Claremont Colleges
Scholarship @ Claremont

All HMC Faculty Publications and Research	HMC Faculty Scholarship

12-1-1988

Quasidegenerate Variational Perturbation Theory and the Calculation of First-Order Properties from Variational Perturbation Theory Wave Functions

Robert J. Cave
Harvey Mudd College

Ernest R. Davidson
Indiana University - Bloomington

Recommended Citation

Quasidegenerate variational perturbation theory and the calculation of first-order properties from variational perturbation theory wave functions. Robert J. Cave and Ernest R. Davidson, J. Chem. Phys. 89, 6798 (1988), DOI: 10.1063/1.455354

This Article is brought to you for free and open access by the HMC Faculty Scholarship at Scholarship @ Claremont. It has been accepted for inclusion in All HMC Faculty Publications and Research by an authorized administrator of Scholarship @ Claremont. For more information, please contact scholarship@cuc.claremont.edu.

Quasidegenerate variational perturbation theory and the calculation of first-order properties from variational perturbation theory wave functions

Robert J. Cave and Ernest R. Davidson[a)]
Department of Chemistry, Indiana University, Bloomington, Indiana 47405

(Received 18 July 1988; accepted 16 August 1988)

In previous work on the treatment of correlation in molecular systems we have applied a multireference version of second-order Hylleraas variational perturbation theory. The choice made for the partitioning of H treated the interactions between the correlating functions to infinite order and gave the corrections to the wave function to first order. The method was shown to be accurate in many cases, but became less so when near degeneracies occurred between the reference energy and other eigenvalues of H_0. In this article we introduce an effective Hamiltonian method that is analogous to variational perturbation theory, but which is significantly more accurate when near degeneracies are important. This quasidegenerate variational perturbation theory (QDVPT) is an explicitly multireference procedure and treats the entire reference space as a quasidegenerate space. A novel method for solving the QDVPT equations is introduced that avoids explicit construction of the effective Hamiltonian. As a result, the work involved in application of QDVPT is on the roder of that required for variational perturbation theory. We also present an approximate method for calculating first-order atomic and molecular properties based on Hylleraas variational perturbation theory, multireference linearized coupled cluster, and QDVPT wave functions. The properties are calculated as derivatives of the energy with respect to the field strength. Construction of a one-electron density matrix based on the energy derivative expression allows rapid evaluation of one-electron properties. Results are presented and compared to full and truncated CI results. Good agreement is found in the cases examined.

I. INTRODUCTION

One of the goals in the development of *ab initio* quantum chemical methods is to obtain procedures which yield size-consistent (or size-extensive, we use the two terms interchangeably here) results.[1] A size-consistent method is one in which the energy of the system scales linearly with the number of particles. Some examples of size-consistent methods are restricted and unrestricted Hartree–Fock theory, Møller–Plesset perturbation theory, some types of complete-active-space SCF, coupled-cluster theory, and full configuration interaction calculations. Truncated configuration interaction (CI) is an example of a size-inconsistent method; for a singles and doubles CI the correlation energy scales as $\sqrt{n}$, where n is the number of particles. However, it has been shown in systems containing only a few electrons and a small basis set that multireference singles and doubles CI (MRSDCI) results can accurately reproduce full CI results.[2] Comparisons have not been made for larger systems because the full CIs cannot be performed at the present time. For treatment of large systems it will be imperative to develop methods that are more nearly size-consistent than single-reference based SDCI.

Until recently, the predominant size-consistent correlation methods (Møller–Plesset perturbation theory and coupled-cluster theory) were applied almost exclusively as single-reference based procedures. In part this is due to the added computational complexity of the multireference based procedures, but also because of the rather severe requirements on the reference space in the early formulations of multireference theories.[3] With large reference spaces problems arose due to the presence of intruder states, giving rise to numerical instabilities or poor convergence of the perturbation series.[4] In addition, it has been shown that in many cases single-reference based procedures can be quite robust and can overcome the rather severe limitations imposed by restriction to a single reference function. In a study by Laidig *et al.*[5] it was shown that a coupled-cluster model including single, double, and triple excitations was able to describe the potential curve for breaking a single bond with quite high accuracy.

However, a host of problems exist for which a single-configurational description is inappropriate. Excited states of the same symmetry as the ground state, or higher lying states of other symmetries than the ground state are cases where adequate single-configurational descriptions may be difficult to obtain. In addition, points on the ground state surface may be inherently multiconfigurational, such as some transition states. It is therefore desirable to have multiconfigurational methods that are size consistent. The earliest applications of multireference coupled-cluster theory[5–12] were all based on complete-active-space SCF reference spaces. In previous applications of multireference coupled-cluster theory, the coupled-cluster equations have been truncated at second order to yield manageable calculations. In

---

[a)] Author to whom correspondence should be addressed.

© 1988 American Institute of Physics

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

most cases,[5,6,9–11] the orthogonal complement of the reference space was excluded from the expansion of the wave functions. When this approximation is made one is dependent on the complete-active-space SCF to yield an accurate estimate of the relative weights of the configurations in the refrence space. In more recent developments the requirement of a complete-active-space SCF reference space has been relaxed.[13,14] A method related to multireference coupled-cluster approaches is the multireference averaged coupled-pair-functional approach of Gdanitz and Ahlrichs.[15] In this method the orthogonal complement of the reference wave function is included in the wave function expansion. While not strictly size consistent, it has been shown to be quite accurate for a variety of small- and moderate-sized systems.[15]

We have recently proposed a version of variational perturbation theory[16–18] based on a multireference zeroth-order space. It was shown to differ from the multireference linearized coupled-cluster[5–7] (MRLCC) method in that the orthogonal complement of the reference space was included in the wave function expansion. Thus, variational perturbation theory allows correlation effects to alter the relative weights of the zeroth-order configurations in the final wave function. In test calculations[18] variational perturbation theory (VPT) gave excitation energies and total energies in good agreement with MRLCC and full CI results. However, in further testing of the method we have found that the inclusion of the orthogonal complement functions in the wave function can make the method more susceptible to intruder state effects than, e.g., MRLCC. In Sec. II we discuss the origin of this effect and introduce a simple model to illustrate the problem. It will be shown that this effect is a result of the coupling of the orthogonal complement of the zeroth-order wave function to *all* single and double excitations. In Sec. V computational results on this model will be presented to support ehe qualitative discussion of Sec. II.

In many cases the intruder state problem in VPT does not manifest itself, but when it does one may be unwilling to merely remove the orthogonal complement functions from the wave function and use MRLCC theory. In. Sec. III we present an effective Hamiltonian based analog of VPT, which we call quasidegenerate variational perturbation theory (QDVPT). Quasidegenerate variational perturbation theory treats the reference wave function (Ψ_0) and its orthogonal complement on a more equal basis. The partitioning made of H into H_0 and V is similar to that made in VPT,[18] except that the reference space (**P**) now contains Ψ_0 and its orthogonal complement, while the correlation space (**Q**) only contains the single and double excitations relative to **P**. We retain the full coupling of the single and double excitations between themselves in H_0, thus yielding an infinite order treatment of their interactions as in VPT. In the limit that the effective interaction within the reference space goes to zero, QDVPT yields results identical with MRLCC. When the effective coupling is small but nonzero QDVPT gives results similar to VPT. However, where intruder state problems arise is variational perturbation theory, or where correlation brings on significant reference space readjustments, results indicate that QDVPT is superior to VPT. QDVPT will be shown to be not strictly size consistent, but to be much more nearly so than (MRSDCI).

In Sec. IV we introduce a method for estimating first-order one-electron properties based on VPT and QDVPT wave functions. Not only do the one-electron properties provide additional probes of size-inconsistency effects, but it is sometimes the case that one-electron properties are of more interest in a theoretical study than bond energies or excitation energies. Also, comparison of calculated molecular properties with experimental values can provide a means of gauging the quality of a calculational procedure.[19] It is thus useful to be able to evaluate molecular properties in an accurate and efficient manner. This is particularly true for correlated wave functions, where one has some hope of systematically approaching agreement with experimental quantities.

The Hellmann–Feynman theorem[20] states that for the exact wave function one can obtain equivalent results for first-order properties by calculating the properties as derivatives of the energy with respect to the perturbation of interest, or as expectation values of the perturbation over the unperturbed wave function. This is also true for wave functions that are optimal with respect to all variable parameters, such as SCF, complete-active-space multiconfigurational SCF, and full configuration interaction.[21] Most other commonly employed wave functions (truncated configuration interaction,[22] many-body perturbation theory,[22] coupled-cluster approaches,[1] coupled-pair functional theory,[15] and variational perturbation theory[16–18]) are not optimal with respect to *all* parameters and differences are expected between the energy derivative and expectation value methods of property evaluation.

The disadvantage of the energy-derivative methods applied in a a finite-field form[23] is that several calculations of the wave function must be performed for each property desired. The expectation value method, where a reduced one-particle density matrix can be defined, allows efficient evaluation of many properties at once. However, for some correlated wave functions in current use (most notably coupled-cluster types of wave functions) calculation of the one-particle density matrix can be more difficult than repeated application of the energy-derivative method.

In this report we examine the utility of an approximate method for evaluation of properties based on second-order Hylleraas variational perturbation theory wave functions (and related wave functions) and QDVPT wave functions. The properties are formulated as the derivative of the second-order energy expression with respect to the perturbation strength. We neglect derivatives of the molecular orbital basis with respect to the perturbation. Due to the form of the energy expression used, a reduced density matrix can be defined. A similar method for property evaluation has been used for coupled-pair functional theory wave functions.[15] Results are compared for the three systems examined previously in our tests of variational perturbation theory.[18] Variational perturbation theory, QDVPT, multireference linearized coupled-cluster,[5–7] and CI results are also presented for the model system examined in Secs. II and III which is designed to assess the effects of size inconsistency on the energy and first-order properties.

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

II. VARIATIONAL PERTURBATION THEORY AND SIZE INCONSISTENCY

In this section we discuss the source of the size inconsistency in variational perturbation theory and introduce a simple model that illustrates this problem. We first review the relevant equations.

We adopt the following conventions for designating the configuration space. Ψ_0 designates the zeroth-order reference function for VPT or MRLCC. Ψ_0 need not be the lowest root of the zeroth-order space. When the reference space contains two functions, we designate the orthogonal complement of Ψ_0 as Ψ_c. When the entire reference space is being considered, we designate a member of this space as Ψ_0^i $(i = 1,...,n)$, where n is the number of functions in the reference space. Finally, when the reference space functions and the single and double excitations from the refrence space are being considered together, these functions are designated as Φ_k $(k = 1,...,N)$ with the first n Φ_k being the reference space functions. With these definitions the configuration space is partitioned into three sets:

$$\Psi_0 = \Psi_0^1 = \Phi_1 = \sum_{i=1}^{n} d_0^i \phi_i, \tag{1a}$$

$$\Psi_0^k = \Phi_k = \sum_{i=1}^{n} d_k^i \phi_i, \quad k = 2,...,n, \tag{1b}$$

$$\Phi_k = \phi_k, \quad k = n + 1,...,N. \tag{1c}$$

The $N - n$ ϕ_k are all the single and double excitations relative to the reference configurations. The projection operators for these three spaces are denoted $\mathbf{P}$, $\mathbf{Q}_0$, and $\mathbf{Q}_1$, respectively. The sum of $\mathbf{Q}_0$ and $\mathbf{Q}_1$ is denoted as $\mathbf{Q}$. The Hamiltonian is partitioned as

$$H_0 = \mathbf{P}H\mathbf{P} + \mathbf{Q}H\mathbf{Q}, \tag{2a}$$

$$V = \mathbf{P}H\mathbf{Q} + \mathbf{Q}H\mathbf{P}. \tag{2b}$$

Using Eqs. (1) and (2) and assuming intermediate normalization $(\langle\Psi_0|\Psi\rangle = 1)$, the expression for the second-order correction to the variational perturbation theory energy is obtained as[16–18]

$$E_2 = 2\langle\Psi_0|H|\Psi_1\rangle + \langle\Psi_1|H - E_0|\Psi_1\rangle \tag{3}$$

with $E_0 = \langle\Psi_0|H|\Psi_0\rangle$ and Ψ_1 composed of the Φ_k $(k = 2,...,N)$. That is, Ψ_1 is defined as

$$\Psi_1 = \sum_{k=2}^{N} C_k \Phi_k. \tag{4}$$

The variation of E_2 with respect to the C_k $(k = 2,...,N)$ yields

$$0 = \langle\Phi_k|H|\Psi_0\rangle + \langle\Phi_k|H - E_0|\Psi_1\rangle \tag{5}$$

or, in matrix form,

$$\mathbf{Q}H\mathbf{P} + \mathbf{Q}(H - E_0)\mathbf{Q}\mathbf{C} = 0. \tag{6}$$

Equations (3) and (6) are the defining equations for variational perturbation theory. We note that when Eq. (6) is satisfied the expression for E_2 reduces to

$$E_2 = \langle\Psi_0|H|\Psi_1\rangle \tag{7}$$

which is identical to the usual Rayleigh–Schrödinger expression for the second-order correction to the energy.

