Optimized partitioning in perturbation theory: Comparison to related approaches

Cite as: J. Chem. Phys. **112**, 4438 (2000); https://doi.org/10.1063/1.481006
Submitted: 04 October 1999 . Accepted: 15 December 1999 . Published Online: 28 February 2000

P. R. Surján, and Á. Szabados

Optimized partitioning in perturbation theory: Comparison to related approaches

P. R. Surján[a] and Á. Szabados
Eötvös University, Department of Theoretical Chemistry, H-1518 Budapest 112, POB 32, Hungary

(Received 4 October 1999; accepted 15 December 1999)

A generalized Epstein–Nesbet type perturbation theory is introduced by a unique, ''optimal'' determination of level shift parameters. As a result, a new *partitioning* emerges in which third order energies are identically zero, most fifth order terms also vanish, and low (2nd, 4th) order corrections are quite accurate. Moreover, the results are invariant to unitary transformations within the zero order excited states. Applying the new partitioning to many-body perturbation theory, the perturbed energies exhibit appealing features: (i) they become orbital invariant if all level shifts are optimized in an excitation subspace; and (ii) meet the size-consistency requirement if no artificial truncations in the excitation space is used. As to the numerical results, low order corrections do better than those of Møller–Plesset partitioning. At the second order, if the single determinantal Hartree–Fock reference state is used, the CEPA-0 (=LCCD) energies are recovered. Higher order corrections provide a systematic way of improving this scheme, numerical studies showing favorable convergence properties. The theory is tested on the anharmonic linear oscillator and on the electron correlation energies of some selected small molecules. © *2000 American Institute of Physics.* [S0021-9606(00)31210-7]

I. INTRODUCTION

Perturbation theory (PT) offers an efficient tool for estimating energetics of weak interactions, and is widely used in various areas of physics and chemistry. It is based on separating a zero order part of the Hamiltonian from a residual interaction operator, the perturbation. This separation specifies the *partitioning* in PT.

In a recent Letter,[1] we proposed a repartitioning of the Hamiltonian which emerged by ''optimizing'' the energy denominators in PT, i.e., by introducing appropriate level shifts for which a linear algebraic equation has been derived. Our aim in this paper is to present a more elaborate theory, to put the method into the context of other approaches, and to apply it to a wider range of examples. We shall show, for instance, that, as applied to the correlation problem in a many-electron system with the Hartree–Fock reference state, the *second* order correction in the new partitioning is the same as that one would obtain with the LCCD method (linearized coupled cluster with doubles).[2] (This particular method has already been introduced to quantum chemistry under various names: linearized CPMET,[3,4] CEPA-0,[5] and D-MBPT(∞).[6–8]) Higher order results will also be resulted demonstrating substantial improvements in the convergence properties at the first 10–20 orders of the PT series, even though at the very high orders, features of asymptotic convergence were noticed in some cases.

The paper is organized as follows. The exposition of the theory is presented in Sec. II., while numerical results are discussed in Sec. III. The theoretical section is though preceded by an introduction collecting our notations and discussing some previous results in this field.

[a]Electronic mail: surjan@para.chem.elte.hu

A. Perturbation theory

On solving the Schrödinger equation, $H\Psi=E\Psi$, by PT, we split the Hamiltonian H into a zero order part H^0 and a perturbation W:

$$H=H^0+W, \tag{1}$$

and suppose that the problem of H^0 has been fully solved:

$$H^0|k\rangle=E_k^0|k\rangle, \quad k=0,1,2,\ldots \ . \tag{2}$$

Then, the exact wavefunction Ψ and the energy E, assuming convergence, can be developed in terms of the zero order quantities as[2,7,9]

$$|\Psi\rangle=|0\rangle+\sum_{n=1}^{\infty}[R(W-\Delta E)]^n|0\rangle, \tag{3}$$

$$E=E_0^0+\sum_{n=0}^{\infty}\langle 0|W[R(W-\Delta E)]^n|0\rangle, \tag{4}$$

where the intermediate normalization $\langle\Psi^0|\Psi\rangle=1$ is used, the reduced resolvent of H^0 is specified in spectral resolution as

$$R=-\sum_{k\neq 0}\frac{|k\rangle\langle k|}{E_k^0-E_0^0}, \tag{5}$$

and the energy correction is $\Delta E=E-E_0^0$. The orders of PT are defined by the powers of W. At a given order, using merely the estimation from the previous orders for ΔE in Eq. (4), one arrives at the Rayleigh–Schrödinger perturbation theory (RSPT).

B. Level shifts

To achieve a satisfactory convergence of PT, a proper choice of H^0 is crucial. For any choice of H^0, one can freely modify the partitioning — without affecting the zero order states — by adding/subtracting weighted projectors as

$$H=\left(H^0+\sum_{k\neq 0}\lambda_k|k\rangle\langle k|\right)+\left(W-\sum_{k\neq 0}\lambda_k|k\rangle\langle k|\right)$$
$$=H^{0\prime}+W', \tag{6}$$

where the weighting factors λ_k are called *level shifts*, since they affect the zero order excited energy levels. Several authors have discussed and used such shifts in PT for accelerating or ensuring convergence of the series, which is especially important in quasi-degenerate situations.[10–14] Complex shift parameters were also investigated in some cases.[15–17]

Level shift operators as introduced in Eq. (6) provide examples to general operators A that are nilpotent when acting on the zero order ground state: $A|0\rangle=0$. Such operators, which clearly do not affect the zero order ground state energy, but modify the excited levels, were considered a long time ago.[18–20] Kutzelnigg[21] presented a many-body representation of operators like this, and assigned the name *''generalized Epstein–Nesbet perturbation theory''* to such a repartitioning. This name is justified because by a special choice of the level shift parameters λ_i one may arrive at the Epstein–Nesbet partitioning[22,23] where all diagonal matrix elements of the perturbation operator W' are zero.

