APPENDIX TO "STUDIES IN PERTURBATION THEORY": THE PROBLEM OF PARTITIONING

Péter R. Surján and Ágnes Szabados

Department of Theoretical Chemistry, Eötvös University, H-1518 Budapest POB. 32.

surjan@chem.elte.hu

Abstract   The problem of partitioning in perturbation theory is reviewed starting from the classical works by Epstein and Nesbet or by Møller and Plesset, up to optimized partitionings introduced recently. Equations for optimal sets of level shift parameters are presented. Attention is paid to the specific problems appearing if the zero order solution is not a single Slater determinant. A special formalism for multi-configurational perturbation theories is outlined. It is shown that divergent perturbation series, like that of an anharmonic oscillator, can be converted to a convergent series by an appropriate redefinition of the zero order Hamiltonian via level shifts. The possible use of effective one-particle energies in many-body perturbation theory is also discussed. Partitioning optimization in a constant denominator perturbation theory leads to second order correction familiar from connected moment expansion techniques. Ionization potentials, computed perturbatively, are found sensitive to the choice of partitioning, and ordinary approximations are improved upon level shift optimization.

1. Introduction

In his series of seminal papers entitled "Studies in Perturbation Theory"[1–12], Per-Olov Löwdin has summarized a vast amount of knowledge accumulated in perturbation theory at that time, with many ideas originating in his own studies, but incorporating lots of information about results obtained by former and contemporary researchers. The guideline of these papers was certainly to present fundamental aspects, and not be lost in particular details of technical problems.

The present appendix aims to augment the fundamental papers of Per-Olov Löwdin with a detailed discussion on the partitioning problem. While it could have been viewed formerly as a small detail, several recent results indicate the conceptual importance of this subject. Of course, the present review can only be considered as a foot-hill of Per-Olov's papers of everlasting value.

To begin with our discussion, a few general words are due on perturbation theory (PT). Students in physics and chemistry nowadays usually meet this theory in course of their studies in quantum mechanics, when learning Rayleigh-Schrödinger PT (RSPT). However, it is worth to recall that PT is a much older discipline: it was developed centuries ago for treating small disturbances of planetary motions caused by the mutual interaction between planets in the solar system, a problem which cannot be solved exactly thus needing a refineable approximate method. The Latin word 'perturbo, perturbare' (i.e., to 'annoy', 'trouble', 'bother', or 'disturb') refers to this origin. Moreover, it is also worth mentioning that the title of Rayleigh's book, which is most often referred to when citing RSPT, is "The Theory of Sound[1] " [13] – indicating that this mathematical theory can be applied to a variety of physical problems. The present quantum mechanical formalism of RSPT is due to Erwin Schrödinger [14, 15] in 1926. Although PT has soon become one of the fundamental tools of quantum theory, its mathematical backgrounds have only been studied in sufficient detail considerably later[16–19], many of these studies being summarized in the comprehensive book by Kato[20].

Perturbation theory is a mathematical method to account for small disturbances. It is usually assumed that the solution of the unperturbed problem is known, and the aim of PT is to give formulae describing the effect of small perturbations. Although in some mathematical studies researchers are interested in large perturbations as well, this should be considered as a (sometimes very interesting) mathematical curiosity and it is quite far from the original spirit of PT.

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[1] The first edition of this book dates back to 1877 (MacMillan &Co., London)

Since its introduction in 1926, quantum mechanical formulation of PT has been studied in great detail. Nevertheless, we are still facing several unsolved problems. To name a few, we do not know the necessary and sufficient conditions for the convergence of the PT series, we do not have a general and robust method to deal with the case of quasi-degenerate zero order, and there is no established method to fix the best partitioning. In addition, in many-body PT (MBPT), the handling of multi-reference zero order state(s) is an open issue[21–33], just like a clear and general theory to correct coupled-cluster type wave functions perturbatively[34–45]. The handling of symmetry in PT can also be a difficult task, especially when the zero order problem has lower symmetry than the perturbed problem, a situation one meets e.g. when studying molecular interactions[12, 46–56]. Among all these problems, we shall be concerned here with that of the partitioning.

The organization of this review is as follows. After briefly introducing the concept of partitioning, we discuss the standard (or traditional) partitionings as used in quantum chemistry. Then level shifts will be used to modify these standard partitionings, after which an ingenious method, the so called Feenberg scaling will be reviewed. The concept of the optimal partitioning, as introduced in our laboratory as well as used by other authors, will be next outlined in some detail, including its applications to energy calculations in single- and multi-reference cases. In the context of many-body perturbation theory, the choice of optimal orbital energies and optimal orbitals will also be mentioned. Then a further criterion for establishing level shifts is discussed – the minimization of norm of operator $\hat{R}\hat{W}$. A somewhat peculiar, but useful, version of perturbation theory that uses constant denominators will also be treated, in connection with partitioning optimization. Finally we consider the application of the optimal partitioning to the calculation of ionization potentials.