The solution of Eq. (6) is the point at which the intruder state problems of the VPT equations can be seen formally. In general, Eq. (6) has a solution when the determinant of $\mathbf{Q}(H - E_0)\mathbf{Q}$ is nonzero.[24] By performing a unitary transformation on $\mathbf{Q}H\mathbf{Q}$ to diagonalize it, one sees that this condition is equivalent to requiring that no eigenvalue of $\mathbf{Q}H\mathbf{Q}$ be equal to E_0. Near points where an eigenvalue of $\mathbf{Q}H\mathbf{Q}$ equals E_0 one expects the solutions of Eq. (6) to behave badly. The problem for VPT is that when the orthogonal complement of the reference space is included in $\mathbf{Q}$ one can always expect a crossing of an eigenvalue of $\mathbf{Q}H\mathbf{Q}$ and E_0 as the system size increases. This is because all single and double excitations relative to the reference space are included in $\mathbf{Q}$ and these single and double excitations correlate the orthogonal complement configurations as well as Ψ_0. As the correlation energy in the system increases, the lowest eigenvalue of $\mathbf{Q}H\mathbf{Q}$ (dominated by an orthogonal complement function for large systems) can be made to sweep through E_0, causing instabilities in the resulting solutions. Thus the orthogonal complement functions (dressed by their interactions with the single and double excitations in H_0) become intruder states[4] as the system size is increased for this nondegenerate treatment. Intruder state effects are less likely to occur for MRLCC since the orthogonal complement functions are excluded from $\mathbf{Q}$, and the single and double excitations do not correlate each other to the extent that they do $\mathbf{Q}_0$. Therefore, in MRLCC the lowest eigenvalue of $\mathbf{Q}H\mathbf{Q}$ can remain separated from E_0 even as the system size increases. To illustrate these features we introduce a simple model system.

The model system we wish to consider is the lowest ${}^1A_1$ state of CH_2He_n, where CH_2 is at the equilibrium geometry for its lowest ${}^1A_1$ state and the He are well separated from one another and from CH_2. For simplicity we assume two AOs are centered on each He. Our treatment will be based on a two-configurational description of CH_2He_n, the two configurations differing only in the orbitals occupied by the CH_2 lone pair electrons. The occupied and virtual orbitals are assumed localized on their respective centers; the SCF results reported below support this assumption. All doubly excited configurations on the He relative to both reference configurations and all double excitations on CH_2 will be considered.

We designate the optimal two-configuration SCF function as Ψ_0 (with energy E_0) and its orthogonal complement in the reference space Ψ_c (with energy E_c). Of the double excitations out of He orbitals, only those involving excitation of a pair of electrons on one He into an orbital on the same He will have nonzero matrix elements with Ψ_0, due to the assumed large distance between the He. Furthermore, for the two configurations corresponding to a double excitation on a given He one can transform to a new set of functions ϕ_0^i and ϕ_c^i (using the two-configuration SCF CI coefficients) that have the following properties:

$$\begin{gathered}\langle\Psi_0|H|\Psi_0\rangle = E_0, \quad \langle\Psi_c|H|\Psi_c\rangle = E_c,\\ \langle\Psi_0|H|\Psi_c\rangle = 0 \quad \langle\Psi_0|H|\phi_0^i\rangle = H_{0,\mathrm{He}},\\ \langle\Psi_c|H|\phi_0^i\rangle = 0, \quad \langle\Psi_0|H|\phi_c^i\rangle = 0,\\ \langle\Psi_c|H|\phi_c^i\rangle = H_{c,\mathrm{He}} = H_{0,\mathrm{He}},\\ \langle\phi_0^i|H|\phi_0^i\rangle = E_0 + \epsilon_{\mathrm{He}},\\ \langle\phi_c^i|H|\phi_c^i\rangle = E_c + \epsilon_{\mathrm{HE}}, \quad \langle\phi_c^i|H|\phi_0^i\rangle = 0.\end{gathered} \tag{8}$$

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

In Eq. (8) ϵ_{He} is the energy of the doubly excited configuration on He relative to the ground state SCF value. We also make use of $\epsilon_c = (E_c - E_0)$. Finally, we denote the set of doubly excited configurations on CH_2 as (the vector) ϕ_{CH2}, the associated vectors of connecting matrix elements being $\mathrm{H}_{0,\mathrm{CH2}}$ and $\mathrm{H}_{c,\mathrm{CH2}}$. Note that these double excitations do not connect with the He double excitations.

Since the He are equivalent it is clear that each He double excitation will enter Ψ with the same coefficient, and that one can write Ψ in the form

$$\Psi = |\Psi_0\rangle + C_c|\Psi_c\rangle + C_{\mathrm{CH2}}|\phi_{\mathrm{CH2}}\rangle + C^0_{\mathrm{He}}|\chi_0\rangle + C^c_{\mathrm{He}}|\chi_c\rangle, \tag{9}$$

where C_{CH2} is a vector of coefficients and we have defined the normalized functions χ_0 and χ_c as

$$\chi_0 = \sum_{i=1}^{n} \phi^i_0/\sqrt{n}, \tag{10a}$$

$$\chi_c = \sum_{i=1}^{n} \phi^i_c/\sqrt{n}. \tag{10b}$$

Note that n indicates the number of He. With these definitions the VPT equations defining the coefficients [Eq. (6)] become

$$\begin{pmatrix} \epsilon_{\mathrm{He}} & 0 & 0 & 0 \\ 0 & \epsilon_c + \epsilon_{\mathrm{He}} & \sqrt{n}H_{0,\mathrm{He}} & 0 \\ 0 & \sqrt{n}H_{0,\mathrm{He}} & \epsilon_c & H_{c,\mathrm{CH2}} \\ 0 & 0 & H_{c,\mathrm{CH2}} & H_{\mathrm{CH2}} - E_0 \end{pmatrix} \begin{pmatrix} C^0_{\mathrm{He}} \\ C^c_{\mathrm{He}} \\ C_c \\ C_{\mathrm{CH2}} \end{pmatrix} = -\begin{pmatrix} \sqrt{n}H_{0,\mathrm{He}} \\ 0 \\ 0 \\ H_{0,\mathrm{CH2}} \end{pmatrix}. \tag{11}$$

With the definitions

$$H^e_{0,0} = H_{0,\mathrm{CH2}}(E_0 - H_{\mathrm{CH2}})^{-1}H_{\mathrm{CH2},0}, \tag{12a}$$

$$H^e_{c,c} = \epsilon_c + H_{c,\mathrm{CH2}}(E_0 - H_{\mathrm{CH2}})^{-1}H_{\mathrm{CH2},c}, \tag{12b}$$

$$H^e_{0,c} = H^e_{c,0} = H_{c,\mathrm{CH2}}(E_0 - H_{\mathrm{CH2}})^{-1}H_{\mathrm{CH2},0}, \tag{12c}$$

Eq. (11) can be solved to yield

$$\begin{aligned} C^0_{\mathrm{He}} &= -\sqrt{n}H_{0,\mathrm{He}}/\epsilon_{\mathrm{He}}, \\ C^c_{\mathrm{He}} &= \sqrt{n}H_{0,\mathrm{He}}H^e_{c,0}/D, \\ C_c &= -H^e_{0,c}(\epsilon_c + \epsilon_{\mathrm{He}})/D, \\ C_{\mathrm{CH2}} &= (E_0 - H_{\mathrm{CH2}})^{-1}H_{\mathrm{CH2},0} \\ &\quad - (E_0 - H_{\mathrm{CH2}})^{-1}H_{\mathrm{CH2},c}H^e_{c,0}(\epsilon_c + \epsilon_{\mathrm{He}})/D \end{aligned} \tag{13}$$

with

$$D = H^e_{c,c}(\epsilon_c - \epsilon_{\mathrm{He}}) - nH^2_{0,\mathrm{He}}. \tag{14}$$

The total energy $E = E_0 + \langle\Psi_0|H|\Psi_1\rangle$ becomes

$$\begin{aligned} E = E_0 - n|H_{0,\mathrm{He}}|^2/\epsilon_{\mathrm{He}} - H_{0,\mathrm{CH2}}(H_{\mathrm{CH2}} - E_0)^{-1} \\ \times H_{\mathrm{CH2},0} - |H^e_{0,c}|^2(\epsilon_c - \epsilon_{\mathrm{He}})/D. \end{aligned} \tag{15}$$

The last term in Eq. (15) manifests the size inconsistency in variational perturbation theory for the present model system. The $D/(\epsilon_c + \epsilon_{\mathrm{He}})$ factor in the last term of Eq. (15) approximately represents the energy of Ψ_c after being correlated by the configurations in ϕ_{CH2} and χ_c. This quantity changes with increasing He, while the factor multiplying it does not, thus leading to size inconsistency. In addition, this term also leads to the numerical instability in the VPT equations with increasing He. For the present model, $H^e_{c,c}(\epsilon_c + \epsilon_{\mathrm{He}})$ is positive and since $-nH^2_{0,\mathrm{He}}$ is negative, D will go thrugh zero as n is increased. At the point $D = 0$, the VPT equations have no solution, and near this point they are unstable with respect to variation of n. Thus, as noted above, the dressed Ψ_c becomes an intruder state in VPT. In the computations presented below it will be seen that this singularity is encountered between 9 and 13 He for the basis sets used. However, it will be shown that this singularity does not have a large effect on the total energy, and that the largest errors actually occur in the one-electron properties.

For cases where D is not near zero we can expand the denominator in Eq. (15) to obtain

$$\begin{aligned} E \simeq E_0 - n|H_{0,\mathrm{He}}|^2/\epsilon_{\mathrm{He}} - H_{0,\mathrm{CH2}}(H_{\mathrm{CH2}} - E_0)^{-1} \\ \times H_{0,\mathrm{CH2}} - |H^e_{c,0}|^2/H^e_{c,c} - n|H_{0,\mathrm{He}}|^2|H^e_{c,0}|^2/ \\ \{(H^e_{c,c})^2(\epsilon_c - \epsilon_{\mathrm{He}})\}. \end{aligned} \tag{16}$$

The second and third terms of Eq. (16) present the second-order Rayleigh–Schrödinger contributions to the energy lowering based on the direct coupling of the He and CH_2 double excitations to Ψ_0. The last two terms represent coupling of Ψ_c to Ψ_0 through ϕ_{CH2}. The direct coupling between Ψ_c and Ψ_0 is zero when Ψ_0 is an eigenfunction of H_0. When the He are well separated from CH_2 the coupling of Ψ_c to Ψ_0 through the He double excitations is also zero. However, since one cannot transform away the coupling of Ψ_0 and Ψ_c through the double excitations on CH_2, this coupling will remain.

When no CH_2 double excitations are included in the present model the effective coupling between Ψ_0 and Ψ_c is zero and variational perturbation theory yields the same size-consistent result as MRLCC. However, in this model the He double excitations are least like "normal" correlating configurations in most molecular calculations. That is, in general, Ψ_0 and Ψ_c will be coupled through most or all of the double excitations. Thus, for a multireference case, these effects are always present for variational perturbation theory, and intruder state problems can arise whenever the correlation energy is larger than the energy separation between Ψ_0 and an orthogonal complement function. This fact suggests that VPT should be modified for cases were the correlation energy is substantial.

III. QUASIDEGENERATE VARIATIONAL PERTURBATION THEORY (QDVPT)

Variational perturbation theory and most other multireference coupled-cluster or perturbation methods[5,6,9–12,25] treat the zeroth-order space as a multiconfigurational nondegenerate space. Thus, the orthogonal complement functions are treated as minor contributors to the final wave function. However, there are occasions where such an approach may be inadequate. One example was given in Sec. II, where inclusion of Ψ_c in Ψ_1 led to size-inconsistency effects because Ψ_c is coupled to all single and double excitations. A

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

second example occurs where correlation significantly alters the relative weights of the configurations comprising Ψ_0 in the final wave function. In this case neglect of the orthogonal complement configurations will lead to errors. Alternatively, inclusion of the orthogonal complement functions via VPT will lead to large (usually inaccurate) coefficients for these functions because VPT is only first order in its treatment of the corrections to Ψ.

In such cases it is important to be able to treat all the reference functions on a more equal basis, thus moving from a nondegenerate to a quasidegenerate formalism. Several groups have discussed[3,7,8,13,26–28] and applied methods of this type.[8,13,14] Below we present a modification to variational perturbation theory based on an effective Hamiltonian constructed from a multireference zeroth-order space. It is derived using partitioning theory[29] applied to the full CI Hamiltonian matrix and is aimed at treating the quasidegenerate problem. It also alleviates the problems encountered in nondegenerate multireference perturbation theory caused by the crossing of E_0 by eigenvalues of H_0 when the orthogonal complement of Ψ_0 is included in **Q**. The method will be shown to reduce to VPT when the effective interaction between zeroth-order configurations is weak, and to MRLCC when the effective interaction is zero. But, since the current method treats the interaction between the reference functions to all orders it remains stable when strong zeroth-order mixing occurs. It will be shown that the model is not strictly size consistent, due to an assumption which eliminates the dominant intruder state effects. Nevertheless, in applications of the model its size inconsistency will be shown to be much weaker than that of comparable CI calculations.