C. Perturbation theory by projectors

A unifying formalism for many perturbational treatments is offered by Löwdin's partitioning technique.[9,24] In this approach, two Hermitian and orthogonal projectors, O and P, are introduced so that

$$O+P=1.$$

The full Schrödinger equation is partitioned as

$$(OHO+OHP)\Psi=EO\Psi, \tag{7}$$

for the O-block, and

$$(PHO+PHP)\Psi=EP\Psi \tag{8}$$

for the P-block. Specifically, if one chooses

$$O=|0\rangle\langle 0|,$$

with $|0\rangle$ being the zero order ground state, and splits the Hamiltonian according to Eq. (1), one gets for the energy

$$E=\langle 0|H|0\rangle+\langle 0|W|P\Psi\rangle, \tag{9}$$

and for the P-component of the wave function,

$$PW|0\rangle+PH^0|P\Psi\rangle+PW|P\Psi\rangle=E_0^0|P\Psi\rangle+\Delta E|P\Psi\rangle,$$

where $\Delta E=E-E_0^0$. This latter equation can be rearranged as

$$|P\Psi\rangle=RW|0\rangle+RW|P\Psi\rangle-\Delta ER|P\Psi\rangle, \tag{10}$$

where, the inverse being taken in the P-space,

$$R=(E_0^0-PH^0)^{-1}P$$

is the same reduced resolvent as introduced in Eq. (5). An iterative solution of Eqs. (9) and (10) yields the exact result, while various approximations and strategies cover different PT schemes. (Note that a variety of notations has been introduced for the quantities O, P and R in literature. Here we adopt those introduced by Löwdin.[9])

II. THEORY

In this section we determine a set of level shift parameters by imposing an approximate variational condition[1] which results in a system of linear algebraic equations. The solution of these will be shown to be equivalent to eliminating any third-order type terms in the new partitioning defined by the level-shifted zero order Hamiltonian, $H^{0\prime}$. Then we show how the second order energy in the new partitioning can be obtained as a partial resummation of the initial series. The resummation results in a compact formula, which can easily be obtained by the projector operator technique. This formula, within the framework of many-electron theory as applied to the correlation problem, is equivalent to the energy expression in the CEPA-0 or LCCD[2,5] method. Going to higher orders in the new partitioning appears to be natural way for a systematic improvement of this latter scheme.

A. Optimal level shifts

To begin with, let us start from a perturbative splitting of the Hamiltonian and simultaneously redefine the zero order and the perturbation operator, as indicated in Eq. (6). Level shift parameters, λ_i, introduced like this, do affect individual terms of the perturbation series, but not the converged sum. This can be expressed by the variational like condition,

$$\frac{\partial}{\partial\lambda_k}\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}=0, \quad k=1,2,\ldots \tag{11}$$

In this spirit, one may regard level shifts as variational parameters and set stationary the Rayleigh quotient taken with a trial wavefunction. For example, with the aim of optimizing low order results, one may write

$$\frac{\partial}{\partial\lambda_k}\frac{\langle\Psi^{[1]}|H|\Psi^{[1]}\rangle}{\langle\Psi^{[1]}|\Psi^{[1]}\rangle}=0, \quad k=1,2,\ldots, \tag{12}$$

where $\Psi^{[1]}$ is the first order Ansatz for the wavefunction having the expansion

$$|\Psi^{[1]}\rangle=|0\rangle-\sum_{k\neq 0}\frac{W_{k0}}{E_k^0-E_0^0+\lambda_k}|k\rangle. \tag{13}$$

Since the total number of level shift parameters can be as large as the free parameters in $\Psi^{[1]}$, the solution of Eq. (12) may, in some cases, yield even the exact result. [In reality, however, the situation is a bit more complicated since from Eq. (12) one can only determine those λ_k values for which $W_{0k}\neq 0$. In electron correlation theory, for example, the solution of Eq. (12) gives CID.] As we do not seek exact results, rather a meaningful approximation to the level shift parameters to be used in PT, we rewrite the Rayleigh-quotient as

$$\frac{\langle\Psi^{[1]}|H|\Psi^{[1]}\rangle}{\langle\Psi^{[1]}|\Psi^{[1]}\rangle}=E^{0'}+E^{1'}+E^{2'}+E^{3'}+\mathcal{O}(4). \tag{14}$$

Here and further on, primes refer to the new partitioning. Neglecting $\mathcal{O}(4)$ terms, the variational requirement takes the form

$$\frac{\partial}{\partial\lambda_k}(E^{2'}+E^{3'})=0, \quad k=1,2,\ldots \ . \tag{15}$$

Here the zero and first order terms are left out since $E^{0'}+E^{1'}=\langle 0|H|0\rangle$ is independent of level shifts. Substituting the expressions of $E^{2'}$ and $E^{3'}$ into Eq. (15), and carrying out the variation, one finds

$$\langle 0|WR'|k\rangle\langle k|W'R'W|0\rangle-W_{00}\langle 0|WR'|k\rangle\langle k|R'W|0\rangle =0, \quad k=1,2,\ldots, \tag{16}$$

where the resolvent of the shifted zeroth order is

$$R'=-\sum_{i\neq 0}\frac{|i\rangle\langle i|}{\Delta_i}, \tag{17}$$

with the shifted denominators $\Delta_i=E_i^0-E_0^0+\lambda_i$. Equation (16) defines the level shifts in the new partitioning.

An interesting feature of this partitioning is that the third order energy is explicitly zero. This fact can be understood by putting down the third order RSPT formula,

$$E^{3'}=\langle 0|WR'W'R'W|0\rangle-W_{00}\langle 0|WR'^2W|0\rangle =\sum_{k\neq 0}E_k^{3'}, \tag{18}$$

where, writing out the resolvents explicitly,

$$E_k^{3'}=\frac{W_{0k}}{\Delta_k}\left(\sum_{i\neq 0}\frac{W_{ki}W_{i0}}{\Delta_i}-(W_{00}+\lambda_k)\frac{W_{k0}}{\Delta_k}\right). \tag{19}$$

