

Perturbation Calculation of Correlation Energies for Polyatomic Molecules

I. Initial Results

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The calculation of correlation energies for polyatomic molecules is discussed. Four second-order perturbation expressions are considered; only the simplest, a Rayleigh-Schroedinger expansion with the Moller-Plesset partitioning of the Hamiltonian is invariant to an arbitrary mixing of degenerate orbitals and has the correct dependence on the number of particles. In the absence of degeneracies an iterative Brillouin-Wigner method is proposed. Calculations predict that correlation effects favor the non-classical form of carbonium ions.

Key words: Polyatomic molecules, correlation energies for \sim – Carbonium ions

1. Introduction

The results of *ab initio* molecular orbital (MO) calculations have proved to be extremely useful in understanding and interpreting modern chemistry [1]. With the proliferation of efficient computer programs, there are now *ab initio* MO calculations on an increasing wide variety of polyatomic molecules. Depending somewhat on the basis set used, one generally expects moderately accurate results for equilibrium geometries and one-electron properties. In certain cases, where the effects of correlation cancel, molecular orbital total energies may even be used to predict heats of reaction [2]. This effective cancellation of correlation effects is implicit in all MO calculations¹ which use the calculated total energy.

Quite apart from those cases where MO calculations may be expected to be reliable, there are a multitude of situations where correlation effects are known to be large. The simple homolytic cleavage of a bond is an example which is well known.² Similarly, MO calculations cannot describe dispersion interactions [3].

¹ We are dealing here solely with restricted molecular orbital theory for closed shells and do not consider the complicated effects implicit in an unrestricted or complex molecular orbital calculation. Any lowering of the energy from the restricted MO result is considered to be an effect of correlation.

² The incorrect dissociation limit of, for example, H_2 is basically a symmetry problem associated with the restricted single determinant. An unrestricted single determinant will dissociate correctly but in our context this is described as an effect of correlation.

When and where correlation effects are important, in those situations to which MO theory is routinely applied, is not as clear.

A large number of methods for including the effects of correlation have been proposed [4–6]. Most of these have only been applied to atoms or diatomic molecules for reasons that are discussed below. If in a MO calculation on a molecule of $2N$ electrons, one uses a basis set of K atomic orbitals, the limiting step in the calculation is the manipulation of $\sim K^4$ two-electron integrals. As shown by the calculations of Clementi [7], and others,³ this K^4 procedure can be practical for values of $K \sim 100$. Our interest here is in calculating the effects of correlation when either N or K become large. Davidson [8] has discussed some of these practical problems and our discussion is closely related to his. Since, by definition, we are interested in relatively large molecules, we are restricted to considering only extremely simple methods. It is not our desire to calculate all the effects of correlation but rather to investigate simple *correlation corrections* to the MO result, which, while including the major effects, remain practical. It is then hoped that the cancellation of terms difficult to include in a calculation will be an order of magnitude better than in the corresponding MO calculation. We will only consider two possibilities⁴ – low-order perturbation theory and configuration interaction (CI) which includes only doubly-excited configurations⁵.

The unavoidable first step in these two methods, and probably any others, is the matrix transformation of two-electron integrals from atomic to molecular orbitals. If all the integrals are required, as is the case for CI or perturbation theory beyond second-order, then the number of operations in this step is proportional to K^5 . We thus immediately have a problem which is an order of K more difficult than the original MO calculation. For practical purposes then, we will not consider any procedure in which the limiting step is not this integral transformation. If we consider second-order perturbation theory then not all the transformed integrals are normally required and the transformation step can be reduced to an NK^4 operation. In practice the difference between NK^4 and K^5 may be important⁶.

As shown by Davidson [8], the cost of a doubly-excited CI calculation is proportional to N^2K^4 while that for a p th order perturbation calculation is N^2K^{2p-2} . Thus for large N and K both CI and third-order perturbation theory, while comparable to each other, are an order of N more difficult than the transformation and two orders of N more difficult than the MO calculation. Once the transformation has been accomplished, however, a second-order perturbation calculation involves N^2K^2 operations and is relatively easy. Thus, as a practical correction to large molecular orbital calculations, we limit ourselves, for the present, to second-order perturbation theory and any modifications which do not include a step more expensive than a K^5 transformation.

³ For example, see Ermler, W.C., Kern, C.W.: J. Chem. Phys. **58**, 3457 (1973).

⁴ There are a number of other possibilities we might consider but none seem to us as simple and practical for large molecules as the perturbation schemes suggested here.

⁵ We could include singly-excited states in a simple manner but their effect on the total energy is generally small. We are discussing all double excitations and not a truncated expansion as might perhaps be used in conjunction with a natural orbital analysis.

⁶ NK^4 and K^5 are of course the limiting values assuming all integrals are held in core. In practice, for values of $K \sim 40$, the transformation may actually be faster than the MO calculation.

2. Second-Order Perturbation Theory

In this section we present the appropriate perturbation equations describing our calculations and briefly discuss previous related calculations.

