

# Resolvent operator approach to many-body perturbation theory. III. Applications

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The resolvent-based closed- and open-shell MBPT developed in the previous papers have been applied for the calculation of ionization potentials (I.P.), electron affinities (E.A.), excitation energies (E.E.), and correlation energies (C.E.) of several prototype atomic and molecular systems. The calculations for I.P., E.A., and C.E. have been performed through third order and the E.E.'s have been calculated through second order. The results presented here are intended to illustrate the utilization of our new MBPT technique and to permit us to compare and check our results with those of other workers who have calculated the above properties using different methods.

## I. INTRODUCTION

In this paper we present some specific applications of our open- and closed-shell<sup>1</sup> MBPT in the Rayleigh-Schrödinger (RS) form as developed in the preceding papers, which are referred to as I and II. We give explicit equations for the calculation of ionization potential (I.P.), electron affinity (E.A.), excitation energy (E.E.), correlation energy (C.E.) of a closed-shell ground state, and state energies up to third order in electron repulsion. Our applications are confined to the RS case because it possesses the desirable features of potential size consistency,  $\omega$ -independence of  $\Sigma$ , and the possibility of choosing  $\Sigma$  as Hermitian. We emphasize here that our theory yields state energies relative to the *perturbed* vacuum energy.<sup>2</sup> Since for the systems studied the chosen vacuum is the unperturbed ground state, we obtain the difference energies directly as the I.P., E.A., or E.E. of the correlated ground state. However, the model space itself contains several configurations  $\Omega_i^+|\Phi\rangle$ . For situations where several configurations are needed due to physical reasons for the zeroth order description of the ground state, the vacuum cannot serve as the unperturbed ground state itself. In such cases, one has to take explicit differences between the roots to get the difference energies. However, they can be treated without any modification of our theory. Such applications will be treated in forthcoming publications.

To implement our resolvent-based MBPT, one must specify a partition of the Hamiltonian  $H$  into  $H^0$  and  $V$  as  $\Sigma^{\text{RS}}$  is a power series in  $V$ . The  $H$  in normal order relative to a vacuum  $|\Phi\rangle$  has the form

$$H = \langle \Phi | H | \Phi \rangle + \sum_{ij} \langle i | f | j \rangle N[a_i^+ a_j] + \frac{1}{2^2} \sum_{ijkl} \langle ij | kl \rangle_a N[a_i^+ a_j^+ a_l a_k], \quad (1)$$

where

$$\langle i | f | j \rangle = h_{ij} + \sum_{\alpha \in |\Phi\rangle} \langle i\alpha | j\alpha \rangle_a = h_{ij} + v_{\text{HF},ij}. \quad (2)$$

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In all the applications presented here we choose the vacuum  $|\Phi\rangle$  to be the Hartree-Fock (HF) ground state and the orbitals to be the HF orbitals. Thus  $H$  becomes

$$H = E_{\text{HF}} + \sum_i \epsilon_i N[a_i^+ a_i] + \frac{1}{2^2} \sum_{ijkl} \langle ij | kl \rangle_a N[a_i^+ a_j^+ a_l a_k], \quad (3)$$

which we choose to partition as

$$H^0 = E_{\text{HF}} + \sum_i \epsilon_i N[a_i^+ a_i] \quad (4)$$

and

$$V = \frac{1}{2^2} \sum_{ijkl} \langle ij | kl \rangle_a N[a_i^+ a_j^+ a_l a_k]. \quad (5)$$

The perturbation appearing in the expression for  $\Sigma^{\text{RS}}$  [Eq. (52) of paper II] is  $V$  in the interaction representation

$$V_I(t) = \frac{1}{2^2} \sum_{ijkl} \langle ij | kl \rangle_a N[a_{i1}^+(t) a_{j1}^+(t) a_{l1}(t) a_{k1}(t)]. \quad (6)$$

The model space functions for the ion or excited states are written as  $|\Phi_i\rangle = \Omega_i^+|\Phi\rangle$ , where  $\Omega_i^+$  are one-hole or one-particle creation operators for the ions or hole/particle pair creation operators for the excited states.

With the above choices,  $\Sigma^{\text{RS}}$  is a one-body operator for the ions and up to a two-body operator for excited states. As the calculated energy shifts  $\Delta E$  are relative to the correlated vacuum energy, the respective state energies for ions and excited states may be obtained by simply adding the ground state energy to the calculated  $\Delta E$ 's. The ground state energy can, of course, be easily calculated from the closed-shell RS theory. The difference energies can be obtained as eigenvalues of the equation

$$\omega A_j = [(E_0^j - E_0)\mathbf{1} + \Sigma^{\text{RS}}] A_j, \quad (7)$$

where  $A_j$  is a vector and  $\Sigma^{\text{RS}}$  is a matrix.

## II. APPLICATIONS

### A. $\Sigma^{\text{RS}}$ for I.P.

For I.P. calculations, the valence creation operators  $\{\Omega_i^+\}$  are one-hole operators of the type  $a_\alpha$ , so that  $\Sigma^{\text{RS}}$  consists of boxes having one ingoing and one outgoing open hole line. A box consists here of all the connected

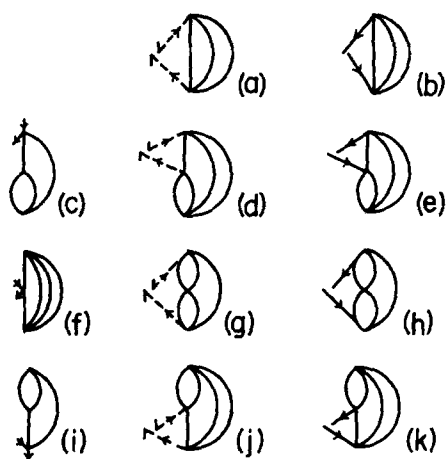


FIG. 1. Skeletons for all folded diagrams up to third order that contribute to  $\Sigma^{\text{RS}}$  for I.P.