Substituting formulas for the resolvent R' and the shifted perturbation operator W' into Eq. (16), its left hand side turns out to be equal $E_k^{3'}$. That is, Eq. (16) is equivalent to the requirement

$$E_k^{3'}=0, \quad k=1,2,\ldots \ .$$

The above condition implies that, in Eq. (19) the expression in curly brackets should be zero:

$$\sum_{i\neq 0}\frac{W_{ki}W_{i0}}{\Delta_i}-(W_{00}+\lambda_k)\frac{W_{k0}}{\Delta_k}=0, \quad k=1,2,\ldots, \tag{20}$$

which is quite useful for the practical determination of λ_k's. This system of equations can be brought to the form[1]

$$\sum_{j\neq 0}A_{kj}\frac{1}{\Delta_j}=1, \quad k=1,2,\ldots, \tag{21}$$

where

$$A_{kj}=\delta_{kj}(E_j^0-E_0^0-W_{00})+\frac{W_{kj}W_{j0}}{W_{0k}}. \tag{22}$$

This shows that, if matrix **A** is nonsingular, nonzero energy denominators Δ_k are uniquely determined as the solution of an inhomogeneous linear system of equations. Those shifts, which do not emerge in the expansion of the first order wavefunction are certainly not defined by Eq. (21). The simplest choice is to set these parameters to zero.

Vanishing of all $E_k^{3'}$'s has important consequences for higher orders, too. Explicitly, all terms containing the expression

$$\langle k|(W'-W_{00})R'W|0\rangle \tag{23}$$

will be zero for all states k which contribute to $E^{3'}$, i.e., which directly interact with the ground state. In particular, of the fifth order formula,

$$\begin{aligned}E^{5'}=&\langle 0|WR'(W'-W_{00})R'(W'-W_{00})R'\\&\times(W'-W_{00})R'W|0\rangle\\&-2E^{2'}\langle 0|WR'^2(W'-W_{00})R'W|0\rangle\\&-E^{3'}\langle 0|WR'^2W|0\rangle,\end{aligned} \tag{24}$$

the last term is zero due to the vanishing of $E^{3'}$, while the second term is zero due to Eq. (23). Consequently, merely the first term may contribute if there are excitations in the two middle resolvents, which do appear here, but are absent in $E^{3'}$. The fifth order contribution is therefore expected to be very small. It may even be zero in a model where neither of the W_{0k} matrix elements vanish. Similar considerations apply for higher orders, too.

The fact that there is no third order correction in the new partitioning remounts to earlier works by Feenberg, Goldhammer and Amos.[25–27] In these studies possibilities for choosing one single repartitioning parameter were investigated, the redefined splitting written as

$$H^{0'}=\mu^{-1}H^0, \quad W'=W+\frac{\mu-1}{\mu}H^0.$$

Requiring that third order energy term in this new partitioning vanishes proved to be considerably successful.[25,26] However, it may be easily shown that a perturbation series emerging like this does not provide size consistent correction at finite orders.

Another way of optimizing zero order energies was followed by Finley *et al.*[28] Their strategy is to select a relatively small subspace of the most important zero order eigenfunctions and, within this space, minimize the functional

$$|E_{\mathrm{gs}}-E_3|+|E_{\mathrm{gs}}-E_4|, \tag{25}$$

with respect to the zero order excited eigenvalues. In this functional, E_{gs} is full CI ground state energy, E_3 and E_4 are the 3rd and 4th order PT energies, and all the three quantities are computed within the subspace chosen. Inclusion of the fourth order term in (25) assures unique determination of the selected zero order energies. Test calculations result improved low order estimations and show convergent series when ordinary partitionings (MP, EN) diverge.[29,30] Clearly, the choice for the subspace for optimization is a crucial point, and should be reconsidered for each system, and each basis set.

B. Resummation of RS-PT series

A useful transformation of formula (20), suitable for an iterative treatment, is given by[1]

$$\Delta_i = \Delta_i^0 \frac{W_{0i}}{W_{0i} - \Sigma_{j\neq 0}(W_{ij}W_{j0}/\Delta_j)} \quad (i\neq 0), \tag{26}$$

where $\Delta_i^0 = E_i^0 - E_0^0$ is the unshifted denominator. Equation (26) is fully equivalent to Eq. (20) if W_{00} is zero, which can be set in the initial partitioning without loss of generality. It is not difficult to see that the second order guess to the energy,

$$E^{2'} = -\sum_{i\neq 0} \frac{|W_{0i}|^2}{\Delta_i}, \tag{27}$$

is equivalent to an infinite order partial resummation of the original partitioning. Substituting Eq. (26) into (27) we get

$$\begin{aligned} E^{2'} &= -\sum_{i\neq 0} \frac{|W_{0i}|^2}{\Delta_i^0} + \sum_{i,k\neq 0} \frac{W_{0i}W_{ik}W_{k0}}{\Delta_i^0 \Delta_k} \\ &= \langle 0|WRW|0\rangle + \langle 0|WRWR'W|0\rangle. \end{aligned} \tag{28}$$

Here the first term is the original second order energy. The second term is of order 3, and it can be further expanded by substituting Eq. (26) repeatedly to yield

$$\begin{aligned} E^{2'} &= \langle 0|WRW|0\rangle + \langle 0|WRWRW|0\rangle \\ &\quad + \langle 0|WRWRWRW|0\rangle + \ldots \\ &= \sum_{n=1}^{\infty} \langle 0|W(RW)^n|0\rangle, \end{aligned} \tag{29}$$

which is clearly a part of the infinite order (exact) PT energy; cf. Eq. (4). More precisely, we see that all type of terms of the PT series have been summed up which would emerge also in Brillouin–Wigner (BW) theory.[31,32] We may call these contributions BW type terms, which differ only from true BW results in that the resolvent R is constructed from zeroth order excitation energies $(E_k^0 - E_0^0)$, and not from BW denominators $(E_k^0 - E_0)$ containing the exact energy E_0.

