
Constant Denominator Perturbative Schemes and the Partitioning Technique

PÉTER R. SURJÁN, ÁGNES SZABADOS

Department of Theoretical Chemistry and Structural Chemistry Research Group of Hungarian Academy of Sciences, Eötvös University, H-1518 Budapest 112, Hungary

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ABSTRACT: With the aid of Löwdin's partitioning theory, an infinite series for the eigenvalue of the Schrödinger equation is derived which does not contain energy differences in denominators. The resulting formulae are compared to those of constant denominator methods, such as perturbation theory within the Unsöld approximation and the connected moment expansion (CMX). The Unsöld formulae are easily obtained from partitioning theory by a suitable choice of the zero order Hamiltonian. Optimizing the value of the energy denominator using the first order wave function in a size-consistent way, the third order Unsöld correction vanishes, and the corresponding energy correction formula of the CMX is recovered at the second order. © 2002 Wiley Periodicals, Inc. *Int J Quantum Chem* 90: 20–26, 2002

Key words: multi-reference perturbation theory; constant-denominator perturbation theory; connected moment expansion; optimized partitioning; quasi-degeneracy perturbation theory

Introduction

Löwdin's partitioning technique [1], besides providing an energy-dependent effective Hamiltonian, serves as a unifying tool to derive different variants of perturbation theory (PT), such as the Brillouin–Wigner [2, 3] or the Rayleigh–Schrödinger [4, 5] formalisms. These points have been repeatedly emphasized by Löwdin in his fundamental series of papers entitled “Studies in Perturbation Theory” [1, 6–11].

Correspondence to: P. Surján; e-mail: surjan@para.chem.elte.hu.
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Among standard formulation of perturbation theories, the Rayleigh–Schrödinger (RS) formalism is preferred in the many-body problem, due to its extensive property which is often of utmost importance. This theory, however, is plagued with the quasi-degeneracy problem, i.e., the diverging nature of standard nondegenerate PT formulae in the limit of small energy denominators. Several solutions have been proposed [12–20] to deal with quasi-degenerate situations. These usually collect the quasi-degenerate levels into a zero order subspace and approximate the exact solution by Löwdin's partitioning theory or a variant thereof. Another possibility is to shift the zero order energy levels and find the level shift parameters by some physical/intuitive consideration, by an em-

pirical analysis [21], or by an optimization technique [22–24]. Two substantially simpler (though less exact) approaches also have to be mentioned: (i) damping of small energy denominators by imaginary level shifts [25, 26], and (ii) using constant (average) energy denominators. Of the latter, the so called Unsöld approximation results from standard RS-PT formulae by setting each denominator equal, permitting one to perform the sum-over-states in the PT formulae explicitly. A second approach of the latter type is the connected moment expansion (CMX) [27] which offers a convergent energy series using the (connected) moments of the Hamiltonian.

The CMX method, some time ago [28], was applied to calculate correlation energies in small molecules with medium success. Later [29], this approach was criticized by Wolinski and Pulay, who remarked that any constant denominator PT or the CMX formulae were ab ovo inappropriate to compute molecular characteristics like potential curves or force constants. They argued that, though at large distances these methods are free from the dissociation catastrophe, at the same time they lack the important effect of decreasing energy denominators upon prolongating covalent bonds at around equilibrium.

However, in accordance with most numerical experience we had with CMX, the above criticism is relevant only if one has a single configurational reference state. Having computed a qualitatively correct potential curve in a multiconfigurational framework, one no longer needs the effect of decreasing denominators, and one may wonder if constant denominator PTs, due to their simplicity, are valuable tools in accounting for the dynamical part of correlation energy.

Application of constant denominator PTs is strongly motivated by the fact that, besides being simpler, permitting one to evaluate easily fourth [30] or even fifth [31] order corrections, they are free from the quasi-degeneracy problem. The price to pay for this is slow convergence and reduced accuracy at low orders; therefore such theories can only be suggested for use if the zero order wave function is already sufficiently accurate. In quantum chemistry, multireference states may serve as such zero orders.

In this article, we first present a simple derivation of Löwdin’s implicit energy formula. Being exact, this formula may serve as a starting point to derive basically any approximate energy correction schemes. We shall analyze some of them and show how the simple Unsöld approximation

can be obtained by an appropriate splitting of the full Hamiltonian. Then, following the philosophy of our previous papers [22, 23] we shall optimize the Unsöld denominator and show that the resulting second order formula is the same as the analogous expression of CMX theory. A few numbers will illustrate the equations.

