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Projected unrestricted Møller–Plesset second-order energies

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A practical scheme for obtaining unrestricted Møller–Plesset energies at second order (UMP2), with spin contamination removed from the wave function, is described and demonstrated. The algebra increases with the number of spin projections, and it appears to be practical to include only two spin projections. Full formulas are given, for which the cost is proportional to M^3, where M is the number of basis functions. The results of these calculations give remarkably enhanced accuracy at fractionally extra cost. Four examples are included to demonstrate this: (i) the potential curve for the symmetric dissociation of H_2O; (ii) the potential curve for the abstraction of H from CH_4; (iii) the barrier for the addition of H to C_2H_4; and (iv) the electron affinity of CN. It is recommended that this procedure should be added at the end of all UMP2 calculations.

I. INTRODUCTION

The problem of spin contamination in unrestricted Hartree–Fock calculations has been known ever since UHF calculations were introduced by Pople and Nesbet.[1] It is not possible for a UHF determinant $\mathscr{A}(\phi_1^\alpha \phi_2^\alpha \cdots \phi_n^\alpha \bar{\phi}_1^\beta \bar{\phi}_2^\beta \cdots \bar{\phi}_m^\beta)$ $(\phi_i \neq \bar{\phi}_i)$ to be an eigenfunction of $\hat{S}^2$. For some molecules the problem is thought to be unimportant: for NH_2, using a 6-31G* basis set, the expectation value of $\hat{S}^2$ for the UHF wave function $\langle \hat{S}^2 \rangle$ is 0.76. For some molecules the problem is severe: for CN, with a 6-311 + G(d,f) basis, $\langle \hat{S}^2 \rangle$ is 1.13.

At this UHF level, it was suggested by Amos and Hall[2] that spin projection should be used, using a projection operator $\hat{O}$ which removed all spin contaminants. Thus the projected unrestricted Hartree–Fock formula (PUHF) was obtained. However, this formula is not often used because of the difficulty of evaluation. We shall comment on this aspect in this paper.

Although the UHF method introduces some electron correlation effects between orbitals of different spin, it is extremely desirable to introduce more general correlation effects. The easiest and most straightforward way to do this is through perturbation theory[3]—this is called unrestricted Møller–Plesset theory (UMP), and it is based on the Hamiltonian partitioning $\hat{H} = \hat{H}_0 + \hat{H}_1$, where $\hat{H}_0 = \Sigma_i F(i) + \Sigma_{\bar{i}} F(\bar{i})$ ($i,\bar{i}$ denote occupied α, β orbitals). It is thus possible to derive formula for the second-, third-, and fourth-order corrections UMP2, UMP3, and UMP4, and nowadays these are routinely calculated.[3]

For closed shell molecules at equilibrium geometries we have recently shown that MP2 calculations give very accurate geometries and properties,[4] provided a large basis set is used. As one breaks a bond in a molecule, it is reasonable to consider using the UHF method, because this method can give the correct form for the wave function at equilibrium and dissociation. Therefore, it is reasonable to consider that a UMP2 calculation should give a good representation of the whole surface. But it does not! Indeed it is particularly poor in that region which may be called "halfway" to dissociation.

We have examined the convergence of the UMPn series,[5] and we have shown that the series is very slowly con-

vergent when $\langle \hat{S}^2 \rangle$ is very different from $S(S + 1)$. We must suspect that this fact and the one in the previous paragraph are related. Therefore, it is highly desirable to devise a practical scheme to evaluate a projected UMPn series; i.e., one for which spin contamination in the perturbation series for the wave function has been removed.

In a previous paper,[6] we have addressed this problem, and we came forward with two schemes for spin projection. We demonstrated both schemes using our full CI program,[7] and showed that after spin projection excellent results may be obtained for the UMPn series. Those calculations were limited, because only very small basis sets may be used in the full CI calculations. The purpose of this paper is to show that one of the schemes is practical for large scale calculations.

As the number of projections required to remove all the spin contaminants increases, unfortunately the algebra becomes very messy, and in practice we have restricted our calculations to the removal of the two worst contaminants. We shall discuss the deficiencies in this approach. We give full formula for this projected UMP2 energy, because we recommend that this projection should automatically be carried out after all UMP2 calculations. It is not expensive, the cost varying as M^3, where M is the number of basis functions.

To demonstrate the greatly increased accuracy that is achieved after the projection of UMP2 calculations, we report four investigations:

(i) Calculations in C_{2v} symmetry for the dissociation of H_2O. These benchmark calculations with small basis sets show that the projected UMP2 values with two projections [denoted PMP2(2)] give a potential curve which is almost parallel to the full curve.

(ii) Calculations with a 6-31G** basis set for the abstraction of H and CH_4. The PMP2(2) calculations are shown to be size consistent for this problem. Furthermore the medium–long range part of the potential curve is much more reasonable (Morse-like) than UMP4 calculations, and the dissociation energy is within 4 kcal/mol of the exact value.

(iii) The barrier for the addition of H to C_2H_4. This is a classic problem for which MP2 and MP4 calculations obtain

a barrier which is approximately 8 kcal/mol too high; our PMP2(2) calculations predict a barrier which is approximately 1 kcal/mol too high.

(iv) The electron affinity of CN. UHF calculations on CN give $\langle \hat{S}^2 \rangle = 1.1$, that is high spin contamination. Good UHF calculations give an electron affinity which is about 25 kcal/mol too low, MP2 calculations being the equivalent amount too high. Our PMP2(2) calculations with a very large basis set give an electron affinity which is about 5 kcal/mol too high, a very significant improvement.

Schlegel has presented two papers[8,9] on the elimination of spin contamination in UMP calculations, and we have compared our calculations with his in some cases. His first paper[8] involved an approximate scheme to remove the largest spin contaminant in ψ_0 and higher terms in the perturbation series; his second paper was more general, but we believe both of his formulas for the projected UMP2 energy are not satisfactory; they involve the expression $\langle \psi_0 | \hat{H}\hat{O} | \psi_1 \rangle / \langle \psi_0 | \hat{O} | \psi_1 \rangle$, where $\hat{O}$ is the projection operator, and because $[\hat{H}_0, \hat{O}] \neq 0$, it involves terms in both first and second order in the perturbation parameter, and this does appear to be the correct formalism. Our theory, given in the next section does not suffer from this problem, and it will be seen that these arguments are supported by the calculations.

II. THE PROJECTED UMP2 SCHEME

The theory has been introduced in full in a recent paper.[6] Here we shall concentrate on those aspects which are important for practical computation.