2. The concept of partitioning

Let us be concerned with the time-independent Schrödinger equation $\hat{H}\Psi = E\Psi$, having the form of an eigenvalue problem of the Hamiltonian $\hat{H}$. To approximate the solutions to this equation, we split the Hamiltonian as

$$\hat{H} = \hat{H}^{(0)} + \hat{W}, \tag{1.1}$$

where $\hat{H}^{(0)}$ is supposed to be close to $\hat{H}$, so that $\hat{W}$ is small in some sense. This splitting of the Hamiltonian is called the partitioning. It is usually supposed that the Schrödinger equation for the zero order

Hamiltonian $\hat{H}^{(0)}$

$$\hat{H}^{(0)}\Psi_K^{(0)} = E_K^{(0)}\Psi_K^{(0)}$$

can be solved, and that one may develop the exact solutions E and Ψ in terms of the zero order solutions and the perturbation operator $\hat{W}$. It is also customary to insert a perturbation parameter λ in front of $\hat{W}$, i.e., instead of (1.1) one may write

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{W}. \tag{1.2}$$

Then, the exact wave functions and energies, i.e., eigenvectors and eigenvalues of $\hat{H}$, are looked for in form of a power series of λ:

$$\Psi_K = \Psi_K^{(0)} + \lambda\Psi_K^{(1)} + \lambda^2\Psi_K^{(2)}\ldots$$

and

$$E_K = E_K^{(0)} + \lambda E_K^{(1)} + \lambda^2 E_K^{(2)}\ldots$$

The perturbation parameter may have three interpretations. It can be just a formal parameter merely guiding our eyes when deriving n-th order corrections that are proportional to λ^n, and, after getting the results, one substitutes $\lambda = 1$ into the final formulae. Oppositely, if $\lambda\hat{W}$ is considered a physical perturbation, like an external field acting on a molecule, then λ measures the field strength which can have any real value. Finally, λ can be considered as a mathematical parameter scaling a given $\hat{W}$; the Hamiltonian $\hat{H}(\lambda)$ as well as its eigenvalues become λ-dependent in this interpretation, with $\hat{H}(0) = \hat{H}^{(0)}$. In this latter case λ can even be complex, which leads to a powerful tool to study convergence properties of the PT expansion via investigating the analyticity of the complex function $E(\lambda)$[20, 57].

From our point of view, it is the second case when we may speak about a natural partitioning of the problem. A good example is a molecule in a weak external field. In this case $\hat{H}^{(0)}$ is the *in vacuo* Hamiltonian, and $\lambda\hat{W}$ describes the interaction between the molecule and the field. A related example is a weakly anharmonic oscillator:

$$\hat{H} = -\frac{1}{2m}p^2 + \frac{1}{2}kq^2 + \lambda q^4$$

with a small λ scaling the anharmonic (quartic) term. Here the 'natural' partitioning of the problem is $\hat{H}^{(0)} = -\frac{1}{2m}p^2 + \frac{1}{2}kq^2$ (the Hamiltonian of the harmonic oscillator), while λq^4 constitutes the perturbation.

The above two examples are quite instructive since they remind us that a partitioning that seems very natural from the physical point of view may be quite unfortunate mathematically. In fact, the PT series of

the quartic oscillator *never converges* in the above partitioning[58, 59], even for infinitesimally small λ values. However, good convergence can be achieved by a more appropriate partitioning[60] or resummation techniques[61–63]. Similarly, the PT series for the Hydrogen atom embedded in a small magnetic field is also known to be divergent at any field strength[61, 64], while an external electric field brings the H atom unstable[61, 65]. These observations underline the essential importance of investigations of the problem of partitioning in PT.

3.   Traditional partitionings in quantum chemistry

3.1   Epstein-Nesbet partitioning

A natural way of partitioning a matrix, whose eigenvalues are to be approximated by PT, is to collect its diagonal elements to form a zero order (diagonal) matrix, and let all off-diagonals to constitute the perturbation. All diagonal elements of the perturbation are zero in this case, which is usually referred to as the Epstein-Nesbet (EN) partitioning[66, 67] in quantum chemistry. In the language of operators, the EN partitioning is defined just by requiring that all diagonal matrix elements of the perturbation operator, $W_{KK} = \langle \Psi_K^{(0)} | \hat{W} | \Psi_K^{(0)} \rangle$, are zero. Note that the EN partitioning cannot be formulated without explicit reference to the basis $\{\Psi_K^{(0)}\}$.

The EN partitioning has several advantages and disadvantages. One advantage is that it can be defined at any level of theory, i.e. it is not bound to, say, the many-body problem. In the case of the anharmonic oscillator EN is quite different from the natural partitioning quoted above, where one does have diagonal perturbations. In fact, it gives much better results than the 'natural' partitioning[68], since it reassigns at least the diagonal elements of the perturbation operator to the zero order. The absence of diagonal perturbations is clearly an advantage. However, there's a big price to pay: the values of matrix elements W_{KK} are basis set dependent, i.e., the partitioning is not invariant against unitary transformations of the basis set $\{\Psi_K^{(0)}\}$. This means that *the EN partitioning is not well defined.* Quoting an example from many-body theory: if the electron correlation is to be accounted for by PT, then the EN partitioning yields different results if one deals with pure determinants as zero order excited states, or with spin-adapted configurations thereof. Moreover, the EN partitioning is not invariant against changing the spin adaptation scheme: having more than one singlet e.g. in a configuration, the EN partitioning is again ill-defined.

Numerical experience with the EN partitioning is mingled. Very good results have been obtained in some cases[69–71], while in other cases an overestimation of low-order contributions and bad convergence properties have been reported[70, 72, 73]. A successful compromise between using pure determinants and spin-adapted configurations is represented by the barycentric expression introduced in Malrieu's group[74].

An important question about any partitionings is whether it obeys the requirement of *size-extensivity*. This involves that the energy of two noninteracting subsystems, as computed by the given method, is equal to the sum of energies of the two isolated systems computed separately. It is sometimes quoted that the EN partitioning is not size-extensive[75, 76]. However, a closer look into the problem reveals that it does not necessarily violate this important principle. The problem is quite delicate; it is connected to the ill-defined nature of the EN partitioning. Let us check the example of a configuration interaction (CI) matrix, having the elements $\langle K|\hat{H}|L\rangle$, with K and L denoting two Slater-determinants. Using EN partitioning, the perturbation denominators will be $\langle K|\hat{H}|K\rangle - \langle 0|\hat{H}|0\rangle$ where $|0\rangle$ is the reference determinant. Extensivity can be met if, upon infinite separation of the two subsystems, the excited determinant $|K\rangle$ is factorized in a way that one subsystem remains unexcited, symbolically: $|K\rangle = |K_A 0_B\rangle$ (note that anti-symmetrization becomes irrelevant at infinite separation). When constructing the excited determinants, this can easily be achieved if the molecular orbitals remain localized on the constituting fragments A and B. Since the orbitals of separated systems may be degenerate (they necessarily are, if the two subsystems are identical), localization may not be fulfilled automatically. Therefore, if a second order calculation is performed for a dissociating system in terms of canonical orbitals, the results are expected to be arbitrary and can violate the extensivity requirement. However, localization can be ensured e.g. by applying any of the well-known localization criteria[77–82].