Löwdin’s Implicit Energy Formula

Using standard notations of partitioning technique, we define two orthogonal projectors,

$$\hat{O}^2 = \hat{O} \quad \hat{P}^2 = \hat{P} \quad \hat{O}\hat{P} = 0, \quad (1)$$

that span the full space under consideration:

$$\hat{O} + \hat{P} = 1. \quad (2)$$

The Schrödinger equation $\hat{H}\Psi = E\Psi$ is then partitioned as

$$\begin{aligned} (\hat{O}\hat{H}\hat{O} + \hat{O}\hat{H}\hat{P})\Psi &= E\hat{O}\Psi \\ (\hat{P}\hat{H}\hat{O} + \hat{P}\hat{H}\hat{P})\Psi &= E\hat{P}\Psi, \end{aligned} \quad (3)$$

leading to the standard energy formula [1]

$$E = \langle \Phi | \hat{H} | \Phi \rangle + \langle \Phi | \hat{H} (E - \hat{P}\hat{H})^{-1} \hat{P}\hat{H} | \Phi \rangle \quad (4)$$

where

$$\Phi = \hat{O}\Psi$$

is the O -component of the exact wave function. In practical methods one often chooses an appropriate reference function Φ and defines the \hat{O} projector as

$$\hat{O} = |\Phi\rangle\langle\Phi|. \quad (5)$$

The energy expression (4) is most useful to derive several practical approximative formulae. It can be, however, brought to a somewhat simpler form by the identical transformation

$$\begin{aligned} &\langle \Phi | \hat{H} (E - \hat{P}\hat{H})^{-1} \hat{P}\hat{H} | \Phi \rangle \\ &= \langle \Phi | \hat{H} (E - \hat{P}\hat{H})^{-1} (\hat{P}\hat{H} - E) | \Phi \rangle \\ &\quad + E \langle \Phi | \hat{H} (E - \hat{P}\hat{H})^{-1} | \Phi \rangle \\ &= -\langle \Phi | \hat{H} | \Phi \rangle + E \langle \Phi | \hat{H} (E - \hat{P}\hat{H})^{-1} | \Phi \rangle \end{aligned} \quad (6)$$

where an auxiliary term was added and subtracted to get rid of the inverse in the first term. Substituting this into the general energy expression (4) and dividing by E we get the compact result

$$1 = \langle \Phi | \hat{H} (E - \hat{P}\hat{H})^{-1} | \Phi \rangle. \quad (7)$$

This equation is an *exact* implicit formula for the energy which, as was discussed by Löwdin [32],

can also be obtained using resolvent techniques and may serve as a starting point to derive diverse theoretical and computational methods of quantum mechanics, including perturbation theory.

It is worth comparing Eq. (7) to the so-called Weinstein function, which is the expectation value of the resolvent of the Hamiltonian taken with the reference function Φ :

$$\langle \Phi | (z - \hat{H})^{-1} | \Phi \rangle. \quad (8)$$

The main difference is that expression (8) is singular at any exact energies $z = E$, while Eq. (7) is a fully regular formula.

Expansion of the Implicit Energy Formula

An interesting result is obtained by expanding the inverse in Eq. (7) by the repeated use of the fundamental operator identity,

$$(\hat{A} - \hat{B})^{-1} = \hat{A}^{-1} + \hat{A}^{-1}\hat{B}(\hat{A} - \hat{B})^{-1} \quad (9)$$

which, with the choice $\hat{A} = E$ and $\hat{B} = \hat{P}\hat{H}$, leads to the following infinite series:

$$1 = \left\langle \Phi \left| \frac{\hat{H}}{E} + \frac{\hat{H}\hat{P}\hat{H}}{E^2} + \frac{\hat{H}\hat{P}\hat{H}\hat{P}\hat{H}}{E^3} + \dots \right| \Phi \right\rangle. \quad (10)$$

