experimentation or detailed analysis, it is difficult to determine if shifts are required, and of what magnitude. Thus the influence of small energy denominators on the perturbative convergence further complicates the choice of the reference space.

The kinds of uncertainties that appear in the selection of the reference space also appear to a lesser extent for the selection of the orbitals. For example, ground-state CASSCF orbitals provide the ‘‘optimal’’ first-order description of this state as determined by the variational theorem. However, CASSCF orbitals usually introduce a larger energy spread to the reference space prior to forcing degeneracy, compared to the spread from a set of valence orbitals obtained from V^{N-1} potentials [35]. (V^{N-1} potential orbitals are defined in Ref. [13].) Therefore the CASSCF orbitals yield a better first-order description but produce larger diagonal elements of V and also shrink many of their perturbative energy denominator factors more severely when the valence orbitals are forced to be degenerate. Thus, as in the selection of the reference space, this trade-off complicates the choice of orbitals for FD perturbation computations. (As a rule of thumb, CASSCF orbitals are poor for large reference spaces.)

Another complication for the FD method arises from the common occurrence of incorrect energy ordering, especially for larger valence spaces. The beryllium atom computations above have a Rydberg state incorrectly ordered, but since this CSF provides a very small contribution to the states of interest, the convergence is usefully asymptotic. Unfortunately, if the Q space contains incorrectly ordered valence-like states that contribute significantly to the, say, valence-like states of interest, divergent behavior can occur in low orders, or the low-order estimates may be inaccurate from errors incurred from perturbation terms involving the incorrectly ordered states. (See Fig. 4 of Ref. [5] for order-by-order results from an incorrectly ordered two-state system.) Convergence may be improved by enlarging the reference space to include these important CSF's. Unfortunately, the increase in the reference space size has limits and involves the trade-offs discussed above.

VIII. PROBLEMS WITH OPT PARTITIONING

The OPT method does not suffer from many of the above difficulties if the reference space is maintained within the method's range of applicability. However, the use of a CAS reference space may introduce problems in some applications of the OPT method. These problems emerge because some of the CSF's from the CAS may have very high-lying energies, and therefore some of these CSF's may be strongly coupled to Q (orthogonal) space states. Consider just one pair of coupled interspace states from a computation that has many other P and Q space states. Let these two states have a large off-diagonal matrix element V_{pq}, and let the difference ΔH between their diagonal matrix elements of H be small. This pair of coupled interspace states produces a very large $V_{pq}/\Delta H$ ratio. A perturbation expansion involving only these two states is divergent or very slowly convergent. The slow convergence occurs only if the two states have their zeroth-order energies properly ordered and greatly separated [5]. Therefore it is essential with any partitioning method that these two strongly coupled interspace states are not important in describing the state(s) of interest, since a low-order perturbative treatment only recovers a small portion of the correlation energy emerging from perturbation terms with these large V_{pq} factors. Let us now contrast how the FD and OPT methods handle these strongly coupled interspace states.

The FD method significantly enlarges the zeroth-order excitation energy $(\epsilon_p - \epsilon_q)$ which thereby greatly diminishes the potentially problematic large perturbative ratios $V_{pq}/(\epsilon_p - \epsilon_q)$ that are otherwise present when forced degeneracy is not imposed. Furthermore, if $(\epsilon_p - \epsilon_q)$ and ΔH have opposite signs, FD partitioning usually yields an error in each order [5]. Thus the FD partitioning can produce satisfactory energies only when these errors from incorrect ordering are small.

Now let the reference space states be nondegenerate, as is the case for OPT partitioning. The zeroth-order energies for a pair of coupled interspace states with a large $V_{pq}/\Delta H$ ratio can be chosen to be correctly energy ordered and to be well separated energetically, a pair of conditions that is often necessary for convergence. Unfortunately, this OPT energy shifting could induce other problems. Consider, in addition to the strongly coupled interspace pair $|p\rangle$ and $|q\rangle$, another pair of interspace states $|p_d\rangle$ and $|q_h\rangle$ that contribute significantly to the state of interest. Assume further that the diagonal elements of H satisfy the orderings $\langle q_h|H|q_h\rangle > \langle p|H|p\rangle > \langle q|H|q\rangle > \langle p_d|H|p_d\rangle$ and that the lowest-lying state $|p_d\rangle$ is a good zeroth-order description for the state of interest. In order to obtain a convergent series, we must have the zeroth-order energies of the two strongly coupled states $|p\rangle$ and $|q\rangle$ be well separated and correctly energy ordered. Explicitly, we must (usually) then have $\epsilon_p \gg \epsilon_q$. Unfortunately, correct energy ordering also requires $\epsilon_{q_h} > \epsilon_p$ and $\epsilon_q > \epsilon_{p_d}$. Therefore the combination of these requirements yields $\epsilon_{q_h} \gg \epsilon_{p_d}$, a condition that may slow the convergence since the important perturbation terms with factors of $V_{p_d,q_h}/(\epsilon_{p_d} - \epsilon_{q_h})$ are now made too small because $(\epsilon_{p_d} - \epsilon_{q_h})$ is very large. Hence, in such circumstances, it may be preferable simply to neglect the offending V_{pq} matrix elements or any interspace matrix elements that produce large $V_{pq}/\Delta H$ factors. A related approach appears in the early work of Stern and Kaldor [36,37] with the neglect of certain zeroth-order states in a complete active space multireference treatment for excited states of H_2 and BH. This approach is made successful only if the reference space is chosen so that these types of matrix elements can be neglected. Usually, the larger the reference space, the better is this approximation.