The situation is illustrated in Figs. 1.1-1.6 on the example of the potential curve of the Helium dimer computed in 6-311G** basis set. For comparison, the full-CI (FCI) potential curve is shown in Fig. 1.5, and PT results in the Møller-Plesset (MP) partitioning (*vide infra*) in Fig. 1.6. Choosing the Hartree-Fock solution as zero order, the second order results obtained in the EN partitioning with canonical orbitals are shown in Fig. 1.1. Here the EN partitioning was made without spin-adaptation, i.e., in a determinantal basis. The resulting curve is very erratic: it has an (exaggerated) minimum at a wrong distance (just above 2 Å), then it tends to be saturated at an extensivity-violating limit up to 8 Å, when it exhibits an unphysical sudden jump with unphysical oscillations,
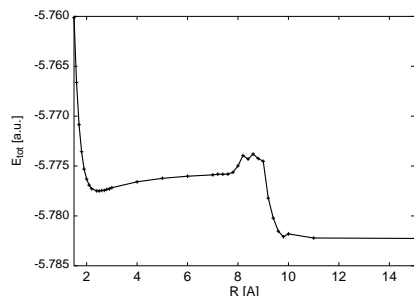
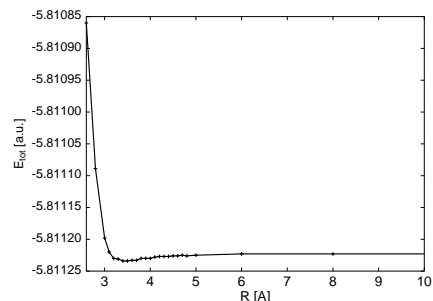*Figure 1.1.* Potential curve of the He dimer (EN partitioning in determinantal basis with canonical MOs)

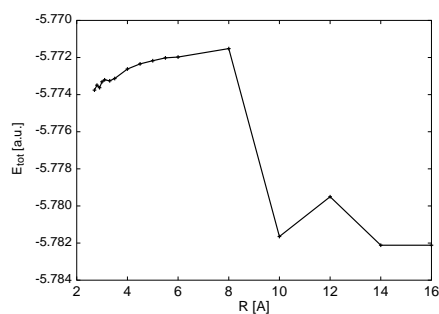*Figure 1.2.* The same as Fig.1.1, but with Boys' localized MOs

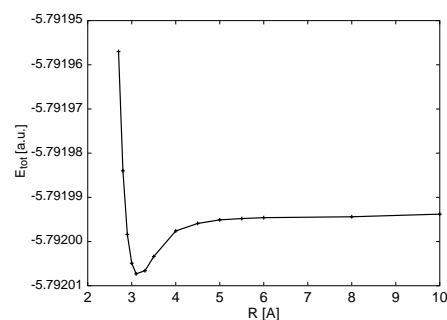*Figure 1.3.* The same as in Fig.1.1, but in spin-adapted basis with canonical MOs

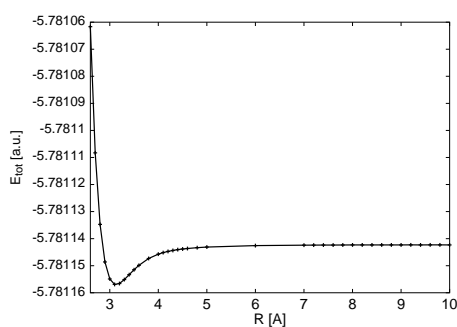*Figure 1.4.* The same as in Fig.1.3, but with Boys' localized MOs

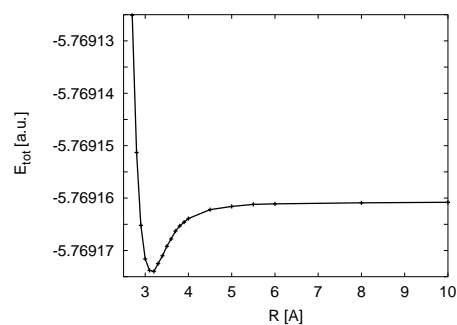*Figure 1.5.* Full CI potential curve for the He dimer

Figure 1.6. Second order potential curve for He$_2$ in the MP partitioning

finally ending at the correct infinite limit. The jumps and oscillations appear due to the non-invariance of the EN partitioning with respect to rotating degenerate levels. The situation is similar (although not the same), if canonical orbitals but a spin-adapted configuration basis is used to make the EN partitioning (see Fig. 1.3). If the orbitals are *a priori*

localized by Boys' criterion, a more smooth curve is obtained with the correct (extensive) dissociation feature, but one still may observe small oscillations along the curve due to the numerical problems that appear in course of the localization procedure (see Figs. 1.2 and 1.4). Note that these latter two curves are also different, indicating the dependence of the EN partitioning on the spin-adaptation scheme.

In concluding, the EN partitioning, in spite of its simplicity, does not represent a reliable PT method in the many-body problem. The main shortcomings are due to the lack of orbital invariance and the invariance against altering the spin adaptation scheme. All of this underlines the importance of a detailed study of the partitioning problem in perturbation theory.