We are considering restricted closed-shell molecular orbital calculations which produce K molecular orbitals ψ_i and orbital energies ε_i , which satisfy the Fock equation,

$$f_i(1)\psi_i(1) = \varepsilon_i\psi_i(1) \quad (2.1)$$

where $f_i(1)$ is the one-electron Fock operator. N of the K molecular orbitals, ψ_a, ψ_b, \dots are occupied in the closed-shell ground state ψ_0^0 and are termed occupied or hole orbitals. The other $K-N$ orbitals ψ_r, ψ_s, \dots are termed virtual or particle orbitals. Two particle orbitals ψ_r and ψ_s replace two hole orbitals ψ_a and ψ_b in ψ_0^0 to give the doubly-excited spin-adapted configurations ψ_n^0 that we will be considering.

The usual procedure in perturbation theory, particularly many-body perturbation theory, is to choose the Moller-Plesset [9] (MP) unperturbed Hamiltonian \mathcal{H}^0 which is a sum of the one-electron Fock operators minus a constant term,

$$\mathcal{H}^0 = \sum_{i=1}^N f_i - \sum_a \sum_b 2(bbaa) - (baba), \quad (2.2)$$

such that ψ_0^0 and ψ_n^0 are eigenfunctions of \mathcal{H}^0 with respective eigenvalues E_0^0 and E_n^0 ,

$$\begin{aligned} E_0^0 &= \sum_a 2\varepsilon_a - \sum_a \sum_b 2(bbaa) - (baba) \\ &= \langle \psi_0^0 | \mathcal{H} | \psi_0^0 \rangle = E_0^{HF}, \end{aligned} \quad (2.3)$$

$$E_n^0 = E_0^0 + \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b, \quad (2.4)$$

where \mathcal{H} is the exact electronic Hamiltonian and by definition the excited state ψ_n^0 is formed from ψ_0^0 by the excitations $\psi_a \rightarrow \psi_r$ and $\psi_b \rightarrow \psi_s$. The two-electron integrals are defined by,

$$(ijkl) = \int \psi_i^*(1)\psi_j(1) \left(\frac{1}{r_{12}} \right) \psi_k^*(2)\psi_l(2) d\tau_1 d\tau_2. \quad (2.5)$$

With this particular partitioning of the Hamiltonian, the first-order energy E_0^1 is zero. Two common expressions for the second-order energy of the ground state are those of the Brillouin-Wigner (BW) expansion,

$$E_0^2(\text{BW}) = - \sum_n \frac{|\langle \psi_0^0 | \mathcal{V} | \psi_n^0 \rangle|^2}{E_n^0 - E_0^0}, \quad (2.6a)$$

and the Rayleigh-Schroedinger (RS) expansion,

$$E_0^2(\text{RS}) = - \sum_n \frac{|\langle \psi_0^0 | \mathcal{V} | \psi_n^0 \rangle|^2}{E_n^0 - E_0^0}, \quad (2.7)$$

where $\mathcal{V} = \mathcal{H} - \mathcal{H}^0$ and E_0 is the exact electronic energy in our original basis of K orbitals,

$$E_0 = E_0^0 + E_0^1 + E_0^2 + \dots \quad (2.8)$$

The prime on the summations denotes that the ground state, ψ_0^0 is explicitly excluded from the sum over the states ψ_n^0 . If in Eq.(2.6a) we take for E_0 its value to second-order, we obtain the iterative closed form,

$$E_0^2(\text{BW}) = - \sum'_n \frac{|\langle \psi_0^0 | \mathcal{V} | \psi_n^0 \rangle|^2}{E_n^0 - E_0^0 - E_0^2(\text{BW})}. \quad (2.6b)$$

The above choice for the unperturbed Hamiltonian is not unique [10] and in particular we wish to consider one other choice, the Epstein [11]-Nesbet [12] (EN) unperturbed Hamiltonian $\overline{\mathcal{H}}^0$,

$$\overline{\mathcal{H}}^0 = \mathcal{H}^0 + \sum_n \langle \psi_n^0 | \mathcal{V} | \psi_n^0 \rangle | \psi_n^0 \rangle \langle \psi_n^0 |, \quad (2.9)$$

$$\overline{\mathcal{V}} = \mathcal{H} - \overline{\mathcal{H}}^0. \quad (2.10)$$

This particular choice⁷ applied to the Rayleigh-Schroedinger expansion has been termed Epstein-Nesbet perturbation theory by Claverie *et al.* [13] and modified Rayleigh-Schroedinger perturbation theory by Rubinstein and Yaris [14]. This choice is such that the eigenvalues of $\overline{\mathcal{H}}^0$ (i.e., \overline{E}_0^0 and \overline{E}_n^0) are the expectation values of the full Hamiltonian,

$$\overline{E}_0^0 = \langle \psi_0^0 | \mathcal{H} | \psi_0^0 \rangle = E_0^{\text{HF}} = E_0^0, \quad (2.11)$$

$$\begin{aligned} \overline{E}_n^0 &= \langle \psi_n^0 | \mathcal{H} | \psi_n^0 \rangle \\ &= \overline{E}_0^0 + \Delta E_n. \end{aligned} \quad (2.12)$$