We shall use the Löwdin spin projection operator[10]

$$\hat{O}_l = \prod_{J=S+1}^{S+l} \frac{\hat{S}^2 - J(J+1)}{S(S+1) - J(J+1)}. \tag{1}$$

Here we shall assume that $S = \frac{1}{2}(N_\alpha - N_\beta)$, and therefore the full spin projection operator $\hat{O}$ is obtained when $l = N_\beta$, the number of β electrons.

The UMP wave function series $\Sigma_n \lambda^n \psi_n$ is derived[11] from the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_1$. The exact wave function obeys

$$\hat{H}\psi = E\psi \tag{2}$$

and, since $[\hat{O}, \hat{H}] = 0$,

$$\hat{H}\hat{O}\psi = E\hat{O}\psi. \tag{3}$$

We represent ψ by the same UMP series $\Sigma_n \lambda^n \psi_n$, arguing that the component of this series of the correct spin symmetry may be a good representation of the wave function. We substitute this into Eq. (3), project on the left by ψ_0, and introduce a new energy series $\Sigma_n \lambda^n \tilde{E}_n$, which is different to the UMP energy series $\Sigma_n \lambda^n \tilde{E}_n$. Thus,

$$\left\langle \psi_0 | (\hat{H}_0 + \lambda \hat{H}_1)\hat{O} | \sum_n \lambda^n \psi_n \right\rangle$$

$$= \sum_m \lambda^m \tilde{E}_m \left\langle \psi_0 | \hat{O} | \sum_n \lambda^n \psi_n \right\rangle. \tag{4}$$

Comparing coefficients of powers of λ yields the new energies $\tilde{E}_n$. Here we are only concerned to second order:

$$\tilde{E}_0 + \tilde{E}_1 = \langle \psi_0 | \hat{H}\hat{O} | \psi_0 \rangle / \langle \psi_0 | \hat{O} | \psi_0 \rangle$$

$$\equiv E_{\text{PUHF}}, \tag{5}$$

$$\tilde{E}_2 = \langle \psi_0 | \hat{O} | \psi_0 \rangle^{-1} (\langle \psi_0 | \hat{H}\hat{O} | \psi_1 \rangle - \tilde{E}_{\text{UHF}} \langle \psi_0 | \hat{O} | \psi_1 \rangle). \tag{6}$$

We now discuss the practical implementation of the formulas (5) and (6). To work with the full projection operator appears to be extraordinarily messy—this may be understood by a realization that every time $\hat{S}^2$ is introduced, two extra levels of excitation are introduced. It appears that $\hat{O}\psi_0$ is a linear combination of all the determinants that appear in a full CI calculation, so it does not appear to be practical to work with a full $\hat{O}$. We shall work with $\hat{O}_2$, Eq. (1), which we shall argue is very satisfactory for most problems.

We therefore define

$$\tilde{E}_{\text{UHF},l} = \langle \psi_0 | \hat{O}_l | \psi_0 \rangle^{-1} \langle \psi_0 | \hat{H}\hat{O}_l | \psi_0 \rangle \tag{7}$$

and

$$\tilde{E}_{2,l} = \langle \psi_0 | \hat{O}_l | \psi_0 \rangle^{-1} (\langle \psi_0 | \hat{H}\hat{O}_l | \psi_1 \rangle$$

$$- \tilde{E}_{\text{UHF},l} \langle \psi_0 | \hat{O}_l | \psi_1 \rangle). \tag{8}$$

To evaluate Eqs. (7) and (8), we find it convenient to use second quantization notation. Thus, $\hat{S}^2$ is represented as

$$\hat{S}^2 = \hat{S}_z^2 + \hat{S}_z + N_\beta - \hat{R}, \tag{9}$$

where

$$\hat{R} = \sum_{\substack{pq \\ \bar{r}\bar{s}}} S_{p\bar{s}} S_{q\bar{r}} \hat{E}_{pq} \hat{E}_{\bar{r}\bar{s}} \tag{10}$$

with $\hat{E}_{pq}, \hat{E}_{\bar{r}\bar{s}}$ being the annihilation–creation operators for α and β orbitals, respectively, and $S_{p\bar{s}}$ is the overlap matrix

$$S_{p\bar{s}} = \langle \phi_p | \bar{\phi}_s \rangle. \tag{11}$$

In Eq. (10), $p, q, \bar{r}, \bar{s}$ run over all orbitals of the appropriate spin.

It is therefore possible to write the projection operator $\hat{O}_l$ as

$$\hat{O}_l = \sum_{j=0}^{l} f_{jl} \hat{R}^j \tag{12}$$

with $f_{j,l}$ given by the recursion relation

$$f_{0,0} = 1; \quad f_{j,0} = 0 \text{ for } j \neq 0,$$

$$f_{j,l+1} = f_{j,l} + \frac{N_\beta f_{j,l} - f_{j-1,l}}{(S+l)(S+l+1) - S(S+1)}. \tag{13}$$

In the following we shall use the notations $i, j, k, \ldots$ to denote occupied orbitals, $a, b, c, \ldots$ to denote virtual orbitals, and $p, q, r, \ldots$ to denote all orbitals. A bar is added to denote β orbitals.

We also need the action of the Hamiltonian on the reference. This is given by

$$\hat{H} | \psi_0 \rangle = E_{\text{UHF}} | \psi_0 \rangle + \hat{H}^{\alpha\alpha} | \psi_0 \rangle + \hat{H}^{\alpha\beta} | \psi_0 \rangle + \hat{H}^{\beta\beta} | \psi_0 \rangle, \tag{14}$$

where (using repeated suffix notation)

$$\hat{H}^{\alpha\alpha} = \frac{1}{4} H_{ab}^{ij} \hat{E}_{ai} \hat{E}_{bj}; \quad \hat{H}^{\alpha\beta} = H_{ab}^{i\bar{j}} \hat{E}_{ai} \hat{E}_{\bar{b}\bar{j}};$$

$$\hat{H}^{\beta\beta} = \frac{1}{4} H_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} \hat{E}_{\bar{a}\bar{i}} \hat{E}_{\bar{b}\bar{j}} \tag{15}$$

and

$$H_{ab}^{ij} = (ai|bj) - (aj|bi); \quad H_{\bar{a}\bar{b}}^{\bar{i}\bar{j}} = (\bar{a}\bar{i}|\bar{b}\bar{j}) - (\bar{a}\bar{j}|\bar{b}\bar{i});$$

$$H_{ab}^{i\bar{j}} = (ai|\bar{b}\bar{j}). \tag{16}$$

$(ai|bj)$, etc., are the usual two electron integrals met in the expression for the second-order MP2 energy E_2.