3.2   Adams partitioning

Adams defined[83] the following zero order Hamiltonian:

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

leading to the perturbation

$$\hat{W} = \hat{O}\hat{H}\hat{P} + \hat{P}\hat{H}\hat{O}$$

where $\hat{O}$ and $\hat{P}$ are two Hermitian projectors satisfying $\hat{O} + \hat{P} = 1$. In matrix language this means that one partitions the full space into two parts; the full matrix will then be separated into four blocks. The two diagonal blocks will be considered as the zero order and the two off-diagonal ones give rise to the perturbation. This partitioning has a conceptual value. To apply it in practice, one has either to diagonalize the two diagonal blocks to get a diagonal $\hat{H}^{(0)}$, or one has to deal with a non-diagonal resolvent. An interesting property of the Adams partitioning is that all odd-order energy corrections are zero[83].

3.3   Møller-Plesset partitioning

In the many-body problem, especially in evaluating the electron correlation energy, the most widely used partitioning is due to Møller and Plesset [84] (MP). It can be defined as

$$\hat{H} = \hat{F} + \hat{W} \tag{1.3}$$

where $\hat{F}$ is the Fockian operator, playing the role of the zero order Hamiltonian. It is apparent that this partitioning is formulated within the framework of many-body theory, thus lacks the generality of EN partitioning which can be formulated at the level of quantum mechanics. To

give an example, it would be difficult to define an MP-type partitioning
for the anharmonic oscillator. On the other hand, the MP partitioning
is defined with the aid of operators without any reference to any partic-
ular basis sets, thus it is basis-independent. If one works with canonical
molecular orbitals (MOs) φ_i which diagonalize the Fockian, the latter
can be specified as

$$\hat{F} = \sum_i \varepsilon_i \; \varphi_i^+ \varphi_i^-$$

where ε_i-s are orbital energies, and the superscripts $\pm$ on φ_i indicate
creation and annihilation operators. The many-electron eigenstates of
this zero order operator are Slater-determinants with various excitation
levels from the ground-state determinant, thus the PT denominators in
this partitioning have the form

$$\varepsilon_p - \varepsilon_a$$

for singly excited states,

$$\varepsilon_p + \varepsilon_q - \varepsilon_a - \varepsilon_b$$

for doubles, etc. (We adopt the convention that letters $a, b, \ldots$ denote
occupied orbitals while $p, q, \ldots$ stand for virtual labels. Letters from the
middle of the alphabet $(i, j, \ldots)$ indicate generic indices.)

The MP partitioning is free from the problems discussed above in con-
nection with the EN partitioning. The MP results are invariant against
spin adaptation and against orbital transformations among degenerate
MOs. Usually, since the EN denominators are smaller than the cor-
responding orbital energy differences, low order MP results are mostly
smaller in absolute value than EN ones. Apart from rare cases, MP2
underestimates the true correlation energy of the given basis set. The
error of an MP2 calculation is rather systematic, thus this method forms
a basis of a stable, reliable tool in quantum chemistry. It can be usually
improved by going to higher orders (MP3, MP4). The 4th order results
are often quite accurate, although rather expensive to compute. This
is because (unlike MP2 and MP3 which need only double substitutions)
MP4 requires three- and four-fold excitations to evaluate.

If one wants to compute MPn results in orbital sets other than the
canonical one, care should be taken to the fact that in those basis sets the
Fockian is not diagonal. The actual expressions for the energy and wave
function corrections will therefore be changed. This is not a conceptual
but merely a technical problem, and efficient formulations have been
reported to evaluate second and higher order results with non-diagonal
zero order[85–87]. Evaluation of the correlation energy in terms of lo-

calized molecular orbitals is a typical example when such a formulation is needed.

Up to this point the discussion about MP referred to the case when the zero order wave function is a single Slater determinant (using the standard *terminus technicus*: the case of 'single reference'). This is an acceptable approximation at around equilibrium geometries of closed-shell systems. Energetics of dissociating covalent bonds, however, cannot be studied in this partitioning. Generalization of the MP partitioning for multi-reference cases, that can also describe dissociating bonds, will shortly be discussed later.

Eq.(1.3) defines the MP partitioning in a strict sense. Speaking about a *generalized MP partitioning* one may think about either a different expression for the Fockian (such as the generalized Fockian in a multi-reference theory, see Section 1.10) or, using a partitioning in which the PT denominators are constituted by the differences of some effective one-particle energies, different from canonical ε_i-s. Examples to this latter case will be provided in section 1.8.

4.   Level shifts

4.1   Basic definition

A given partitioning of the Hamiltonian, $\hat{H} = \hat{H}^{(0)} + \hat{W}$, can always be changed by adding and subtracting an operator that is diagonal in the basis of the eigenvectors of $\hat{H}^{(0)}$:

$$\hat{H} = \underbrace{\hat{H}^{(0)} + \sum_K \eta_K |K\rangle\langle K|}_{\hat{H}^{(0)'}} + \underbrace{\hat{W} - \sum_K \eta_K |K\rangle\langle K|}_{\hat{W}'} \qquad (1.4)$$

where η_K-s are arbitrary parameters called level shifts (here and further on, the shorthand $|K\rangle = |\Psi_K^{(0)}\rangle$ is used). One usually sets $\eta_0 = 0$ to fix the energy origin. Level shifts obviously do not modify the zero-order wave functions, they merely affect the zero-order energy levels.

Level shift parameters have been applied in a number of works with various purposes[26, 88–93], among which the removal of (quasi)degeneracies from the zero order spectrum is an important issue.