If the ψ_n^0 are chosen as spin-adapted configurations, then the actual form of the excitation energy ΔE_n , in terms of orbital energies and two-electron integrals, depends on the particular type of doubly-excited state. With this choice of the unperturbed Hamiltonian the first-order energy \overline{E}_0^1 is also zero and since $\langle \psi_0^0 | \mathcal{V} | \psi_n^0 \rangle = \langle \psi_0^0 | \overline{\mathcal{V}} | \psi_n^0 \rangle$, we have

$$\overline{E}_0^2(\text{BW}) = - \sum'_n \frac{|\langle \psi_0^0 | \mathcal{V} | \psi_n^0 \rangle|^2}{\overline{E}_n^0 - E_0^0}, \quad (2.13a)$$

$$\overline{E}_0^2(\text{RS}) = - \sum'_n \frac{|\langle \psi_0^0 | \mathcal{V} | \psi_n^0 \rangle|^2}{E_n^0 - E_0^0}. \quad (2.14)$$

If we again make the approximation of setting E_0 to its second-order value, we obtain

$$\overline{E}_0^2(\text{BW}) = - \sum'_n \frac{|\langle \psi_0^0 | \mathcal{V} | \psi_n^0 \rangle|^2}{\overline{E}_n^0 - \overline{E}_0^0 - \overline{E}_0^2(\text{BW})}. \quad (2.13b)$$

⁷ Note that the summation without the prime is meant to include ψ_0^0 .

We are thus considering four procedures, either an RS or BW perturbation expansion and either an MP or EN partitioning of the Hamiltonian. The numerators in each of the cases are identical and the calculations differ in the choice of energy denominators. The two Brillouin-Wigner procedures require an iterative calculation, but since the second-order sum goes as N^2K^2 compared to the NK^4 or K^5 transformation, this is not a practical problem. Setting the self-consistent term in the denominator of the two BW procedures (Eqs.(2.6b) and (2.13b)) to zero, reduces them to the two RS procedures (Eqs.(2.7) and 2.14), so that the RS calculations provide convenient initial guesses and lower bounds to the corresponding iterative BW calculations. The EN procedures, using the Epstein-Nesbet partitioning of the Hamiltonian, have in their energy denominators the difference in the expectations values of the true Hamiltonian for ψ_0^0 and ψ_n^0 , i.e., $\overline{\Delta E}_n$, while the MP procedures, using the Moller-Plesset partitioning of the Hamiltonian, have the difference in orbital energies of the molecular orbitals involved in the double excitation, i.e., $\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b$.

The RS,MP procedure has not yet been extensively applied to molecules; finite basis set calculations have been reported for H_2 [15], N_2 [16], butadiene [13], and linear polyenes [17]. Most calculations to date have favored the Epstein-Nesbet partitioning of the Hamiltonian and a number of RS,EN calculations have recently appeared [13, 17-27]. Grimaldi [16] has calculated the BW,EN terms for N_2 . No BW,MP calculations appear to have been reported. At this point it seems convenient to consider the four procedures in relation to a model system.

3. Two-Orbital Model System

Here we wish to illustrate certain aspects of the four perturbation procedures using a model system. The general results are not new, but the model provides an explicit demonstration of several considerations. For simplicity we consider a minimal basis calculation on H_2 at a bondlength of 1.4 a.u., with an optimum Slater-orbital exponent of 1.19. We thus have one hole-orbital ψ_1 with orbital energy $\varepsilon_1 = -0.594931$ a.u. and a particle-orbital ψ_2 with orbital energy $\varepsilon_2 = +0.607689$ a.u. The two-electron integrals are

$$J_{11} = (1111) = 0.652613 \text{ a.u.}, \quad (3.1)$$

$$J_{22} = (2222) = 0.676110 \text{ a.u.}, \quad (3.2)$$

$$J_{12} = (2211) = 0.642272 \text{ a.u.}, \quad (3.3)$$

$$K_{12} = (2121) = 0.172548 \text{ a.u.} \quad (3.4)$$

The ground state ψ_0^0 has energy $E_0^{HF} = E_0^0 = \overline{E}_0^0 = 2\varepsilon_1 - J_{11}$ and the one doubly-excited state ψ_1^0 has energy $E_1^0 = E_0^{HF} + 2(\varepsilon_2 - \varepsilon_1)$ or $\overline{E}_1^0 = E_0^{HF} + 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12} = E_0^{HF} + 2(\varepsilon_2 - \varepsilon_1) + D$. The four expressions for the second-order energy are

$$E_0^2(\text{RS}) = \frac{-K_{12}^2}{2(\varepsilon_2 - \varepsilon_1)} = -0.012378 \text{ a.u.} \quad (3.5)$$