Writing this result more compactly becomes possible by introducing the reaction operator T:

$$\langle 0|T|0\rangle = W_{00} + E^{2'}, \tag{30}$$

where, from (29),

$$T = W + WRW + WRWRW \ldots \tag{31}$$

that satisfies an equation of the Lippman-Schwinger type,

$$T = W + WRT, \tag{32}$$

since the iteration of (32) with $T^{(0)} = 0$ leads immediately to (31). The formal solution of (32) is

$$T = (1 - WR)^{-1}W, \tag{33}$$

indicating that the second order energy in the optimized partitioning can be compactly expressed as

$$\begin{aligned} E^{2'} &= \langle 0|(1 - WR)^{-1}W|0\rangle - W_{00} \\ &= \langle 0|W(1 - RW)^{-1}RW|0\rangle. \end{aligned} \tag{34}$$

The last equality can be seen by subtracting and adding the term $\langle 0|W(1-RW)^{-1}|0\rangle$. It is of course also possible to express the resolvent R' of the shifted zero order in terms of the initial resolvent R. Comparing Eq. (34) to Eq. (27), since the latter can be rewritten with the shifted resolvent R' as $E^{2'} = \langle 0|WR'W|0\rangle$

$$R' = (1 - RW)^{-1}R. \tag{35}$$

To accelerate convergence of the PT series, Dietz *et al.*[33,34] have proposed introducing a damping operator Λ when solving Eq. (31) iteratively. Besides a simple diagonal approximation to Λ, they applied the formula

$$\Lambda = \frac{RW}{RW - 1}$$

as well. Comparing Eq. (35) with this expression, the relation between their damping operator and our shifted resolvent is found to be

$$\Lambda = -R'W.$$

Besides the apparent similarity of the formulation of the theory, the procedure followed by Dietz et al. and the present level shift technique differ in two major features. One concerns the subspace, in which the matrix R' or Λ is essentially constructed. The above authors study several different ways of choosing a model space, while in our case only those levels contribute to R', which directly interact with the ground state. The other important point is that, in the case of an RS expansion, we completely neglect terms originating from the second term of Eq. (10), as shown in the next section. Though these terms are kept in Refs. 33,34, without eliminating them in our case, size consistency of the RS scheme would be broken.

C. Derivation by projection operator technique

In the spirit of the partitioning technique, the P-component of the wavefunction is defined by Eq. (10). If we neglect the last term in this equation (which can be numerically justified only if the energy correction is a second order quantity), we have

$$|P\Psi\rangle = RW|0\rangle + RW|P\Psi\rangle, \tag{36}$$

having the formal solution

$$|P\Psi\rangle = (1 - RW)^{-1}RW|0\rangle. \tag{37}$$

Iteration of Eq. (36), or the expansion of the inverse in (37), yields

$$|P\Psi\rangle = RW|0\rangle + RWRW|0\rangle + \cdots = RT|0\rangle. \tag{38}$$

On substituting this result into the energy formula (9) we find

$$\begin{aligned} E &= \langle 0|H|0\rangle + \langle 0|WRT|0\rangle = \langle 0|H|0\rangle + \langle 0|WRW|0\rangle \\ &\quad + \langle 0|WRWRW|0\rangle \cdots, \end{aligned} \tag{39}$$

in perfect agreement with (29).

The equivalence of these results can also be seen on the compact formulas. Inserting (37) into Eq. (9),

$$E=\langle 0|H|0\rangle+\langle 0|W(1-RW)^{-1}RW|0\rangle$$
$$=E_0^0+\langle 0|W+W(1-RW)^{-1}RW|0\rangle, \quad (40)$$

which agrees with (34). This derivation, of course, does not contribute to any new result as compared to the formulas of the previous section, but it makes transparent how the BW-type terms, accounted for by $E^{2'}$, emerge by neglecting ΔE in Eq. (10).

D. Connection to CEPA-0

An interesting feature of the optimized partitioning is that, as applied to the correlation problem in many-electron theory, the well known CEPA-0 energy formula is recovered at the second order. This can be demonstrated in several ways, since the very same method has been described in the literature in different manners. The CEPA-0 equations,[5]

$$\langle \phi_{ij}^{ab}|H-\langle 0|H|0\rangle|\Psi^{[1]}\rangle=0 \quad (41)$$

(ϕ_{ij}^{ab} denoting doubly excited configurations) originate from the variational problem of the functional,

$$F=\langle \Psi^{[1]}|H-\langle 0|H|0\rangle|\Psi^{[1]}\rangle, \quad (42)$$

which upon substituting the first order Ansatz with shifted denominators, can be expanded as

$$F=\langle 0|(1+WR')(H-\langle 0|H|0\rangle)(R'W+1)|0\rangle$$
$$=\langle 0|WR'W|0\rangle+\langle 0|WR'W'R'W|0\rangle$$
$$-W_{00}\langle 0|WR'^2W|0\rangle=E^{2\prime}+E^{3\prime}. \quad (43)$$

This was just the functional we used in Eq. (15) to get the level shifts, which, if only doubles are taken into account, are just the free parameters in $\Psi^{[1]}$.

Equivalence of $E^{2'}$ and the CEPA-0 correlation energy can also be inferred from the energy formula (34), which is clearly the same as the energy formula in the LCCD method,[2,35] the latter being known to be equivalent to CEPA-0. The analogy between the resummation discussed in Sec. II B and the D-MBPT(∞) method (another variant of deriving the same energy[6–8]) is also obvious.

E. Properties of the optimized partitioning

Based on the derivation by projector operator technique and as suggested by the equivalence of the second order result and LCCD, a few properties of $E^{2'}$ are immediately evident. Namely, we get an energy which is, though not variational, size extensive, and invariant to unitary transformations among zeroth order excited states. In particular, $E^{2'}$ (more generally, $E^{n'}$ if computed in the subspace present in $\Psi^{[1]}$) is invariant to orbital rotations within the occupied MOs (and also to those within virtuals). This is an especially appealing feature as this makes it possible to perform the calculations, e.g., in terms of localized orbitals without affecting the PT formulas. This property markedly distincts the optimized partitioning from that of Epstein[22] and Nesbet,[23] as well as from that of Møller and Plessett,[36] since the former is not orbital invariant at all, while the orbital invariant formulation of the latter[37,38] requires the use of nondiagonal resolvents. In the optimized partitioning the same second order formula (27) gives the same result whatever orbitals (canonical or localized) are used.