diagrams such that a horizontal line drawn between two successive vertices of a diagram does not cross one hole line only (see Sec. II of paper II). As  $V_I$  is a two-body operator, one cannot draw a diagram having one open line with one  $V_I$ ; thus there are no first-order diagrams. We display in Fig. 1 skeletons of all the "folded" diagrams of  $\Sigma^{\text{RS}}$  for I.P. up to third order in  $V_I$ . Notice that because the lowest order diagram in a box is second order, the MC and TC diagrams begin to appear in fourth order only and, hence, need not be considered here since calculations have been performed up to third order. The contributions of these skeletons (Fig. 1) to  $\Sigma^{\text{RS}}$  can be calculated using the rules for evaluating folded boxes given in paper II. For I.P. calculations, since the  $E_j^0 - E_0$  are  $-\epsilon_\alpha$  for all holes  $\alpha$ , Eq. (7) takes the form

$$\omega A = (-\epsilon + \Sigma^{\text{RS}})A, \quad (8)$$

where  $\epsilon_{\alpha\beta} \equiv \epsilon_\alpha \delta_{\alpha\beta}$ . Explicit expressions for  $\Sigma_{\alpha\beta}^{\text{RS}}$  up to third order are given in the Appendix.

### B. $\Sigma^{\text{RS}}$ for E.A.

In E.A. calculations the valence creation operators  $\{\Omega_i^+\}$ , for our choice of the vacuum as  $\Phi_{\text{HF}}$ , are one-particle operators of the type  $a_p^\dagger$ , so that  $\Sigma^{\text{RS}}$  consists of boxes having one ingoing and outgoing open particle line. Thus the  $\Sigma^{\text{RS}}$  for E.A. will be the diagrams in which the hole and particle lines of  $\Sigma^{\text{RS}}$  for I.P. (Fig. 1) have been reversed. Since the  $E_j^0 - E_0 = a_p$  for all  $p$ , the equation determining E.A.'s is

$$\omega A = (\epsilon + \Sigma^{\text{RS}})A, \quad (9)$$

where  $\epsilon_{pq} = \epsilon_p \delta_{pq}$ .



FIG. 2. Skeletons for all folded diagrams up to second order that contribute to  $\Sigma^{\text{RS}}$  for E.E.



FIG. 3. Skeletons for all the closed diagrams up to third order that contribute to the correlation energy of the ground state.

### C. $\Sigma^{\text{RS}}$ for E.E.

In E.E. calculations, the valence creation operators  $\{\Omega_i^+\}$  are one hole-one particle operators  $a_p^\dagger a_\alpha$ , so that  $\Sigma^{\text{RS}}$  consists of boxes having a pair of hole-particle ingoing and outgoing open lines. The  $\Sigma^{\text{RS}}$  for E.E. would contain up to two-body operators. We show in Fig. 2 all connected skeletons up to second order that comprise  $\Sigma^{\text{RS}}$ . Expressions for  $\Sigma_{p\alpha, q\beta}^{\text{RS}}$  up to second order are given in the Appendix.

### D. $\Sigma^{\text{RS}}$ for C.E.

For our choice of the vacuum as  $\Phi_{\text{HF}}$ , the ground state energy  $E_c$  can be calculated by adding the closed diagrams, the correlation contributions  $\Delta E_c$ , to  $E_{\text{HF}}$ . The ground state energy  $E_c$ , when added to the energy differences, I.P., E.A., and E.E., yields the corresponding ion and excited state energies. The skeletons for the C.E. up to third order are shown in Fig. 3, and expressions for C.E. up to third order are given in the Appendix.

## III. COMPUTATIONAL CONSIDERATIONS

We have implemented on the Utah DEC-2060 computer our resolvent MBPT for the calculation of state and difference energies (I.P., E.A., E.E.). The first step in this implementation is the generation of an orthonormal set of orbitals  $\{\chi_p\}$  which are eigenfunctions of an appropriately chosen one-body Hamiltonian  $h_0$ , where  $\sum_i h_0(i) = H_0$  specifies the partition of the Hamiltonian  $H$ . The next step involves the specification of the model space functions  $\{\phi_i\}$  and classification of the orbital set into holes and particles, corresponding to a conveniently chosen vacuum  $\Phi$ . Once  $\Phi$  and  $\{\Omega_i^+\}$  are chosen, the final step is the calculation of  $\Sigma^{\text{RS}}$  up to a given order, the organizational aspects of which form the content of this section. The computational procedure that we discuss for  $\Sigma^{\text{RS}}$  is independent of the choice of the orbitals.

As shown in the Appendix, the expression for each diagram of an  $n$ th-order term contributing to  $\Sigma^{\text{RS}}$  involves a sum over products of  $n$  two-electron integrals with an associated energy denominator. The chief problem encountered here in constructing  $\Sigma^{\text{RS}}$  is that simultaneous access to  $n$  random integrals is required, whereas the complete list of two-electron integrals is too large to be kept in the computer's fast memory. Moreover, a  $p$ -body contribution to  $\Sigma^{\text{RS}}$  involves  $l = 2n + p$  hole or particle lines and leads to  $\sim m^l$  computational steps, where  $m$  is the size of the "active" orbital basis, since each line (open or internal) manifests itself as a  $\text{D}\emptyset$ -loop index. To address ourselves to these problems, we note certain general patterns arising in the expressions for a  $p$ -body  $\Sigma^{\text{RS}}$  element, keeping in mind that we want to have a procedure which is equally applicable to correlation energy, I.P., E.A., or E.E. calculations.