The first order wave function is given by

$$|\psi_1\rangle = \tfrac{1}{4}C^{ij}_{ab}\hat{E}_{ai}\hat{E}_{bj}|\psi_0\rangle + C^{i\bar{j}}_{ab}\hat{E}_{ai}\hat{E}_{\bar{b}\bar{j}}|\psi_0\rangle$$
$$+ \tfrac{1}{4}C^{\bar{i}\bar{j}}_{ab}\hat{E}_{\bar{a}\bar{i}}\hat{E}_{\bar{b}\bar{j}}|\psi_0\rangle$$
$$= |\psi_1^{\alpha\alpha}\rangle + |\psi_1^{\alpha\beta}\rangle + |\psi_1^{\beta\beta}\rangle, \qquad (17)$$

where

$$C^{ij}_{ab} = H^{ij}_{ab}(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1}, \quad \text{etc.} \qquad (18)$$

We are now in a position to derive the formulas for

$\langle\psi_0|\hat{H}|\psi_0\rangle$, $\langle\psi_0|\hat{H}|\psi_1\rangle$, $\langle\psi_0|\hat{R}|\psi_0\rangle$, $\langle\psi_0|\hat{R}|\psi_1\rangle$,

$\langle\psi_0|\hat{R}\hat{H}|\psi_0\rangle$, $\langle\psi_0|\hat{R}\hat{H}|\psi_1\rangle$, $\langle\psi_0|\hat{R}^2|\psi_0\rangle$, $\langle\psi_0|\hat{R}^2|\psi_1\rangle$,

$\langle\psi_0|\hat{R}^2\hat{H}|\psi_0\rangle$ and $\langle\psi_0|\hat{R}^2\hat{H}|\psi_1\rangle$

which are required to evaluate $\tilde{E}_{2,0}$, $\tilde{E}_{2,1}$, and $\tilde{E}_{2,2}$. The procedure we have used, if we discuss the most difficult term $\langle\psi_1|\hat{R}^2\hat{H}|\psi_0\rangle$, is to substitute in expressions for $\hat{H}\psi_0$ [Eq. (14)], ψ_1 [Eq. (17)], and $\hat{R}$ [Eq. (12)]. $\hat{R}$ has to be represented in terms of the occupied orbitals and virtual orbitals through

$$\hat{E}_{pq} = \delta_{pi}\delta_{qj}\hat{E}_{ij} + \delta_{pa}\delta_{qi}\hat{E}_{ai} + \delta_{pi}\delta_{qa}\hat{E}_{ia} + \delta_{pa}\delta_{qb}\hat{E}_{ab} \qquad (19)$$

and similarly for $\hat{E}_{\bar{r}\bar{s}}$. The matrix element can then be split into α and β parts and the key is then the evaluation of expressions such as

$$\langle\psi_0|\hat{E}_{ia}\hat{E}_{jb}\hat{E}_{pq}\hat{E}_{rs}\hat{E}_{ck}\hat{E}_{dl}|\psi_0\rangle. \qquad (20)$$

This may be evaluated using standard commutation relations.[12] We have used a computer algebra program RE-DUCE,[13] forcing operators such as $\hat{E}_{ck}$ to the left and operators such as $\hat{E}_{kc}$ to the right. The resulting expressions for all the required matrix elements are given in Table I. The completeness relations

$$S_{p\bar{q}}S_{p\bar{s}} = \delta_{\bar{q}\bar{s}}; \quad S_{q\bar{p}}S_{r\bar{p}} = \delta_{qr} \qquad (21)$$

have been used in the derivations to minimize summations over virtual orbitals. For these reasons there are many equivalent expressions to those given in Table I.

It is seen that we have defined quantities such as

$$D^{ij}_{a\bar{p}} = C^{ij}_{ab}S_{b\bar{p}} \qquad (22)$$

which occur many times in the resulting expressions. The time to evaluate this is proportional to $M^3 N^2$ (where N is the number of α or β orbitals, and M is the number of basis functions). Once these have been formed, the time to evaluate all the expressions is proportional to $M^2 N^p$ ($p = 0,1,2,3$). In other words the time to evaluate these expressions grows far less rapidly with M than the time to evaluate the integrals H^{ij}_{ab} by transformation of the atomic orbital basis integrals, which is proportional to $M^4 N$. Note furthermore that no new two electron integrals are required beyond those required for a standard UMP2 calculation. Also the evaluation of all terms proceeds most efficiently using matrix multiply routines on a vector computer.

Our tests of this method, reported in the earlier paper,[6] used the full CI program as explained earlier. These were all with very small basis sets, but the results served as a very useful check on the formula presented in Table I and its computer implementation.

In the following, PUHF(1), PUHF(2), PMP2(1), PMP2(2) will denote the projected UHF energies and projected UMP2 energies, obtained with this method with one and two spin projections.

III. RESULTS USING THE PROJECTED UMP METHOD

A. Small basis set calculations on H₂O

We first represent some results from the full CI program on H_2O, and compare them with various other approaches. See Table II.

In this table, two different basis sets have been employed:

(i) a 6-21G basis defined in Ref. 5, with calculations performed at (r_e,θ_e), $(1.5r_e,\theta_e)$, and $(2r_e,\theta_e)$;

(ii) a DZ basis defined in Ref. 14, with calculations at the same values of r_e and θ_e given in Ref. 14.

The calculations with the 6-21G basis held the $1a_1$ orbitals at their SCF form, and it was treated as a frozen orbital with no excitations from it.

The results in Table II are almost self-explanatory. The first group demonstrate the well known fact that Møller–Plesset energies based on RHF orbitals cannot describe the dissociation of a molecule. The second group demonstrate that this is also true for MP calculations based on UHF orbitals. In particular there is a most unacceptable hump at $1.5r_e$.

The projected UHF and UMP calculations show a different picture; the first set of results are with the full projector $\hat{O}$ and the second set and third set are obtained with $\hat{O}_1$ and with $\hat{O}_2$, respectively. The results with $\hat{O}_1$ are disastrous; the removal of one spin contaminant is not sufficient for this problem. The results for $\hat{O}_2$ and the full projector are negligibly different for the purpose of this discussion. The PUHF error decreases as r increases, a very different behavior to RHF and UHF. The PMP2 results are by far the best results so far in this table; the surface is parallel to the full CI within 4.0 mhartree. The projected UMP4 results are much better in magnitude, but show a variation of 4.7 mhartree over the surface. The significant point is that for very little extra work, the results with PMP2 are a factor of 5 better than UMP2.