This expansion is challenging to discuss. We see, first, that if the reference function Φ happens to be an eigenvector of \hat{H} , then all terms but the first vanish at the right-hand side due to the orthogonality of the P and O spaces (i.e., for $\hat{P}\Phi$ being zero), and one is left with

$$1 = \left\langle \Phi \left| \frac{\hat{H}}{E} \right| \Phi \right\rangle \quad (11)$$

which is an immediate consequence of the Schrödinger equation. If, however, Φ is just a trial function, the terms in (10) containing projector \hat{P} survive; consequently Eq. (11) does not hold. Nevertheless, Eq. (10) may still be useful provided that the series is convergent. Assuming that sufficiently good approximation can be reached after m terms, one can rearrange Eq. (10) to have

$$E^m = \langle \Phi | \hat{H} | \Phi \rangle E^{m-1} + \langle \Phi | \hat{H}\hat{P}\hat{H} | \Phi \rangle E^{m-2} + \dots + \langle \Phi | (\hat{H}\hat{P})^{m-1} \hat{H} | \Phi \rangle \quad (12)$$

which is an algebraic equation of order m for the energy. In particular, for $m = 2$, one may write

$$E^2 = \langle \Phi | \hat{H}E + \hat{H}\hat{P}\hat{H} | \Phi \rangle, \quad (13)$$

having the solutions

$$E^{[2]} = \frac{\langle \Phi | \hat{H} | \Phi \rangle \pm \sqrt{\langle \Phi | \hat{H} | \Phi \rangle^2 + 4\langle \Phi | \hat{H}\hat{P}\hat{H} | \Phi \rangle}}{2} \quad (14)$$

where, for bound states, the negative sign corresponds to the ground state. Here the quantity $\langle \hat{H}\hat{P}\hat{H} \rangle$ (we dropped the reference function from this shorthand) can be transformed as

$$\langle \hat{H}\hat{P}\hat{H} \rangle = \langle \hat{H}(1 - \hat{O})\hat{H} \rangle = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 \quad (15)$$

which is the distribution of the Hamiltonian, also called the second connected moment [33]. Using the abbreviation

$$\langle \hat{H}^2 \rangle_c = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2,$$

Eq. (14) becomes

$$E^{[2]} = \frac{\langle \hat{H} \rangle}{2} \pm \sqrt{\frac{\langle \hat{H} \rangle^2}{4} + \langle \hat{H}^2 \rangle_c} \quad (16)$$

which, assuming $\langle \hat{H}^2 \rangle_c \ll \langle \hat{H} \rangle^2$, can be approximated by the Taylor expansion of the square root as

$$E^{[2]} = \langle \hat{H} \rangle + \frac{\langle \hat{H}^2 \rangle_c}{\langle \hat{H} \rangle} + \dots \quad (17)$$

which is a simple (nonperturbative) energy correction formula. Since it does not contain energy differences in denominators, it is free from the quasi-degeneracy problem of PT; thus it may be of potential use in some cases.

The applicability of the previous equations relies upon the fast convergence of the series expansion in (10). Unfortunately, this series is not at all convergent in general. The condition of its convergence is that the norm of operator $\hat{P}\hat{H}/E$ should be less than 1, but this condition is not satisfied in many cases. We have checked for example the hydrogen molecule using the Hartree–Fock (HF) wave function as the reference state and the exact (full-CI) value for E . In minimal basis set we have $\|\hat{P}\hat{H}/E\| = 0.4793$ which means that the series is nicely convergent, but in a DZ, TZ, and TZP bases we obtained for $\|\hat{P}\hat{H}/E\|$ the values 1.3784, 4.2943, and 4.3716, respectively. Similar results were found for the helium atom and the water molecule. Although one may apply Padé approximants or other techniques to sum up a divergent series, the low-order estimations like Eq. (17) remain useless. The second order truncation typically provides a negligible improvement if the norm is around 1, while it is unphysically large if $\|\hat{P}\hat{H}/E\| \gg 1$. To treat these cases one must search better approximations, e.g., in the field

of perturbation theory, where splitting the Hamiltonian for a “larger” and a “smaller” part one has a better hope that higher powers of the “smaller” one can be neglected.

Constant Denominator PT

It is well known [1] that PT can be derived from the partitioning technique, and in particular, the perturbative series of the energy can be derived from the implicit energy formula (7). Here we aim to extract the PT formulae in the so called Unsöld approximation that uses averaged energy denominators. To this end, we split the total Hamiltonian into a zero order part \hat{H}^0 and a perturbation \hat{V} , so that

$$\hat{H} = \hat{H}^0 + \hat{V}, \quad (18)$$

where

$$\hat{H}^0 = E^0 \hat{O} + \nu \hat{P}. \quad (19)$$

In this expression ν stands for an “averaged” value of excited energy levels; thus $\nu - E^0$ is an Unsöld type excitation energy.