(a) Whenever two consecutive vertices in a diagram are joined by  $j(\leq 4)$  lines, then orbital indices for such lines appearing in the product of the two integrals associated with these vertices and the corresponding denominator will not occur anywhere else in the expression for the diagram.

(b) Each vertex contributes a factor  $[C_1\langle ij|kl\rangle - C_2\langle ij|lk\rangle]$  in Dirac notation after spin integration, with an implied loop over each of the orbital indices.

(c) Two vertices that have at least two common hole ( $h$ ) or particle ( $p$ ) lines  $i$  and  $j$  joining them will contribute a product of integrals  $[C_1\langle ij|kl\rangle - C_2\langle ij|lk\rangle] \times [C_3\langle ij|pq\rangle - C_4\langle ij|qp\rangle]$  in Dirac notation after spin integration.

(d) Diagrams which are mirror images of each other (with the sense of arrows preserved) about a horizontal mirror plane contribute to matrix elements of  $\Sigma^{\text{RS}}$  which are transposes of one another.

Based on observations (b) and (c), we have sorted the list of two-electron integrals  $\langle ij|kl\rangle$  into Dirac distributions  $\langle ij|$  with  $i \geq j$ , where each  $\langle ij|$  distribution contains integrals  $\langle ij|kl\rangle$  for all  $k$  and  $l$ . Furthermore, each distribution is divided into subdistributions according to the hole or particle nature of the indices  $k, l$  as  $\langle ij|hh\rangle, \langle ij|hp\rangle, \langle ij|ph\rangle, \langle ij|pp\rangle$ , of lengths  $m_h^2, m_h m_p, m_p m_h,$  and  $m_p^2$ , respectively. The list of such sorted integrals are stored in a direct-access file with one subdistribution per record. Here  $m_h$  and  $m_p$  are the total number of active hole and particle orbitals, respectively.

Such a sorted list of integrals can be exploited for calculating the terms of  $\Sigma^{\text{RS}}$ . According to (a), the total expression for a diagram may be calculated as a product of contributions arising from groups of consecutive vertices. Thus, at any stage of the calculation one would require at most two Dirac distributions simultaneously in the fast memory, with each distribution  $\langle ij|$  contributing two integrals  $\langle ij|kl\rangle$  and  $\langle ij|lk\rangle$  for each vertex. Moreover, a partial sum may be performed over the orbitals common to these two vertices. Observation (c) indicates that whenever two consecutive indices are joined by  $hh$  or  $pp$  lines, one needs only one distribution to calculate the partial sum involving these two vertices. These are also the cases where a partial sum leads to a reduction in computational steps. Observation (d) may be exploited by considering only one of the pair of diagrams which are mirror images by suitably choosing the limits of the  $D\emptyset$ -loop parameters for the open lines of  $\Sigma^{\text{RS}}$ . A general reduction of the computational steps is possible by constraining the  $D\emptyset$ -loop indices to run over only those values which, by symmetry, give nonzero contributions to  $\Sigma^{\text{RS}}$  (because  $\Sigma^{\text{RS}}$  is an effective Hamiltonian, it belongs to totally symmetric representation). This is accomplished by setting the limits of orbital indices according to symmetry that ensures use of the nonzero integrals only. All the above aspects have been incorporated in our working program.

## IV. RESULTS AND DISCUSSION

### A. General remarks

We present here a few general points common to all the studies undertaken. The effective Hamiltonian  $\Sigma^{\text{RS}}$  in our theory is  $\omega$ -independent. Therefore, the poles of  $S(\omega)$ , which correspond to the pertinent difference energies (I.P., E.A., or E.E.), are calculated simply as roots of the same eigenvalue Eq. (7). This situation contrasts with theories of the BW form, like the Bloch-Horowitz theory,<sup>3</sup> or the so-called Green's function theory,<sup>4</sup> in which the effective operator  $\Sigma^{\text{RS}}$  is  $\omega$ -dependent, thereby requiring an iterative solution for each root. From this point of view, ours is a one-shot procedure and is thus computationally more attractive. An additional desirable feature of our theory is the Hermiticity of  $\Sigma^{\text{RS}}$ . The above two features allow us to easily include the interactions among the components  $\Phi_i = \Omega_i^+|\Phi\rangle$  of the multiconfiguration model space through the solution of Eq. (7). These interactions are at least of the order of  $n^2$ , where  $n$  is the lowest order term of the perturbation in the off-diagonal elements of  $\Sigma^{\text{RS}}$ . This is obvious if we expand each root of Eq. (7) as a series containing the off-diagonal terms of  $\Sigma^{\text{RS}}$ . However, the cumulative effect of all such off-diagonal terms is of the order of number of model space functions times  $n^2$ . Such interactions can, in principle, be taken into account in other theories as well, such as those developed by Brandow,<sup>5</sup> and Kvasnička.<sup>6</sup> However, until now, most applications of these theories have been performed with one model space configuration.<sup>7-9</sup> Presumably, in Brandow's theory this was done to avoid complications involving a non-Hermitian eigenvalue problem (see, however, Ref. 10).

We should also mention a potential source of instability that one may encounter if, for a given root, the model space functions  $\Phi_i$  are not good zeroth-order functions. There may exist configurations outside the model space (virtual configurations) which are also dominant in the expansion of the wave function corresponding to that root. Such dominant configurations tend to be quasidegenerate with respect to the unperturbed Hamiltonian  $H_0$ . Since the energy denominators appearing in  $\Sigma^{\text{RS}}$  essentially consist of differences of unperturbed energies between the model space functions and the functions outside the model space, the presence of such quasidegenerate virtual configurations will manifest themselves in the calculations as large matrix elements of  $\Sigma^{\text{RS}}$ . In some of our calculations we have indeed encountered such difficulties for certain roots. To achieve a meaningful perturbation expansion of such roots, the model space should be extended to include the quasidegenerate configurations. It may be noted here that this kind of instability would also show up in any other open-shell formalism whenever there are functions outside the model space which are quasidegenerate with some model space functions. Such offending configurations have been termed "intruder states" in the literature.<sup>10,13</sup> This behavior has been observed by earlier workers in their respective theories.<sup>7,10-12</sup> In a forthcoming publication we shall treat such roots by including the effect of the quasidegenerate configurations

TABLE I. Difference energies for  $N_2$ . Energies in hartrees.