A. Method

The full CI Hamiltonian is partitioned into **P**, **Q**, and **R** spaces, in a similar way to that done for VPT. This partitioning was used by Kutzelnigg in work on perturbation theory.[30] Based on this partitioning we obtain

$$\begin{aligned} \mathbf{H}_0 &= \mathbf{PHP} + \mathbf{QHQ} + \mathbf{RHR}, \\ \mathbf{V} &= \mathbf{PHQ} + \mathbf{QHP} + \mathbf{QHR} + \mathbf{RHQ} + \mathbf{PHR} + \mathbf{RHP}. \end{aligned} \tag{17}$$

If one assumes that **P** comprises all of the reference functions, **Q** all single and double excitations from **P**, and **R** all higher excitations from **P**, then the fifth and sixth terms of **V** in Eq. (17) are zero. The CI equations for this partitioning can be written as

$$\begin{pmatrix} \mathbf{PHP} & \mathbf{PHQ} & 0 \\ \mathbf{QHP} & \mathbf{QHQ} & \mathbf{QHR} \\ 0 & \mathbf{RHQ} & \mathbf{RHR} \end{pmatrix} \begin{pmatrix} \mathbf{C_P} \\ \mathbf{C_Q} \\ \mathbf{C_R} \end{pmatrix} = \mathbf{E} \begin{pmatrix} \mathbf{C_P} \\ \mathbf{C_Q} \\ \mathbf{C_R} \end{pmatrix}. \tag{18}$$

We rearrange Eq. (18) using

$$\mathbf{C_R} = \{\mathbf{R(E-H)R}\}^{-1}\mathbf{RHQC_Q} \tag{19}$$

to yield

$$\begin{pmatrix} \mathbf{PHP-E} & \mathbf{PHQ} \\ \mathbf{QHP} & \mathbf{QHQ} + \mathbf{QHR}\{\mathbf{R(E-H)R}\}^{-1}\mathbf{RHQ-E} \end{pmatrix} \begin{pmatrix} \mathbf{C_P} \\ \mathbf{C_Q} \end{pmatrix} = \mathbf{0}, \tag{20}$$

where $\{\mathbf{R(E\text{-}H)R}\}^{-1}$ is shorthand for the Lowdin T matrix[29] defined as $\mathbf{R}[\alpha(\mathbf{P+Q})+\mathbf{R(E\text{-}H)R}]^{-1}\mathbf{R}$, where α is a constant. Note that $[\alpha(\mathbf{P+Q})+\mathbf{R(E\text{-}H)R}]^{-1}$ is block diagonal so that $\mathbf{P}[\alpha(\mathbf{P+Q})+\mathbf{R(E\text{-}H)R}]^{-1}\mathbf{R}$ and $\mathbf{Q}[\alpha(\mathbf{P+Q})+\mathbf{R(E\text{-}H)R}]^{-1}\mathbf{R}$ equal zero. At this point, Eq. (20) is equivalent to the full CI equations and is impractical to solve, due to the coupling of the single and double excitations (**Q**) to all higher excitations. A means of truncating the equations is needed. We do so in the following way. For the root within the reference space most like the state of interest we define $E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$ and set $E = E_0 + E_{\text{corr}}$ in the block of H over the **Q** configurations. (Various choices for Ψ_0 will be discussed below.) Realizing that the effect of higher excitations contained in the term $\mathbf{QHR}\{\mathbf{R(E\text{-}H)R}\}^{-1}\mathbf{RHQ}$ is to dress (or correlate) the single and double excitations, we approximate the **Q** block by replacing this term by the diagonal matrix $\mathbf{E_{corr}}$. That is, we assume that the correlation energy for the single and double excitations is similar to that of the state of interest. [This is not completely accurate, since the E in the term $\mathbf{QHR}\{\mathbf{R(E\text{-}H)R}\}^{-1}\mathbf{RHQ}$ is that of the state under consideration, and thus this term is not entirely equivalent to the correlation energy of each of the single and double excitations.] With this approximation Eq. (20) becomes

$$\begin{pmatrix} \mathbf{PHP-E} & \mathbf{PHQ} \\ \mathbf{QHP} & \mathbf{QHQ-E_0} \end{pmatrix} \begin{pmatrix} \mathbf{C_P} \\ \mathbf{C_Q} \end{pmatrix} = \mathbf{0}. \tag{21}$$

Equation (21) can itself be rearranged using

$$\mathbf{C_Q} = \{\mathbf{Q(E_0-H)Q}\}^{-1}\mathbf{QHPC_P} \tag{22}$$

[where $\{\mathbf{Q(E_0\text{-}H)Q}\}^{-1}$ is defined analogously to $\{\mathbf{R(E-H)R}\}^{-1}$] to give the effective Schrödinger equation

$$\{\mathbf{PHP+PHQ}\{\mathbf{Q(E_0-H)Q}\}^{-1}\mathbf{QHP}\}\mathbf{C_P} = \mathbf{EC_P}. \tag{23}$$

The effective Hamiltonian defined by Eq. (23) is Hermitian and is defined only over the reference space. We stress that, as in VPT or MRLCC, **QHQ** is the full interaction matrix for the single and double excitations, not just the diagonal elements as in the B_K[31] or Rayleigh–Schrödinger B_K[32] approaches. The direct method of solution for QDVPT uses this partitioning and solves Eqs. (22) and (23). In contrast to MRLCC where a specific C_P is chosen and Eq. (22) is solved, C_P is not known in QDVPT. As a result one must essentially solve n MRLCC problems, one for each function in the **P** space. We have implemented the solution of the QDVPT equations using this direct method and have obtained QDVPT wave functions by diagonalizing Eq. (23). While this approach is possible, it turns out to be unwieldy for large reference spaces, requiring essentially n times the work of a VPT or MRLCC calculation. In the Appendix we present an iterative method for solving Eq. (21) which proves to be much more efficient. This treatment takes only somewhat more effort than a MRLCC or VPT calculation.

Since we require E_0 for the root of the reference space most like the state of interest, we normally begin the calculation by diagonalizing H_0 over the reference space and defining H in terms of the eigenfunctions of H_0 in the reference space. (This is not a necessary step, since given an E_0 the

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

QDVPT equations are invariant to a unitary transformation within the reference space. Rather, we perform this operation to make obvious the relation of QDVPT to MRLCC and VPT, where this prediagonalization of the reference space is necessary.) When this is done, **PHP** is diagonal and any coupling that occurs between the zeroth-order states now arises due to the $\mathbf{PHQ\{Q(E_0\text{-}H)Q\}^{-1}QHP}$ term. If this term becomes large, significant mixing will occur within the **P** space. In this case, E_0 is no longer the appropriate reference energy to use in solving Eq. (21) and it is best to iterate these equations, using the new E_0 defined by $E_0 = \mathbf{C}_\mathbf{P}^\dagger \mathbf{H}_0 \mathbf{C}_\mathbf{P}$ with $\mathbf{C}_\mathbf{P}^\dagger \mathbf{C}_\mathbf{P} = 1$ (note this expression contains H_0 and not the effective H), repeating this process until convergence is reached.

In the other extreme, when both **PHP** and $\mathbf{PHQ\{Q(E_0-H)Q\}^{-1}QHP}$ yield no coupling within the reference space, Eqs. (22) and (23) can be shown to yield the MRLCC energy and wave function for the root corresponding to the E_0 chosen. The diagonal elements corresponding to the remaining configurations are

$$H_{jj} = E_0^j + \langle \Psi_0^j | \mathbf{HQ\{Q(E_0-H)Q\}^{-1}QH} | \Psi_0^j \rangle. \quad (24)$$

Thus the remaining diagonal elements do not correspond to the MRLCC energies for these roots, due to the presence of E_0 in their effective matrix elements, rather than E_0^j. However, it is just this approximation that inhibits the problems encountered with intruder states. Were the effective Hamiltonian to reduce to separate MRLCC calculations on each root when no effective coupling existed, one would have quite high values of E_0^j in the effective matrix elements, leading to crossings with eigenvalues of **QHQ** and instabilities in the equations as were encountered in VPT.

B. Relation to other methods

The present method is somewhat similar to the B_K[31] and Rayleigh–Schrödinger B_K[32] methods. Referring to Eq. (20), the first difference between QDVPT and the B_K method is that in QDVPT we substitute $-E_0$ for $\{-E + \mathbf{QHR\{R(E-H)R\}^{-1}RHQ}\}$, whereas the B_K method neglects $\mathbf{QHR\{R(E-H)R\}^{-1}RHQ}$ and retains E, thus yielding a size inconsistency similar to that of MRSDCI. The second difference between B_K and QDVPT is that the B_K method only retains the diagonal elements in the **QHQ** block, whereas QDVPT retains the full **QHQ** matrix. Rayleigh–Schrödinger B_K perturbation theory differs from QDVPT only in the second of these two ways, since it makes the same substitution of $-E_0$ for $\{-E + \mathbf{QHR\{R(E-H)R\}^{-1}RHQ}\}$ as QDVPT does. The expected improvement in accuracy of QDVPT over Rayleigh–Schrödinger B_K perturbation theory should be similar to that found in proceeding from conventional Rayleigh–Schrödinger PT to the nondegenerate second-order VPT defined in Sec. II and Ref. 18.

The relation between the present method and MRLCC was discussed above. The difference between QDVPT and MRSDCI consists in that CI neglects $\mathbf{QHR\{R(E-H)R\}^{-1}RHQ}$ in the **Q** block, but retains E, rather than substituting E_0. Variational perturbation theory will be shown below to be related to QDVPT in a perturbative sense; i.e., by solving the effective Schrödinger equation perturbatively (when such an expansion is appropriate) one recovers the VPT results in low orders.

Finally, QDVPT can be shown to be similar to the recently introduced multireference averaged coupled-pair functional method of Gdanitz and Ahlrichs.[15] In the multireference averaged coupled-pair functional method the configuration space (outside Ψ_0) is broken up into two parts: Ψ_a comprises all configurations with orbital occupations that are the same as the reference configurations outside the active space, and Ψ_e is made up of all other configurations. A modified CISD energy expression is used in which the normalization terms in the denominator corresponding to Ψ_a and Ψ_c are weighted by the factors g_a and g_c, respectively. Gdanitz and Ahlrichs choose $g_a = 1$ (reasoning that no renormalization is needed for the **a** space) and $g_e = 2/n$, where n is the number of electrons being correlated. The definition of g_e is obtained by requiring that the energy functional employed have the proper dependence on particle number for a system of separated electron pairs. QDVPT can be obtained from their energy functional by setting $g_e = 0$ and $g_a = 1$.

C. Application of QDVPT to 1 $^1A_1$ CH$_2$(He)$_n$

Using the same definitions of the components of Ψ as were used in Sec. II we now have

$$\mathbf{P} = |\Psi_0\rangle\langle\Psi_0| + |\Psi_c\rangle\langle\Psi_c|,$$
$$\mathbf{Q} = |\phi_{\mathrm{CH2}}\rangle\langle\phi_{\mathrm{CH2}}| + |\chi_0\rangle\langle\chi_0| + |\chi_c\rangle\langle\chi_c|. \quad (25)$$

With the definitions for the Hamiltonian matrix elements used in Sec. II we obtain the effective Hamiltonian

$$\mathbf{H}_{\mathrm{eff}} - \mathbf{E}_0 = \begin{pmatrix} H_{0,0}^e - nH_{0,\chi 0}^2/\epsilon_{\mathrm{He}} & H_{0,c}^e \\ H_{c,0}^e & H_{c,c}^e - nH_{c,\chi c}^2/(\epsilon_c + \epsilon_{\mathrm{He}}) \end{pmatrix}. \quad (26)$$

Because the He do not interact with CH$_2$, $H_{c,\chi c} = H_{0,\chi 0} = H_{0,\mathrm{He}}$. Defining the matrix elements of Eq. (26) as M_{ij} and solving for the lowest root of the effective Schrödinger equation we obtain

$$\begin{aligned} E_1 &= E_0 + (M_{11} + M_{22})/2 + [(M_{11} - M_{22})/2] \\ &\quad \times [(1 + 4(M_{12})^2/(M_{11} - M_{22})]^{1/2} \\ &= E_0 + M_{11} + (M_{12})^2/(M_{11} - M_{22}) \\ &\quad - (M_{12})^4/(M_{11} - M_{22})^3 + O[(M_{12})^6]. \end{aligned} \quad (27)$$

Substituting for the M_{ij} one obtains

$$\begin{aligned} E_1 = E_0 &- nH_{0,\mathrm{He}}^2/\epsilon_{\mathrm{He}} - H_{0,\mathrm{CH2}}(E_0 - H_{\mathrm{CH2}})^{-1}H_{\mathrm{CH2,0}} \\ &+ |H_{c,0}^e|^2/[H_{0,0}^e - H_{c,c}^e - nH_{0,\chi 0}^2/ \\ &\quad \epsilon_{\mathrm{He}} + nH_{c,\chi c}^2/(\epsilon_c + \epsilon_{\mathrm{He}})] \\ &- |H_{c,0}^e|^4/[H_{0,0}^e - H_{c,c}^e - nH_{0,\chi 0}^2/\epsilon_{\mathrm{He}} \\ &+ nH_{c,\chi c}^2/(\epsilon_c + \epsilon_{\mathrm{He}}]^3 + O(H_{ij}^{12}). \end{aligned} \quad (28)$$

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

For comparison with the VPT results we expand out the $M_{11}-M_{22}$ denominators around $H^{e}_{c,c}$ and obtain

$$E \simeq E_0 - n|H_{0,\mathrm{He}}|^2/\epsilon_{\mathrm{He}} - H_{0,\mathrm{CH2}}(E_0 - H_{\mathrm{CH2}})^{-1}H_{\mathrm{CH2},0} - |H^{e}_{c,0}|^2/H^{e}_{c,c} + H^{e}_{0,0}|H^{e}_{c,0}|^2/(H^{e}_{c,c})^2 - n|H_{0,\mathrm{He}}|^2|H^{e}_{c,0}|^2\{1/(\epsilon_c+\epsilon_{\mathrm{He}}) - 1/\epsilon_{\mathrm{He}}\}/(H^{e}_{c,c})^2. \tag{29}$$

The only differences between Eq. (28) and the VPT result are the fifth and seventh terms of Eq. (28), which do not appear in Eq. (16). Thus, in the regions where $1/D$ or $1/(M_{11}-M_{22})$ can be expanded as above, the VPT and QDVPT results are expected to be quite close.