To derive the second order energy correction formula, one substitutes the partition (18) and the special form of the zero order Hamiltonian (19) into the implicit energy formula (7),

$$1 = \frac{1}{E} \left\langle \Phi \left| \hat{H} \left(1 - \frac{\nu}{E} \hat{P} - \frac{\hat{P} \hat{V}}{E} \right)^{-1} \right| \Phi \right\rangle$$

where

$$\hat{H}^0 \hat{P} = \nu \hat{P}$$

is utilized, which is a simple consequence of (19) and (1). One now expands the inverse operator using the fundamental identity (9) with $\hat{A} = (1 - (\nu/E)\hat{P})$ and $\hat{B} = \hat{P}\hat{V}/E$ to get

$$1 = \langle \Phi | \hat{H} (E - \nu \hat{P})^{-1} | \Phi \rangle + \langle \Phi | \hat{H} (E - \nu \hat{P})^{-1} \times \hat{P} \hat{V} (E - \nu \hat{P})^{-1} | \Phi \rangle + \mathcal{O}(3).$$

This result is substantially simplified noting that

$$(E - \nu \hat{P})^{-1} | \Phi \rangle = \frac{1}{E} | \Phi \rangle,$$

by which, upon multiplying with E , one obtains the Brillouin–Wigner variant of Unsöld PT:

$$E = \langle \Phi | \hat{H} | \Phi \rangle + \langle \Phi | \hat{H} (E - \nu \hat{P})^{-1} \hat{P} \hat{V} | \Phi \rangle + \mathcal{O}(3). \quad (20)$$

The Rayleigh–Schrödinger–Unsöld formula emerges from this by expanding the energy E in the

inverse and recollecting the terms of various orders,

$$\begin{aligned} E &= \langle \Phi | \hat{H} | \Phi \rangle + \langle \Phi | \hat{H} (E^0 - \nu \hat{P})^{-1} \hat{P} \hat{V} | \Phi \rangle + \mathcal{O}(3) \\ &= \langle \Phi | \hat{H} | \Phi \rangle + \frac{\langle \Phi | \hat{V} \hat{P} \hat{V} | \Phi \rangle}{E^0 - \nu} + \mathcal{O}(3), \end{aligned} \quad (21)$$

where we used the identity

$$(E^0 - \nu \hat{P})^{-1} = \frac{\hat{O}}{E^0} + \frac{\hat{P}}{E^0 - \nu}$$

and the fact that

$$\langle \Phi | \hat{H}^0 \hat{P} = 0.$$

The energy expression Eq. (21) is a standard RS-PT expansion, apart from the restriction of using a unified excitation energy $\nu - E^0$. It can be obtained from the usual second order RS-PT formula by setting all energy levels equal and performing the sum-over-states in a trivial manner.

Optimized Denominators and the CMX Correction

Appearance of the averaged excited levels ν in the energy expression of the previous section, Eq. (21), gives rise to the problem of establishing this parameter. Among numerous possible ways to determine ν , here we choose the one that introduces the concept of *optimized partitioning* in PT [22, 23]. We may consider ν as a level shift parameter, as can be seen if regrouping the terms of the Hamiltonian as

$$\hat{H} = \hat{H}^0 + (\hat{H} - E^0 \hat{O} - \nu \hat{P})$$

where both the zero order operator, Eq. (19), and the perturbation (the three terms in parentheses) are ν -dependent. Changing the level shift parameter ν affects the partitioning of the Hamiltonian, which can now be optimized by finding a proper value for ν .

In the spirit of constant denominator theory, parameter ν is now state independent, which represents a substantial simplification to the general theory of optimized partitioning [23]. The optimization [22, 23] is based on the wavefunction correct up to first order in PT,

$$|\Psi^{(1)}\rangle = |\Phi\rangle + \frac{\hat{P} \hat{V}}{E^0 - \nu} |\Phi\rangle,$$

and requires that the Rayleigh quotient taken with $\Psi^{(1)}$ and written up to $\mathcal{O}(3)$ has an extremum at the desired ν :

$$\frac{\partial}{\partial \nu} \frac{\langle \Psi^{(1)} | H | \Psi^{(1)} \rangle}{\langle \Psi^{(1)} | \Psi^{(1)} \rangle} = 0. \quad (22)$$

Neglecting $\mathcal{O}(4)$ terms of the left-hand side and carrying out the derivation one arrives at

$$v = E^0 + \frac{\langle \hat{H}^3 \rangle_c}{\langle \hat{H}^2 \rangle_c} \quad (23)$$

where $\langle \hat{H}^3 \rangle_c$ is the third connected moment of the Hamiltonian [33].