$$E_0^2(\text{BW}) = \frac{-K_{12}^2}{2(\varepsilon_2 - \varepsilon_1) - E_0^2(\text{BW})} = -0.012315 \text{ a.u.} \quad (3.6)$$

$$\bar{E}_0^2(\text{RS}) = \frac{-K_{12}^2}{2(\varepsilon_2 - \varepsilon_1) + D} = -0.019717 \text{ a.u.} \quad (3.7)$$

$$\bar{E}_0^2(\text{BW}) = \frac{-K_{12}^2}{2(\varepsilon_2 - \varepsilon_1) + D - \bar{E}_0^2(\text{BW})} = -0.019467 \text{ a.u.} \quad (3.8)$$

The RS,MP result corresponds to the usual second-order result of many-body perturbation theory. The RS,EN result is identical except that the energy denominator has been *shifted* by the quantity D . By expanding the RS,EN denominator it is seen that the additional terms introduced in going from the RS,MP to the RS,EN result are just the particle-particle, hole-hole and particle-hole ladders first summed by Kelly [28] and noticed previously by Claverie *et al.* [13]. The additional self-consistent correction in the BW results corresponds to the summation of the so-called rearrangement diagrams [29]. In our model the effect of the rearrangement diagrams is small, but in systems with large correlation energies this correction can be expected to be significant. Since we have only one particle orbital and one hole orbital, all diagrams are diagonal and the BW,EN result is equal to the exact CI result⁸. In the general case, it is easy to show that the BW,EN result corresponds to diagonalizing the doubly-excited CI matrix, if the matrix elements corresponding to interactions between different doubly-excited states are neglected. At this point the BW,EN procedure appears to be the obvious one to use. There are, however, other considerations to be taken into account, as can be seen by slightly expanding on our previous model.

We consider now *two* minimal basis hydrogen molecules separated by a large distance so that they do not interact⁹. A molecular orbital calculation will thus lead to two hole orbitals ψ_1 , which we consider to be *localized* on the first molecule and ψ'_1 , localized on the second molecule, both with orbital energies ε_1 equal to our previous value. Similarly, we will have two particle orbitals ψ_2 and ψ'_2 with orbital energy ε_2 . There are now two doubly-excited states which contribute, corresponding to excitation of 2 electrons localized on one *or* the other of the two molecules. The formulae for the second-order energies are identical to (3.5)–(3.8) except that K_{12}^2 is replaced by $2K_{12}^2$. The calculated second-order energies are, of course, twice the previous result for the RS procedures, but because of the self-consistent term, the correlation energy (calculated from doubly-excited CI, or either of the BW procedures) for two non-interacting H_2 molecules is not twice the correlation energy of one H_2 molecule. This deficiency of the BW expansion or of doubly-excited CI is a basic result of many-body theory as discussed by Brueckner [30] and Goldstone [31]. The numerical values are $E_0^2(\text{BW}) = -0.024507$ a.u.

⁸ In this model the singly-excited state is of different symmetry and the CI with one doubly-excited state gives the exact result for the basis.

⁹ A discussion of the additivity problem similar to ours has been given by J. P. Malrieu, *Application des techniques de théorie des champs aux problèmes à N-corps* (unpublished lecture notes), and by K. Shulten, Ph.D. Thesis, Harvard University (1974), unpublished.

and $\bar{E}_0^2(\text{BW}) = -0.038456$ a.u. It is necessary in the CI calculation to include a quadruply excited state (i.e., simultaneous double excitations on each molecule) in order that the energy be additive. For n non-interacting minimal basis H_2 molecules, the correlation energy calculated from BW or doubly-excited CI becomes $n^{\frac{1}{2}}K_{12}$ for large n .

Another problem becomes apparent when we consider the degeneracy of ψ_1 and ψ'_1 or ψ_2 and ψ'_2 . In particular, consider the equivalent *delocalized* orbitals,

$$\tilde{\psi}_1 = 2^{-\frac{1}{2}}(\psi_1 + \psi'_1), \quad (3.9)$$

$$\tilde{\psi}'_1 = 2^{-\frac{1}{2}}(\psi_1 - \psi'_1), \quad (3.10)$$

$$\tilde{\psi}_2 = 2^{-\frac{1}{2}}(\psi_2 - \psi'_2), \quad (3.11)$$

$$\tilde{\psi}'_2 = 2^{-\frac{1}{2}}(\psi_2 + \psi'_2), \quad (3.12)$$

There are now five doubly-excited states which interact with the ground state. Evaluating the appropriate matrix elements, one finds that $E_0^2(\text{RS})$ and $E_0^2(\text{BW})$ are identical to the localized orbital expressions, but that the RS,EN result¹⁰ is not Eq.(3.7) multiplied by a factor of two, but is instead,

$$\bar{E}_0^2(\text{RS}) = \frac{-K_{12}^2}{2(\varepsilon_2 - \varepsilon_1) + D/2} - \frac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1) + D + 2J_{12} - K_{12}} = -0.026564 \text{ a.u.} \quad (3.13)$$