State	Method	Zeroth order			Second order			Third order			Expt.
I.P. $1\sigma_g, 2\sigma_g, 3\sigma_g$	Present	15.7192,	1.5276*	0.6245	14.8621,	0.5184	15.3488,	0.5582	$3\sigma_g: 0.57^b$		
	$GF^a$						15.096,	1.393,	0.5479		
	$GF^c$			0.6243		0.5394			0.5894		
$1\sigma_u, 2\sigma_u$	Present	15.7157,	0.7725		14.8605,	0.6027	15.3432,	0.7019	$2\sigma_u: 0.69^b$		
	$GF^a$						15.094,	0.645			
	$GF^c$		0.7717			0.6247		0.7107			
$1\pi_u$	Present	0.6260			0.6410		0.6113		0.624 <sup>b</sup>		
	$GF^a$						0.633				
	$GF^c$	0.6258			0.6232		0.6210				

<sup>a</sup>Reference 12.<sup>b</sup>Reference 17.<sup>c</sup>Reference 11.

within the model space itself. In the present calculations, however, we are interested in only those roots which are well described by our choice of model spaces, i. e., one-hole and one-particle functions  $a_\alpha|\Phi\rangle$  and  $a_p^+|\Phi\rangle$  for I.P. and E.A., respectively, and hole-particle functions  $a_p^+a_\alpha|\Phi\rangle$  for E.E. Operationally, the offending functions in the model space appropriately tend to make themselves noninteracting with other model space functions due to their large contribution to the diagonal terms of  $\Sigma^{RS}$  relative to others.

## B. Numerical results

With the above general observations in mind we now briefly outline the individual case studied here. These calculations were intended to provide us with a basis for comparing our results with those of others rather than to produce new chemical information. Therefore our discussion of the results will be rather brief.

$N_2$ : The basis set is the same as that used by Cederbaum *et al.*<sup>11</sup> and consists of (4s, 2p) contracted Gaussian functions. The results are shown in Table I. The table also includes, for comparison, the Green's function I.P. results using the MBPT<sup>11</sup> and superoperator methods.<sup>12</sup> It should be noted that the I.P. calculation for the  $2\sigma_g$ -hole state could not be performed because of its near degeneracy with a function outside the model space.

$F_2$ : For  $F_2$ , we have again used Cederbaum's basis,<sup>11</sup> and the results are shown in Table II. Our results for I.P. parallel closely the Green's function results of Cederbaum *et al.* We have marked by asterisks in the

table the results that show potential instability due to the presence of a quasidegenerate configuration outside the model space. We particularly mention here the I.P. calculation for the  $2\sigma_u$ -hole state for which a comparison with Cederbaum's Green's function result could be made. With both the methods, the third-order results become unstable. Let us also emphasize here that quite often the diagonal elements of  $\Sigma^{RS}$  show strong quasidegeneracy, indicating that interactions among all the corresponding functions must be included in the model space. As an example, the two E.E. roots 0.88 and 1.05 for the  $^3\Sigma_g$  states shown in the table exhibit such quasidegeneracy.

$H_2O$ : For  $H_2O$ , we utilized the fairly extended basis set (5s, 4p, 1d/3s + polarization) used by Yamamoto *et al.*<sup>8</sup> in their MBPT calculations of E.A. and E.E. The results are shown in Table III. For comparison, we have also included the results of Green's function<sup>11</sup> and MBPT<sup>8</sup> calculations. For  $H_2O$ , I.P. calculations using a smaller basis set have been performed by Yamamoto *et al.*<sup>8</sup> and Hubac *et al.*<sup>9</sup> This smaller basis was also explored by us because it allows us to check our program in calculations on those symmetries for which there is only one model space function per symmetry. As mentioned in paper II, for one model space function our MBPT series coincides with the perturbation series of Brandow<sup>5</sup> and Kvasnička.<sup>6</sup> Since our SCF results (along with occupied and virtual orbital energies) agreed with the results quoted by Hubac,<sup>9</sup> our perturbation results coincided with their calculations at all orders. The values of the virtual orbital energies quoted by Yamamoto *et al.*<sup>8</sup> do not agree with our or Hubac's val-

TABLE II. Difference energies for  $F_2$ . Energies in hartrees.

State	Method	Zeroth order			Second order			Third order			Expt.
I.P. $1\sigma_g, 2\sigma_g, 3\sigma_g$	Present	26.4346,	1.7763,	0.7410	25.1234,	1.5226,	0.7229	26.0239,	1.6569,	0.7720	$3\sigma_g = 0.772$
	$GF^a$			0.7426			0.7199			0.7588	
	$GF^c$										
$\pi_u$	Present	0.8165			0.5734			0.7218			0.6908 <sup>b</sup>
	$GF^a$	0.8198			0.6221			0.6956			
	$GF^c$	26.4344,	1.5043		25.1232,	0.9631*		26.0232			
$1\sigma_u, 2\sigma_u$	Present		1.4874			1.2612					0.5817 <sup>b</sup>
	$GF^a$										
	$GF^c$	0.6766			0.4798			0.6012			
$\pi_g$	Present	0.6805			0.5082			0.5832			
	$GF^a$										
	$GF^c$										
E.A. $3\sigma_u$	Present	-0.0642			-0.0196*						
	$GF^a$	-0.0635			-0.0415			-0.0286			
	$GF^c$										

<sup>a</sup>Reference 11.<sup>b</sup>Reference 16.