This optimized averaged energy is now to be substituted into the PT correction formulae, which in the Unsöld approximation read as

$$\begin{aligned} E^{(2)} &= -\frac{\langle \hat{V}^2 \rangle_c}{\omega} = -\frac{\langle \hat{H}^2 \rangle_c}{\omega} \\ E^{(3)} &= \frac{\langle \hat{V}^3 \rangle_c}{\omega^2} = -\frac{\langle \hat{H}^2 \rangle_c}{\omega} + \frac{\langle \hat{H}^3 \rangle_c}{\omega^2} \end{aligned} \quad (24)$$

where $\omega = v - E^0$ is the averaged excitation energy. Substituting expression (23) for v we arrive at

$$E_{\text{opt}}^{(2)} = -\frac{\langle \hat{H}^2 \rangle_c^2}{\langle \hat{H}^3 \rangle_c} \quad (25)$$

$$E_{\text{opt}}^{(3)} = 0. \quad (26)$$

That is, the third order energy correction in the optimized partitioning is zero, in agreement with the general result [23].

Determination of parameter v in constant denominator PT by means of a variational optimization procedure with the first order Ansatz was suggested some time ago by Cullen and Zerner [30]. The difference between their results and those presented above is that they did not neglect $\mathcal{O}(4)$ terms in the Rayleigh quotient. This has the consequence that their second order result is not size extensive but gives an upper bound to the energy. Their third order formula is thus not zero but represents an approximate correction for extensivity in Davidson's philosophy.

The second and third order Unsöld formulae (25) and (26) have to be compared to those resulting from the CMX [27]. The CMX expansion is a nonperturbative, convergent technique to approach the exact energy, which can, e.g., be obtained by utilizing the properties of the Horn–Weinstein functional [33]. The lowest order corrections read [27]

$$\begin{aligned} E^{(\text{CMX1})} &= \langle \hat{H} \rangle \\ E^{(\text{CMX2})} &= -\frac{\langle \hat{H}^2 \rangle_c^2}{\langle \hat{H}^3 \rangle_c} \\ E^{(\text{CMX3})} &= -\frac{1}{\langle \hat{H}^3 \rangle_c} \frac{(\langle \hat{H}^4 \rangle_c \langle \hat{H}^2 \rangle_c - \langle \hat{H}^3 \rangle_c^2)^2}{\langle \hat{H}^5 \rangle_c \langle \hat{H}^3 \rangle_c - \langle \hat{H}^4 \rangle_c^2} \end{aligned} \quad (27)$$

where $\langle \hat{H}^n \rangle_c$'s are the higher connected moments of the Hamiltonian [33] defined recursively as

$$\langle \hat{H}^{n+1} \rangle_c = \langle \hat{H}^{n+1} \rangle - \sum_{p=0}^{n-1} \binom{n}{p} \langle \hat{H}^{p+1} \rangle_c \langle \hat{H}^{n-p} \rangle.$$

It is apparent that the second order optimized Unsöld approximation coincides with the CMX2 energy; the latter can therefore be considered as a constant denominator PT result with optimized partitioning. The third order CMX correction, however, is not zero, and we shall see that it often represents a considerable improvement.

Numerical Examples

As mentioned briefly in the Introduction, the simple denominator-free energy correction formula can only be useful if one uses a multiconfigurational reference state. In this case static correlation effects are already described by the reference function, and the role of the perturbative formulae is just to describe dynamical correlation effects. However, small energy denominators may still prevent one from applying standard PT formulae, and the constant denominator approximation can be useful in such a case.

In Figure 1 we have presented a situation like that: the potential curve of symmetrical stretching of water in a split valence basis set. The reference function we use is the energy-optimized antisymmetrized product of strongly orthogonal geminals (APSG) [34–36] with four spatial orbitals for each two-center bond and two for each lone pair. The 1s core is left uncorrelated. This is a highly correlated size-consistent reference function which qualitatively describes the dissociation, but, as inferred from Figure 1, it is still not sufficiently accurate. Inaccuracy of APSG is known to be a consequence of neglecting intergeminal correlation effects, which, being small, can be taken into account by means of perturbation theory. For the symmetrical stretching of two bonds, however, PT is not trivial to apply, since both dissociating bonds generate vanishing energy differences in PT denominators. Thus the standard formulae diverge.