A more natural choice about which to expand the QDVPT energy is $1/(H^{e}_{c,c}-H^{e}_{0,0})$, in which both Ψ_0 and Ψ_c are dressed by their interactions with the CH_2 double excitations. The fifth term in Eq. (28) arises because we instead expanded about $1/H^{e}_{c,c}$, and the ratio $H^{e}_{0,0}/H^{e}_{c,c}$ gives information regarding the appropriateness of VPT for a given problem. When this factor becomes large one expects intruder state effects to be important. Note that QDVPT is still valid, it merely indicates that this choice for expansion of the QDVPT denominator is inappropriate. In fact, one need not perform any expansion in the QDVPT case and then the QDVPT energy expression is valid even when $(M_{11}-M_{22})$ is zero. (In the calculations presented below we, of course, do not expand out the QDVPT energy expression. This expansion is performed here for illustrative purposes.) It should be noted that it is the presence of the factor $1/(M_{11}-M_{22})$ rather than $1/D$ which contributes to the stability of the QDVPT equations. As shown above D will go through zero as the number of He is increased, whereas one expects $(M_{11}-M_{22})$ to be nearly constant with increasing He. When D becomes small the VPT equations cannot be solved either perturbatively or exactly.

Finally, we comment on the lack of size consistency in QDVPT. Within the present simple model it can be shown that $M_{12}(=M_{21})$ is constant as the number of He is increased. However, the difference between M_{11} and M_{22} will change as the number of He is increased. This is due to the presence of E_0 in the expression for H^{e}_{cc}, rather than E_c as would be found in a MRLCC calculation on Ψ_c. That is, given that the He are well separated from CH_2 one would expect the same He double excitation coefficients (and thus the same contribution to the correlation energy of each state) from the expressions $\{\mathbf{Q}(\mathbf{E}_0-\mathbf{H})\mathbf{Q}\}^{-1}\mathbf{QH}\Psi_0$ and $\{\mathbf{Q}(\mathbf{E}_c-\mathbf{H})\mathbf{Q}\}^{-1}\mathbf{QH}\Psi_c$. This is not the case for $\{\mathbf{Q}(\mathbf{E}_0-\mathbf{H})\mathbf{Q}\}^{-1}\mathbf{QH}\Psi_c$ which is the expression used in QDVPT to generate the effective matrix elements for the orthogonal complement to Ψ_0. This leads to the energy contribution per He to M_{22} being somewhat different from that to M_{11}. In the calculations performed below $M_{11}-M_{22}$ becomes more negative with increasing He, and in the limit of an infinite number of He in the present system the QDVPT result would reduce to an MRLCC calculation on the lowest state. However, it will also be shown below that this effect is quite small relative to the size inconsistency of truncated CI and should not be a major factor, even for calculations on quite large molecules.

IV. PROPERTY EVALUATION

While the methods for evaluation of first-order one-electron properties for VPT and QDVPT are formally similar, some differences exist between the two. We first present the theory for VPT and MRLCC and then proceed to QDVPT.

A. VPT/MRLCC properties

The full CI Hamiltonian for a fixed many-electron basis in the presence of the perturbation G is written as

$$\mathbf{H} = \mathbf{H}^{\mathrm{f}} + \mu G, \tag{30}$$

where the superscript f denotes the field-free Hamiltonian for the system of interest. We partition the field-dependent Hamiltonian in the usual way for VPT or MRLCC and E_0, E_2, Ψ_0, and Ψ_1 are then functions of the strength of the perturbation μ. To the extent that E_0+E_2 for VPT or MRLCC is able to approximate the eigenvalue of the full CI matrix, the property $\langle G\rangle$ is given by $\partial E/\partial\mu|_{\mu=0}$. The derivative of the total VPT or MRLCC energy with respect to μ evaluated at $\mu=0$ is

$$\frac{\partial E}{\partial\mu} = \frac{\partial E_0}{\partial\mu} + \frac{\partial E_2}{\partial\mu},$$
$$\frac{\partial E_2}{\partial\mu} = \left\langle\frac{\partial\Psi_0}{\partial\mu}|H^f|\Psi_1\right\rangle + \langle\Psi_0|G|\Psi_1\rangle + \left\langle\Psi_0|H^f|\frac{\partial\Psi_1}{\partial\mu}\right\rangle. \tag{31}$$

After some manipulations, one obtains the expression (for real wave functions)

$$\frac{\partial E}{\partial\mu} = (1-|\Psi_1|^2)\langle\Psi_0|G|\Psi_0\rangle + 2\langle\Psi_1|G|\Psi_0\rangle + \langle\Psi_1|G|\Psi_1\rangle + 2\left\langle\frac{\partial\Psi_0}{\partial\mu}|H^f - E_0 - E_2|\Psi_0+\Psi_1\right\rangle - 2|\Psi_1|^2\left\langle\Psi_0|H^f|\frac{\partial\Psi_0}{\partial\mu}\right\rangle. \tag{32}$$

When Ψ_0 is an eigenfunction of H^f_0, the last term in Eq. (32) is zero. Furthermore, when Ψ_0 is an eigenfunction of H^f_0, $\partial\Psi_0/\partial\mu$ is easily obtained as $\{\mathbf{Q}_0(\mathbf{E}^{\mathrm{f}}_0-\mathbf{H}^{\mathrm{f}})\mathbf{Q}_0\}^{-1}\mathbf{G}\Psi_0$ and Eq. 32) becomes for VPT:

$$\frac{\partial E_{\mathrm{VPT}}}{\partial\mu} = (1-|\Psi_1|^2))\Psi_0|G|\Psi_0\rangle + 2\langle\Psi_1|G|\Psi_0\rangle + \langle\Psi_1|G|\Psi_1\rangle - 2E_2\langle\Psi_0|G|\{\mathbf{Q}_0-\mathbf{E}^{\mathrm{f}}_0-\mathbf{H}^{\mathrm{f}})\mathbf{Q}_0\}^{-1}\Psi_1\rangle, \tag{33}$$

whereas for MRLCC Eq. (32) becomes

$$\frac{\partial E_{\mathrm{MRLCC}}}{\partial\mu} = (1-|\Psi_1|^2))\Psi_0|G|\Psi_0\rangle + 2\langle\Psi_1|G|\Psi_0\rangle + \langle\Psi_1|G|\Psi_1\rangle + 2\langle\Psi_0|G|\{\mathbf{Q}_0-\mathbf{E}^{\mathrm{f}}_0-\mathbf{H}^{\mathrm{f}})\mathbf{Q}_0\}^{-1}\mathbf{H}\Psi_1\rangle. \tag{34}$$

Alternatively, one could choose to not allow the coefficients defining Ψ_0 to change with application of the field. In this case $\partial\mathbf{P}/\partial\mu = \partial\mathbf{Q}/\partial\mu = 0$ and the expression for both the VPT and MRLCC properties reduces to

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

$$\frac{\partial E}{\partial \mu} = (1-|\Psi_1|^2))\rangle\Psi_0|G|\Psi_0\rangle + 2\langle\Psi_1|G|\Psi_0\rangle + \langle\Psi_1|G|\Psi_1\rangle. \quad (35)$$

We denote properties calculated using Eq. (35) as $\langle G\rangle_{\rm fix}$ below, and refer to these fixed or frozen Ψ_0 properties, since the coefficients defining Ψ_0 are fixed at their zero-field values. The properties obtained from Eq. (35) are equivalent to those obtained using the modified expectation value

$$\langle G\rangle = \langle\Psi_0|G|\Psi_0\rangle + \langle\Psi_0+\Psi_1|G-G_0|\Psi_0+\Psi_1\rangle, \quad (36)$$

where $G_0 = \langle\Psi_0|G|\Psi_0\rangle$. Equation (36) can be obtained in a somewhat different manner by writing

$$\langle G\rangle = \langle\Psi_0+\Psi_1|G|\Psi_0+\Psi_1\rangle/\langle\Psi_0+\Psi_1|\Psi_0+\Psi_1\rangle \quad (37)$$

expanding the denominator, and keeping terms up to second order in Ψ_1. The equivalence of Eqs. (35) and (36) when the coefficients defining Ψ_0 are fixed at their zero-field values arises because the C_j are obtained variationally via Eq. (6). This may be viewed as a modified Hellmann–Feynman theorem for the energy expression used above [Eq. (3)], with the assumption that the atomic and molecular orbitals are fixed.

In general, Eqs. (33) and (34) are expected to be more accurate than Eq. (35), since they take into account the variation of Ψ_0 with the perturbation strength. However, when Ψ_0 is not an eigenfunction of H_0^f we have chosen to use Eq. (35) to evaluate molecular properties, thus using the form equivalent to the expectation value in Eq. (36). We choose this due to the ambiguity in the derivative of the d_0^i associated with an arbitrarily chosen Ψ_0. One could use standard first-order Rayleigh–Schrödinger perturbation theory to define $\partial\mathbf{d}_0/\partial\mu$, but we have chosen to discard the term arising from $\partial\mathbf{d}_0/\partial\mu$. In using Eqs. (32) or (34) an effective one-particle density matrix can be defined for the variational perturbation theory or MRLCC wave functions as

$$\rho = (1-\langle\Psi_1|\Psi_1\rangle)\rho_0 + (\rho_{01}+\rho_{10}) + \rho_1 + (\rho_{01}^X + \rho_{10}^X) \quad (38)$$

with X either VPT or MRLCC and where

$$\rho_0 = \int\cdots\int dr_2\cdots dr_M\, \Psi_0^*(r_1,\ldots,r_M)\Psi_0(r_1,\ldots,r_M), \quad (39a)$$

$$\rho_{01} = \int\cdots\int dr_2\cdots dr_M\, \Psi_0^*(r_1,\ldots,r_M)\Psi_1(r_1,\ldots,r_M), \quad (39b)$$

$$\rho_{10} = \int\cdots\int dr_2\cdots dr_M\, \Psi_1^*(r_1,\ldots,r_M)\Psi_0(r_1,\ldots,r_M), \quad (39c)$$

$$\rho_1 = \int\cdots\int dr_2\cdots dr_M\, \Psi_1^*(r_1,\ldots,r_M)\Psi_1(r_1,\ldots,r_M) \quad (39d)$$

and

$$\rho_{01}^{\rm VPT} = -E_2\int\cdots\int dr_2\cdots dr_M\, \Psi_0^*(r_1,\ldots,r_M) \times\{\mathbf{Q}_0(\mathbf{E}_0^{\rm f}-\mathbf{H}^{\rm f})\mathbf{Q}_0\}^{-1}\Psi_1(r_1,\ldots,r_M), \quad (40a)$$

$$\rho_{10}^{\rm VPT} = -E_2\int\cdots\int dr_2\cdots dr_M\, \{\mathbf{Q}_0(\mathbf{E}_0^{\rm f}-\mathbf{H}^{\rm f})\mathbf{Q}_0\}^{-1} \times\Psi_1^*(r_1,\ldots,r_M)\Psi_0(r_1,\ldots,r_M), \quad (40b)$$

$$\rho_{01}^{\rm MRLCC} = \int\cdots\int dr_2\cdots dr_M\, \Psi_0^*(r_1,\ldots,r_M) \times\{\mathbf{Q}_0(\mathbf{E}_0^{\rm f}-\mathbf{H}^{\rm f})\mathbf{Q}_0\}^{-1}\mathbf{H}\Psi_1(r_1,\ldots,r_M), \quad (41a)$$

$$\rho_{10}^{\rm MRLCC} = \int\cdots\int dr_2\cdots dr_M \{\mathbf{Q}_0(\mathbf{E}_0^{\rm f}-\mathbf{H}^{\rm f})\mathbf{Q}_0\}^{-1}\mathbf{H} \times\Psi_1^*(r_1,\ldots,r_M)\Psi_0(r_1,\ldots,r_M). \quad (41b)$$

When fixed properties are calculated ρ is obtained using Eq. (42), with the various terms defined as in Eq. (39):

$$\rho = (1-\langle\Psi_1|\Psi_1\rangle)\rho_0 + (\rho_{01}+\rho_{10}) + \rho_1. \quad (42)$$

One-electron properties are obtained via Eq. (43):

$$\langle G\rangle = {\rm Tr}(\rho G). \quad (43)$$

Finally, we point out that there is an effective inconsistency in Eqs. (33) and (34) in the order of the terms included from the field-free wave function. Since Ψ_1 is the first-order correction to the wave function, the expressions for $\langle G\rangle$ contain zeroth-order terms (G_0), first-order terms ($\langle\Psi_0|G|\Psi_1\rangle$), and some of the second-order terms ($\langle\Psi_1|G-G_0|\Psi_1\rangle$). The other second-order terms, of the form $\langle\Psi_0|G|\Psi_2\rangle$, do not appear since the expression for the properties presented above is based on the second-order energy expression. These terms do not enter into the energy at second order.