TABLE III. Difference energies for H<sub>2</sub>O. Energies in hartrees.

State	Method	Zeroth order			Second order			Third order			Expt.
I. P.	$1a_1, 2a_1, 3a_1$	Present	20.5619,	1.3535,	0.5870	19.4262,	1.0847*,	0.4787	20.2919,	0.5776	$2a_1 = 1.183^c$
		GF <sup>a</sup>		1.3431,	0.5758		1.2101,	0.4843		0.5578	$3a_1 = 0.544^c$
		MBPT <sup>b</sup>	20.558,	1.345,	0.575	19.477,	1.170,	0.484	20.192,	1.255,	0.566
	$1b_1$	Present	0.5109			0.3916			0.4906		0.4696 <sup>c</sup>
		GF <sup>a</sup>	0.5023			0.4012			0.4788		
		MBPT <sup>b</sup>	0.502			0.395			0.470		
$1b_2$	Present	0.7196			0.6511			0.7249		0.6879 <sup>c</sup>	
	GF <sup>a</sup>	0.7092			0.6504			0.7063			
	MBPT <sup>b</sup>	0.710			0.655			0.707			
E. A.	$4a_1$	Present	-0.0229			-0.0195					
		MBPT <sup>b</sup>	-0.026			-0.029			-0.030		
	$2b_2$	Present	-0.0465			-0.0455					
		MBPT <sup>b</sup>	-0.049			-0.050			-0.050		
E. E.	$^1A_1$	Present				0.2946,	0.3011,	0.3797			0.355 <sup>b</sup>
		MBPT <sup>b</sup>				0.313					
	$^1B_1$	Present				0.2167,	0.2483,	0.3297			0.275 <sup>d</sup>
		MBPT <sup>b</sup>				0.222,	0.306				0.368 <sup>e</sup>
	$^1B_2$	Present				0.3747					
	$^1A_2$	Present				0.2860,	0.3486				0.334 <sup>d</sup>
		MBPT <sup>b</sup>				0.290,	0.302				0.374 <sup>e</sup>
	$^3A_1$	Present				0.2688,	0.3020,	0.3858			
		MBPT <sup>b</sup>				0.303					
	$^3B_1$	Present				0.2092,	0.2961,	0.3252			0.265 <sup>f</sup>
		MBPT <sup>b</sup>				0.150,	0.305				
	$^3B_2$	Present				0.3694					
	$^3A_2$	Present				0.2823,	0.3460				
		MBPT <sup>b</sup>				0.289,	0.298				
C. E.	Present	(-76.02936)			-0.20142			-0.20593			

<sup>a</sup>Reference 11.<sup>b</sup>Reference 8.<sup>c</sup>Reference 18.<sup>d</sup>Reference 19.<sup>e</sup>Reference 20.<sup>f</sup>Reference 21.

ues, leading to corresponding discrepancies in the perturbation results. It is a bit disheartening to note that although no instability is encountered for the I. P. calculation on the  $a_1$  states with the smaller basis, use of the extended basis set (with more diffuse functions) leads to an instability for the  $2a_1$  state. The virtual orbitals for the calculations, having been obtained from an SCF calculation on the ground state, are arbitrary to the extent that they are just orthogonal to the occupied orbitals but not adapted to the virtual configurations. As

a result, the orbital energies for the virtual orbitals often change substantially with change (increase) in the basis set leading to unphysical energies for the virtual configurations. For all open-shell MBPT calculations this situation may often lead to instabilities of certain roots which are not caused by any quasidegeneracy expected on *physical* grounds. Just as in the E. E. calculations on  $F_2$ , we have encountered strong mixing among the model space configurations due to near degeneracy of the corresponding diagonal elements of  $\Sigma^{RS}$ . A par-

TABLE IV. Difference energies for C<sub>2</sub>H<sub>4</sub>. Energies in hartrees.

State	Method	Zeroth order			Second order			Third order			Expt.
I. P.	$1a_g, 2a_g, 3a_g$	Present	11.2530,	1.0416,	0.5898	10.5898,	0.8966,	0.5154	10.7849,	0.9060,	0.5407
		Present	0.6499			0.5665			0.5919		
		Present	0.3805			0.3673			0.3813		0.386 <sup>b</sup>
	$1a_u, 2a_u$	MBPT <sup>a</sup>	0.387			0.378			0.389		
		Present	11.2514,	0.7937		10.5885,	0.6907		10.7832,	0.7134	
		Present	0.5073			0.4498			0.4708		
E. A.	$b_{3g}$	Present	-0.1453			-0.1175			-0.1252		-0.065 <sup>c</sup>
		MBPT <sup>a</sup>	-0.136			-0.115			-0.124		
E. E.	$^1A_u$	Present				0.3299					0.281 <sup>b,d</sup>
		MBPT <sup>a</sup>				0.312					
	$^1B_{1u}$	Present				0.3772					
		Present				0.1626					0.169 <sup>b,d</sup>
	$^3B_{1u}$	Present				0.155					
C. E.	Present	(-78.00055)			-0.18454			-0.20507			

<sup>a</sup>Reference 8.<sup>b</sup>Reference 22.<sup>c</sup>Reference 23.<sup>d</sup>Reference 24.

TABLE V. Difference energies for H<sub>2</sub>. Energies in hartrees.