An alternative method for dealing with intruder states is provided by the intermediate Hamiltonian [38] approach which removes problematic energy denominators. A change of ket basis can also be employed to reduce large, problematic, interspace couplings [e.g., as in the CAS perturbation theory (CASPT) method [39–43]]. It may be beneficial to employ the OPT partitioning with these methods. In addition, since multireference coupled cluster (MRCC) [44–55] computations for complete reference spaces (and even for incomplete reference spaces) frequently encounter poor convergence problems due to the presence of intruder states, the OPT partitioning might provide an improved initial guess to overcome some of these convergence difficulties.

IX. CONCLUSIONS

Electronic-structure computations for the beryllium atom exhibit many of the fundamental difficulties encountered in attempting to extend single-reference perturbative methods to treatments based on multiple reference spaces. The present work demonstrates how a proper selection of the zeroth-order Hamiltonian H_0 enables us to achieve intruder-state-free, optimal, low-order perturbative convergence for multireference spaces with accurate energies in low orders. The third-order OPT energy for the beryllium atom differs from the FCI eigenvalue by 0.01 kcal/mol for the ground state and by 1.4 kcal/mol for the second excited state. The FD partitioning yields an energy ordering in zeroth order between the $|1s^2 2p^2\rangle$ P space and the $|1s^2 2s 3s\rangle$ Q space states that differs from the energy ordering provided by the expectation value of the Hamiltonian. This incorrect ordering between these interspace states ultimately destroys the perturbative convergence for the beryllium atom using FD partitioning. However, since the coupling between these states is small, the FD perturbation series is usefully asymptotic in the sense that low-order truncations provide good approximations. The present computations again emphasize the utility of simple models for providing convergence criteria and for assessing the quality of possible choices for multireference perturbative computations. An analysis of interspace two-state models yields an indication of probable impediments to the perturbative convergence and of possible remedies for these problems.

ACKNOWLEDGMENTS

This research is supported, in part, by the National Science Foundation, Grant No. CHE9307489. We thank Steve Biondi for useful discussions regarding incorrect energy ordering.

---

[1] I. Lindgren, J. Phys. B **7**, 2441 (1974).
[2] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, 2nd ed., Springer Series on Atoms and Plasmas Vol. 3 (Springer, New York, 1986).
[3] T. H. Schucan and H. A. Weidenmüller, Ann. Phys. (N.Y.) **73**, 108 (1972).
[4] T. H. Schucan and H. A. Weidenmüller, Ann. Phys. (N.Y.) **76**, 483 (1973).