The $\bar{E}_0^2(\text{BW})$ result is identical to the above except for the self-consistent term in each denominator and leads to a second-order energy of -0.026250 a.u. As opposed to the MP partitioning, the EN procedures are not invariant to an arbitrary mixing of degenerate orbitals. This result is true in general; the MP Hamiltonian (2.2) is invariant to an arbitrary unitary transform of degenerate orbitals, whereas the EN Hamiltonian (2.9) is not. The doubly-excited CI result is, of course, invariant, but since the mixing of degenerate orbitals changes the relative magnitude of various off-diagonal CI matrix elements, the neglect of certain ones, as in the BW,EN procedure, leads to invariance.

Thus of the four procedures only the simplest, the RS,MP procedure, is invariant to a mixing of degenerate orbitals and has the correct dependence on the number of particles. It appears that as a general unambiguous procedure for investigating the major effects of correlation in polyatomic systems, the RS,MP procedure is unique. In special cases all four procedures may be appropriate, and the relative convergence of the four perturbation expansions is of interest. In the many-body sense, the RS,EN; BW,MP; BW,EN procedures all include higher terms or diagrams and might be expected to be more accurate, order by order, than the RS,MP procedure. Claverie *et al.* [13] indeed found the RS,EN procedure to converge faster than the RS,MP procedure for butadiene, and this group has consistently preferred the EN partitioning. Grimaldi [16] has studied the convergence to the doubly-excited CI result of the RS,MP and BW,EN procedures

¹⁰ This calculation uses the 2 by 2 diagonalization of the four open-shell problem discussed in the next section.

for N_2 and in contrast to our model example or the results of Claverie *et al.* [13], he found the RS,MP expansion to be more accurate at all orders. It appears that the relative converge of the various procedures to the appropriate CI result will require further study. It may be that the convergence properties will depend on the particular system.

4. Details of the Calculations : Ambiguity of the 4-Open-Shell Case

In this section we give details of the second-order perturbation calculation in order to describe a second invariance problem associated with the EN Hamiltonian.

The doubly-excited states can be divided into closed-shell, 2-open-shell and 4-open-shell cases. The closed-shell wavefunctions are

$$\psi_{\substack{a \rightarrow r \\ a \rightarrow r}} = |\bar{r}\bar{r}\rangle, \quad (4.1)$$

where the bar refers to beta spin and $|\bar{r}\bar{r}\rangle$ is a normalized single determinant which does not explicitly show the electrons not involved in the excitation. The relevant matrix elements are

$$\langle \psi_0^0 | \mathcal{V} | \psi_{\substack{a \rightarrow r \\ a \rightarrow r}} \rangle = (rara), \quad (4.2)$$

$$\langle \psi_{\substack{a \rightarrow r \\ a \rightarrow r}} | \mathcal{H} | \psi_{\substack{a \rightarrow r \\ a \rightarrow r}} \rangle = \bar{E}_n^0 = \bar{E}_0^0 + 2\varepsilon_r - 2\varepsilon_a + (aaaa) + (rrrr) - 4(rraa) + 2(rara). \quad (4.3)$$

The 2-open-shell wavefunctions and matrix elements are

$$\psi_{\substack{a \rightarrow r \\ a \rightarrow s}} = 2^{-\frac{1}{2}} \{ |r\bar{s}\rangle + |s\bar{r}\rangle \}, \quad (4.4)$$

$$\psi_{\substack{a \rightarrow r \\ b \rightarrow r}} = 2^{-\frac{1}{2}} \{ |a\bar{b}\rangle + |b\bar{a}\rangle \}, \quad (4.5)$$

$$\langle \psi_0^0 | \mathcal{V} | \psi_{\substack{a \rightarrow r \\ a \rightarrow s}} \rangle = 2^{\frac{1}{2}} (sara), \quad (4.6)$$

$$\langle \psi_0^0 | \mathcal{V} | \psi_{\substack{a \rightarrow r \\ b \rightarrow r}} \rangle = 2^{\frac{1}{2}} (rbra), \quad (4.7)$$

$$\begin{aligned} \langle \psi_{\substack{a \rightarrow r \\ a \rightarrow s}} | \mathcal{H} | \psi_{\substack{a \rightarrow r \\ a \rightarrow s}} \rangle &= \bar{E}_0^0 + \varepsilon_r + \varepsilon_s - 2\varepsilon_a \\ &+ (aaaa) + (ssrr) + (srsr) - 2(ssaa) - 2(rraa) + (sasa) + (rara), \end{aligned} \quad (4.8)$$

$$\begin{aligned} \langle \psi_{\substack{a \rightarrow r \\ b \rightarrow r}} | \mathcal{H} | \psi_{\substack{a \rightarrow r \\ b \rightarrow r}} \rangle &= \bar{E}_0^0 + 2\varepsilon_r - \varepsilon_a - \varepsilon_b \\ &+ (rrrr) + (bbaa) + (baba) - 2(rrbb) - 2(rraa) + (rbrb) + (rara). \end{aligned} \quad (4.9)$$

The calculation with these excited states is straightforward. The calculation of hole-hole and particle-particle integrals ($bbaa$), ($baba$), ($ssrr$) and ($srsr$), however, requires a K^5 step as opposed to the particle-hole integrals which require only a NK^4 step. These hole-hole and particle-particle integrals are only needed in the EN procedures.