	State	Method	Zeroth order	Second order	Third order	Accurate
I.P.	1σ <sub>g</sub>	Present	0.5945	0.5974	0.60025	0.6050 <sup>b</sup>
		MBPT <sup>a</sup>	0.5946	0.6004	0.6021	
E.E.	1Σ <sub>g</sub> <sup>+</sup>	Present		0.4716, 0.5432		0.4825 <sup>c</sup>
	1Π <sub>u</sub>	Present		0.4819, 0.5481		0.4859 <sup>c</sup>
	1Σ <sub>u</sub> <sup>+</sup>	Present		0.4240, 0.5273		0.4687 <sup>c</sup>
	1Π <sub>g</sub>	Present		0.5434		
	3Σ <sub>g</sub> <sup>+</sup>	Present		0.4534, 0.5415		0.4608 <sup>c</sup>
	3Π <sub>u</sub>	Present		0.4626, 0.5395		
	3Σ <sub>u</sub> <sup>+</sup>	Present		0.3833, 0.5241		0.3892 <sup>c</sup>
	3Π <sub>g</sub>	Present		0.5436		
C.E.	1Σ <sub>g</sub> <sup>+</sup>	Present	(-1.13294)	-0.02899	-0.03527 (-1.16822)	-1.17447 <sup>c</sup>

<sup>a</sup>Reference 8.<sup>b</sup>Reference 25.<sup>c</sup>Reference 26.

ticularly telling example is the pair of <sup>1</sup>A<sub>2</sub> excited states which mix with the weights of magnitude ~0.8 and 0.5, indicating that use of only one model space function at a time for such cases may be quite inadequate.

C<sub>2</sub>H<sub>4</sub>: We have used the (3s2p/2s) contracted Gaussian basis of Dunning<sup>14</sup> and the geometry given by Duncan<sup>15</sup> (r<sub>CH</sub> = 2.04 a.u., r<sub>CC</sub> = 2.52 a.u., θ<sub>HCH</sub> = 117.37°). The results are given in Table IV. For comparison, we have also collected in the same table the MBPT results of Yamamoto *et al.*<sup>8</sup> who use a very similar geometry and the same basis set. The two sets of results parallel very closely.

H<sub>2</sub>: For H<sub>2</sub>, we have used a hybrid basis set of 9s, 4p, and 1d basis functions obtained from the basis sets of Shulman-Kaufman<sup>7</sup> and Kaldor.<sup>7</sup> The results of calculations are shown in Table V. For I.P., we have compared our results with the results of Yamamoto *et al.*<sup>8</sup> For E.E., once again quasidegeneracy within the model space was encountered for nearly all the symmetries. Kaldor *et al.*<sup>7</sup> and Yamamoto *et al.*<sup>8</sup> report the total electronic energies for the excited states rather than the E.E.'s, and therefore have not been quoted in Table V. However, our values, calculated by adding the ground state energy up to second order to the corresponding E.E.'s, agree well with those of Kaldor *et al.*<sup>7</sup> As an example, the electronic energies for the first two 1Σ<sub>g</sub><sup>+</sup> states agree within mH of Kaldor's results. For the ground state, we have shown the total energy in brackets under C.E. at the third order and compared it with the accurate value of Kolos *et al.*<sup>26</sup>

## V. CONCLUDING REMARKS

The results presented in this paper demonstrate the viability of our resolvent-based open-shell MBPT for

the calculation of difference energies. The calculations clearly indicate that it is often imperative to include more than one configuration in the model space, particularly when these configurations are quasidegenerate and mix quite strongly. The majority of previous workers in MBPT have used only one model space configuration in their calculations.

The effective operator Σ<sup>RS</sup> in our theory is ω-independent, so that the solution of Eq. (7) for the roots as difference energies is a simple diagonalization procedure. This leads to computational simplifications in our theory. Furthermore, the Hermiticity of Σ<sup>RS</sup> in our theory allows us to incorporate the effect of interactions within the model space in a computationally stable manner.

Finally, we again point out that one may encounter instabilities due to quasidegeneracy (intruder states) between the model space functions and those outside the model space. For a proper treatment of such situations, one should include all such virtual configurations within the model space itself. In a forthcoming publication we shall come back to such cases. Unfortunately, this instability may also arise due to a particular choice of the virtual orbital set and thus may be an unphysical artifact of the basis set. To locate such instabilities, variation of the results against a change in the virtual orbital basis should be followed carefully.

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## APPENDIX

In this appendix we give detailed expressions for the matrix elements of Σ<sup>RS</sup> appropriate to the calculations of I.P., E.A., E.E., and correlation energy of the vacuum. The order of each contribution to Σ is indicated in parentheses (e.g., Σ<sub>αβ</sub><sup>(2)</sup> is second order).

Σ<sup>RS</sup> for I.P.

$$\Sigma_{\alpha,\beta}^{(2)} = \sum_{\gamma,\delta,\rho} \frac{\langle \gamma\delta | \alpha\rho \rangle (2\langle \beta\rho | \gamma\delta \rangle - \langle \beta\delta | \gamma\rho \rangle)}{\epsilon_\gamma + \epsilon_\delta - \epsilon_\rho - \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta)} - \sum_{\gamma,\rho,q} \frac{\langle \beta\gamma | \rho q \rangle (2\langle \rho q | \alpha\gamma \rangle - \langle \rho q | \gamma\alpha \rangle)}{\frac{1}{2}(\epsilon_\alpha + \epsilon_\beta) + \epsilon_\gamma - \epsilon_\rho - \epsilon_q}, \quad (\text{A1})$$