We note that the equivalence between $E^{2'}$ and the CEPA-0 (or LCCD) energy holds only if one uses the Hartree–Fock wavefunction as the reference state $|0\rangle$. The optimization of the partitioning by level shifts is, therefore, a more general procedure, with a possibility of a wider range of applications. These may include truly one-electron problems (an example for this will be shown in Sec. III A), or multi-configurational reference states in the many-body problem.

To investigate size extensivity of finite order contributions in the optimized partitioning in general, let us consider two noninteracting subsystems A and B, characterized by the equations $H^0=H_A^0+H_B^0$, $W=W_A+W_B$, $|0\rangle=|0_A0_B\rangle$. Assuming that eigenvectors of H_A^0 are not mixed with those of system B if they belong to a degenerate subspace, it is enough to show that in the noninteracting situation level shifts can be assigned to subsystem A or B. Regarding the structure of matrix $\mathbf{A}$ in Eq. (22), it is apparent that a nonzero intersystem element may only emerge in the case where $\langle k|=\langle k_A0_B|$ and $|i\rangle=|i_B0_A\rangle$. (This is because matrix elements of type $\langle k_Ai_B|W|0_B0_A\rangle$ are all zero.) In the former special case, since

$$W_{ki}=\langle k_A|W_A|0_A\rangle\langle 0_A|i_B\rangle+\langle 0_B|W_B|i_B\rangle\langle k_A|0_A\rangle=0, \quad (44)$$

A_{kl} again proves to be zero. This means that matrix $\mathbf{A}$ is blockdiagonal if subsystems A and B are infinitely apart, consequently level shifts are determined solely by expressions of one subsystem or another. If, however, mixing between degenerate eigenvectors of system A and B may occur, size consistency of finite order corrections is violated only if PT expressions are not invariant to unitary transformations within a degenerate subspace. The Epstein–Nesbet partitioning represents such an example. In our case, however, owing to the invariance of the optimized partitioning to unitary transformation of zeroth order excited states, the size consistency requirement is fulfilled at second order, even if degenerate eigenvectors belonging to different subsystems are mixed. As to fourth and higher orders, size consistency is recovered only if terms including unaffected levels are also invariant to unitary transformation of degenerate eigenvectors. Therefore, MP partitioning is preferred to EN, for these levels.

An important advantage of this reformulation is that, once the new partitioning is defined, one may go beyond the second order in a straightforward manner. A few preliminary higher order results in the new partitioning will be presented in the following section. The convergence properties of PT in the new partitioning will also be studied.

Since, as the linear nature of Eq. (21), or the equivalence with LCCD shows, the optimized partitioning is unique, it can be found by starting from any initial partitioning. One has to recall, however, that only levels of those states will be determined which directly interact with the reference state. Accordingly, when 4th and higher order results for the correlation energy are computed, the singles, triples, and qua-

druples are treated in the original partitioning. This problem could be, in principle, circumvented by using a more accurate Ansatz instead of $\Psi^{[1]}$, but this method does not seem to yield equations that are easily tractable.

III. EXAMPLES

A. Anharmonic oscillator

The eigenvalue problem of a perturbed one dimensional harmonic oscillator is one of the most simple study cases. Considering a perturbation proportional to the fourth power of the coordinate q, the Hamiltonian can be written in arbitrary units as

$$H=\tfrac{1}{2}(p^2+q^2)+\gamma q^4=H^0+W, \tag{45}$$

with p being the operator of momentum and the scalar γ measuring the strength of the perturbation. Most easily one may start off with the partitioning suggested by the physics of the problem, as indicated in Eq. (45), considering γq^4 as the perturbation, with the solution of the zeroth order of the well known form

$$H^0|n\rangle=\left(n+\tfrac{1}{2}\right)|n\rangle. \tag{46}$$

In this case there are only two levels that interact with the ground state, for the corresponding matrix element of W is

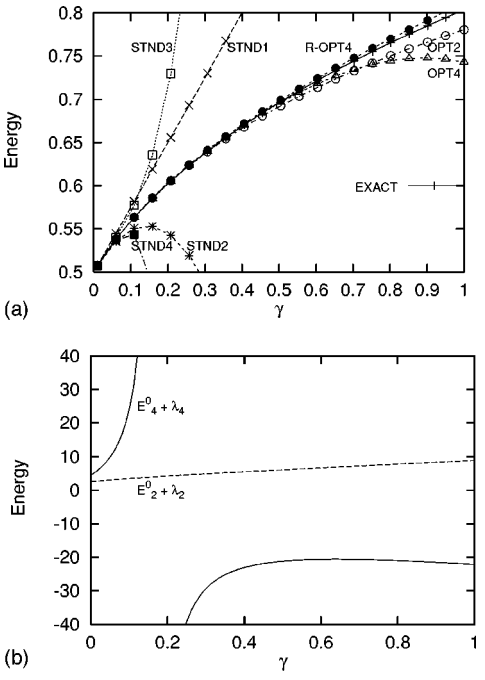

FIG. 1. Ground state energy of the anharmonic oscillator (a), and shifted zeroth order energies (b) as a function of the coupling strength γ in arbitrary units. Results of the standard partitioning, i.e., considering the anharmonic term as a perturbation, are identified by STNDn. Optimized partitioning is referred to as OPT; for details see the text. An exact result (solid line) was obtained by solving the Schrödinger equation numerically. Labels of (b) are those used in text.