The constant denominator (CMX) corrections do a good job in this case. Already CMX2 offers a significant improvement, and the CMX3 curve approaches quite well the full-CI line at around equilibrium geometry. The APSG energies are considerably improved also at large bond distances. The

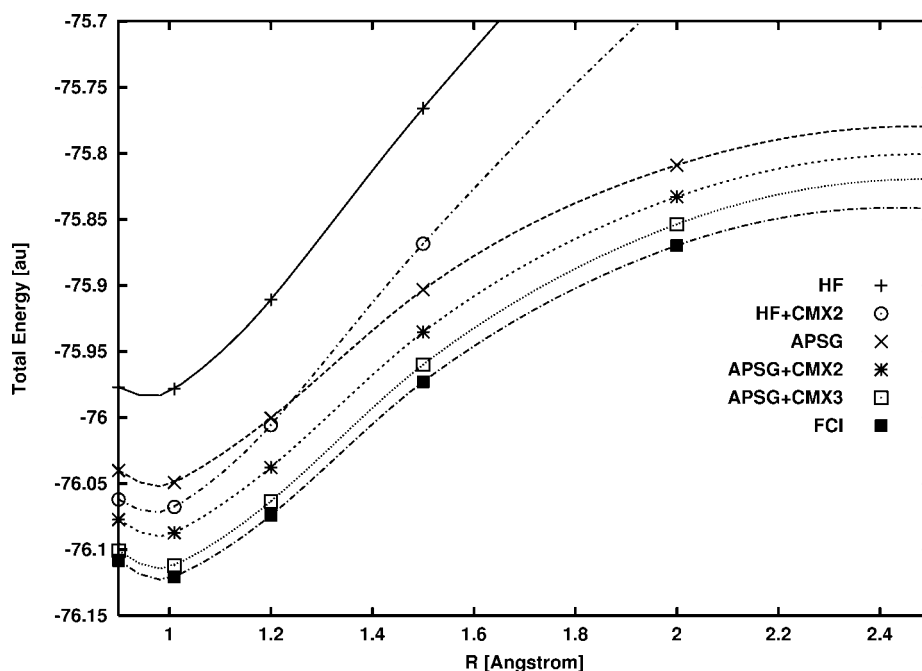


FIGURE 1. Potential curves of the symmetric dissociation of water in 6-31G basis set. The $\angle(\text{HOH})$ angle was kept at 104.0° . For notations, see text.

CMX2 correction can also be performed with the HF reference function, but, despite eliminating divergent denominators, the HF-CMX2 curve remains quite pathological, reflecting the improper features of the HF wave function.

TABLE I
Perturbative corrections [a.u.] to the energy of the Be atom in two different basis sets, the zero order approximations being Hartree-Fock or antisymmetrized products of strongly orthogonal geminals (APSG). Acronym MP2 stands for the Møller-Plesset second order correction; CMX2 and CMX3 label the connected moment expansion second and third order, respectively. Full configuration interaction (FCI) energies are given for comparison.

	3-21G	6-311G**
HF	-14.48682	-14.57187
MP2	-14.51026	-14.59847
HF + CMX2	-14.49996	-14.58179
HF + CMX3	-14.51520	-14.58789
APSG	-14.53083	-14.61734
APSG + CMX2	-14.53136	-14.63210
APSG + CMX3	-14.53144	-14.63323
FCI	-14.53144	-14.63338

To inspect some numbers, too, we present Tables I and II reporting data for the Be atom and the water molecule. For beryllium, the APSG wave function is very accurate; actually it is equivalent to a frozen-core full CI. Accordingly, the APSG-CMX2 energy is already very accurate, and the APSG-CMX3 result coincides with full CI to four to six digits depending on the basis set. The results for water also

TABLE II
Total energies [a.u.] for the H₂O molecule in 3-21G basis, with the geometry $d_{\text{OH}} = 1.01 \text{ \AA}$ and $\alpha(\text{HOH}) = 104.0^\circ$. To both zero order approximations HF and APSG, the connected moment expansion (CMX) is given up to third order; Møller-Plesset (MP) PT corrections are also indicated for the HF reference state. The FCI energy is shown for comparison.

Order and type of PT	Reference state	
	HF	APSG
0	-83.679551	-83.726373
MP2	-83.719698	
MP3	-83.730842	
CMX2	-83.718400	-83.730758
CMX3	-83.731190	-83.734895
FCI	-83.73624257	

exhibit significant improvements upon performing the CMX corrections.

The few numerical results presented above are clearly insufficient to draw final conclusions about applicability of constant-denominator PT corrections to multireference states. More experience is needed for many molecules and especially in larger basis sets; work in this line is in progress.

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