$$\begin{aligned}
\Sigma_{\alpha,\beta}^{(3)} = & (1 + P_{\alpha\beta}) \sum_{\gamma\delta\lambda,pq} \frac{(2\langle\beta\gamma|\alpha p\rangle - \langle\beta\gamma|p\alpha\rangle)\langle\lambda\delta|\gamma q\rangle(2\langle pq|\lambda\delta\rangle - \langle pq|\delta\lambda\rangle)}{(\epsilon_\gamma - \epsilon_p)(\epsilon_\lambda + \epsilon_\delta - \epsilon_p - \epsilon_q)} \\
& - (1 + P_{\alpha\beta}) \sum_{\gamma\delta,rs} \frac{(2\langle\beta\gamma|\alpha p\rangle - \langle\beta\gamma|p\alpha\rangle)\langle p\delta|rs\rangle(2\langle rs|\gamma\delta\rangle - \langle rs|\delta\gamma\rangle)}{(\epsilon_\gamma - \epsilon_p)(\epsilon_\gamma + \epsilon_\delta - \epsilon_p - \epsilon_s)} \\
& + (1 + P_{\alpha\beta}) \sum_{\gamma\delta\lambda,pq} \{ (2\langle\gamma\delta|\alpha p\rangle - \langle\gamma\delta|p\alpha\rangle)[\langle\beta\lambda|\gamma q\rangle(2\langle qp|\lambda\delta\rangle - \langle qp|\delta\lambda\rangle) - \langle\beta\lambda|q\gamma\rangle\langle qp|\lambda\delta\rangle] \\
& - (2\langle\gamma\delta|p\alpha\rangle - \langle\gamma\delta|\alpha p\rangle)\langle\beta\lambda|q\gamma\rangle\langle qp|\delta\lambda\rangle\} / [\epsilon_\gamma + \epsilon_\delta - \epsilon_p - \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta)](\epsilon_\lambda + \epsilon_\delta - \epsilon_p - \epsilon_q) \\
& + (1 + P_{\alpha\beta}) \sum_{\gamma\delta,rs} \frac{\langle\gamma\delta|\alpha p\rangle\langle\beta p|rs\rangle(2\langle rs|\delta\gamma\rangle - \langle rs|\gamma\delta\rangle)}{[\epsilon_\gamma + \epsilon_\delta - \epsilon_p - \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta)](\epsilon_\gamma + \epsilon_\delta - \epsilon_r - \epsilon_s)} \\
& + (1 + P_{\alpha\beta}) \sum_{\gamma\delta,pqr} [- (2\langle\beta\gamma|pq\rangle - \langle\beta\gamma|qp\rangle)\langle p\delta|\alpha r\rangle(2\langle rq|\delta\gamma\rangle - \langle rq|\gamma\delta\rangle) + \langle\beta\gamma|pq\rangle\langle p\delta|\alpha r\rangle(2\langle rq|\delta\gamma\rangle - \langle rq|\gamma\delta\rangle) \\
& + \langle\gamma\beta|pq\rangle\langle p\delta|\alpha r\rangle(2\langle rq|\gamma\delta\rangle - \langle rq|\delta\gamma\rangle)] / [\epsilon_\gamma + \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta) - \epsilon_p - \epsilon_q](\epsilon_\gamma + \epsilon_\delta - \epsilon_r - \epsilon_q) \\
& + (1 + P_{\alpha\beta}) \sum_{\gamma\delta\lambda,pq} \frac{\langle\beta\gamma|qp\rangle\langle\delta\lambda|\alpha\gamma\rangle(2\langle qp|\delta\lambda\rangle - \langle qp|\lambda\delta\rangle)}{[\epsilon_\gamma + \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta) - \epsilon_p - \epsilon_q](\epsilon_\delta + \epsilon_\lambda - \epsilon_p - \epsilon_q)} + \sum_{\gamma\delta\lambda,\mu,p} \frac{\langle\delta\gamma|\alpha p\rangle\langle\mu\lambda|\delta\gamma\rangle(2\langle\beta p|\mu\lambda\rangle - \langle\beta p|\lambda\mu\rangle)}{[\epsilon_\gamma + \epsilon_\delta - \epsilon_p - \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta)](\epsilon_\mu + \epsilon_\lambda - \epsilon_p - \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta))} \\
& + \sum_{\gamma\delta\lambda,pq} [(2\langle\gamma\delta|\alpha p\rangle\langle p\lambda|\delta q\rangle - \langle\gamma\delta|\alpha p\rangle\langle p\lambda|q\delta\rangle - \langle\gamma\delta|p\alpha\rangle\langle p\lambda|\delta q\rangle)(2\langle\beta q|\gamma\lambda\rangle - \langle\beta q|\lambda\gamma\rangle) \\
& - \langle\gamma\delta|p\alpha\rangle\langle p\lambda|q\delta\rangle(2\langle\beta q|\lambda\gamma\rangle - \langle\beta q|\gamma\lambda\rangle)] / [\epsilon_\delta + \epsilon_\gamma - \epsilon_p - \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta)](\epsilon_\gamma + \epsilon_\lambda - \epsilon_q - \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta)) \\
& - \sum_{\gamma,pqrs} \frac{\langle\beta\gamma|pq\rangle\langle pq|rs\rangle(2\langle rs|\alpha\gamma\rangle - \langle rs|\gamma\alpha\rangle)}{[\epsilon_\gamma + \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta) - \epsilon_p - \epsilon_q][\epsilon_\gamma + \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta) - \epsilon_r - \epsilon_s]} \\
& + \sum_{\gamma\delta,pqr} [(-2\langle\beta\gamma|pq\rangle\langle q\delta|\gamma r\rangle + \langle\beta\gamma|pq\rangle\langle q\delta|\gamma r\rangle + \langle\beta\gamma|pq\rangle\langle q\delta|\gamma r\rangle)(2\langle pr|\alpha\delta\rangle - \langle pr|\delta\alpha\rangle) \\
& + \langle\beta\gamma|qp\rangle\langle q\delta|\gamma r\rangle(2\langle pr|\delta\alpha\rangle - \langle pr|\alpha\delta\rangle)] / [\epsilon_\gamma + \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta) - \epsilon_p - \epsilon_q][\epsilon_\delta + \frac{1}{2}(\epsilon_\alpha + \epsilon_\beta) - \epsilon_p - \epsilon_r] \\
& + \sum_{\gamma\delta\lambda,pq} \frac{(2\langle\gamma\lambda|pq\rangle\langle\beta\delta|\alpha\gamma\rangle - \langle\gamma\lambda|pq\rangle\langle\beta\delta|\gamma\alpha\rangle)(2\langle pq|\delta\lambda\rangle - \langle pq|\lambda\delta\rangle)}{(\epsilon_\gamma + \epsilon_\lambda - \epsilon_p - \epsilon_q)(\epsilon_\delta + \epsilon_\lambda - \epsilon_p - \epsilon_q)} \\
& + \sum_{\gamma\delta,pqr} \frac{(-2\langle\gamma\delta|pr\rangle\langle\beta p|\alpha q\rangle + \langle\gamma\delta|pr\rangle\langle\beta p|\alpha q\rangle)(2\langle qr|\gamma\delta\rangle - \langle qr|\delta\gamma\rangle)}{(\epsilon_\gamma + \epsilon_\delta - \epsilon_p - \epsilon_r)(\epsilon_\gamma + \epsilon_\delta - \epsilon_q - \epsilon_r)}. \tag{A2}
\end{aligned}$$