B. Quasidegenerate variational perturbation theory properties

As was the case for VPT properties we obtain the QDVPT properties as derivatives of the total energy with respect to the strength of the applied perturbation. Beginning with the effective Schrödinger equation [Eq. (23)] we have

$$E(\mu)C_P(\mu) = H_{\rm eff}(\mu)C_P(\mu), \quad (44)$$

where the dependence on μ has been made explicit. Assuming that C_P is normalized we have

$$E(\mu) = C_P'(\mu)H_{\rm eff}(\mu)C_P(\mu). \quad (45)$$

From here on we drop the explicit reference to the μ dependence. We assume that the basis states for $H_{\rm eff}$ are an arbitrary set of μ-independent linear combinations of the reference space configurations. The case where $H_{\rm eff}$ and C_P are defined in terms of field-dependent zeroth-order functions can be shown to be equivalent to what follows since, as long as the reference space *configurations* are fixed the field-dependent and field-independent zeroth-order states are related by a unitary transformation. Thus the effective Hamiltonians and C_P in the two bases are related in the usual way and the energy is invariant to this transformation.

Traking the derivative of E with respect to μ and using the facts that C_P is an eigenfunction of $H_{\rm eff}$ and that $\partial(C_P'C_P)/\partial\mu = 0$ one obtains

$$\langle G\rangle = \frac{\partial E}{\partial\mu} = C_P'\frac{\partial H_{\rm eff}}{\partial\mu}C_P. \quad (46)$$

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

In an entirely analogous manner to the procedure for VPT one obtains the effective one-electron density matrix (noting that $\partial \mathbf{Q}/\partial\mu = 0$, since $\mathbf{P}$ contains Ψ_0 and its orthogonal complement)

$$\rho = \rho_0 + (\rho_{01} + \rho_{10}) + \rho_1 - \langle\Psi_1|\Psi_1\rangle\rho_0^0 \tag{47}$$

when E_0 is defined by the eigenvector of H_0 in the reference space, or

$$\rho = \rho_0 + (\rho_{01} + \rho_{10}) + \rho_1 - \langle\Psi_1|\Psi|\rangle \times \left\{\rho_0 + 2\left\langle C_P|H^f|\frac{\partial C_P}{\partial\mu}\right\rangle\right\} \tag{48}$$

when E_0 is defined self-consistently in terms of the final C_P. In either case ρ_0, ρ_{01}, ρ_{10}, and ρ_1 are given by Eq. (39) and

$$\rho_0^0 = \int\cdots\int dr_2\cdots dr_M\ \Psi_0^{0*}(r_1,\ldots,r_M)\Psi_0^0(r_1,\ldots,r_M), \tag{49}$$

where Ψ_0^0 is the eigenfunction of H_0 corresponding to E_0.

Note that due to the normalization chosen ($C_P^{\prime}C_P = 1$) the trace of ρ_0 is equal to the total electron density, as is the case for ρ_0^0 and ρ. With this choice of normalization we can write Eq. (47) (defining $\Psi_{\mathrm{EVPT}} = \Psi_0 + \Psi_1$)

$$\rho = \rho_{\mathrm{EVPT}} - \langle\Psi_1|\Psi_1\rangle\rho_0^0 \tag{50}$$

with

$$\rho_{\mathrm{EVPT}} = \int\cdots\int dr_2\cdots dr_M \times \Psi_{\mathrm{EVPT}}^*(r_1,\ldots,r_M)\Psi_{\mathrm{EVPT}}(r_1,\ldots,r_M). \tag{51}$$

For the one case considered below where E_0 was defined self-consistently, the last term in Eq. (48) was neglected and ρ_0^0 was replaced by ρ_0 in Eq. (50).

Properties are calculated using Eqs. (43) and (50). Finally, we note that an expression identical to Eq. (50) holds for the fixed coefficient (or frozen Ψ_0) VPT properties. A significant difference exists in the application of this expression to the two types of wave functions, however. In VPT the orthogonal complement configurations of Ψ_0 in the reference space are included in the $\mathbf{Q}$ space and contribute to Ψ_1, and the intermediate normalization applied sets the coefficient of Ψ_0 to one. In QDVPT all linear combinations of the reference space functions are included in the $\mathbf{P}$ space, thus $\langle\Psi_1|\Psi_1\rangle$ contains no contributions from the reference space. In addition, the intermediate normalization applied has the sum of the squares of *all* reference space configurations equal to unity.

V. RESULTS

All calculations were performed with the MELDF suite of electronic structure codes from this laboratory.[33] The BeH_2,[34] CH_2,[2(c)] and ethylene[35] basis sets and geometries were those used in Ref. 18 to allow comparison with previous full CI results.[2(c),2(d),36] The He basis is the 3-12G basis of Binkley *et al.*[37] In all cases except the $^1B_{1u}$ states of ethylene the MO basis sets were the SCF or two-configurational SCF (TCSCF) orbitals, with canonical virtual orbitals. For the $^1B_{1u}$ states of ethylene the average natural orbitals[38] for the two lowest $^1B_{1u}$ states from a preliminary CI were used as an MO basis.[18,39,40] Properties are presented from multireference singles and doubles configuration interaction calculations (MRSDCI) (calculated as the expectation value of the given property operator), variational perturbation theory, QDVPT, and multireference linearized coupled-cluster wave functions. We have used second-order Rayleigh–Schrödinger perturbation theory to select correlating configurations in some cases.[18] Where this is done we also note the percentage of the second-order energy accounted for by the configurations retained in the variational part of the treatment. When perturbation theory selection was used we retained all single excitations relative to the reference functions.

We first present results based on QDVPT calculations on the systems examined in Ref. 18. Only for the $^1B_{1u}$ states of ethylene did we perform an iteration of the QDVPT equations to redefine E_0. In all other cases the results were based on using the appropriate eigenvalue of H_0 in the reference space as E_0.

In Table I results are presented from calculations at sev-

TABLE I. BeH_2 two-reference (MRSDCI) and QDVPT results, C_{2v} geometries.

$r(\mathrm{BeH_2})$[a]	$r(\mathrm{H_2})$[a]	TCSCF[b]	Corr. E[c]	ΔMRSDCI[d]	ΔQDVPT[d]
1.00	4.16	− 15.7054	31.8	0.3	− 0.5
2.00	3.24	− 15.6330	41.8	0.4	− 1.4
2.50	2.78	− 15.5696	53.3	0.9	− 2.9
2.75	2.55	− 15.5386	64.3	2.0	− 4.7
3.00	2.32	− 15.5583	66.7	3.1	− 5.5
3.50	1.86	− 15.6372	56.0	2.1	− 2.3
4.0	1.4	− 15.6872	50.4	2.5	− 0.8
6.0	1.4	− 15.7107	50.2	1.6	− 1.8

[a] Distances in bohr. $r(\mathrm{BeH_2})$ is the distance from Be to the H_2 midpoint. $r(\mathrm{H_2})$ is the H_2 bond length.

[b] Energy of the two configuration SCF wave function, in hartree.

[c] Correlation energy, in millihartree, relative to the two configuration SCF energy, using the full CI energies of Ref. 36.

[d] Error relative to the full CI energies of Ref. 36, in millihartree. (MRSDCI) designates singles and doubles CI results [in this case a two-reference (MRSDCI)] and QDVPT denotes uniterated quasidegenerate variational perturbation theory results.

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

TABLE II. MRSDCI and MRLCC, VPT, and QDVPT results for CH_2, C_{2V} symmetry.

State	Refs.[a]	ΔMRSDCI[b]	ΔMRLCC[b]	ΔVPT	ΔQDVPT[b]	Full CI[c]
$1\,^3B_1$	1	4.7			− 1.3[d]	− 39.0463
$1\,^1A_1$	1	8.9			− 3.0[d]	− 39.0272
$1\,^1A_1$	2	5.0	− 1.3	− 1.3	− 1.3	
$1\,^1A_1$	20	1.7	− 1.3	− 1.7	− 1.7	
$1\,^1A_1$	29	1.1	− 1.2	− 1.6	− 1.6	

[a] The number of spin-adapted configurations in the reference space.

[b] Errors relative to the full CI, in millihartree. The labels are defined in Table I.

[c] Results from Ref. 2(c), in hartree.

[d] In the one-reference case, the MRLCC, VPT, and QDVPT methods are equivalent.

eral geometries of BeH_2. In Ref. 18 it was shown that while MRLCC and VPT generally gave good agreement with full CI energies, the geometry $r(BeH_2) = 2.75\ a_0\ r(H_2) = 2.55\ a_0$ was particularly troublesome for either method. The VPT results gave a grossly incorrect ratio of the coefficients of the two reference functions in the final wave function, and the error in the total energy changed sign relative to the preceding or following points in the series, leading to a bumpy surface. A smooth surface and accurate relative sizes of the coefficients of the zeroth-order configurations were only recovered when the reference space size was increased significantly. MRLCC gave a smooth surface but because the reference space coefficients were taken from diagonalizing H_0, their ratio in the final wave function was also incorrect. It is seen that the uniterated QDVPT results compare favorably with MRSDCI (relative to the full CI energies). The ratio of the coefficients of the two reference functions (x in Ref. 18) was found to be − 0.89 for QDVPT, − 0.82 for MRSDCI, − 0.57 for MRLCC, and + 0.04 for VPT. The full CI value is − 0.85, indicating that QDVPT is capable of treating the strong mixing between the two zeroth-order functions much more easily than VPT.

In Table II we present results from MRSDCI, VPT, MRLCC, and QDVPT calculations on CH_2, and compare them to the full CI results of Bauschlicher and Taylor.[2(c)] It is seen that excellent agreement is obtained.

TABLE III. Total energies for CH_2He_n, C_{2V} symmetry.

n	State	Refs.[a]	%PTK[b]	ΔMRSDCI[c]	Δ(MR)LCC[c]	ΔVPT[c]	QDVPT[c]
0	$1\,^3B_1$	1	100	4.7		− 1.3	
0	$1\,^1A_1$	1	100	8.9		− 3.0	
0	$1\,^1A_1$	2	100	5.0	− 1.3	− 1.3	− 1.3
1	$1\,^3B_1$	1	100	5.7		− 1.4	
1	$1\,^1A_1$	1	100	10.3		− 3.0	
1	$1\,^1A_1$	2	100	6.1	− 1.3	− 1.3	− 1.3
3	$1\,^3B_1$	1	100	8.0		− 1.5	
3	$1\,^1A_1$	1	100	13.2		− 3.1	
3	$1\,^1A_1$	2	100	8.4	− 1.4	− 1.4	− 1.4
5	$1\,^3B_1$	1	100	10.5		− 1.6	
5	$1\,^1A_1$	1	100	16.3		− 3.2	
5	$1\,^1A_1$	2	> 99.9	11.0	− 1.6	− 1.6	− 1.6
9	$1\,^3B_1$	1	> 99.9	16.4		− 1.7	
9	$1\,^1A_1$	1	> 99.9	23.2		− 3.4	
9	$1\,^1A_1$	2	> 99.9	17.1	− 1.7	− 1.7	− 1.7
12	$1\,^1A_1$	2	> 99.9	22.2	− 1.8	− 1.7	− 1.8
13	$1\,^3B_1$	1	> 99.9	23.3		− 1.9	
13	$1\,^1A_1$	1	> 99.9	31.0		− 3.6	
13	$1\,^1A_1$	2	> 99.9	24.0	− 1.9	− 1.9	− 1.9
17	$1\,^3B_1$	1	> 99.9	31.2		− 2.1	
17	$1\,^1A_1$	1	> 99.9	39.7		− 3.8	
17	$1\,^1A_1$	2	> 99.9	32.1	− 2.1	− 2.1	− 2.1
25	$1\,^3B_1$	1	> 99.9	49.8		− 2.5	
25	$1\,^1A_1$	1	> 99.9	59.5		− 4.1	
25	$1\,^1A_1$	2	> 99.9	50.8	− 2.5	− 2.5	− 2.5

[a] The number of spin-adapted configurations in the reference space. In the one-reference case, the LCC, QDVPT, and VPT methods are equivalent.

[b] The percentage of the second-order energy accounted for by the configurations treated variationally. A value of 100 indicates all single and double excitations were included. All single excitations from the reference functions were included in all cases.

[c] Errors relative to the full CI [Ref. 2(c)] in millihartree. (MR)LCC denotes a (multireference) linearized coupled-cluster calculation. VPT denotes a variational perturbation theory calculation. The remaining labels are defined in Table I and the text.

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

TABLE IV. Results from correlated treatments for C_2H_4,[a] D_{2h} symmetry.

State	Refs.[b]	PTK[c]	Conf.[d]	MRSDCI	MRLCC	VPT	QDVPT
$1\,^1A_g$	1	100	5 252	−78.3272	···	−78.3615	···
$1\,^1A_g$	4	100	23 762	−78.3330	−78.3616	−78.3618	−78.3617
$1\,^1A_g$	4	96.5	3 242	−78.3319	−78.3563	−78.3610	−78.3592
$1\,^1A_g$	2	100	10 226	−78.3356	−78.3610	−78.3622	−78.3616
$1\,^1B_{1u}$	2[e]	100	21 062	−78.0287	−78.0614	−78.0614	−78.0614
$2\,^1B_{1u}$	2[e]	100	21 062	−77.9911	−78.0206	−78.0206	−78.0206

[a] All energies in hartree. The labels are defined in Tables I and III.