The second order energy correction in the shifted partitioning becomes

$$E^{(2)'} = -\sum_{K \neq 0} \frac{\langle 0|\hat{W}|K\rangle\langle K|\hat{W}|0\rangle}{E_K^{(0)} - E_0^{(0)} + \eta_K} \qquad (1.5)$$

Note that the second order numerator does not depend on η-s. This induces an ambiguity for the second order expression: by the η-dependence

of the denominator one can arrive at *any* second order result by changing level shift parameters. The $E^{(2)'}(\eta_K)$ function is not even bounded. At the third order, numerators become also η-dependent:

$$E^{(3)'} = \sum_{K,L(\neq 0)} \frac{\langle 0|\hat{W}|K\rangle\langle K|\hat{W} - W_{00} + \eta_K|L\rangle\langle L|\hat{W}|0\rangle}{(E_K^{(0)} - E_0^{(0)} + \eta_K)(E_L^{(0)} - E_0^{(0)} + \eta_L)}$$

which causes that the third order results are less ambiguous.

4.2   Connection between MP and EN

Evaluating the correlation energy of an N-electron system perturbatively in the MP and EN partitionings, we find that the numerators of the second order terms, $|\langle 0|\hat{W}|K\rangle|^2$, are the same in both cases. This is because these numerators (unlike higher order ones) do not contain diagonal elements of $\hat{W}$. The denominators, however, are different:

$$\Delta_K^{EN} = \hat{H}_K - \hat{H}_0 = \Delta_K^{MP} + \eta_K,$$

where Δ_K^{MP}-s are orbital energy differences, while $\eta_K - s$ can be interpreted as level shifts. Conversely, starting from the MP partitioning, one may prove that a resummation of certain terms appearing in the higher orders of MP, namely those having contributions from diagonal perturbations, is equivalent to a suitable modification of the energy denominators[69, 94, 95].

4.3   Complex level shifts

One may in principle choose complex or imaginary values for the level shift parameters η_K. This results that finite order corrections will not be necessarily real, and additional assumptions have to be introduced to extract real numbers that may solely have a physical interpretation. One possibility is to take the modulus (absolute value) of each term[96–98]. Optimization of complex level shift parameters have not yet been reported, merely ad hoc formulae for setting imaginary parameters were proposed[96–99]. The formula

$$E_{damped}^{(2)} = -\sum_{K \neq 0} \frac{|W_{0K}|^2}{\sqrt{\Delta_K + |W_{0K}|^2}}$$

corresponds to taking the term-by-term absolute value of an imaginarily shifted second order expression and requiring that it be exact for a two-level system in the fully degenerate ($\Delta_K = 0$) limit. This formula was tested for molecules[96] and polymers[98]. It has also been compared to other, non-perturbative formulae[100–103]. Imaginary shifts in multireference PT have also been considered[99].

5.　　Feenberg scaling

Feenberg and Goldhammer[104, 105] have investigated the effect of introducing a single scaling parameter in front of the first order wave function, which is equivalent to the repartitioning

$$\hat{H} = \underbrace{\frac{1}{\mu}\hat{H}^{(0)}}_{\hat{H}^{(0)\prime}} + \underbrace{\left(\hat{W} + \frac{\mu-1}{\mu}\hat{H}^{(0)}\right)}_{\hat{W}^{\prime}} \qquad (1.6)$$

discussed also by Amos[106]. Requiring that the third order energy correction in this new partitioning vanishes leads to

$$E^{(2)\prime} = \frac{\left(E^{(2)}\right)^2}{E^{(2)} - E^{(3)}} \qquad (1.7)$$

which proved to be considerably successful[104, 105]. It was noted[107–109] that Feenberg's procedure is equivalent to a Padé approximation[2] scheme[116], as the above equation indeed suggests.

An important question is whether the extensivity is maintained by the above modification, for which affirmative answers were already published [117, 118]. However, a closer look into the problem reveals that Eq.(1.7) is separable for non-interacting subsystems only if the latter are identical [119].

In the recent studies by Goodson[118, 120, 121], connection between Padé approximants and Feenberg scaling has further been exploited. Goodson has used quadratic Padé approximants[121], the denominators of which may exhibit not only poles, but also branching points. He suggested to determine the Feenberg scaling parameter μ from the condition that the first branching point is pushed apart from the origin to the maximum possible extent, thereby maximizing the convergence radius of the PT series. (For convergence radii, see e.g. [113].)

Feenberg scaling has been extensively studied by several other authors, too[108, 109, 122–124, 112]. Cremer et al.[117, 125] generalized Feenberg's procedure to any (odd) orders and studied the convergence of the original and the generalized series.

6.　　Optimized partitioning

It is apparent from Eq.(1.6) that the Feenberg scaling can be viewed as a special level shift: all zero order energies are divided by a factor,

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[2]Padé approximants represent a useful tool, widely studied in quantum theory[110–115].

and the perturbation is modified just by a diagonal operator. The success of the optimal selection of μ suggests that it is useful to consider a more general case, when all level shift parameters are varied independently. This section is devoted to discuss some possibilities for an optimal selection of the η_K parameters introduced in (1.4).

6.1   General formulation

In order to set the level shift parameters η_K, one may proceed in the following way. Parameters η_K affect individual terms of the perturbation series, but not the converged sum. One may expect even for approximate wave functions that the 'best' η_K values are those for which the energy is stationary. This can be expressed by the variational like condition

$$\frac{\partial}{\partial \eta_K} \frac{\langle \Psi^{[1]'}|\hat{H}|\Psi^{[1]'}\rangle}{\langle \Psi^{[1]'}|\Psi^{[1]'}\rangle} = 0 \qquad K = 1, 2, \ldots \qquad (1.8)$$

where $\Psi^{[1]'} = \Psi^{(0)} + \Psi^{(1)'}$ is the first order Ansatz for the wave function. To set the connection to PT, let us expand the Rayleigh-quotient as

$$\frac{\langle \Psi^{[1]'}|\hat{H}|\Psi^{[1]'}\rangle}{\langle \Psi^{[1]'}|\Psi^{[1]'}\rangle} = E^{(0)'} + E^{(1)'} + E^{(2)'} + E^{(3)'} + \mathcal{O}(4) \qquad (1.9)$$