The 4-open-shell case generates two linearly independent singlets which we arbitrarily choose to be

$$\psi_{b \rightarrow s}^A = (12)^{-\frac{1}{2}} \{2|\overline{rasb}| + 2|\overline{arbs}| - |\overline{asrb}| + |\overline{arbs}| + |\overline{rabs}| - |\overline{sabr}|\}, \quad (4.10)$$

$$\psi_{b \rightarrow s}^B = \frac{1}{2} \{|\overline{asrb}| + |\overline{arbs}| + |\overline{rabs}| + |\overline{sabr}|\}, \quad (4.11)$$

$$\langle \psi_0^0 | \mathcal{V} | \psi_{b \rightarrow s}^A \rangle = 3^{\frac{1}{2}} \{(rasb) - (rbsa)\}, \quad (4.12)$$

$$\langle \psi_0^0 | \mathcal{V} | \psi_{b \rightarrow s}^B \rangle = (rasb) + (rbsa), \quad (4.13)$$

$$\begin{aligned} \langle \psi_{b \rightarrow s}^A | \mathcal{H} | \psi_{b \rightarrow s}^A \rangle &= \overline{E}_0^0 + \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b + (bbaa) - (baba) + (ssrr) - (srsr) \\ &\quad - (ssbb) - (ssaa) - (rrbb) - (rraa) + (3/2)\{(sbsb) + (sasa) + (rbrb) + (rara)\}, \end{aligned} \quad (4.14)$$

$$\begin{aligned} \langle \psi_{b \rightarrow s}^B | \mathcal{H} | \psi_{b \rightarrow s}^B \rangle &= \overline{E}_0^0 + \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b + (bbaa) + (baba) + (ssrr) + (srsr) - (ssbb) \\ &\quad - (ssaa) - (rrbb) - (rraa) + \frac{1}{2}\{(sbsb) + (sasa) + (rbrb) + (rara)\}. \end{aligned} \quad (4.15)$$

Quite apart from any problems involving orbital degeneracy, there is another invariance problem here, associated with the fact that, since one is neglecting the off-diagonal matrix element,

$$\langle \psi_{b \rightarrow s}^A | \mathcal{H} | \psi_{b \rightarrow s}^B \rangle = (3^{\frac{1}{2}}/2)\{(sbsb) - (sasa) - (rbrb) + (rara)\}, \quad (4.16)$$

the calculation will give different results depending on which particular representation of the two linearly-independent singlets one chooses, since (4.16) depends on this choice. Other authors [32] have avoided this problem by using for each energy denominator, the average of (4.14) and (4.15). We have chosen instead to diagonalize each 2×2 problem in the process of performing the second-order sum. The results of some initial calculations are given in the next section.

5. Results

Since the EN procedures are most directly related to a perturbation expansion of the doubly-excited CI matrix, we have initially applied the RS,EN and BW,EN methods to potential curves for H_2 and HF and compared the results with those obtained from a doubly-excited CI calculation, as shown in Figs. 1 and 2, respectively. The MO calculation on H_2 is that of Fraga and Ransil [33] using $1s$, $2s$, and $2p_\sigma$ Slater atomic orbitals with equal but optimized exponents at each internuclear distance. The MO calculation on HF is a minimal basis Slater orbital calculation [34] with fixed best-atom exponents. The BW calculations properly correct for the poor dissociation behavior of the restricted MO calculations. The RS calculations, on the other hand, blow up at large bondlengths when the correlation energy becomes large and the self-consistent term in the BW denominators becomes critical in reproducing the CI result. The BW results appear to be a lower bound¹¹

¹¹ The bounding properties of Brillouin-Wigner perturbation theory have been discussed by P. O. Löwdin, *Perturbation theory and its applications in quantum mechanics*. C. H. Wilcox (Ed.) New York: Wiley 1966.

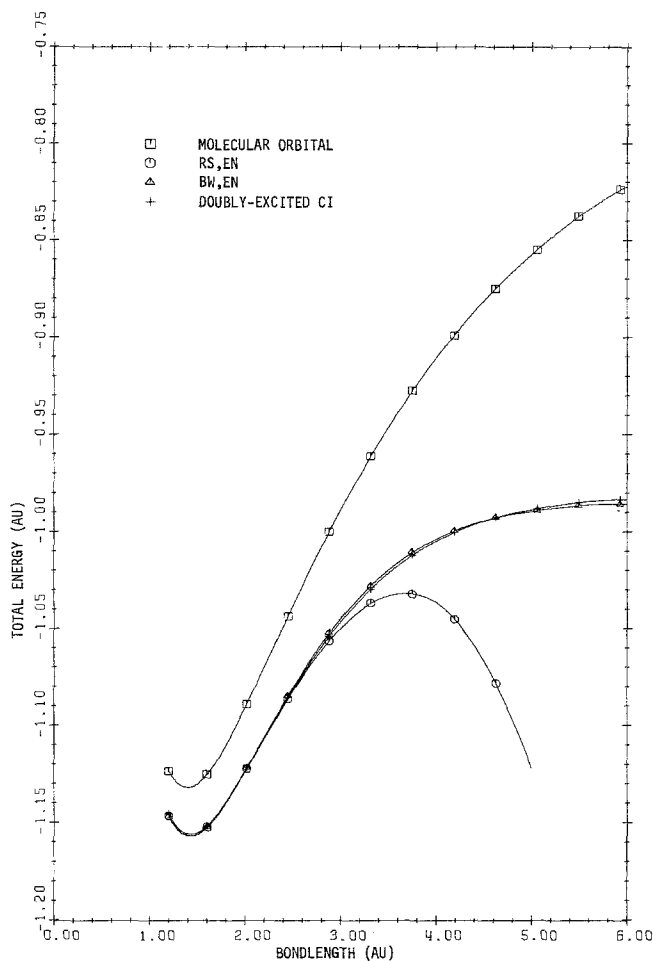


Fig. 1. Potential Curves for H_2 using Epstein-Nesbet Partitioning

to the CI values for the HF calculation but not for the H_2 calculation. The BW perturbation calculations approximate the CI results very well, even at long bondlengths. A BW rather than an RS expansion is thus required if second-order perturbation theory is to properly correct for the poor dissociation behavior of a restricted MO calculation.

There has recently been considerable theoretical interest in the relative stability of classical and non-classical carbonium ions [35-41]. As a test of our four procedures we have calculated correlation energies for the classical and non-classical forms of the vinyl and ethyl cations, using the *ab initio* STO-3G basis of Hehre *et al.* [42], with standard exponents, and the 4-31G basis of Ditchfield *et al.* [43]. The calculations were performed on an IBM 370/155. The largest calculation ($N=6$, $K=28$) required the following times for the various steps: integral evaluation, 4.1 min.; SCF, 7.5 min.; short (NK^4) transformation, 3.6 min.; long (K^5)

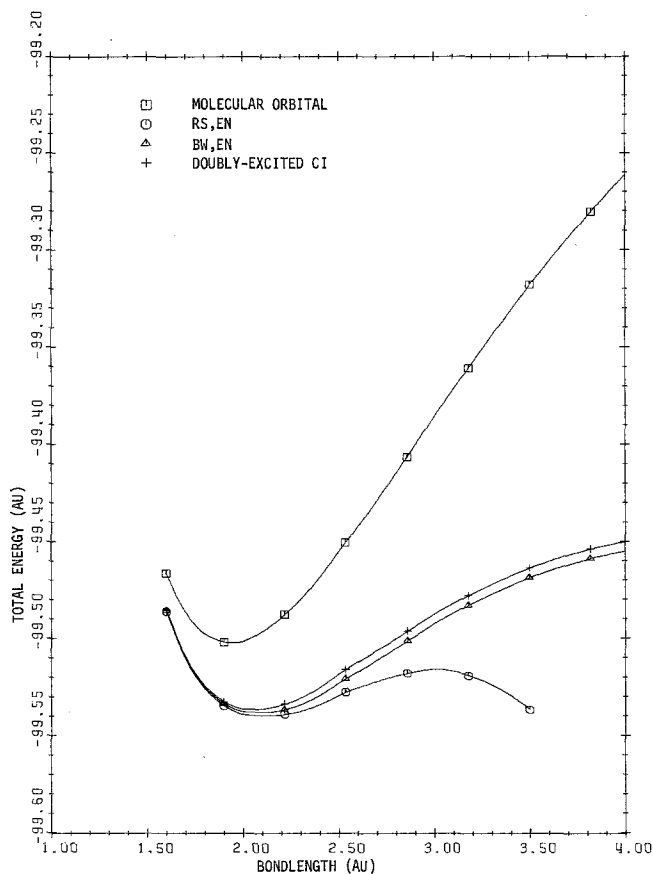


Fig. 2. Potential Curves for HF using Epstein-Nesbet Partitioning

transformation, 14.9 min., correlation calculation, 0.2 min. The molecular orbital results [38, 40] are given in Table 1. The STO-3G and 4-31G MO calculations strongly favor classical structures for both cations, although the larger basis reduces the relative stability of the classical ethyl cation. More elaborate MO calculations [40, 41], using basis sets which include polarization functions, reduce the relative stability of the classical vinyl cation from our 19–20 kcal mol⁻¹ to 5 [41] or 6 [40] kcal mol⁻¹ and predict the classical and non-classical forms of the ethyl cation to have energies which differ by 1 kcal mol⁻¹ or less. Zurawski *et al.* [41], using a pair approximation based on natural orbitals have, with their polarized basis sets, calculated the effects of correlation on the relative stability of vinyl and ethyl cations. They find that the correlation energy favors the non-classical forms.