[b] Number of spin-adapted configurations in the reference space. For the $^1B_{1u}$ states the average NOs were used (see the text) as an MO basis. For the two-reference $1\,^1A_g$ calculation the TCSCF orbitals were used. For the remaining $1\,^1A_g$ calculations the one-reference SCF orbitals were used.

[c] Percentage of the second-order Rayleigh–Schrödinger perturbation theory energy accounted for by the configurations retained. All single excitations were kept.

[d] Number of spin-adapted configurations treated beyond second-order Rayleigh–Schrödinger perturbation theory.

[e] The choice of E_0 for the QDVPT equation was iterated once. The coefficients defining ψ_0 for MRLCC and VPT were chosen to be the coefficients of the reference space configurations used to define E_0 in the final iteration of the QDVPT equations.

In Table III we present results from MRSDCI, MRLCC, VPT, and QDVPT calculations on the model system CH_2He_n. The He are placed at 10 a_0 intervals along the $+z$ axis (defined as the symmetry axis of CH_2, C is at the origin and the H atoms lie in $-z$ half-plane). The nearest He is 10 a_0 from the C. Since we have used the same basis for CH_2 as in the results of Table II and since the He are well separated from each other and from CH_2, we can calculate the full CI energy for this system from the results of Ref. 2(c) and full CI on He ($E_{\mathrm{He}} = -2.850\,576\,7$ hartree). The energy values for the various methods are reported relative to the computed full CI values (based on the expression

TABLE V. BeH_2 properties at selected geometries.[a]

$r(BeH_2)$	$r(H_2)$	Refs.	Quantity	Ref. space[b]	MRSDCI	MRLCC	VARPT	QDVPT	Full CI
1.0	4.16	2	$\langle z\rangle$	0.794	0.686	0.674	0.671	0.671	0.689
			$\langle x^2\rangle$	4.80	4.84	4.84	4.85	4.85	4.84
			$\langle z\rangle_{\mathrm{fix}}$			0.674	0.671		
			$\langle x^2\rangle_{\mathrm{fix}}$			4.84	4.85		
3.5	1.86	2	$\langle z\rangle$	−1.011	−0.907	−0.847		−0.859	−0.889
			$\langle x^2\rangle$	7.51	7.48	7.44	7.46	7.46	7.47
			$\langle z\rangle_{\mathrm{fix}}$			−0.829	−0.863		
			$\langle x^2\rangle_{\mathrm{fix}}$			7.38	7.48		
6.0	1.4	2	$\langle z\rangle$	−0.093	−0.079	−0.073	−0.073	−0.073	−0.077
			$\langle x^2\rangle$	7.02	6.95	6.92	6.93	6.92	6.94
			$\langle z\rangle_{\mathrm{fix}}$			−0.072	−0.073		
			$\langle x^2\rangle_{\mathrm{fix}}$			6.88	6.93		
2.0	3.24	2	$\langle z\rangle$	1.48	1.26	1.23	1.21	1.21	1.26
			$\langle x^2\rangle$	5.05	5.08	5.09	5.10	5.10	5.09
			$\langle z\rangle_{\mathrm{fix}}$			1.23	1.21		
			$\langle x^2\rangle_{\mathrm{fix}}$			5.08	5.10		
2.0	3.24[c]	9	Energy		−15.6748	−15.6745	−15.6750	−15.6749	···
			$\langle z\rangle$	1.43	1.26	1.28	1.25	1.25	···
			$\langle x^2\rangle$	5.07	5.09	5.08	5.09	5.09	···
			$\langle z\rangle_{\mathrm{fix}}$			1.28	1.25		
			$\langle x^2\rangle_{\mathrm{fix}}$			5.08	5.09		
3.0	2.32	2	$\langle z\rangle$	−1.40	−1.20	−0.954	−0.948	−0.952	−1.16
			$\langle x^2\rangle$	7.68	7.64	7.51	7.50	7.50	7.63
			$\langle z\rangle_{\mathrm{fix}}$			−0.955	−0.947		
			$\langle x^2\rangle_{\mathrm{fix}}$			7.51			
3.0	2.32[c]	9	Energy		−15.6246	−15.6267	−15.6283	−15.6281	···
			$\langle z\rangle$	−1.39	−1.16	−1.14	−1.05	−1.08	···
			$\langle x^2\rangle$	7.82	7.62	7.58	7.54	7.56	···
			$\langle z\rangle_{\mathrm{fix}}$			−1.14	−1.04		
			$\langle x^2\rangle_{\mathrm{fix}}$			7.59	7.51		

[a] All quantities in atomic units. The various methods are defined in Sec. II and the labels are defined in Tables I and III. Properties labeled fix for MRLCC and VPT are calculated using Eq. (36), otherwise Eqs. (34) and (35) are used for VPT and MRLCC, respectively.

[b] The value of the peoperty for the CI within the reference space.

[c] The reference functions were the dominant spin-adapted configurations in the QDVPT calculation at the given geometry.

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

$E^A_{\text{full}} + nE_{\text{He}}$, where A labels the state of interest). The MRSDCI results, as expected, begin to deviate significantly from the full CI energies as the number of He is increased. The MRLCC, VPT, and QDVPT results are all significantly closer to the full CI values as n is increased, but they show some drift away from the full CI values. However, close inspection shows this drift with n is essentially linear. This drift is due to the fact that the total energy for these methods should vary as $E^A_{\text{Meth}} + n(E_{\text{He}})_{\text{LCC}}$, since for the reference spaces chosen (the reference functions involve excitations localized on CH_2) the He are treated at the single reference level. All three methods reduce to the linearized coupled cluster (LCC) method for a single reference function. Thus the change in ΔE with increasing He for MRLCC, VPT, and QDVPT goes as $n[(E_{\text{He}})_{\text{LCC}} - E_{\text{He}}]$.

In Table IV results of (MRSDCI), MRLCC, VPT, and QDVPT calculations are presented for various states of ethylene. The QDVPT results are in good agreement with the MRLCC and VPT results. For the $^1B_{1u}$ states the QDVPT equations were iterated once to redefine E_0, since the final C_P were quite different from those obtained by diagonalizing H_0 over the reference space. The VPT and MRLCC results are based on the coefficients of the QDVPT reference space functions used in the final iteration of the QDVPT equations. The energy values based on these reference functions are quite close to those reported previously where a somewhat different definition of Ψ_0 was used.[18] The excitation energies based on these results are in good agreement with size-consistency corrected CI values.[18]

We next examine the results of calculations of one-electron properties for these wave functions. The results from the calculations on BeH_2 are given in Tables V and VI. For VPT and MRLCC we present both fixed coefficient properties [Eq. (35)] and properties calculated where the coefficients defining Ψ_0 are allowed to change with application of the field [Eqs. (33) and (34)]. Several geometries[36] are examined in Table V for treatments based on two-configuration SCF wave functions. Representative examples for the effects of expansion of the reference space are also given in Table V. Similar results were obtained at other geometries. The full CI property results were obtained in the present study. For the geometries in Table V, the singles and doubles CI results are somewhat closer to the full CI results than MRLCC, VPT, or QDVPT, but in general the agreement for all the methods is quite good. Expansion of the reference space leads to better agreement for the MRLCC, VPT, and QDVPT results. In all cases the fixed coefficient MRLCC or VPT results are not as accurate as the variable coefficient results.

In Table VI results are shown from calculations at a particularly difficult geometry. In the two-reference case the MRLCC and QDVPT energies and properties are reasonably close to the full CI results, but the VPT error in the properties is quite large. Note that the fixed coefficient properties are generally worse. Expansion of the reference space leads to better agreement for all methods, with the QDVPT results converging to the full CI values somewhat quicker.

Results from calculations on CH_2He_n ($n = 0,\ldots,25$) are shown in Table VII; full CI results for $n = 0$[2(d)] are listed as well. Since the He are well separated from each other and

TABLE VI. BeH_2 properties at $r(BeH_2) = 2.75$b, $r(H_2) = 2.55$b.[a]

Refs.	Quantity	Ref. space[b]	MRSDCI	MRLCC	VARPT	QDVPT	Full CI
2[c]	Energy	-15.5386	-15.6009	-15.6053	-15.5986	-15.6076	-15.6029
	$\langle z\rangle$	0.807	0.135	0.191	0.403	-0.111	0.090
	$\langle x^2\rangle$	5.79	6.30	6.23	6.14	6.50	6.35
	$\langle z\rangle_{\text{fix}}$			0.592	1.80		
	$\langle x^2\rangle_{\text{fix}}$			5.84	4.80		
15[d]	Energy	-15.5788	-15.6028	-15.6010	-15.6063	-15.6037	
	$\langle z\rangle$	0.716	0.100	0.306	-0.490	0.024	
	$\langle x^2\rangle$	5.91	6.34	6.12	6.92	6.41	
	$\langle z\rangle_{\text{fix}}$			0.720	-0.990		
	$\langle x^2\rangle_{\text{fix}}$			5.75	7.35		
12[e]	Energy	-15.5814	-15.6029	-15.6026	-15.6038	-15.6033	
	$\langle z\rangle$	0.320	0.093	0.223	-0.060	0.069	
	$\langle x^2\rangle$	6.22	6.39	6.23	6.48	6.37	
	$\langle z\rangle_{\text{fix}}$			0.389	-0.207		
	$\langle x^2\rangle_{\text{fix}}$			6.06	6.63		
17[f]	Energy	-15.5850	-15.6029	-15.6028	-15.6032	-15.6031	
	$\langle z\rangle$	0.052	0.090	0.118	0.083	0.091	
	$\langle x^2\rangle$	6.47	6.35	6.33	6.48	6.35	
	$\langle z\rangle_{\text{fix}}$			0.136	0.055		
	$\langle x^2\rangle_{\text{fix}}$			6.31	6.38		

[a] All quantities in atomic units. The various methods are defined in Sec. II.

[b] Results from CI over the reference space configurations.

[c] The two-reference configurations are from the two-configuration SCF wave function.

[d] The reference configurations are taken from the 15 dominant configurations (Ref. 41) in the two-configuration-based VPT calculation; their coefficients were obtained by diagonalizing H over the reference space.

[e] The reference configurations are taken from the 12 dominant configurations (Ref. 41) in the two-configuration-based MRSDCI calculation. The zeroth-order wave function was defined by diagonalizing H over the reference space.

[f] The reference configurations are taken from the 17 dominant configurations (Ref. 41) in the 12-configuration-based MRSDCI calculation. The zeroth-order wave function was defined by diagonalizing H over the reference space.

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

TABLE VII. Results for CH_2He_n: $\langle z\rangle$ vs n.[a]

n	State	Refs.	PTK[b]	MRSDCI	MRLCC	VARPT	QDVPT
0	$1\,^3B_1$	1	100	− 0.2630	···	− 0.2742	···
	$1\,^1A_1$	1	100	− 0.7538	···	− 0.6835	···
	$1\,^1A_1$	2	100	− 0.7232	− 0.7217	− 0.7232	− 0.7225
	$1\,^1A_1$	20	100	− 0.7192	− 0.7196	− 0.7124	− 0.7149
	$1\,^1A_1$	29	100	− 0.7177	− 0.7183	− 0.7113	− 0.7138
1	$1\,^3B_1$	1	100	− 0.2622	···	− 0.2742	···
	$1\,^1A_1$	1	100	− 0.7567	···	− 0.6835	···
	$1\,^1A_1$	2	100	− 0.7232	− 0.7217	− 0.7233	− 0.7225
3	$1\,^3B_1$	1	100	− 0.2606	···	− 0.2742	···
	$1\,^1A_1$	1	100	− 0.7616	···	− 0.6835	···
	$1\,^1A_1$	2	100	− 0.7231	− 0.7217	− 0.7236	− 0.7225
5	$1\,^3B_1$	1	100	− 0.2593	···	− 0.2742	···
	$1\,^1A_1$	1	100	− 0.7658	···	− 0.6835	···
	$1\,^1A_1$	2	99.9	− 0.7231	− 0.7217	− 0.7241	− 0.7225
9	$1\,^3B_1$	1	99.9	− 0.2569	···	− 0.2739	···
	$1\,^1A_1$	1	99.9	− 0.7720	···	− 0.6832	···
	$1\,^1A_1$	2	99.9	− 0.7229	− 0.7217	− 0.7275	− 0.7225
12	$1\,^1A_1$	2	99.9	− 0.7227	− 0.7217	− 0.6431	− 0.7225
13	$1\,^3B_1$	1	99.9	− 0.2552	···	− 0.2739	···
	$1\,^1A_1$	1	99.9	− 0.7768	···	− 0.6832	···
	$1\,^1A_1$	2	99.9	− 0.7226	− 0.7217	− 0.7076	− 0.7225
17	$1\,^3B_1$	1	99.9	− 0.2538	···	− 0.2739	···
	$1\,^1A_1$	1	99.9	− 0.7805	···	− 0.6832	···
	$1\,^1A_1$	2	99.9	− 0.7224	− 0.7217	− 0.7185	− 0.7224
25	$1\,^3B_1$	1	99.9	− 0.2516	···	− 0.2739	···
	$1\,^1A_1$	1	99.9	− 0.7858	···	− 0.6832	···
	$1\,^1A_1$	2	99.9	− 0.7219	− 0.7217	− 0.7205	− 0.7224

[a] The labels are defined in Tables I and III. Properties are reported in atomic units. The orbitals used for the multireference calculations on the $1\,^1A_1$ state are TCSCF orbitals. The SCF values of $\langle z\rangle$ are $^3B_1$: − 0.243; $^1A_1$ (one-reference): − 0.807; $^1A_1$ (two-reference): − 0.716; the full CI values [Ref. 2(d)] are $^3B_1$: − 0.264; $^1A_1$: − 0.716.