(cf. Wigner's $2n + 1$ rule). Neglecting $\mathcal{O}(4)$ terms, the variational requirement takes the form

$$\frac{\partial}{\partial \eta_K} \left(E^{(2)'} + E^{(3)'} \right) = 0 , \quad K = 1, 2, \ldots \qquad (1.10)$$

Here we left out the zero and first order terms since $E^{(0)'} + E^{(1)'} = \langle 0|\hat{H}|0\rangle$ is independent of level shifts. Substituting the expressions of $E^{(2)'}$ and $E^{(3)'}$ into Eq.(1.10), and carrying out the variation one finds

$$\langle 0|\hat{W}\hat{R}'|K\rangle\langle K|\hat{W}'\hat{R}'\hat{W}|0\rangle - W_{00}\langle 0|\hat{W}\hat{R}'|K\rangle\langle K|\hat{R}'\hat{W}|0\rangle = 0 \quad K = 1, 2, \ldots \qquad (1.11)$$

where the reduced resolvent of the shifted zero order is

$$\hat{R}' = -\sum_{I\neq 0} \frac{|I\rangle\langle I|}{\Delta'_I}$$

with the shifted denominators $\Delta'_I = E^{(0)}_I - E^{(0)}_0 + \eta_I$. Equation (1.11) defines the level shifts in the new partitioning.

This system of equations can be brought to the form [68]

$$\sum_{J\neq 0} A_{KJ} \frac{1}{\Delta'_J} = 1 , \qquad K = 1, 2, \ldots \qquad (1.12)$$

where

$$A_{KJ} = \delta_{KJ}(E_J^{(0)} - E_0^{(0)} - W_{00}) + \frac{W_{KJ}W_{J0}}{W_{0K}} \qquad (1.13)$$

showing that, if matrix $\mathbf{A}$ 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 wave function are not defined by Eq.(1.12). The simplest choice is to set these parameters zero.

6.2   Properties of the optimized partitioning

6.2.1   Vanishing of the third order correction.   One can easily show that in the optimal partitioning the third order energy is zero. Putting down the third order RSPT formula

$$
\begin{aligned}
E^{(3)'} &= \langle 0|\hat{W}\hat{R}'\hat{W}'\hat{R}'\hat{W}|0\rangle - W_{00}\langle 0|\hat{W}\hat{R}'^2\hat{W}|0\rangle \\
&= \sum_{K\neq 0} E_K^{(3)'}
\end{aligned}
$$

and writing out the reduced resolvents explicitly, one has

$$E_K^{(3)'} = \frac{W_{0K}}{\Delta_K'}\left(\sum_{I\neq 0}\frac{W_{KI}W_{I0}}{\Delta_I'} - (W_{00}+\eta_K)\frac{W_{K0}}{\Delta_K'}\right) \quad . \qquad (1.14)$$

Substituting $\hat{R}'$ and the shifted perturbation operator $\hat{W}'$ into Eq.(1.11), one finds that its left hand side equals $E_K^{(3)'}$. That is, Eq.(1.11) is equivalent to the requirement

$$E_K^{(3)'} = 0, \qquad K = 1, 2, \ldots$$

The fact that $E^{(3)'}$ vanishes in the optimized partitioning points back to the Feenberg scaling discussed in Sect.1.5. Having a closer look to the Feenberg procedure it turns out that setting $E^{(3)'} = 0$ is equivalent to the requirement $\partial\left(E^{(2)'} + E^{(3)'}\right)/\partial\mu = 0$ in the one-parameter optimization scheme, too[106, 117]. In fact, the original idea of Feenberg for choosing the single scaling parameter μ was just this latter condition.

6.2.2   Consequences on the higher orders.   Vanishing of all $E_K^{(3)'}$-s has important consequences for higher orders, too. All terms containing the expression

$$\langle K|(\hat{W}' - W_{00})\hat{R}'\hat{W}|0\rangle \qquad (1.15)$$

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

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

the last term is zero due to vanishing of $E^{(3)'}$, while the second term is zero due to Eq.(1.15). Consequently, merely the first term may contribute to $E^{(5)'}$. Similar considerations apply for higher orders, too.

6.2.3   Extensivity.   The repartitioning with level shift parameters obtained from Eqs.(1.12)-(1.13) preserves size extensivity. Consider two noninteracting subsystems A and B, characterized by the equations $\hat{H} = \hat{H}_A^{(0)} + \hat{H}_B^{(0)}$, $\hat{W} = \hat{W}_A + \hat{W}_B$, $|0\rangle = |0_A 0_B\rangle$. Taking a look at the second order correction, e.g., in the new partitioning [cf. Eq.(1.5)], one finds that repartitioning preserves extensivity of the initial series if in the noninteracting situation any level shift can be assigned to the subsystem where that particular level belongs. Regarding the structure of matrix **A** in Eq.(1.13), it is apparent, that a nonzero inter-system element may only emerge in the case where $\langle K| = \langle K_A 0_B|$ and $|J\rangle = |J_B 0_A\rangle$. This is because matrix elements of $\hat{W}$ of the type $\langle K_A J_B|\hat{W}|0_B 0_A\rangle$ are all zero. In the former special case, since

$$
W_{KJ} = \langle K_A|\hat{W}_A|0_A\rangle\langle 0_A|J_B\rangle + \langle 0_B|\hat{W}_B|J_B\rangle\langle K_A|0_A\rangle = 0
$$

A_{KJ} again proves to be zero. This means that matrix **A** is block-diagonal if subsystems A and B are infinitely apart, consequently level shifts are determined solely by expressions of one subsystem or another.