These results should then be compared with results using other standard approaches. The fact that a slightly different basis is used and also that all orbitals are active in the DZ calculations should make no difference for discussion purposes. We observe that PMP2 is a tremendous improvement over RSDCI, and the variation over the surface is approximately the same as for RSDTQCI.[14] The variation over the surface with PMP2 is a factor of 2 better than CCSD.[15] It need hardly be said that the cost of performing the PMP2(2) calculations is very much less than RSDCI, RSDTQCI, and CCSD. The best results are obtained using the CASSCF method,[16] in this instance with seven active orbitals, and as is well known, excellent results are obtained when CISD is performed on top of this.[16]

The conclusion to be drawn is that the projected UMP2 method appears to give remarkable accuracy for the little

TABLE I. Formulas for the evaluation of projected UMP2 energies.

Define

$$D_{ap}^{ij} = C_{ab}^{ij} S_{bp}; \quad D_{ap}^{\bar{ij}} = C_{ab}^{\bar{ij}} S_{pb}; \quad D_{ap}^{i\bar{j}} = C_{ab}^{i\bar{j}} S_{pb}; \quad D_{ap}^{i\bar{j}} = C_{ba}^{i\bar{j}} S_{bp},$$

$$I_{ap}^{ij} = H_{ab}^{ij} S_{bp}; \quad I_{ap}^{\bar{ij}} = H_{ab}^{\bar{ij}} S_{pb}; \quad I_{ap}^{i\bar{j}} = H_{ab}^{i\bar{j}} S_{pb}; \quad I_{ap}^{i\bar{j}} = H_{ba}^{i\bar{j}} S_{bp},$$

and

$$M_{ijkl} = C_{ab}^{ij} H_{ab}^{kl}; \quad M_{i\bar{j}k\bar{l}} = C_{ab}^{i\bar{j}} H_{ab}^{k\bar{l}}; \quad M_{\overline{ij}\overline{kl}} = C_{ab}^{\bar{ij}} H_{ab}^{\overline{kl}},$$

and

$$T_{kj} = S_{k\bar{l}} S_{j\bar{l}}; \quad T_{\overline{kj}} = S_{\bar{i}k} S_{\bar{i}j},$$

$$g = \tfrac{1}{4} N_\alpha + \tfrac{1}{4} N_\beta - \tfrac{1}{2} - T_{ii}.$$

Then the following quantities must be calculated:

(i) For $\tilde{E}_{2,l}$, $l \geqslant 0$:

$$\langle \psi_0 | \hat{H} | \psi_0 \rangle = E_{\text{UHF}},$$

$$\langle \psi_0 | \hat{H} | \psi_1 \rangle = \tfrac{1}{4} M_{ijij} + \tfrac{1}{4} M_{\overline{ij}\overline{ij}} + M_{i\bar{j}i\bar{j}}.$$

(ii) For $\tilde{E}_{2,l}$, $l \geqslant 1$:

$$\langle \psi_0 | \hat{R} | \psi_0 \rangle = T_{ii} = R_1,$$

$$\langle \psi_0 | \hat{R} | \psi_1 \rangle = D_{ai}^{ij} S_{aj},$$

$$\langle \psi_0 | \hat{R} \hat{H} | \psi_0 \rangle = I_{ai}^{ij} S_{aj} + E_{\text{UHF}} T_{ii},$$

$$\langle \psi_1^{\alpha\alpha} | \hat{R} \hat{H}^{\alpha\alpha} | \psi_0 \rangle = \tfrac{1}{4} M_{ijij} T_{kk} - \tfrac{1}{4} M_{ijik} T_{jk} + \tfrac{1}{2} D_{ak}^{ij} I_{ak}^{ij},$$

$$\langle \psi_1^{\alpha\alpha} | \hat{R} \hat{H}^{\alpha\beta} | \psi_0 \rangle = S_{kj} D_{ab}^{ik} H_{ab}^{i\bar{j}},$$

$$\langle \psi_1^{\alpha\beta} | \hat{R} \hat{H}^{\alpha\beta} | \psi_0 \rangle = M_{i\bar{j}i\bar{j}} T_{kk} + M_{i\bar{j}k\bar{l}} S_{i\bar{l}} S_{k\bar{j}} - M_{i\bar{j}i\bar{l}} T_{j\bar{l}} - M_{i\bar{j}k\bar{j}} T_{ik} + D_{ba}^{i\bar{j}} I_{ab}^{i\bar{j}}$$
$$+ D_{ak}^{i\bar{j}} I_{ak}^{i\bar{j}} + D_{bm}^{i\bar{j}} I_{bm}^{i\bar{j}} - D_{bj}^{i\bar{j}} I_{b\bar{l}}^{i\bar{j}} - D_{ai}^{i\bar{j}} I_{ak}^{k\bar{j}}.$$

(iii) for $E_{2,l}$, $l \geqslant 2$:

$$\langle \psi_0 | \hat{R}^2 | \psi_0 \rangle = N_\alpha N_\beta - 4g T_{kk} - 2T_{kk} T_{ll} - 2T_{mn} T_{mn} = R_2$$

$$\langle \psi_0 | \hat{R}^2 | \psi_1 \rangle \quad - \text{equivalent to } \langle \psi_0 | \hat{H} \hat{R}^2 | \psi_0 \rangle,$$

$$\langle \psi_0 | \hat{R}^2 \hat{H}^{\alpha\alpha} | \psi_0 \rangle = -2 I_{bj}^{ij} S_{i\bar{j}} T_{jb},$$

$$\tfrac{1}{4} \langle \psi_0 | \hat{R}^2 \hat{H}^{\alpha\beta} | \psi_0 \rangle = I_{bk}^{i\bar{j}} S_{i\bar{k}} T_{jb} - I_{bk}^{i\bar{j}} S_{i\bar{b}} T_{jk} - I_{bj}^{i\bar{j}} S_{i\bar{k}} T_{bk} - g I_{bj}^{i\bar{j}} S_{i\bar{b}},$$

$$\langle \psi_1^{\alpha\alpha} | \hat{R}^2 \hat{H}^{\alpha\alpha} | \psi_0 \rangle = -4 D_{ak}^{ij} I_{ak}^{ij} T_{kj} - 2 D_{ak}^{ij} I_{al}^{ij} T_{lk} + 4 D_{ak}^{ij} I_{al}^{ij} S_{jk} S_{k\bar{l}} + D_{ak}^{ij} I_{bk}^{ij} T_{ba} - 2g D_{ak}^{ij} I_{ak}^{ij}$$
$$+ M_{ijkl} T_{ik} T_{jl} + M_{ijil} (2 T_{jm} T_{lm} + 2g T_{jl}) + \tfrac{1}{4} M_{ijij} R_2,$$