[b] The percentage of the second-order perturbation theory energy lowering accounted for by the configurations treated variationally. A value of 100 indicates that no perturbation theory selection was performed. For the two-reference cases PT selection was performed on both roots of the zeroth-order space.

from CH_2, and each He makes no contribution to the dipole moment, the full CI dipole moments for $n \neq 0$ would be identical to the $n = 0$ results. In a one-reference wave function MRLCC, VPT, and QDVPT are all equivalent. For the $1\,^1A_1$ state all methods are sensitive to the expansion of the reference space from one function to two, with significantly better agreement obtained in the two-reference case. The VPT result for the one-reference case leads to an error comparable to the one-reference CI wave function. For $n = 0$ we also present results from expanded reference space calculations on the $1\,^1A_1$ state, based on the TCSCF orbitals with canonical virtual orbitals. It is seen that all methods approach the full CI values, although only the CI and MRLCC results appear to converge monotonically.

For $n > 0$ it is seen that the one-reference $^3B_1$ value of $\langle z\rangle$ for the CI wave function changes as the number of He atoms is increased, whereas the VPT value does not. Note that use of perturbation theory selection in VPT alters the computed value of the property by 0.0003 for the $^3B_1$ state. The two-reference $1\,^1A_1$ CI $\langle z\rangle$ changes slowly over the range of n considered here. In part this slow change is due to the small difference between the TCSCF value of $\langle z\rangle$ (to which the MRSDCI value goes as n increases) and the MRSDCI value. The MRLCC and QDVPT results are quite stable as n is increased, the small change in $\langle z\rangle$ for QDVPT arising from the size inconsistency discussed above. The error in the VPT result, which is large even by $n = 9$, arises from a crossing of E_0 by one of the eigenvalues of $\mathbf{Q}H\mathbf{Q}$ between $n = 9$ and 13. In addition to the odd behavior of $\langle z\rangle$, corroborating evidence that this crossing is occurring comes from comparison of the total VPT and MRLCC energies. In Ref. 18 it was shown that E_{VPT} is less than or equal to E_{MRLCC} whenever E_0 is the lowest eigenvalue of H_0 (i.e., when the eigenvalues of $\mathbf{Q}H\mathbf{Q}$ are all greater than E_0). We have found that at $n = 12$ the MRLCC total energy becomes lower than the VPT energy, suggesting that a crossing has occurred. It is interesting to note that the results of Table III show that this crossing has no significant effect on the total VPT energy. Thus, the size inconsistency in VPT manifests itself in the one-electron properties to a much greater extent than in the total energy.

Results obtained for various states of ethylene are shown in Table VIII. Examining the $1\,^1A_g$ results it is seen that all four methods are sensitive to the expansion of the reference space, especially in the two-reference case, where the MOs are from a two-configuration SCF. The fixed and variable coefficient MRLCC and VPT properties agree to the number of significant figures reported. In the $^1B_{1u}$ cases, the CI results differ from the QDVPT, VPT, or MRLCC results to a greater extent. The QDVPT, MRLCC, and VPT values of $\langle x^2\rangle$ for the $1\,^1B_{1u}$ state are somewhat smaller than the CI value. For the $2\,^1B_{1u}$ state the QDVPT, MRLCC, and VPT values are all somewhat larger than the CI values. The coefficients defining Ψ_0 for the $^1B_{1u}$ states in the VPT

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

TABLE VIII. C_2H_4 properties.[a]

State	Refs.	PTK[b]	Quantity	SDCI	MRLCC	VARPT	QDVPT
$1\,^1A_g$	1	100	$\langle x^2\rangle$	11.8	⋯	11.6	⋯
			$\langle y^2\rangle + \langle z^2\rangle$	18.0	⋯	18.1	⋯
$1\,^1A_g$	4	100	$\langle x^2\rangle$	11.8	11.6	11.6	11.6
			$\langle y^2\rangle + \langle z^2\rangle$	18.1	18.2	18.2	18.2
			$\langle x^2\rangle$		11.6	11.6	
			$(\langle y^2\rangle + \langle z^2\rangle)_{\rm fix}$		18.2	18.2	
$1\,^1A_g$	2[c]	100	$\langle x^2\rangle$	11.7	11.7	11.7	11.7
			$\langle y^2\rangle + \langle z^2\rangle$		18.2	18.2	
			$\langle x^2\rangle$		11.7	11.7	
			$(\langle y^2\rangle + \langle z^2\rangle)_{\rm fix}$	18.1	18.2	18.2	18.2
$1\,^3B_{1u}$[e]	1	>99	$\langle x^2\rangle$	11.8	⋯	11.9	
			$\langle y^2\rangle + \langle z^2\rangle$	19.6	⋯	19.8	
$1\,^1B_{1u}$[e]	2[d]	100	$\langle x^2\rangle$	27.8	23.7	23.7	23.3
			$\langle y^2\rangle + \langle z^2\rangle$	38.7	33.4	33.5	32.9
$2\,^1B_{1u}$[e]	2[d]	100	$\langle x^2\rangle$	59.1	70.6	70.5	70.6
			$\langle y^2\rangle + \langle z^2\rangle$	80.0	94.8	94.8	94.8

[a] All quantities in atomic units. The various methods are defined in Sec. II. Calculations based on Hartree–Fock molecular orbitals unless otherwise noted.

[b] Denotes the percentage of the second-order Rayleigh–Schrödinger perturbation theory energy lowering corresponding to the configurations treated variationally.

[c] The molecular orbitals are from a two-configuration SCF that correlates the π electrons.

[d] The molecular orbitals are the average natural orbitals from a preliminary CI calculation (see the results section). The coefficients defining Ψ_0 for VPT and MRLCC were those used to define E_0 in the final QDVPT iteration. The definition of E_0 in the QDVPT results was obtained via the iterative process described in the text.

[e] Since the zeroth-order wave functions are defined iteratively, and not as the eigenfunctions of H_0^f, the B_{1u} properties are evaluated using Eq. (36) for MRLCC and VPT, and the final term in Eq. (48) is neglected for the QDVPT properties.

and MRLCC calculations were those used in the final iteration of the QDVPT equations.

VI. DISCUSSION

Comparison of the VPT results of Ref. 18 and the QDVPT results presented above suggests that QDVPT and VPT are comparable whenever the effective coupling in the reference space is small and/or no instabilities are present in the VPT equations due to crossings of an eigenvalue of **QHQ** and E_0. However, when such instabilities exist for VPT, or when the effective coupling is large, QDVPT remains accurate. The elimination of these problems occurs because, relative to the VPT equations, E_0 has been replaced by $E_{\rm Total}$ in the diagonal elements corresponding to the orthogonal complement reference space configurations. E_0 is retained on the diagonal for the single and double excitations in QDVPT, but since the single and double excitations do not correlate each other to a significant extent, no crossings are expected of the eigenvalues of $\mathbf{Q}H\mathbf{Q}$ with E_0 for QDVPT.

Even with the problems noted above for VPT, it is seen in the results on the CH_2He_n systems that VPT, MRLCC, and QDVPT all yield more nearly size-consistent total energies than does MRSDCI. MRLCC is strictly size consistent for this choice of reference space.

Concerning the properties results the agreement obtained between the CI, MRLCC, VPT, and QDVPT results is quite good. For BeH_2, CH_2, and most states of ethylene we find agreement to within a few percent of the total value of the property. Based on the BeH_2 results and the CH_2 $^3B_1$ one-reference results it can be seen that the CI properties tend to be more rapidly convergent than the VPT, MRLCC, and QDVPT properties. However, increasing the reference space from two to nine functions for the BeH_2 example brought the VPT, MRLCC, and QDVPT results into much closer agreement with the CI results. Similar results were found for the $1\,^1A_1$ state of CH_2 on going from a one- to a multireference based treatment.

The possible sensitivity of the calculated properties to the choice of Ψ_0 is graphically illustrated by the results of Table VI. It is seen that the energy estimate obtained by MRLCC, QDVPT, or VPT can be reasonably accurate (error <4 mhartree), but that the error in the property estimate can still be quite large. For MRLCC and VPT a significant expansion of the reference space was required to obtain good agreement with the full CI property results, and even still the properties were not as accurate as the MRSDCI or QDVPT values. QDVPT gave reasonable results with somewhat less effort. It should be noted that this was also a difficult geometry for the two-reference singles and doubles CI approach, and expansion of the reference space was again required to obtain good agreement with the full CI. However, the error for a given reference space was found to be smaller for the MRSDCI results than the MRLCC, VPT, or QDVPT.

The results for the CH_2He_n system illustrate a number of interesting points. First, the value of $\langle z\rangle$ is dependent on the number of He atoms for the MRSDCI properties, while for MRLCC and QDVPT $\langle z\rangle$ was basically independent of n. The ratio of the MRSDCI error in $\langle z\rangle$ to the SCF error in $\langle z\rangle$ $[\Delta = (G_{\rm SDCI} - T_{\rm Full})/G_{\rm SCF} - G_{\rm Full})]$ changed considerably for the values of n examined here. For the $^3B_1$ state

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

with $n = 0$ Δ equals 0.05, while for $n = 25$ it was 0.57. For the one reference description of the 1 $^1A_1$ state the change in the CI value of $\langle z \rangle$ is quite large, with $\Delta = 0.30$ for $n = 0$, while at $n = 25$ Δ was 0.77. The two configuration SCF value for $\langle z \rangle$ for the $^1A_1$ state is closer to the full CI than any of the correlated treatments. However, it is still the case that an increase in n changes the MRSDCI value of $\langle z \rangle$ significantly. It should be noted that the $^3B_1$ MRSDCI values for $\langle z \rangle$ are closer to the full CI values than those of the perturbative treatments for all but the largest n.

The results of Table VII also highlight the limitations of VPT for multireference cases. It is seen that the error in the VPT value of $\langle z \rangle$ becomes unacceptable when n is equal to 12. With larger n the value of $\langle z \rangle$ again becomes close to the full CI value, but this agreement is most likely fortuitous. However, since the VPT energy agrees with the MRLCC and QDVPT energies to within one in the fourth decimal place it is clear that the coefficients of the single and double excitations from Ψ_0 are similar in all three methods [cf. the energy expression, Eq. (7)]. Due to the variational nature of these methods, the error in the energy goes quadratically with the error in Ψ_1, whereas the error in the property is first order in the error in Ψ_1. The main source of the error in $\langle z \rangle$ is an inordinately large coefficient for the configuration which is the orthogonal complement of Ψ_0. The total energy is basically unaffected because Ψ_0 is taken as the eigenfunction of H in the reference space and $\langle \Psi_c | H | \Psi_0 \rangle$ equals zero. Thus, while Ψ_c can have no direct effect on the energy, it can still have quite a large effect on the properties.

In most cases the ethylene results are in good agreement for all of the methods examined. The QDVPT, MRLCC, and VPT wave functions predict that the 1 $^1B_{1u}$ state is significantly more diffuse than either the ground state or the 1 $^3B_{1u}$ state, in agreement with CI. All three methods show similar sensitivity in the properties to expansion of the reference space, whereas the CI *energies* are much more sensitive to reference space expansion than the VPT or MRLCC energies. The MRLCC, QDVPT, and VPT results predict the 1 $^1B_{1u}$ state to be less diffuse than the MRSDCI result. Previous MCSCF calculations on this state[42] have found similar results and it was suggested that size inconsistency in the MRSDCI may be the cause of the discrepancy. Our results lend support to this suggestion, but must be viewed with some caution. In the VPT, MRLCC, and QDVPT calculations reported where we have neglected the terms in the property expressions [Eqs. (35) or (36) and (45) or (50) and (45)] related to derivatives of the reference space coefficients with respect to perturbation strength. Since for the $^1B_{1u}$ states the reference space coefficients were defined iteratively and not as the eigenfunctions of the zeroth-order Hamiltonian, these terms will, in general, be nonzero. We expect them to be small, but further calculations are required to assess this. Similar comments apply to the 2 $^1B_{1u}$ state, which VPT, MRLCC, and QDVPT predict to be more diffuse than the MRSDCI result. Larger CI, QDVPT, VPT, and MRLCC results for these states are required to answer this question.

The question arises as to which of the three methods (other than CI) is expected to be the most reliable. We believe that QDVPT should generally be the most accurate method because it treats the interaction of the reference functions to infinite order, thus avoiding the numerical instabilities of VPT, while still allowing the weights of the reference configurations to change in the final wave function, unlike MRLCC. However, the results presented above suggest that both MRLCC and QDVPT can be quite accurate and should be useful for large systems where size-inconsistency effects in CI results are of the same order as the errors incurred by basis set and CI truncation.