[5] J. P. Finley, R. K. Chaudhuri, and K. F. Freed, J. Chem. Phys. **103**, 4990 (1995).
[6] S. Solomonson, I. Lindgren, and A. Martensson, Phys. Scr. **21**, 351 (1980).
[7] J. P. Heully and J. P. Daudey, J. Chem. Phys. **88**, 1046 (1988).
[8] B. H. Brandow, Rev. Mod. Phys. **39**, 771 (1967).
[9] T. T. S. Kuo, S. Y. Lee, and K. F. Ratcliff, Nucl. Phys. A **176**, 65 (1971).
[10] V. Kvasnička, Czech. J. Phys. B **24**, 605 (1974).
[11] S. Zarrabian, W. D. Laidig, and R. J. Bartlett, Phys. Rev. A **41**, 4711 (1990).
[12] R. Sawatzki and L. S. Cederbaum, Chem. Phys. Lett. **126**, 430 (1986).
[13] J. P. Finley and K. F. Freed, J. Chem. Phys. **102**, 1306 (1995).
[14] B. Huron, P. Rancurel, and J. P. Malrieu, J. Chem. Phys. **58**, 5745 (1973).
[15] S. Wilson, K. Jankowski, and J. Paldus, Int. J. Quantum Chem. **28**, 525 (1985).
[16] J. M. Leinaas and T. T. S. Kuo, Phys. Lett. **62B**, 275 (1976).
[17] P. J. Ellis and E. Osnes, Rev. Mod. Phys. **49**, 777 (1977).
[18] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).
[19] R. J. Bartlett and E. J. Brandäs, J. Chem. Phys. **59**, 2032 (1972).
[20] W. D. Laidig, G. B. Fitzgerald, and R. J. Bartlett, Chem. Phys. Lett. **113**, 51 (1985).
[21] J. E. Stevens, K. F. Freed, M. F. Arendt, and R. L. Graham, J. Chem. Phys. **101**, 4832 (1994).
[22] R. L. Graham and K. F. Freed, J. Chem. Phys. **96**, 1304 (1992).
[23] C. H. Martin, R. L. Graham, and K. F. Freed, J. Chem. Phys. **99**, 7833 (1993).
[24] S. Y. Lee and K. F. Freed, J. Chem. Phys. **104**, 3260 (1996).
[25] K. F. Freed, *Tests and applications of Complete Model Space Quasidegenerate Many-Body Perturbation Theory for Molecules,* Lecture Notes in Chemistry Vol. 52 (Springer, Berlin, 1989), p. 1.
[26] G. A. Baker, *Essentials of Padé Approximants* (Academic, New York, 1975).
[27] H. F. Kelly, Adv. Chem. Phys. **14**, 129 (1969).
[28] P. A. Schaefer, Ann. Phys. (N.Y.) **87**, 375 (1974).
[29] R. K. Chaudhuri, J. P. Finley, and K. F. Freed (unpublished).
[30] G. Hose and U. Kaldor, J. Phys. B **12**, 3827 (1979).
[31] G. Hose and U. Kaldor, J. Phys. Chem. **86**, 2133 (1982).
[32] G. Hose, Theor. Chim. Acta **72**, 303 (1987).
[33] G. Hose (personal communication).
[34] Y. S. Lee and K. F. Freed, J. Chem. Phys. **77**, 1984 (1982).
[35] J. P. Finley and K. F. Freed (unpublished results for N_2 ground and first excited states).
[36] P. S. Stern and U. Kaldor, J. Chem. Phys. **63**, 2199 (1976).
[37] P. S. Stern and U. Kaldor, J. Chem. Phys. **64**, 2002 (1977).
[38] J.-P. Malrieu, Ph. Durand, and J. P. Daudey, J. Phys. A **18**, 809 (1985).
[39] K. Wolinski and P. Pulay, J. Chem. Phys. **90**, 3647 (1989).
[40] K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, J. Chem. Phys. **94**, 5483 (1990).
[41] K. Andersson, P.-Å. Malmqvist, and B. O. Roos, J. Chem. Phys. **96**, 1218 (1992).
[42] M. P. Fülscher, K. Andersson, and B. O. Roos, J. Chem. Phys. **96**, 9204 (1992).
[43] L. Serrano-Andrés, M. Merchán, I. Nebot-Gil, R. Lindh, and B. O. Roos, J. Chem. Phys. **98**, 3151 (1993).
[44] D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Pramana **4**, 245 (1975).
[45] D. Mukherjee, R. Moitra, and A. Mukhopadhyay, Mol. Phys. **30**, 861 (1975).
[46] D. Mukherjee and S. Pal, Int. J. Quantum Chem. **S20**, 292 (1989).
[47] R. Offermann, W. Ey, and H. Kümmel, Nucl. Phys. **A273**, 249 (1976).
[48] I. Lindgren, Int. J. Quantum Chem. **S12**, 33 (1978).
[49] B. Jeziorski and H. J. Monkhorst, Phys. Rev. A **24**, 1668 (1981).
[50] J. Paldus, in *New Horizons in Quantum Chemistry*, edited by P. O. Löwdin and B. Pullman (Reidel, Dordrecht, 1983), p. 33.
[51] S. Wilson, K. Jankowski, and J. Paldus, Int. J. Quantum Chem. **23**, 1781 (1983).
[52] W. Kutzelnigg, J. Chem. Phys. **80**, 222 (1984).
[53] U. Kaldor, Theor. Chim. Acta **80**, 427 (1991), and references therein.
[54] L. Meissner, S. A. Kucharaski, and R. Bartlett, J. Chem. Phys. **91**, 6187 (1989).
[55] J. Paldus, P. Piecuch, L. Pylypow, and B. Jeziorski, Phys. Rev. A **47**, 2738 (1993), and references therein.