$$\tfrac{1}{4} \langle \psi_1^{\alpha\beta} | \hat{R}^2 \hat{H}^{\alpha\alpha} | \psi_0 \rangle = D_{ak}^{k\bar{l}} I_{ai}^{ij} S_{i\bar{l}} S_{j\bar{l}} + D_{ak}^{i\bar{l}} I_{ai}^{ij} (S_{j\bar{l}} S_{k\bar{l}} - S_{j\bar{l}} S_{k\bar{i}}) + D_{ab}^{i\bar{l}} H_{ab}^{jk} S_{j\bar{l}} T_{ik}$$
$$+ D_{ab}^{i\bar{l}} I_{bi}^{ij} (S_{a\bar{l}} S_{j\bar{l}} - S_{a\bar{i}} S_{j\bar{l}}) - D_{ab}^{i\bar{l}} H_{ab}^{ij} (S_{kl} T_{jk} + g S_{j\bar{l}}),$$

$$\langle \psi_1^{\beta\beta} | \hat{R}^2 \hat{H}^{\alpha\alpha} | \psi_0 \rangle = -D_{ad}^{\bar{ai}} I_{da}^{mk} S_{k\bar{l}} S_{m\bar{n}},$$

$$\tfrac{1}{4} \langle \psi_1^{\alpha\beta} | \hat{R}^2 \hat{H}^{\alpha\beta} | \psi_0 \rangle = -D_{cl}^{k\bar{l}} I_{cl}^{k\bar{l}} T_{ll} - D_{cl}^{k\bar{l}} I_{cl}^{i\bar{l}} T_{ik} - D_{cl}^{k\bar{l}} I_{cl}^{k\bar{l}} T_{\bar{ll}} - D_{ak}^{k\bar{l}} I_{dk}^{i\bar{l}} T_{ik} - D_{ak}^{k\bar{l}} I_{dk}^{k\bar{l}} T_{\bar{ll}}$$
$$- D_{ab}^{k\bar{l}} I_{ba}^{i\bar{l}} T_{ik} - D_{ab}^{k\bar{l}} I_{ba}^{k\bar{l}} T_{\bar{ll}} - D_{ak}^{k\bar{l}} I_{dl}^{i\bar{l}} T_{\bar{ik}} + D_{dl}^{k\bar{l}} I_{dk}^{ik} T_{ik} + D_{ck}^{k\bar{l}} I_{cl}^{i\bar{l}} T_{\bar{ll}}$$
$$- g D_{cl}^{k\bar{l}} I_{cl}^{k\bar{l}} - g D_{db}^{k\bar{l}} I_{ba}^{k\bar{l}} - g D_{ak}^{k\bar{l}} I_{dk}^{k\bar{l}} + g D_{dl}^{k\bar{l}} I_{dk}^{k\bar{l}} + g D_{ck}^{k\bar{l}} I_{cl}^{i\bar{l}}$$
$$- D_{ck}^{k\bar{l}} I_{cl}^{i\bar{l}} S_{i\bar{l}} S_{\bar{ll}} - D_{cl}^{k\bar{l}} I_{ci}^{i\bar{l}} S_{k\bar{l}} S_{l\bar{l}} + D_{ck}^{k\bar{l}} I_{cl}^{i\bar{l}} T_{ll} + D_{cl}^{k\bar{l}} I_{ci}^{i\bar{l}} T_{kl}$$
$$- D_{cl}^{k\bar{l}} I_{bk}^{kk} S_{cl} S_{l\bar{b}} + D_{cl}^{k\bar{l}} I_{bk}^{k\bar{l}} S_{ck} S_{l\bar{b}} + D_{cl}^{k\bar{l}} I_{ci}^{k\bar{l}} S_{i\bar{l}} S_{l\bar{l}} + D_{cl}^{k\bar{l}} I_{cl}^{i\bar{l}} S_{i\bar{l}} S_{k\bar{l}} + D_{db}^{k\bar{l}} I_{ba}^{i\bar{l}} S_{i\bar{l}} S_{k\bar{l}}$$
$$+ D_{db}^{k\bar{l}} I_{bk}^{i\bar{l}} S_{i\bar{k}} S_{k\bar{a}} + D_{ak}^{k\bar{l}} I_{ba}^{i\bar{l}} S_{i\bar{b}} S_{k\bar{k}} - D_{ak}^{k\bar{l}} I_{bk}^{i\bar{l}} S_{i\bar{b}} S_{k\bar{a}} + D_{ak}^{k\bar{l}} I_{di}^{i\bar{l}} S_{i\bar{l}} S_{k\bar{k}} + D_{ak}^{k\bar{l}} I_{dk}^{ik} S_{i\bar{l}} S_{k\bar{l}}$$
$$- D_{ab}^{k\bar{l}} I_{bk}^{ik} S_{i\bar{l}} S_{k\bar{a}} - D_{dl}^{k\bar{l}} I_{ba}^{i\bar{l}} S_{i\bar{b}} S_{k\bar{l}} + D_{dl}^{k\bar{l}} I_{bk}^{ik} S_{i\bar{b}} S_{k\bar{a}} - D_{ak}^{k\bar{l}} I_{di}^{i\bar{l}} S_{i\bar{l}} S_{k\bar{l}} - D_{dl}^{k\bar{l}} I_{dk}^{i\bar{l}} S_{i\bar{k}} S_{k\bar{l}}$$
$$+ D_{dl}^{k\bar{l}} I_{dk}^{k\bar{l}} T_{\bar{lk}} + D_{ak}^{k\bar{l}} I_{di}^{i\bar{l}} T_{k\bar{l}} + D_{dl}^{k\bar{l}} I_{ba}^{i\bar{l}} T_{\bar{lb}} + D_{ab}^{k\bar{l}} I_{bk}^{kk} T_{\bar{al}} - D_{ak}^{k\bar{l}} I_{ba}^{k\bar{l}} T_{kb} - D_{ab}^{k\bar{l}} I_{bk}^{k\bar{l}} T_{k\bar{a}}$$
$$+ M_{kli\bar{j}} (T_{ik} T_{j\bar{l}} - g S_{i\bar{l}} S_{kj} - S_{j\bar{l}} S_{k\bar{j}} T_{ij} - S_{i\bar{l}} S_{j\bar{l}} T_{jk})$$
$$+ M_{kji\bar{j}} (T_{ij} T_{jk} + g T_{ik}) + M_{klkj} (T_{\bar{ij}} T_{\bar{ll}} + g T_{j\bar{l}}) + \tfrac{1}{4} M_{i\bar{j}i\bar{j}} R_2.$$