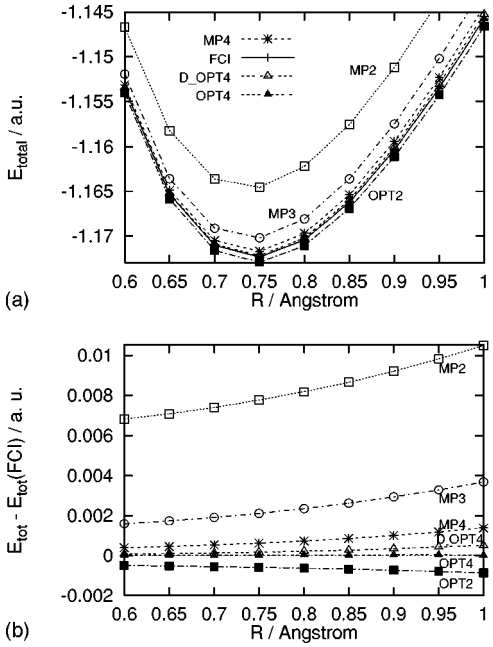

FIG. 2. Absolute energy (a) and deviation from full CI (b) at around the equilibrium on the potential curve of the H_2 molecule in the $[3s2p1d]$ basis set (Ref. 42), in MP and optimized partitioning.

$$W_{0k}=\frac{\gamma}{4}(2+5k+4k^2+(k+1)^2)\,\delta_{0k}+\frac{\gamma}{2}\sqrt{k(k-1)(k+1)^2}\,\delta_{2k}+\frac{\gamma}{4}\sqrt{k(k-1)(k-2)(k-3)}\,\delta_{4k}. \tag{47}$$

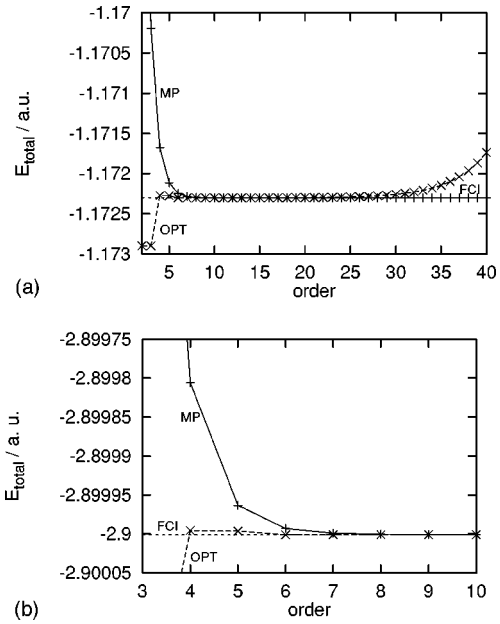

FIG. 3. Illustration of the convergence of perturbation series estimating the total energy of the H_2 molecule in the $[3s2p1d]$ basis set (Ref. 42) (a) and the He atom in the $10s2p1d$ basis set (Ref. 49) (b).

TABLE I. Errors of PT estimates for the total energy of the H_2 molecule ($R=0.75$ Å), as compared to the limit of the series, FCI or CI with doubles (CID). Prefix D refers to the inclusion of doubles only. Atomic energy units are used.

Order	MP−FCI	OPT−FCI	D_MP−CID	D_OPT−CID
2	7.7659×10^{-3}	-5.953×10^{-4}	7.6229×10^{-3}	-7.383×10^{-4}
3	2.1111×10^{-3}	-5.953×10^{-4}	1.9682×10^{-3}	-7.383×10^{-4}
4	6.220×10^{-4}	2.89×10^{-5}	5.564×10^{-4}	3.25×10^{-5}
5	1.873×10^{-4}	2.62×10^{-5}	1.587×10^{-4}	3.25×10^{-5}
6	5.73×10^{-5}	-6×10^{-7}	4.45×10^{-5}	-1.2×10^{-6}
7	1.77×10^{-5}	-8×10^{-7}	1.21×10^{-5}	-1.6×10^{-6}
8	5.5×10^{-6}	3×10^{-7}	3.1×10^{-6}	0
9	1.7×10^{-6}	4×10^{-7}	7×10^{-7}	1×10^{-7}
10	5×10^{-7}	4×10^{-7}	1×10^{-7}	0
11	1×10^{-7}	5×10^{-7}	0	0
12	0	6×10^{-7}	0	0

This leads to the expansion of the first order wavefunction, Eq. (13), to become

$$|\Psi^{[1]}\rangle=|0\rangle-\frac{(\frac{\gamma}{2})\sqrt{18}}{2+\lambda_2}|2\rangle-\frac{(\frac{\gamma}{4})\sqrt{24}}{4+\lambda_4}|4\rangle. \tag{48}$$

Level shifts λ_2 and λ_4 can be determined using Eq. (20) in a straightforward way. Sums appearing in these equations extend only for a few terms, because the matrix of W is sparse on the basis of the zeroth order eigenvectors.

Perturbative results up to fourth order, calculated in the partitioning of Eq. (45) and in the optimized splitting are plotted in Fig. 1(a) as a function of the strength of the perturbation. Standard partitioning of Eq. (45) is labeled by STND; OPT refers to the optimal repartitioning. A third order correction of the optimal partitioning is not shown, for there is no third order contribution in this series. Figure 1(a) shows, that as compared to the optimal partitioning, standard splitting gives meaningful results only in the range of a weak perturbation. Repartitioning by optimal level shifts drastically improves the results even at a relatively large perturbation.

It might be interesting to see, how shifted zeroth order eigenvalues vary with the strength of perturbation. These curves are plotted in Fig. 1(b). It is apparent that the shifted zeroth order energy of the second level is a slowly varying function of γ, while level 4 runs across a singularity at $\gamma=1/6$, eliminating the corresponding term in the perturbation expansion at that point. After the pole the shifted denominator even becomes negative. However, one would beware of assigning any physical interpretation to these values, as they are results of a purely mathematical consideration.

Computing higher than third order of PT, one faces the question of determining shifts, that are not set by optimization, but appear due to the interaction with an excited zeroth order state. These are λ_6 and λ_8, in this special case, at fourth order. One choice is to set these shifts zero; this corresponds to keeping the original partitioning for these diagonal matrix elements. Another possibility is to perform PT in the subspace determined by the levels appearing in the optimization, that is, to neglect at every order terms including levels for which $W_{0i}=0$. The curve labeled OPT4 in Fig. 1(a) is calculated using the former choice, R-OPT4 is obtained by the latter one, ''R'' indicating ''restricted.'' Comparing the performance of the different fourth order schemes, one can see that, in the case of weak or moderate perturbation, OPT4 lies closer to the exact result. Increasing the strength of perturbation to a relatively large value, it is OPT4 that first starts to deviate significantly from the exact curve (at $\gamma\sim0.5$), but it remains still better than OPT2 up to $\gamma\sim0.7$. The R-OPT4 results remain quite close to the exact line within the full range investigated.

We may therefore conclude that, for the problem of an anharmonic oscillator, the optimization of the partitioning in Rayleigh–Schrödinger PT extends its applicability to very strong perturbations. In the next section we address the more difficult problem of electron correlation.

TABLE II. The same as Table I for the He atom $10s2p1d$ basis set.

Order	MP−FCI	OPT−FCI	D_MP−CID	D_OPT−CID
2	6.0941×10^{-3}	-2.911×10^{-4}	6.0719×10^{-3}	-3.134×10^{-4}
3	1.0619×10^{-3}	-2.911×10^{-4}	1.0396×10^{-3}	-3.134×10^{-4}
4	1.949×10^{-4}	5.2×10^{-6}	1.812×10^{-4}	5.9×10^{-6}
5	3.75×10^{-5}	4.5×10^{-6}	3.01×10^{-5}	5.9×10^{-6}
6	7.7×10^{-6}	-1×10^{-7}	4.3×10^{-6}	-1×10^{-7}
7	1.7×10^{-6}	-1×10^{-7}	4×10^{-7}	-2×10^{-7}
8	4×10^{-7}	0	0	0
9	1×10^{-7}	0	0	0
10	0	0	0	0

B. Electron correlation energies

In this section we apply the repartitioned PT to the electron correlation problem for the He atom and the H_2 molecule representing two electron systems, as well as the Be

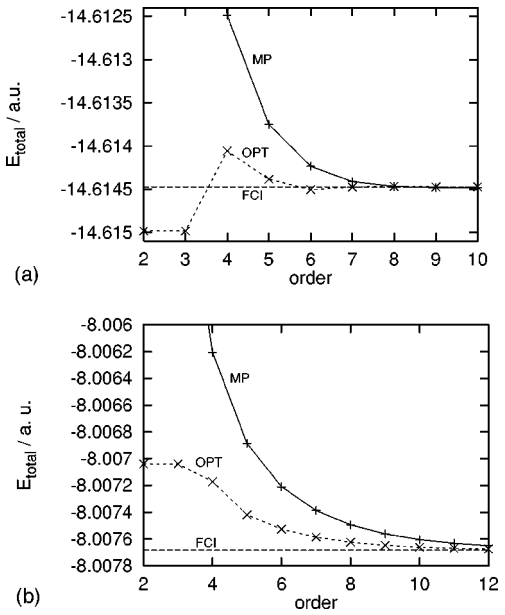

FIG. 4. The same as Fig. 3 for the Be atom in the $4s1p$ basis (Ref. 49) (a) and the LiH molecule (b) using the $[3s1p/2s]$ basis set (Ref. 44). The distance between the Li and the H atom is set to the SCF optimized value 1.607 Å.

TABLE III. Inversion barriers (a.u.) of the NH_3 molecule.

Method	STO3-G	ΔE 6-31G**	6-311G**
MP2	0.052 40	0.023 72	0.020 27
MP3	0.053 06	0.024 15	0.020 75
MP4	0.053 23	0.024 36	0.020 87
OPT2	0.053 60	0.024 25	0.020 83
D_OPT4	0.053 31	0.024 22	0.020 78
CCSD	0.053 61	0.024 14	0.020 74
CCSD(T)	0.053 46	0.024 32	0.020 97
CCSDT	0.053 39	0.024 33	0.020 98
QCISD(TQ)	0.053 43	0.024 29	0.020 81
Full-CI	0.053 41		

atom and the LiH molecule possessing four electrons. The inversion barrier of ammonia will be presented as an example for energy difference.

Basis sets and geometries are specified at the headings of tables and figures. As to other details of calculations, note that the single determinantal HF wavefunction was used as the zeroth order ground state, thus only doubly excited states interact directly with $|0\rangle$. Accordingly, only the level shift parameters of doubles have been optimized. Neglecting all other types of excitations (singles, triples, etc.) entirely, the PT series should converge to CID. (These approximate results, referred to as D_OPT4, are of course not size consistent.) When keeping all types of excitations (results labeled OPT), for the two-electron systems only the single excitations should be dealt with besides of doubles, and we kept the spin adapted EN denominators for these states. For Be and LiH, we have the singles, triples, and quadruples entering from the fourth order on, and we used MP denominators for these levels. For the NH_3 molecule, OPT4 is calculated only in the subspace spanned by doubly excited configurations. Higher order results were generated recursively[39–41] to study how perturbative improvement of LCCD behaves.

In Fig. 2 PT results using MP and the optimal partitioning are compared to the FCI (Full Configuration Interaction) value. Total energies near equilibrium geometry are shown in Fig. 2(a); differences taken with the FCI results are plotted in Fig. 2(b). Both figures show how MP results improve from order to order. However, the fourth order MP curve has roughly the same accuracy as OPT2, with the sign of the error being opposite. Fourth order of the optimal partitioning is considerably closer to the exact curve, with or without exclusion of the singly excited subspace (D_OPT4 or OPT4, respectively). With singles included, OPT4 can hardly be distinguished from FCI.

High order perturbative estimates are plotted in Fig. 3, to give an insight to the convergence properties of the series studied. In these particular cases, the often discussed divergent behavior[43] of the MP series is not observed: MPn data slowly but smoothly seem to converge to FCI. On the example of the He atom, sign of asymptotic convergence is seen at the very high orders of the optimized partitioning, though this series approach the FCI limit much faster than MPn. Similar conclusions can be drawn by the numbers presented in Tables I and II, where we also included PT series obtained using double substitutions exclusively.

In Fig. 4, the PT convergence on four-electron systems is depicted. Again, both series is converging, and neither shows features of asymptotic convergence (we followed the iterations up to 50 orders, but only the first dozen are shown). The accelerated convergence of the optimized partitioning is apparent.

Estimates for the inversion barrier of NH_3 are shown in Table III. Geometry of the pyramidal arrangement was optimized at the SCF level in each basis set, and the same bond lengths were used for the planar geometry. In the minimal basis the FCI value is shown for a comparison, CCSD (Coupled Cluster with Singles and Doubles) and QCISD(TQ), with an approximate account for triple and quadruple excitations is calculated as a reference in each case. Again second order of the optimized partitioning, that is LCCD, is comparable to MP4 in its accuracy. Fourth order results with doubles do not alter the picture significantly.