6.2.4   Resummation of RS-PT series.   Substituting Eq.(1.13) into (1.12), one gets the following formula, suitable for an iterative treatment[68]:

$$
\Delta_I' = \Delta_I \frac{W_{0I}}{W_{0I} - \sum\limits_{J\neq 0} \frac{W_{IJ}W_{J0}}{\Delta_J'}} \qquad (I \neq 0) \qquad (1.16)
$$

where $\Delta_I = E_I^{(0)} - E_0^{(0)}$ is the unshifted denominator, and the condition $W_{00} = 0$ was used which can be set in the initial partitioning without loss of generality. Considering Eq.(1.16), it is not difficult to see that the second order guess to the energy,

$$
E^{(2)'} = -\sum\limits_{I\neq 0} \frac{|W_{0I}|^2}{\Delta_I'} \qquad (1.17)
$$

is equivalent to an infinite order partial resummation of the original partitioning. Substituting Eq.(1.16) into (1.17):

$$
\begin{aligned}
E^{(2)'} &= -\sum_{I \neq 0} \frac{|W_{0I}|^2}{\Delta_I} + \sum_{I,K \neq 0} \frac{W_{0I} W_{IK} W_{K0}}{\Delta_I \Delta_K'} \\
&= \langle 0|\hat{W}\hat{R}\hat{W}|0\rangle + \langle 0|\hat{W}\hat{R}\hat{W}\hat{R}'\hat{W}|0\rangle \ .
\end{aligned}
$$

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.(1.16) repeatedly to yield

$$
\begin{aligned}
E^{(2)'} &= \langle 0|\hat{W}\hat{R}\hat{W}|0\rangle + \langle 0|\hat{W}\hat{R}\hat{W}\hat{R}\hat{W}|0\rangle + \langle 0|\hat{W}\hat{R}\hat{W}\hat{R}\hat{W}\hat{R}\hat{W}|0\rangle + \dots \\
&= \sum_{n=1}^{\infty} \langle 0|\hat{W}(\hat{R}\hat{W})^n|0\rangle
\end{aligned}
\tag{1.18}
$$

which is clearly a part of the infinite order (exact) PT energy. 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 [126, 127]. We may call these contributions BW type terms, which differ only from true BW results in that the reduced resolvent $\hat{R}$ is constructed from zero 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.

To write this result more compactly, let us introduce the reaction operator $\hat{T}$:

$$
\hat{T} = \hat{W} + \hat{W}\hat{R}\hat{W} + \hat{W}\hat{R}\hat{W}\hat{R}\hat{W} + \dots
\tag{1.19}
$$

that satisfies a Lippmann-Schwinger type equation

$$
\hat{T} = \hat{W} + \hat{W}\hat{R}\hat{T}
\tag{1.20}
$$

since the iteration of (1.20) with $\hat{T}^{(0)} = 0$ leads to (1.19). Using (1.18),

$$
\langle 0|\hat{T}|0\rangle = W_{00} + E^{(2)'}
$$

The formal solution of (1.20) is

$$
\hat{T} = (1 - \hat{W}\hat{R})^{-1}\hat{W}
\tag{1.21}
$$

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

$$
\begin{aligned}
E^{(2)'} &= \langle 0|(1 - \hat{W}\hat{R})^{-1}\hat{W}|0\rangle - W_{00} \\
&= \langle 0|\hat{W}\left(1 - \hat{R}\hat{W}\right)^{-1}\hat{R}\hat{W}|0\rangle \ .
\end{aligned}
\tag{1.22}
$$

The last equality can be seen by subtracting and adding the term $\langle 0|\hat{W}(1 - \hat{R}\hat{W})^{-1}|0\rangle$.

Let us recall at this point the damping procedure of Dietz et al.[124, 128, 129], which leads to a second order correction $\langle 0|\hat{W}(1 - \hat{\Lambda})\hat{R}\hat{W}|0\rangle$, where $\hat{\Lambda}$ is an arbitrary damping operator. The authors proposition for $\hat{\Lambda}$: $1 - \hat{\Lambda} = \left[1 - \hat{R}\left(\hat{W} - \Delta E\right)\right]^{-1}$ with $\Delta E = E_0 - E_0^{(0)}$ clearly results in a formula closely related to Eq.(1.22). There are two major differences between the procedure of Dietz et al. and the optimized partitioning. Once, Dietz et al. use several model spaces to construct operator $\hat{\Lambda}$ in, while in the optimized partitioning those K-s are used for which $W_{0K} \neq 0$. Secondly, the infinite order correction, ΔE does not appear in Eq.(1.22). Absence of ΔE from the optimized reduced resolvent has the advantage that finite order PT corrections are extensive in the optimized partitioning.

6.2.5   Derivation by projection operator technique.   In the spirit of Löwdin's partitioning technique[2], the P-component of the wave function, i.e., its projection to the subspace orthogonal to the reference (O-) space, is written as

$$|\hat{P}\Psi\rangle = \hat{R}\hat{W}|0\rangle + \hat{R}\hat{W}|\hat{P}\Psi\rangle - \Delta E \hat{R}|\hat{P}\Psi\rangle$$

If one neglects the last term in this equation (which is justified if the energy correction is a second order quantity), and left multiplies with $\left(1 - \hat{R}\hat{W}\right)^{-1}$ one gets:

$$|P\Psi\rangle = (1 - \hat{R}\hat{W})^{-1}\hat{R}\hat{W}|0\rangle. \tag{1.23}$$

Expansion of the inverse in (1.23), yields

$$|P\Psi\rangle = \hat{R}\hat{W}|0\rangle + \hat{R}\hat{W}\hat{R}\hat{W}|0\rangle + \ldots = \hat{R}\hat{T}|0\rangle.$$

On substituting this result into the energy formula $E = \langle 0|\hat{H}|\Psi\rangle$ one finds:

$$\begin{aligned} E &= \langle 0|\hat{H}|0\rangle + \langle 0|\hat{W}\hat{R}\hat{T}|0\rangle \\ &= \langle 0|\hat{H}|0\rangle + \langle 0|\hat{W}\hat{R}\hat{W}|0\rangle + \langle 0|\hat{W}\hat{R}\hat{W}\hat{R}\hat{W}|0\rangle + \ldots \end{aligned}$$

in perfect agreement with (1.18). This derivation, of course, does not contribute to any new result as compared to the formulae of the previous sections, but it makes transparent how the resummation of BW-type terms emerges from Löwdin's partitioning technique.