(iv) For remaining spin contamination estimate:

$$\langle \psi_0 | \hat{R}^3 | \psi_0 \rangle = 4g(R_1^2 + 4 T_{mn} T_{mn} - 4R_1 - R_2)$$

$$+ R_1 R_2 - 8R_1^2 - 4R_1 + 8 T_{mn} T_{mn} (R_1 - 1) + 12 T_{ij} T_{jk} T_{ki}.$$

effort required. Indeed it can be argued that greater accuracy is achieved than with RSDCI, RMP2, UMP2, RMP4, UMP4, and CCSD. Of course only one set of calculations is presented, but it is reasonable to assume that this state of affairs will hold for all similar situations where bonds are broken. Finally, we note that although not exactly size consistent, the PMP2(2) ansatz gives an energy difference of just 0.53 kcal/mol between the energies of completely disso-

ciated H_2O and $O(^3P) + H(^2S) + H(^2S)$.

The remaining applications are typical of problems where spin contamination of the wave function has disastrous effects on UHF and UMP calculations. All calculations were carried out with the new formulas given above for projected UHF energies with 1 and 2 spin projections PUHF(1) and PUHF(2), and the projected UMP2 energies PMP2(1) and PMP2(2).

TABLE II. Various methods for calculating the correlation energy of H_2O at r_e, $1.5r_e$, and $2.0r_e$.[a]

Method	Basis	r_e	$1.5r_e$	$2.0r_e$	Reference
RHF	6-21G	130.1	192.0	299.9	6
RMP2	6-21G	9.2	25.1	58.2	6
RMP4	6-21G	1.0	6.2	17.9	6
UHF	6-21G	130.1	164.2	91.9	6
UMP2	6-21G	9.2	69.8	36.5	6
UMP4	6-21G	1.0	50.9	28.8	6
PUHF	6-21G	130.1	110.5	70.5	6
PMP2	6-21G	9.2	10.2	13.2	6
PMP4	6-21G	1.0	3.7	5.7	6
PUHF(1)	6-21G	130.1	− 76.4	− 102.9	This work
PMP2(1)	6-21G	9.2	− 22.5	− 147.3	This work
PMP4(1)	6-21G	1.0	− 7.8	− 91.9	This work
PUHF(2)	6-21G	130.1	110.6	71.6	This work
PMP2(2)	6-21G	9.2	10.3	13.6	This work
PMP4(2)	6-21G	1.0	3.7	5.7	This work
RHF	DZ	148.0	211.0	310.1	14
RSDCI	DZ	7.9	22.4	60.4	14
RSDTQCI	DZ	0.3	1.1	4.4	14
CCSD	DZ	1.8	5.6	9.3	15
CASSCF(7)	DZ	1.9	2.0	1.9	16
CASSCF(7) + CI	DZ	1.9	2.0	1.9	16
Full CI	DZ	0	0	0	⋯

[a] Energies in mhartree. In the 6-21G calculations, the $1a_1$ orbital is frozen, and at (r_e,θ_e) the atomic coordinates are taken as (± 1.474 432 3,0,1.078 153 4).

B. The CH dissociation potential for CH_4

This problem has been studied in the past by Duchovic et al.[17] and by Schlegel,[9] using a 6-31G** basis set. The first set of authors performed RHF, UHF, and MPn (n = 2,3,4) calculations at a set of geometries for which the $C\cdots H$ distance R and the pyramidal angle θ were changed. Schlegel[9] then used his first projection scheme to present projected MP4 results. Brown and Truhlar[18] have also examined this problem using a larger basis set [6-311 + + G(df,p)] at the MCSCF and MR-CISD level. The results of these calculations are summarized in Table III, where the zero for each calculation is taken to be the energy for R = 10 Å, θ = $\pi/2$. The table shows the size consistency error[19] calculated from $E(CH_4, R = 10$ Å, $\theta = \pi/2) - E(H) - E(CH_3)$.

Our calculations with one and two projections are reported in the final four columns of Table III, using the 6-31G** basis set.

There are several comments to be made. It is clear that calculations with one projector operator are not sufficient. This was recognized by Schlegel,[9] as evidenced by his 4.6 kcal/mol error. Our PMP2(1) calculation shows this also with the error of 2.3 kcal/mol. With two projections, the PUHF and PMP2 calculations become size consistent [the PMP2(2) calculation is size consistent to 0.006 kcal/mol]. The point here is that in the (CH_4, R = 10 Å, θ = $\pi/2$) calculation, a projection operator is needed for both CH_3 and the coupling of H to CH_3 to form a singlet. After zero and one projections, the values of $\langle\psi_0|\hat{S}^2\hat{O}_i|\psi_0\rangle/\langle\psi_0|\hat{O}_i|\psi_0\rangle$ were 1.01 and − 0.05, respectively. There will be many such

TABLE III. Comparison of $H\cdots CH_3$ potentials for various ab initio methods.[a]

R(Å)	0.757	1.086	1.500	2.000	2.500	3.000	4.000	10.00
θ (deg)	111.33	109.47	105.72	100.57	96.47	91.30	90.00	90.00
$\langle\hat{S}^2\rangle$	0.00	0.00	0.00	0.66	0.93	0.99	1.01	1.01
UHF	3.0	− 87.5	− 51.3	− 10.1	− 2.1	− 0.6	− 0.1	0.0
MP2	− 18.8	− 109.4	− 74.1	− 16.0	− 3.3	− 0.9	− 0.1	0.0
MP4[b]	− 19.7	− 110.6	− 77.0	− 29.6	− 4.1	− 0.9	− 0.1	0.0
MRCI[b]	13.9	− 104.3	− 76.5	− 32.8	− 10.8	− 3.0	⋯	0.0
PUHF(1)[d]	8.8	− 81.6	− 45.5	− 22.7	− 7.6	− 2.0	− 0.1	0.0
PMP2(1)[d]	− 15.4	− 106.0	− 70.7	− 30.7	− 9.7	− 2.6	− 0.2	0.0
PMP4[c,d]	− 13.9	− 104.8	− 71.3	− 28.5	− 9.3	− 2.4	0.1	0.0
PUHF(2)[d]	4.9	− 85.5	− 49.4	− 25.4	− 8.6	− 2.3	− 0.1	0.0
PMP2(2)[d]	− 17.7	− 108.5	− 72.9	− 32.3	− 10.3	− 2.7	− 0.2	0.0

[a] For details of calculation, see the text. Except where otherwise noted, the basis set is 6-31G**, and energies are in kcal/mol.
[b] 6-311 + G(df, p) results from Ref. 18.
[c] Schlegel's calculation, Ref. 8.
[d] Size consistency error $E(CH_4) - E(H) - E(CH_3)$: PUHF(1): − 3.9; PMP2(1): − 2.3; PMP4[c]: − 4.6; PUHF(2): 0.0; PMP2(2): 0.0.

calculations where two projectors are essential for size consistency.