V. CONCLUSIONS

An effective Hamiltonian based method is introduced which eliminates the main intruder state effects encountered in variational perturbation theory. The reference space is treated as quasidegenerate and the effects of single and double excitations from the reference space are obtained in an approximately size-consistent manner. QDVPT preserves the advantages of VPT in that changes in the reference space coefficients brought on by correlation are possible, unlike MRLCC. A novel method for solving the QDVPT equations is introduced that avoids explicit construction of the effective Hamiltonian over the reference space. As a result, QDVPT takes little more computational time than MRLCC or VPT.

Approximate expressions for the evaluation of one-electron properties for variational perturbation theory, quasidegenerate variational perturbation theory, and multireference linearized coupled-cluster wave functions are presented. Results are compared to truncated CI and full CI results and good agreement is obtained.

It is shown that the inclusion of the orthogonal complement of Ψ_0 in the variational perturbation theory wave function leads to size-inconsistency effects. These effects are relatively minor in the total energy, but can be quite large in the one-electron properties.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support of this research by the National Institutes of Health, Grant No. 2 R01 GM34081-03. The calculations were performed in part at the Indiana University Computational Facility, the establishment of which was in part made possible by grants from the National Science Foundation, Grant Nos. CHE-83-09446 and CHE-84-05851.

APPENDIX

The direct solution of Eq. (21) via Eqs. (22) and (23) (i.e., formation of the effective Hamiltonian) requires approximately n times the work of an MRLCC calculation, where n is the number of spin-adapted configurations in the reference space. In this Appendix we introduce an iterative procedure for the solution of Eq. (21) which, for the calculations presented above, converged faster than the effective Hamiltonian method and becomes increasingly faster as n increases.

We begin with Eq. (21) and partition it as one would in a VPT calculation. That is, we single out one function in the

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

reference space (normally that associated with E_0, designated Ψ_0^i), write Ψ in intermediate normalized form based on Ψ_0^i and rewrite Eq. (21) as the two sets of equations:

$$E = E_0 + \sum_{j \neq i} \langle \Psi_0^i | H | C^j_{P'} \Psi_0^j \rangle + \sum_j \langle \Psi_0^i | H | C^j_Q \phi_j \rangle \tag{A1}$$

and

$$\begin{pmatrix} \mathbf{P'HP'-E} & \mathbf{P'HQ} \\ \mathbf{QHP'} & \mathbf{QHQ-E_0} \end{pmatrix} \begin{pmatrix} \mathbf{C_{P'}} \\ \mathbf{C_Q} \end{pmatrix} = - \begin{pmatrix} \mathbf{P'H\Psi_0^i} \\ \mathbf{QH\Psi_0^i} \end{pmatrix}. \tag{A2}$$

$\mathbf{P}'$ represents the orthogonal complement of Ψ_0^i in the reference space. Equations (A1) and (A2) are identical to Eqs. (22) and (23). They are also formally similar to the VPT equations, except that E in the $\mathbf{P}'$ block would be replaced by E_0. It is the presence of E that prevents one from simply solving Eq. (A2) as a set of inhomogeneous linear equations.

Rather than constructing the effective Hamiltonian of Eq. (23) we replace E in Eq. (A2) with an approximation to the total correlation energy and solve Eq. (A2) for approximate $C_{P'}$ and C_Q. Using Eq. (A1) one obtains a new approximation to the total correlation energy based on these $C_{P'}$ and C_Q. Iterating this procedure leads (when it converges) to results identical with the direct solution of Eq. (21) via Eqs. (22) and (23). This iterative method (with the modifications described below to speed convergence) is the one we used to obtain the QDVPT results in the present article, and it affords significant speedups over formation of the effective Hamiltonian, especially when the reference space is large. [Only for cases having two reference functions where the energy was converged to quite high accuracy (better than $1.0E-10$) was the effective Hamiltonian method competitive in the present study. It may also be competitive for two-reference case where a particularly bad initial guess at E is used or for near degeneracies.] After completion we renormalize Ψ to have the proper normalization for property evaluation (i.e., $\Sigma |C_P|^2 = 1$).

One can go a step further to speed convergence, with no increase in work. The above iterative expression has first order errors in $E_{n+1} - E_n$; i.e., it converges linearly with the error in E. Below we develop an iterative procedure which eiliminates the errors linear in $E_{n+1} - E_n$ and obtain an approximately quadratically convergent method. The procedure is analogous to one used to obtain approximately quadratic convergence for the B_K method.[43]

Using the subscript 0 to refer to Ψ_0^i, and with $\mathbf{P}'$ and $\mathbf{Q}$ defined as for Eqs. (A1) and (A2) one can rewrite Eqs. (A1) and (A2) as

$$E = H_{00} + H_{0P'} \{P'(E - H^e_{P'P'})P'\}^{-1} H^e_{P'0} + H_{0Q} \{Q(E_0 - H_{QQ})Q\}^{-1} H^e_{Q0} \tag{A3}$$

with

$$H^e_{P'P'} = H_{P'P'} + H_{P'Q} \{Q(E_0 - H_{QQ})Q\}^{-1} H_{QP'}, \tag{A4}$$

$$H^e_{P'0} = H_{P'0} + H_{P'Q} \{Q(E_0 - H_{QQ})Q\}^{-1} H_{Q0}, \tag{A5}$$

$$H^e_{Q0} = H_{Q0} + H_{QP'} \{P'(E - H^e_{P'P'})P'\}^{-1} H^e_{P'0}. \tag{A6}$$

We assume E_{n+1} is known and is essentially converged. Using Eq. (A3), which is satisfied when E_{n+1} is the converged energy, we expand $(\mathrm{E}_{n+1} - H)^{-1}$ about E_n. [Note, in the iterative scheme E_{n+1} is determined via E_n using Eq. (A3).] Expansion of $\{P'(E_{n+1} - H^e_{P'P'})P'\}^{-1}$ around E_n yields [with $\Delta E_n = (E_{n+1} - E_n)$]

$$\begin{aligned} \{P'(E_{n+1} - H^e_{P'P'})P'\}^{-1} & \\ \simeq \{P'(E_n - H^e_{P'P'})P'\}^{-1} &+ \{P'(E_n - H^e_{P'P'})P'\}^{-1} \\ \times (\Delta E_n) \{P'(E_n - H^e_{P'P'})P'\}^{-1} &+ O[(\Delta E_n)^2]. \end{aligned} \tag{A7}$$

Retaining only the first two terms and substituting back into Eq. (A3), noting that

$$C^{n+1}_{P'} = \{P'(E_n - H^e_{P'P'})P'\}^{-1} \times \{H_{P'0} + H_{P'Q} \{Q(E_0 - H_{QQ})Q\}^{-1} H_{Q0}\} \tag{A8}$$

one obtains the expression

$$\begin{aligned} E_{n+1} = \{E_0 &+ \sum_{j \neq i} \langle \Psi_0^i | H | C^j_{P'} \Psi_0^j \rangle \\ &+ \sum_j \langle \Psi_0^j | H | C^j_Q \phi_j \rangle \\ &+ E_n \Sigma |C_{P'}|^2\} / (1 + \Sigma |C_{P'}|^2), \end{aligned} \tag{A9}$$

where we take $C_{P'}$ and C_Q from the $(n+1)$th iteration. This method yields approximately quadratic convergence for E.

Our method of solution proceeds as follows: (1) Guess an initial value for E, either based on Rayleigh–Schrödinger perturbation theory, size-consistency corrected CI, or a previous MRLCC calculation; (2) solve Eq. (A2) using the method of Ref. 18; (3) use the result of (2) to construct Eq. (A9); (4) check for convergence. If the energy is not converged to the desired accuracy, repeat steps (2) and (3) with this new energy.

In tests on systems with larger reference spaces[44] we have found that the present iterative scheme yields a workable procedure, whereas construction of the effective Hamiltonian becomes too time consuming to undertake.

[1] R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981).

[2] (a) C. W. Bauschlicher, S. R. Langhoff, P. R. Taylor, N. C. Handy, and P. J. Knowles, J. Chem. Phys. **85**, 1469 (1986); (b) C. W. Bauschlicher and P. R. Taylor, *ibid.* **86**, 1420 (1987); (c) **85**, 6510 (1986); (d) Theor. Chim. Acta **71**, 263 (1987).

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

[4] S. Evangelisti, J. P. Daudey, and J.-P. Malrieu, Phys. Rev. A **35**, 4930 (1987).

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

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

[7] J. Paldus, in *New Horizons in Quantum Chemistry*, edited by P.-O. Lowdin and B. Pullman (Reidiel, Dordrecht, 1983), pp. 31–60.

[8] B. Jeziorski and J. Paldus, J. Chem. Phys. **88**, 5673 (1988).

[9] H. Baker and M. A. Robb, Mol. Phys. **50**, 1077 (1983).

[10] K. Tanaka and H. Terashima, Chem. Phys. Lett. **106**, 558 (1984).

[11] (a) A. Banerjee and J. Simons, Int. J. Quantum Chem. **19**, 207 (1981); (b) J. Chem. Phys. **76**, 4548 (1982).

[12] M. R. Hoffmann and J. Simons, J. Chem. Phys. **88**, 993 (1988).

[13] (a) M. A. Haque and D. Mukherjee, J. Chem. Phys. **80**, 5058 (1984); (b) D. Mukherjee, Chem. Phys. Lett. **125**, 207 (1986); (c) D. Sinha, S. K. Mukhopadhyay, M. D. Prasad, and D. Mukherjee, *ibid.* **125**, 213 (1986); (d) S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, *ibid.* **137**, 273 (1987); (e) D. Mukherjee, W. Kutzelnigg, and S. Koch, J.

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

Chem. Phys. **87**, 5902 (1987); (f) S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, *ibid.* **88**, 4357 (1988).

[14] U. Kaldor, J. Chem. Phys. **87**, 467 (1987), and references cited therein.

[15] R. J. Gdanitz and R. Ahlrichs, Chem. Phys. Lett. **143**, 413 (1988).

[16] E. A. Hylleraas, Z. Phys. **65**, 209 (1930).

[17] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems* (Springer, Berlin, 1957), p. 122.

[18] R. J. Cave and E. R. Davidson, J. Chem. Phys. **88**, 5770 (1988).

[19] D. Feller, C. M. Boyle, and E. R. Davidson, J. Chem. Phys. **86**, 3424 (1987).

[20] H. Hellmann, *Einfuehrung in Quantenchemie* (Deuticke, Leipzig, 1937), p. 285; R. P. Feyman, Phys. Rev. **56**, 340 (1939).

[21] A. C. Hurley, Proc. R. Soc. London Ser. A **226**, 179 (1954).

[22] See A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (MacMillan, New York, 1982).

[23] J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, J. Chem. Phys. **49**, 2960 (1968).

[24] J. N. Franklin, *Matrix Theory* (Prentice–Hall, Englewood Cliffs, NJ, 1968), p. 22.

[25] (a) P. Pulay and S. Saebo, Theor. Chim. Acta **69**, 357 (1986); (b) K. Wolinski, H. I. Sellers, and P. Pulay, Chem. Phys. Lett. **140**, 225 (1987).

[26] G. Hose and U. Kaldor, J. Phys. B **12**, 3827 (1979).

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

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

[29] P.-O. Lowdin, in *Perturbation Theory and its Applications in Quantum Mechanics*, edited by C. H. Wilcox (Wiley, New York, 1966), p. 255.

[30] W. Kutzenlnigg, Chem. Phys. Lett. **35**, 283 (1975).

[31] Z. Gershgorn and I. Shavitt, Int. J. Quantum Chem. **2**, 751 (1968).

[32] (a) E. R. Davidson, L. E. McMurchie, and S. J. Day, J. Chem. Phys. **74**, 5491 (1981); (b) D. C. Rawlings and E. R. Davidson, Chem. Phys. Lett. **98**, 424 (1983).

[33] The MELDF series of electronic structure codes was developed by L. E. McMurchie, S. T. Elbert, S. R. Langhoff, E. R. Davidson, and D. Feller, and was extensively modified by D. C. Rawlings.

[34] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

[35] B. R. Brooks and H. F. Schaefer III, J. Chem. Phys. **68**, 4839 (1978).

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

[37] J. S. Binkley, J. A. Pople, and W. J. Hehre, J. Am. Chem. Soc. **102**, 939 (1980).

[38] C. F. Bender and H. F. Schaefer III, J. Chem. Phys. **55**, 4798 (1971).

[39] L. E. McMurchie and E. R. Davidson, J. Chem. Phys. **66**, 2959 (1977).

[40] R. J. Cave and E. R. Davidson, J. Phys. Chem. **91**, 4481 (1987).

[41] The dominant coefficients are defined as follows. The configurations were ordered on the basis of the size of the square of the coefficients in the final wave function. When two or more spin couplings exist for a given orbital occupation the sum of the squares of the coefficients for all spin couplings was used to order the configurations. Thus, it is perhaps more accurate to say that the dominant n-electron orbital products were selected, and all spin-adapted configuration state functions associated with them were included in the reference space.

[42] K. K. Sunil, K. D. Jordan, and R. Shepard, Chem. Phys. **88**, 55 (1984).

[43] L. E. Nitzsche and E. R. Davidson, J. Chem. Phys. **68**, 3103 (1978).

[44] D. Feller, R. J. Cave, and E. R. Davidson (unpublished results).

Downloaded 23 Feb 2011 to 134.173.131.83. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions