

Optimized partitioning in Rayleigh–Schrödinger perturbation theory

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Abstract

Finite-order perturbation corrections are ambiguous since they depend on the partitioning of the Hamiltonian to a zero-order part and perturbation, and any chosen partitioning can be freely modified, e.g. by level shift projectors. To optimize low-order corrections, an approximate variational procedure is proposed to determine level shift parameters from the first-order Ansatz for the wavefunction. The resulting new partitioning scheme provides significantly better second-order results than those obtained by standard partitions like Epstein–Nesbet or Møller–Plesset. We treat the anharmonic oscillator and the atomic electron correlation energy in He, Be and Ne as numerical test cases. © 1999 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

A crucial starting point in any perturbational calculation is the partitioning of the Hamiltonian \hat{H} into a zero-order part \hat{H}^0 and a remainder \hat{W} , the perturbation:

$$\hat{H} = \hat{H}^0 + \hat{W}. \quad (1)$$

In some cases, a natural partitioning is suggested by the physics of the problem (e.g. an atom in a weak external field), while in other cases it is completely arbitrary (e.g., Fockian + correlation operator in a many-electron system). In any case, selecting \hat{H}^0 by some physical or intuitive argument, one can

freely consider a *repartitioning* by any level shift parameters λ_k :

$$\hat{H} = \left(\hat{H}^0 + \sum_k \lambda_k |k\rangle \langle k| \right) + \left(\hat{W} - \sum_k \lambda_k |k\rangle \langle k| \right), \quad (2)$$

with $|k\rangle$ being the eigenfunctions of \hat{H}^0 . This kind of repartitioning neither affects zero-order states, energy correction up to first order, nor off-diagonal matrix elements of \hat{W} and thus is easy to implement. In many-body theory, such level shifts can be applied to connect the Møller–Plesset [1] and Epstein–Nesbet [2,3] partitionings, commonly used to evaluate the correlation energy perturbationally. Level shifts have also been applied by several authors to remove quasidegeneracies from the zero-order spectrum [4–9].

Previously, Feenberg and Goldhammer [10,11] have investigated the effect of introducing a single

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variational parameter in front of the first-order wavefunction, which is equivalent to the repartitioning

$$\hat{H} = \frac{1}{\mu} \hat{H}^0 + \left(\hat{W} + \frac{\mu - 1}{\mu} \hat{H}^0 \right) \quad (3)$$

discussed also by Amos [12]. Feenberg has also considered separate scaling factors at each order of the wavefunction. The requirement for a specific order of the energy to vanish, as an alternative to the variationally optimal choice for μ , was also discussed.

In the framework of many-body perturbation theory (PT), Dietz et al. [13,14] have also studied a ‘one- λ ’ approximation in the previous sense, for the repartitioning of the Hamiltonian. They have checked the convergence properties of the PT series and the damping effect of their repartitioning parameter as well.

2. Theory

In this Letter, we suggest keeping all the relevant shift parameters λ_k in Eq. (2) and optimizing them using the first-order Ansatz of the wavefunction. As a result, a new partitioning scheme emerges, the performance of which will be demonstrated on selected examples (the case of anharmonic oscillator and some ab initio calculations of the electron correlation energy in atomic systems).

As we wish to optimize *low-order* results, we consider the wavefunction of state i up to first order:

$$|\psi_i\rangle = |i\rangle - \sum_{k(\neq i)} \frac{W_{ki}}{E_k^{(0)} + \lambda_k - E_i^{(0)}} |k\rangle, \quad (4)$$

where $E^{(0)}$ are the zero-order energies before applying level shift, W_{ki} are the matrix elements of the perturbation. We have set $\lambda_i = 0$ for the sole state i (normally being the ground state) to fix the energy origin. The Rayleigh quotient of this first-order Ansatz,

$$\langle E \rangle = \frac{\langle \psi_i | \hat{H} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} \quad (5)$$

can, in principle, be made stationary with respect to the variation of parameters λ_k . This would be equivalent to exact diagonalization of the full Hamiltonian

if (i) the zero-order states formed a complete set and (ii) neither of the W_{ik} matrix elements vanished. If only some of these matrix elements are non-zero (as is usually the case), then the variational optimization of λ_k is equivalent to diagonalizing the Hamiltonian in a subspace. Instead of the exact diagonalization, we propose determining λ_k approximately in the spirit of perturbation theory. Carrying out the variation of Eq. (5), and neglecting all $\mathcal{O}(3)$ terms, we get a system of equations for the level shift parameters:

$$\Delta_k = W_{ik} \frac{E_k^{(0)} - E_i^{(0)} - W_{ii}}{W_{ik} - \sum_{j \neq i} \frac{W_{kj} W_{ji}}{\Delta_j}} \quad (k \neq i), \quad (6)$$

where $\Delta_k = E_k^{(0)} - E_i^{(0)} + \lambda_k$ are assumed to be non-zero (that is, we do not shift levels for which $W_{ik} = 0$). This is the working formula of the present Letter.

Expressions of Eq. (6) may be transformed to inhomogeneous equations linear in $1/\Delta_j$

$$\sum_{j \neq i} A_{kj} \frac{1}{\Delta_j} = 1 \quad (k \neq i) \quad (7)$$

where

$$A_{kj} = \delta_{kj} (E_j^{(0)} - E_i^{(0)} - W_{ii}) + \frac{W_{kj} W_{ji}}{W_{ik}}. \quad (8)$$

Therefore, provided that the Δ_j that are equal to zero can be excluded, and assuming that the determinant of matrix \mathbf{A} is non-vanishing, the solutions are uniquely determined. In practice, one is not forced to compute the inverse of \mathbf{A} , as Eq. (6) may be solved by a fast-converging direct iteration procedure.

It may be possible to introduce one further approximation neglecting all $j \neq k$ terms in the denominators of Eq. (6). Then the solutions become

$$\Delta_k = E_k^{(0)} + W_{kk} - E_i^{(0)} - W_{ii} \quad (k \neq i) \quad (9)$$

leading to

$$\lambda_k = W_{kk} - W_{ii} \quad (k \neq i). \quad (10)$$

This means that no diagonal elements of the perturbation survive for $k \neq i$, which is essentially the partitioning of Epstein and Nesbet [2,3].

It is not difficult to see that the repartitioning of the Hamiltonian indicated by Eq. (2) using shifts of Eq. (6) is equivalent to a specific resummation tech-

nique. For example, assuming that W_{ii} is zero, the second-order energy obtained with denominators of the first iteration of Eq. (6) contains the third-order correction in the original partitioning, while the third-order correction in the new partition always vanishes. Further iteration brings in higher-order corrections. A detailed account of this partial resummation would grow out of the limits of this Letter, and will be given in a forthcoming publication.

3. Examples

3.1. Anharmonic oscillator

Consider a one-dimensional harmonic oscillator perturbed by a quartic term

$$\hat{H} = \frac{1}{2}(\hat{p}^2 + \hat{q}^2) + \gamma\hat{q}^4 = \hat{H}^{(0)} + \gamma\hat{V} = \hat{H}^{(0)} + \hat{W} \quad (11)$$

in arbitrary units, γ measuring the strength of anharmonicity. Starting from the well-known solution of the harmonic oscillator, $E_n^{(0)} = n + \frac{1}{2}$, we wish to find the ground state eigenvalue of the anharmonic system perturbatively.

The most straightforward way is to consider the anharmonic term as perturbation, indicated in Eq.

(11), and obtain the eigenvalue corrections order by order with the Rayleigh–Schrödinger (RS) formulae

$$E^{(1)} = W_{00} \quad E^{(2)} = - \sum_{k \neq 0} \frac{|W_{0k}|^2}{E_k^{(0)} - E^{(0)}}. \quad (12)$$

In the basis of the zero-order eigenfunctions, the W_{0k} matrix elements become

$$\begin{aligned} W_{0k} = & \frac{\gamma}{4}(2 + 5k + 4k^2 + (k + 1)^2)\delta_{0k} \\ & + \frac{\gamma}{2}\sqrt{k(k-1)(k+1)^2}\delta_{2k} \\ & + \frac{\gamma}{4}\sqrt{k(k-1)(k-2)(k-3)}\delta_{4k} \end{aligned} \quad (13)$$

leading to

$$\begin{aligned} E^{(1)} = \frac{3}{4}\gamma \quad E^{(2)} = & - \frac{|W_{02}|^2}{E_2^{(0)} - E^{(0)}} - \frac{|W_{04}|^2}{E_4^{(0)} - E^{(0)}} \\ = & - \frac{21}{8}\gamma^2. \end{aligned} \quad (14)$$

Because of the sparseness of matrix \mathbf{W} , Eq. (6) may now be solved for Δ_2 and Δ_4 explicitly.

Second-order results and Rayleigh quotients of Eq. (5) are plotted in Fig. 1 as a function of the strength of anharmonicity. The full anharmonic