This correction of the size consistency error and this new method of spin projection have a significant effect upon the potential curve. There is excellent agreement between the PMP2(2) calculations at R = 4.0, 3.0, 2.5, and 2.0 Å and the more accurate (presumably) MRCI calculations on this long range part of the potential. All other calculations—UHF, MP2, MP4, PUHF(1), PUHF(2), PMP2(1), and PMP4(Schlegel) give values which are too shallow to a greater or lesser extent. In particular the MP2 and MP4 values are very poor at long range (at R = 2.5 Å, values of − 3.3 and − 4.1 compared to − 10.3 for PMP2 and − 10.8 kcal/mol for MRCI). Around equilibrium the MP2 and PMP2(2) values are close, whereas values obtained with one projection and Schlegel's PMP4 value are definitely inferior. Thermodynamic data yields a well depth of 112.4 kcal/mol.[18] The results in Table III indicate that the 4 kcal/mol difference between the PMP2(2) value for the well depth and experiment should be apportioned between the effects of higher order perturbation theory and basis set deficiency. The MRCI calculation, despite the large basis set, certainly appears not to be balanced over the whole potential curve.

Brown and Truhlar[18] discuss the form of this potential curve, and are satisfied that the longer range values for their MRCI curve are much more reasonable than the MP4 curve, principally because the MRCI values lie on a smooth Morse curve. The fact that PMP2(2) values at these R agree closely with the MRCI results, and the fact that the well depth of the PMP2(2) is much closer to the experimental D_e value than the MRCI value, suggests that this PMP2(2) curve is of high accuracy along its whole length. We again comment how inexpensive this PMP2(2) curve is to generate.

C. Barrier height for the addition of hydrogen to ethylene

This is a problem which has recently been discussed by Sosa and Schlegel,[20] for which they say that calculations with large basis sets and correlation energy inclusion predict barriers which are 3–8 kcal/mol too high (they refer to UMPn calculations). Results from Sosa and Schlegel, and our calculations are given in Table IV. All calculations are reported for the 6-31G* basis set. As in Ref. 20, the geometries used for C_2H_4 and the transition state are the optimized Hartree–Fock values for this basis set.[21]

From Table IV it is seen that whereas the UHF barrier height is in good agreement with experiment at 2.90 kcal/mol, the MP2 and MP4 values are too large by 9.8 and 8.0 kcal/mol, respectively. The projected UHF value is unacceptable at − 5.8 kcal/mol; Sosa and Schlegel attribute this to the fact that the PUHF curve has a spurious minimum in a region where a bond is partially broken.[20] We feel that this is not the case. The UHF wave function has some electron correlation effects already in it, but it is contaminated by a quartet and therefore too high in energy. On the other hand, PUHF has the contamination removed, yet still has some correlation effects, which the asymptote H + C_2H_4 does not, and therefore the PUHF energy will give a barrier which is

TABLE IV. Hydrogen addition to ethylene.[a]

	(i) Energies (in hartree)	
H + C_2H_4	PUHF − 78.529 948	PMP2 − 78.791 914
Transition state (0[b])	− 78.525 32	− 78.772 966
Transition state (1[b])	− 78.539 542	− 78.786 881
Transition state (2[b])	− 78.539 244	− 78.786 735

(ii) Barrier height (in kcal/mol)	
UHF	2.90
MP2	11.80
MP4	10.05
PUHF(1)	− 6.02
PUHF(2)	− 5.83
PMP2(1)	3.16
PMP2(2)	3.25
PMP2[c]	− 1.84
PMP4[c]	1.58
Experiment	2.04 ± 0.08

[a] 6-31G* basis set.
[b] Number of spin projections l in $\hat{O}_l$.
[c] Reference 20.

too low. Our value for the PMP2(2) barrier is most acceptable at 3.25 kcal/mol, and shows once again that proper treatment of spin projection can yield good values. Schlegel's approximate scheme with one spin projection is shown to be deficient here.

Here therefore is another example where spin contamination is the principal cause for deficient UMP2 calculations. At the transition state $\langle \hat{S}^2 \rangle$ = 0.99. A little extra work from UMP2 to PMP2(2) has reduced the barrier from 11.80 to 3.25 kcal/mol, in better agreement with the experimental value of 2.04 kcal/mol. Sosa and Schlegel[20] mention the problem of hydrogen addition to CH_2O and substituted olefins (C_2H_3F, C_2H_3Cl, C_2H_3OH), where the same problem of too high barriers resulting from spin contamination occurs. Application of this projection scheme should cure these problems.

D. The electron affinity of CN

Recently Nobes et al.[22] have observed that the slow convergence of the Møller–Plesset series for CN leads to MP4 values for the electron affinity of CN which is considerably overestimated. Using a large basis set [6-311 + G(df)], UHF, MP2, and MP4 values for the electron affinity of CN were calculated to be 283, 435, and 414 kJ/mol to be compared to the experimental value of 367 ± 3 kJ/mol. The $\langle \hat{S}^2 \rangle$ value for CN was 1.13.