Here  $P_{\alpha\beta}$  stands for a permutation of the labels  $\alpha$  and  $\beta$  which generates the expressions for the mirror image diagrams.

An expression for  $\Sigma^{\text{RS}}$  appropriate to E. A. calculation may be obtained from Eqs. (A1) and (A2) by interchanging hole and particle indices.

$\Sigma^{\text{RS}}$  for E.E.

$$\Sigma_{p\alpha,q\beta}^{(1)} = 2\langle\alpha q|p\beta\rangle - \langle\alpha q|\beta p\rangle, \tag{A3}$$

$$\begin{aligned}
\Sigma_{p\alpha,\alpha\beta}^{(2)} = & \sum_{\gamma r} \frac{(2\langle\alpha\gamma|pr\rangle - \langle\alpha\gamma|rp\rangle)(2\langle qr|\beta\gamma\rangle - \langle qr|\gamma\beta\rangle)}{\frac{1}{2}(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q) + \epsilon_\gamma - \epsilon_r} \\
& + \sum_{rs} \frac{\langle\alpha q|rs\rangle(2\langle rs|p\beta\rangle - \langle rs|\beta p\rangle)}{\frac{1}{2}(\epsilon_\alpha + \epsilon_\beta + \epsilon_p + \epsilon_q) - \epsilon_r - \epsilon_s} + \sum_{\gamma\delta} \frac{\langle\gamma\delta|p\beta\rangle(2\langle\alpha q|\gamma\delta\rangle - \langle\alpha q|\delta\gamma\rangle)}{\epsilon_\gamma + \epsilon_\delta - \frac{1}{2}(\epsilon_p + \epsilon_q + \epsilon_\alpha + \epsilon_\beta)} \\
& - (1 + P_{\alpha\beta}P_{pq}) \sum_{\gamma r} \frac{\langle q\gamma|rp\rangle(2\langle r\alpha|\beta\gamma\rangle - \langle r\alpha|\gamma\beta\rangle) + \langle q\gamma|pr\rangle(2\langle r\alpha|\gamma\beta\rangle - \langle r\alpha|\beta\gamma\rangle)}{\epsilon_\gamma - \epsilon_r + \frac{1}{2}(\epsilon_\beta - \epsilon_p + \epsilon_q - \epsilon_\alpha)} + \Sigma_{p\alpha}^{(2)}\delta_{\alpha\beta} + \Sigma_{\alpha\beta}^{(2)}\delta_{pq}, \tag{A4}
\end{aligned}$$

where  $\Sigma_{\alpha\beta}^{(2)}$  is given by Eq. (A1) and  $\Sigma_{pq}^{(2)}$  is its  $h$ - $p$  interchanged counterpart.

$\Sigma^{\text{RS}}$  for vacuum correlation energy

$$\Sigma^{(2)} = \sum_{\alpha\beta,pq} \frac{\langle\alpha\beta|pq\rangle(2\langle\alpha\beta|pq\rangle - \langle\alpha\beta|qp\rangle)}{\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q}, \tag{A5}$$

$$\begin{aligned}
\Sigma^{(3)} = & 2 \sum_{\alpha\beta\gamma,pqr} \{ (2\langle pr|\alpha\gamma\rangle - \langle pr|\gamma\alpha\rangle)[\langle\alpha\beta|pq\rangle(2\langle q\gamma|\beta r\rangle - \langle q\gamma|r\beta\rangle) - \langle\alpha\beta|qp\rangle\langle q\gamma|\beta r\rangle] \\
& - \langle\alpha\beta|qp\rangle\langle q\gamma|r\beta\rangle(2\langle pr|\gamma\alpha\rangle - \langle pr|\alpha\gamma\rangle)] / (\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)(\epsilon_\alpha + \epsilon_\gamma - \epsilon_p - \epsilon_r) \\
& + \sum_{\alpha\beta,pqrs} \frac{\langle\alpha\beta|pq\rangle\langle pq|rs\rangle(2\langle rs|\alpha\beta\rangle - \langle rs|\beta\alpha\rangle)}{(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)(\epsilon_\alpha + \epsilon_\beta - \epsilon_r - \epsilon_s)} + \sum_{\alpha\beta\gamma\delta,pq} \frac{\langle\alpha\beta|pq\rangle\langle\gamma\delta|\alpha\beta\rangle(2\langle pq|\gamma\delta\rangle - \langle pq|\delta\gamma\rangle)}{(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)(\epsilon_\gamma + \epsilon_\delta - \epsilon_p - \epsilon_q)}. \tag{A6}
\end{aligned}$$

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