ACKNOWLEDGMENTS

The authors are indebted to P. Szalay (Budapest) and M. Nooijen (Princeton) for useful discussions. Also, we are grateful to L. Füsti-Molnár (Budapest) for kindly providing us his version of the Schrödinger-equation solving code.[45,46] Standard CCSD-type calculations were performed using the ACES II program system.[47] The MBPT results were computed with the MUNGAUSS program,[48] to which special routines were added. Many-electron full-CI results were obtained with the code of Knowles and Handy.[49] For four-electron systems, full-CI calculations and the PT iterations were performed with a simple routine constructing and diagonalizing the CI matrix explicitly, written with E. Rosta (Budapest). This work was supported by Grants No. OTKA T021179-023052-030435 and No. FKFP 0165/1999.

[1] Á. Szabados and P. R. Surján, Chem. Phys. Lett. **308**, 303 (1999).
[2] R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. **14**, 561 (1978).
[3] J. Čížek, Adv. Chem. Phys. **14**, 35 (1969).
[4] J. Čížek, J. Chem. Phys. **45**, 4256 (1966).
[5] R. Ahlrichs and P. Scharf, Adv. Chem. Phys. **67**, 501 (1987).
[6] R. J. Bartlett and I. Shavitt, Chem. Phys. Lett. **50**, 190 (1977).
[7] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. **68**, 2114 (1978).
[8] R. J. Bartlett and I. Shavitt, Chem. Phys. Lett. **57**, 157 (1978).
[9] P.-O. Löwdin, J. Math. Phys. **3**, 969 (1962).
[10] D. Hegarty and M. A. Robb, Mol. Phys. **37**, 1455 (1979).
[11] I. Shavitt and L. T. Redmon, J. Chem. Phys. **73**, 5711 (1980).
[12] U. Kaldor, Int. J. Quantum Chem. **28**, 103 (1985).
[13] J. Mášik, I. Hubač, and P. Mach, Int. J. Quantum Chem. **53**, 207 (1995).
[14] V. I. Alexandrov, A. V. Zaitevskii, and A. I. Dementev, Chem. Phys. Lett. **218**, 206 (1993).
[15] P. R. Surján and Á. Szabados, J. Chem. Phys. **104**, 3320 (1996).
[16] P. R. Surján and Á. Szabados, Acta Univ. Debreceniensis, Ser. IV, Phys. Chim. **30**, 97 (1995).
[17] N. Forsberg and P.-Å. Malmqvist, Chem. Phys. Lett. **274**, 196 (1997).
[18] S. T. Epstein, J. Chem. Phys. **41**, 1045 (1964).
[19] S. T. Epstein. *Perturbation Theory and its Applications in Quantum Mechanics* (Wiley, New York, 1966), p. 49.
[20] E. Steiner, J. Chem. Phys. **46**, 1717 (1967).
[21] W. Kutzelnigg, in *Modern Theoretical Chemistry, The Methods of Electronic Structure Theory* (Plenum, New York, 1977), Vol. 3, p. 129.
[22] P. S. Epstein, Phys. Rev. **28**, 695 (1926).
[23] R. K. Nesbet, Proc. R. Soc. London, Ser. A **230**, 312 (1955).
[24] P. O. Löwdin, J. Mol. Spectrosc. **10**, 12 (1963).

[25] P. Goldhammer and E. Feenberg, Phys. Rev. **101**, 1233 (1955).
[26] E. Feenberg, Phys. Rev. **103**, 1116 (1956).
[27] A. T. Amos, J. Chem. Phys. **52**, 603 (1970).
[28] J. P. Finley, R. K. Chaudhuri, and K. F. Freed, J. Chem. Phys. **103**, 4990 (1995).
[29] J. P. Finley, R. K. Chaudhuri, and K. F. Freed, Phys. Rev. A **54**, 343 (1996).
[30] R. K. Chaudhuri, J. P. Finley, and K. F. Freed, J. Chem. Phys. **106**, 4067 (1997).
[31] L. Brillouin, J. Phys. Radium **3**, 373 (1932).
[32] E. Wigner, Math. Naturw. Anz. ungar. Akad. Wiss. **53**, 477 (1935).
[33] K. Dietz, Ch. Schmidt, M. Warken, and B. A. Heβ, J. Phys. B **26**, 1885 (1993).
[34] K. Dietz, Ch. Schmidt, M. Warken, and B. A. Heβ, J. Phys. B **26**, 1897 (1993).
[35] A. Szabó and N. S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1989).
[36] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
[37] P. Pulay and S. Saebø, Theor. Chim. Acta **69**, 357 (1986).
[38] S. Saebø and P. Pulay, J. Chem. Phys. **86**, 914 (1987).
[39] P. J. Knowles, K. Somasundram, N. C. Handy, and K. Hirao, Chem. Phys. Lett. **113**, 8 (1985).
[40] N. C. Handy, P. J. Knowles, and K. Somasundram, Theor. Chim. Acta **68**, 87 (1985).
[41] P. R. Surján and J. G. Ángyán, Phys. Rev. A **28**, 45 (1983).
[42] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
[43] O. Christiansen, J. Olsen, and P.-A. Malmquist, Chem. Phys. Lett. **261**, 369 (1996).
[44] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).
[45] F. Gogtas, G. G. Balint-Kurti, and C. C. Marston, *QCPE Program No. 647*, 1993.
[46] G. G. Balint-Kurti, R. N. Dixon, and C. C. Marston, Int. Rev. Phys. Chem. **11**, 317 (1992).
[47] J. F. Stanton, J. Gauss, J. D. Watts, W.J. Lauderdale, and R. J. Bartlett, Program ACES II, Quantum Theory Project, University of Florida, 1991.
[48] R. A. Poirier and M. Peterson, Program MUNGAUSS, Department Chemistry, Memorial University St. Johns, Canada, 1989.
[49] P. J. Knowles and N. C. Handy, Comput. Phys. Commun. **54**, 75 (1989).