We decided to tackle this problem using four different basis sets. The first was STO-3G, for which all types of calculations can be done, including full CI. See the results in Table V. The MP2 value (− 112 kJ/mol) and MP4 value (− 156 kJ/mol) are much in error from the full CI value of − 244 kJ/mol. When the projection operator is applied, much better results are obtained with the PMP2(2) value of − 205 kJ/mol being in error by 39 kJ/mol for this basis. Further spin projection at MP2 will have no effect (after two spin projections in the STO-3G basis, there was virtually no re-

TABLE V. The electron affinity of CN.[a]

Basis	STO-3G[b]	[321]	[4321]	[4321 + diffuse]
$\langle \hat{S}^2 \rangle$	1.228	1.110	1.117	1.121
UHF	− 215	245	267	280
MP2	− 112	379	433	456
PUHF(1[c])	− 306	182	202	214
PUHF(2[c])	− 293	189	209	222
PMP2(1[c])	− 216	308	359	382
PMP2(2[c])	− 205	314	366	389

[a] Electron affinity in kJ/mol. Geometry: for CN⁻, $r = 1.1607$ Å; for CN, $r = 1.1619$ Å. The experimental electron affinity is 367 ± 3.
[b] Additional data for STO-3G: PMP2(6) − 205; PMP4(6) − 215; PMP6(6) − 221; full CI − 244.
[c] Number of spin projections l in $\hat{O}_l$.

maining spin contamination). These results already tell us that larger basis set calculations at the PMP2(2) level will not give us exact results because it is clear that higher orders of perturbation theory will contribute the equivalent of 39 kJ/mol at the STO-3G basis. However, the fact remains that the PMP2(2) value is a great improvement over the MP2 and MP4 value.

The larger basis set calculations used the atomic natural orbital basis sets of Almlöf and Taylor,[23] which may be denoted [$lmn\cdots$] to represent l "s," m "p," n "d" basis functions, each of which is a general contraction, based on atomic natural orbitals, of a large primitive set. The basis sets [321], [4321] which we used are exactly as described in Ref. 23. Our largest basis, denoted [4321] + diffuse, is the [4321] basis with the last s, p functions uncontracted, and augmented by an additional s and p function of exponents 0.04, 0.03(C) and 0.055, 0.04(N). The calculations show how critical the results are on the level of basis set—the UHF electron affinities are 245, 267, and 280 kJ/mol. The trends are as might be expected: the UHF is too low, the PUHF(2) results are far too low, the MP2 results are far too high and the PMP2(2) results are very reasonable for large basis sets. If we concentrate on the largest basis set, the MP2 value is in error by 89 kJ/mol, whereas the PMP2(2) value is in error by only 22 kJ/mol. This is entirely acceptable, bearing in mind the earlier comments of the effects of higher order perturbation theory. It is probable that this basis is very close to a complete basis set.

The conclusion from this study of CN and CN⁻ is that spin projection is essential if the properties of CN are going to be studied through UHF theory. Once again we find that a most difficult property, the electron affinity, has improved in accuracy by a factor of 4 to an approximate error of 20 kJ/mol with the PMP2(2) calculation and a large basis set. It is difficult to see how a better result than this could have been expected with a second-order perturbation theory method.

IV. CONCLUSION

In the previous sections we have given the theory and formulas for the evaluation of projected unrestricted Møller–Plesset second-order energies with two spin contaminants eliminated: the PMP2(2) calculations. We have also demonstrated the greatly improved accuracy which is

achieved in four calculations where spin contamination is significant.

We must also point our remaining deficiencies and associated remarks which can be made about this projection procedure.

(a) Unless the full Löwdin projection operator $\hat{O}$ is used, then these projected calculations are not exactly size consistent. However, we believe that two spin projections is all that is necessary for them to be size consistent in practice, for most calculations. For example, we showed that our $H + CH_3 \rightarrow CH_4$ calculations were size consistent to 0.006 kcal/mol. One can have an idea of the number of spin projections required by considering the number of bonds being broken or formed, and the number of open shell species which have spin contamination, in the products. An evaluation of

$$\langle \hat{S}^2 \rangle = \frac{\langle \psi_0 | \hat{S}^2 \hat{O}_2 | \psi_0 \rangle}{\langle \psi_0 | \hat{O}_2 | \psi_0 \rangle}$$

will give an estimate of the remaining spin contamination error after two spin projections.

(b) Our experience is that any spin contamination effect should be removed, however small. For example, in $H + CH_3 \rightarrow CH_4$ after one spin projection for $R = 10$ Å, $\theta = \tau/2$, $\langle \hat{S}^2 \rangle = -0.048$, and for this the size consistency error was 2.3 kcal/mol for PMP2(1). Certainly if there is a greater than 5% contamination, it must be removed.

(c) All our reported calculations show that the PUHF method is very poor, and usually inferior to UHF. We understand this by arguing that most investigations involve a comparison of UHF calculations at one geometry and RHF at another geometry. The UHF calculations include some correlations effects, which are often more than compensated by spin contamination from higher states. The removal of the spin contamination therefore leads, e.g., to barriers which are too low.

(d) The formulas in Table I are indeed complicated, but they can all be vectorized and programmed efficiently. If one stores most of the matrices on disk, only a few M^2 dimensional arrays in memory are necessary at any one time. Some 2000 lines of FORTRAN are necessary for this program. It is repeated that no new two electron integrals are needed over those required for standard MP2 calculations.

(e) Formulas such as these have a much wider use if the energy gradient can be calculated. Simandiras et al.[24] have shown how to calculate efficiently the gradient of the MP2 energy. The same theory can be applied to the PMP2(2) energy expression, but the algebra will be most unpleasant. However, it only has to be done once, and we shall attempt it.

(f) There is a well known point in closed shell molecules where the RHF and UHF potential surfaces split into two. We examined this behavior for the C_{2v} dissociation of H_2O in our previous paper.[6] Those calculations clearly show that there is a "discontinuity" of some kind in the behavior of projected UHF and projected UMP calculations, which is only finally removed at a high order of perturbation theory. In other words the behavior of PMP2(2) calculations in the neighborhood of this geometry is unsatisfactory, but those calculations showed that the degree of this problem is im-

proved by a factor of around 4 compared to UMP2 calculations. We shall investigate this question further when we have a gradient routine available.

(g) The first important recent paper on this topic was by Schlegel,[8] where he made a first attempt to remove one spin contaminant. We believe that his next paper,[9] although an improved version of the problem, does not give the best representation of the projected UMP2 energy, primarily because it mixes up different orders of perturbation theory. This is probably the principal reason why his values are deficient when compared to our calculations. Our formulation is consistent, order by order.

(h) We are not recommending this projected UMP2 scheme as the answer to all problems, but it is an almost size consistent method which gives good accuracy over the whole of a ground state potential surface. If greater accuracy is required, then a method involving configuration interaction should be used. MCSCF is an ideal choice, with some additional CI if necessary, but if this is done then a size consistency error will appear. Of course we recognize the importance of the developments in this field; indeed one of us is actively involved in an "internally contracted" CI scheme,[25] which has excellent features across a complete surface. The purpose of this paper is to observe that remarkable accuracy can be achieved with little effort through the PMP2(2) approach; if greater accuracy is required, at least an order of magnitude more work is required using a far more sophisticated method.

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