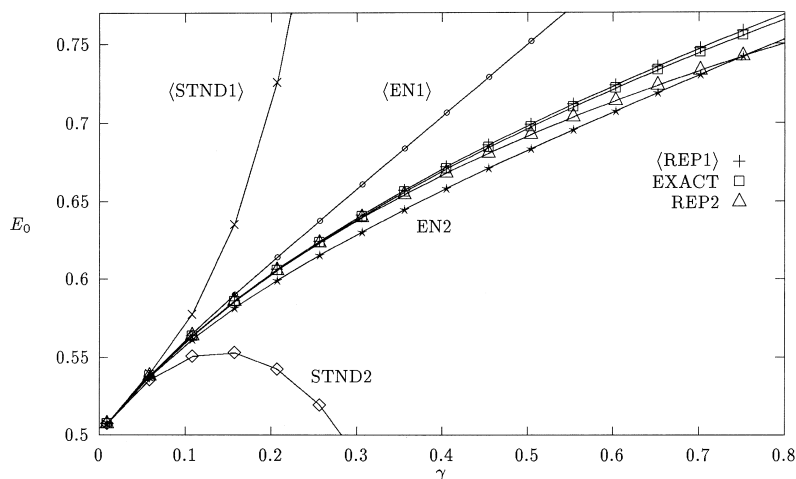


Fig. 1. Ground state eigenvalue of a one-dimensional oscillator as a function of the anharmonicity of the potential (γ) as obtained from exact diagonalization and by second-order RS perturbation theory in different partitionings. STND, standard (see text); EN, Epstein–Nesbet; REP, the present repartitioning. Rayleigh quotients with first-order wavefunctions are indicated by $\langle \dots \rangle$. Energy and γ are measured in arbitrary units.

Hamiltonian was diagonalized exactly [15,16] to check the accuracy of perturbative results. Of the three partitionings shown, that of Eq. (11) (standard, labelled by STND) gives a reliable estimation only at very weak perturbation. Higher-order terms do not improve this result in the moderate perturbation range. We also tested the Epstein–Nesbet (EN) partitioning up to the second order. It results in reasonable values at relatively broad perturbation range, the second-order value approaching closer to the exact curve than the expectation value with the first-order wavefunction. Significantly better results are obtained using the partitioning defined by Eq. (6). The second-order correction gives a curve which starts to deviate from the exact one only above $\gamma \sim 0.3$ in our scale, while the first-order expectation value remains close to the exact result within the full range investigated, including γ values of relatively strong anharmonicity.

3.2. Atomic electron correlation energies

To investigate the power of the proposed partitioning, calculations have been performed for the correlation energies of atoms He, Be and Ne in a few basis sets (Tables 1 and 3). Results of second-order perturbation theory (PT) are compared to those of standard quantum chemical methods. Of these, CCD

(CCSD) are values from the coupled-cluster (CC) method with double (and single) substitutions, while CID (CISD) refers to the configuration interaction (CI) technique. Whenever it was possible, exact diagonalization (denoted by FULL-CI) was performed in the actual basis set. Notations RS and BW stand for the Rayleigh–Schrödinger and Brillouin–Wigner variants of PT [17,18]. Different partitionings are indicated by MP (Møller–Plesset), EN (Epstein–Nesbet) on the spin-adapted CI matrix, and REP, the latter referring to the repartitioning proposed here. The BW-REP2 results presented here are BW corrections in the partitioning optimized within the RS scheme. The CC calculations were done with the GAUSSIAN 94 program system [19], others were performed with special routines added to the MUNGAUSS program [20], which was also interfaced to the FULL-CI code by Knowles and Handy [21].

We are of course aware of the fact that the BW variant of PT does not meet the size-consistency requirement. Since the presented preliminary calculations were done on single atoms, the BW results are still informative. We strongly emphasize that within the RS scheme the proposed repartitioning *does not destroy* the size-consistent feature. This was checked by numerical calculations but can also be shown explicitly by inspecting Eq. (8). Assume $\hat{W} = \hat{W}_A +$

Table 1
Results of PT calculations in different partitionings for He atom

Basis set method	(5s)/[3s] 2p1d		10s2p1d	
	E_{tot} (au)	Percentage of E_{corr} covered	E_{tot} (au)	Percentage of E_{corr} covered
Hartree–Fock	–2.859895	0.0	–2.861669	0.0
RS-MP2	–2.891578	84.1	–2.893907	84.1
RS-MP3	–2.896550	97.3	–2.898939	97.2
RS-EN2	–2.898574	102.7	–2.899759	99.4
RS-REP2	–2.897846	100.7	–2.900292	100.8
BW-MP2	–2.886941	71.8	–2.889212	71.9
BW-EN2	–2.898256	101.8	–2.899472	98.6
BW-REP2	–2.897542	99.9	–2.899978	99.9
CID	–2.897542	99.9	–2.899979	99.9
CCD	–2.897542	99.9	–2.899979	99.9
FULL-CI	–2.897564	100.0	–2.900001	100.0

Total electronic energies and electron correlation energy fractions are shown in two different Huzinaga type basis sets [17]. See text for the meaning of acronyms.

Table 2
Results of PT calculations in different partitionings for Be atom

Basis set	(9s)/[5s] 2p		(9s5p)/[5s2p] 1d	
method	E_{tot} (au)	Percentage of E_{corr} covered	E_{tot} (au)	Percentage of E_{corr} covered
Hartree–Fock	– 14.571951	0.0	– 14.571951	0.0
RS-MP2	– 14.609264	64.7	– 14.610932	65.3
RS-MP3	– 14.621400	85.7	– 14.622507	84.7
RS-EN2	– 14.638488	115.3	– 14.633372	102.9
RS-REP2	– 14.632764	105.4	– 14.636236	107.7
BW-MP2	– 14.587492	26.9	– 14.587755	26.5
BW-EN2	– 14.631939	104.0	– 14.628401	94.6
BW-REP2	– 14.627801	96.8	– 14.629739	96.8
CID	– 14.627811	96.8	– 14.629793	96.9
CISD	– 14.628462	97.9	– 14.630258	97.7
CCD	– 14.628814	98.6	– 14.630980	98.9
CCSD	– 14.629512	99.8	– 14.631475	99.7
FULL-CI	– 14.629652	100.0	– 14.631639	100.0

Total electronic energies and electron correlation energy fractions are shown in two different Huzinaga-type basis sets [17]. See text for the meaning of acronyms.

\hat{W}_B , A and B representing two non-interacting subsystems, and suppose that excited state k describes an excitation localized either on A or B . (Mixed type excitations do not contribute in the non-inter-

acting case.) Clearly, matrix A in Eq. (8) has a block-diagonal form in the basis of local excitations. Consequently, the presence of subsystem B will not affect the energy denominators Δ_k of subsystem A

Table 3
Results of PT calculations in different partitionings for Ne atom

Basis set	(9s5p)/[3s2p]		(9s5p)/[3s2p] 1d
method	E_{tot} (au)	Percentage of E_{tot} E_{corr} covered	(au)
Hartree–Fock	– 128.522354	0.0	– 128.522354
RS-MP2	– 128.622712	97.7	– 128.671277
RS-MP3	– 128.620756	95.8	– 128.671872
RS-EN2	– 128.643544	118.0	– 128.701569
RS-REP2	– 128.621929	97.0	– 128.673259
BW-MP2	– 128.530709	8.1	– 128.536350
BW-EN2	– 128.639945	114.5	– 128.694690
BW-REP2	– 128.619896	95.0	– 128.669126
CID	– 128.619897	95.0	– 128.669127
CISD	– 128.621178	96.3	– 128.670869
CCD	– 128.622502	97.5	– 128.672798
CCSD	– 128.623366	98.4	– 128.673994
FULL-CI	– 128.625027	100.0	

Total electronic energies and electron correlation energy fractions are shown in two different Huzinaga type basis sets [17]. See text for the meaning of acronyms.

resulting from Eq. (7). This is exactly the requirement of size-consistency in RS-PT.

The results can be summarized as follows.

In the case of the He atom (Table 1), all the perturbative methods presented above give relatively high percent of the correlation energy, as expected for a two-electron system. Still one can see that the good approximation presented by RS-MP can be improved turning to RS-EN. It is interesting to note that the performance of EN has the strongest basis set dependence among the methods studied. This is a quite general feature which can be inferred from the other examples too. Another notable observation is that combination of MP partitioning with BW2 is necessarily inappropriate for the estimation of correlation energy since energy denominators, already too large in RS-MP, are further increased during BW iteration. The accuracy of REP2 is much better than that of MP3 in both PT expansions, in fact it provides the best PT estimates, the error being less than +0.8% (RS) and -0.1% (BW).

For the Be atom (Table 2), the estimation given by RS-MP is unusually poor, and again considerable improvement may be achieved by EN partitioning. With the repartitioning defined by Eq. (6) one gets significantly better approximations in both RS and BW schemes for this system as well.

Considering the Ne atom (Table 3), the RS-MP2 estimations are astonishingly good. In the larger basis, we were not able to get the FULL-CI solution, thus we can judge the accuracy of the REP2 results by comparison with CCSD. One may observe that, in both basis sets, the RS-REP2 results are again better than RS-MP3. The RS-REP2 energy is not lowered below the exact value, and the BW iteration pulls it back to the variational CID level.

The examples studied above give rise to the following qualitative conclusions. The proposed repartitioning of the Hamiltonian significantly improves RS-MP results. Values gained by RS-REP2 are better than RS-MP3 though the former may present a slight overestimation of the exact correlation energy. This property of the RS-REP2 scheme is compensated by turning to BW-REP2 as the latter applies increased energy denominators. Since the determination of shift parameters and is not concerned with those levels which directly interact with the ground state, we did not compute higher-order results. It is

in accordance with the central idea of the present proposition, which was to increase the accuracy of low-order corrections. Although figures presented for total and correlation energies are quite promising, we do not claim that the conclusions drawn on the simple examples studied in this Letter are fully general. Other examples and the question of chemical energy differences are still to be investigated.

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