Our results for the correlation energy are given in Table 2. Both basis sets and all four procedures give the same qualitative results. The calculations predict that correlation effects strongly favor the non-classical structure, in agreement with Zurawski *et al.* [41]. In particular, our simplest RS,MP procedure with the larger

Table 1. Molecular orbital energies

	Total energy (Hartrees)		$\Delta E(\text{kcal mol}^{-1})$
	Non-classical	Classical	
C_2H_3^+			
STO-3G	-76.13374 ^a	-76.16540 ^b	19.87
4-31G	-76.94913 ^c	-76.97973 ^d	19.20
C_2H_5^+			
STO-3G	-77.38986 ^e	-77.40805 ^f	11.41
4-31G	-78.18680 ^g	-78.19852 ^h	7.35

^a The optimum STO-3G geometry has not been published so we used the optimum 4-31G geometry, Ref. 40.

^b Optimum geometry, Ref. 38.

^c Optimum structure V, Ref. 40.

^d Optimum structure IV, Ref. 40.

^e Optimum structure III, Ref. 38.

^f Optimum structure I, Ref. 38.

^g Optimum structure VIII, Ref. 40.

^h Optimum structure VI, Ref. 40.

Table 2. Valence correlation energies (kcal mol^{-1})

	RS,MP	BW,MP	RS,EN	BW,EN
STO-3G				
C_2H_3^+				
Non-classical	-81.82	-77.23	-117.61	-104.53
Classical	-70.43	-66.98	-101.49	-91.23
Difference	-11.39	-10.25	-16.12	-13.30
C_2H_5^+				
Non-classical	-71.05	-67.91	-96.60	-88.88
Classical	-61.54	-59.27	-81.40	-76.33
Difference	-9.51	-8.64	-15.20	-12.55
4-31G				
C_2H_3^+				
Non-classical	-110.54	-103.19	-146.65	-129.81
Classical	-97.71	-92.04	-129.15	-115.92
Difference	-12.83	-11.15	-17.50	-13.89
C_2H_5^+				
Non-classical	-108.07	-101.77	-136.86	-124.24
Classical	-100.86	-95.47	-125.41	-115.37
Difference	-7.21	-6.30	-11.45	-8.87

4-31G basis gives $12.8 \text{ kcal mol}^{-1}$ favoring the non-classical vinyl cation and $7.2 \text{ kcal mol}^{-1}$ favoring the non-classical ethyl cation, which are in remarkable agreement with their values of 12.7 and 7.4.

The Brillouin-Wigner calculations necessarily give smaller total correlation energies than the corresponding Rayleigh-Schrodinger calculations. The EN

procedures give larger total correlation energies than the MP procedures. The magnitudes of the total correlation energies thus follow the trend $RS,EN > BW,EN > RS,MP > BW,MP$. The same trend is apparent in the energy differences. Surprisingly, the total valence correlation energy is larger for the vinyl cation than the ethyl cation, with the minimal STO-3G basis. In going to the larger 4-31G basis, the correlation energy difference increases slightly for the vinyl cation, but decreases for the ethyl cation. Without polarization functions, the molecular orbital calculations so strongly favor the classical forms that only for the ethyl cation is the prediction of relative stability overturned by inclusion of the correlation energy; nevertheless, our correlation results, in combination with those of Ref. [41] and the results of larger basis molecular orbital calculations, suggest that the favored species is the non-classical one.

6. Conclusion

Of the standard variational (CI) and perturbation methods for including the effects of correlation, we conclude that, for large calculations on polyatomic molecules, one is presently limited to second-order perturbation theory if the calculation is not to be much more difficult or costly than the original molecular orbital calculation. Of four second-order expressions investigated, the simplest is a Rayleigh-Schrodinger expansion with Moller-Plesset partitioning. This procedure which uses differences in orbital energies for excitation energies is the only one which is both invariant to mixing of degenerate orbitals and has the correct dependence on the number of particles. It is preferred as a general unambiguous first correction to the Hartree-Fock result. When degeneracies are not a problem, Brillouin-Wigner expansion with the Epstein-Nesbet partitioning appears to be most likely to reproduce doubly-excited CI results. The BW,EN procedure corrects for the poor behavior of restricted molecular orbital calculations on dissociation, so that it may make practical the calculation of potential surfaces for larger systems. Calculations on vinyl and ethyl cations correlate well with the recent results of Zurawski *et al.* [41], on the importance of correlation in the non-classical carbonium ions. In future papers we plan to further explore the effects of correlation in polyatomic systems.

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