6.3   The example of the anharmonic oscillator

The Hamiltonian of the harmonic oscillator perturbed by a quartic term can be written in arbitrary units as

$$\hat{H} = \frac{1}{2}\left(p^2 + q^2\right) + \lambda q^4 = \hat{H}^{(0)} + \hat{W} \qquad (1.24)$$

One may start off with the partitioning suggested by the physics of the problem, as discussed in Sect.1.2, with the solution of the zero order

$$\hat{H}^{(0)}|n\rangle = \left(n + \frac{1}{2}\right)|n\rangle \ .$$

In this case there are only two levels that interact with the ground state, since

$$W_{0K} = \frac{\lambda}{4}(2 + 5K + 4K^2 + (K+1)^2)\delta_{0K} + \frac{\lambda}{2}\sqrt{K(K-1)(K+1)^2}\delta_{2K}$$
$$+ \frac{\lambda}{4}\sqrt{K(K-1)(K-2)(K-3)}\delta_{4K},$$

leading to the first order wave function

$$|\Psi^{[1]}\rangle = |0\rangle - \frac{\frac{\lambda}{2}\sqrt{18}}{2 + \eta_2}|2\rangle - \frac{\frac{\lambda}{4}\sqrt{24}}{4 + \eta_4}|4\rangle \ .$$

Level shifts η_2 and η_4 can be determined using Eqs. (1.12) and (1.13) in a straightforward way.

Perturbative results up to fourth order, calculated in the partitioning of Eq.(1.24) and in the optimized splitting are plotted in Fig. 1.7 as a function of the strength of the perturbation. Standard partitioning of Eq.(1.24) is labeled by STND, OPT refers to the optimal partitioning.

Computing higher than third order of PT, one faces the question of determining shifts, that are not set by optimization. These are η_6 and η_8, in this special case, at fourth order. Calculating the curve labeled OPT4 in Fig.1.7, η_6 and η_8 were set zero, which means keeping the original partitioning for these levels. Inspecting Fig.1.7, it is apparent that the PT expansion in the STND partitioning diverges already for small λ values, while the corrections in the OPT partitioning remain meaningful even at relatively large values of the coupling parameter. In concluding, for the problem of anharmonic oscillator the optimization of the partitioning in Rayleigh-Schrödinger PT extends its applicability to strong perturbations.

7.   Optimized partitioning in single reference PT

Now we turn to the problem of calculating electronic (correlation) energies in atoms and molecules. Let us consider first a simple case, when
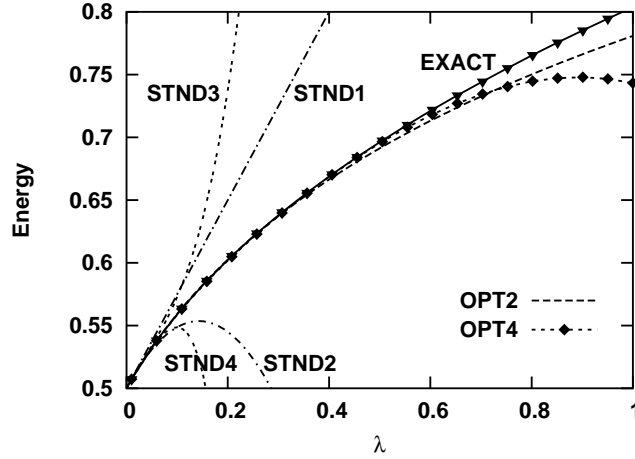
Figure 1.7. Ground state energy of the anharmonic oscillator as a function of the coupling strength λ in arbitrary units. Results of the standard partitioning are identified by STNDn. Optimized partitioning is referred to as OPT, for details see text. Exact result (solid line) was obtained by solving the Schrödinger equation numerically.

the lowest eigenvector of $\hat{H}^{(0)}$ is a single Slater determinant, typically the Hartree-Fock solution.

An interesting feature of the optimized partitioning is that, as applied to the correlation problem in many-electron theory, the well known CEPA-0 (equivalently: coupled pair many-electron theory (CPMET) [130, 131], linearized coupled-cluster (LCCD)[132], or D-MBPT∞[133–135]) energy formula is recovered at the second order. This can be demonstrated in several ways, since the very same method has been described in literature in different manners. The CEPA-0 equations [136]

$$\langle \phi_{ab}^{pq}|\hat{H} - H_{00}|\Psi^{[1]}\rangle = 0$$

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

$$F = \langle \Psi^{[1]}|\hat{H} - H_{00}|\Psi^{[1]}\rangle$$

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

$$
\begin{aligned}
F &= \langle 0|(1 + \hat{W}\hat{R}')\,(\hat{H} - H_{00})\,(\hat{R}'\hat{W} + 1)|0\rangle \\
&= \langle 0|\hat{W}\hat{R}'\hat{W}|0\rangle + \langle 0|\hat{W}\hat{R}'W'R'\hat{W}|0\rangle - W_{00}\langle 0|\hat{W}\hat{R}'^2\hat{W}|0\rangle \\
&= E^{(2)'} + E^{(3)'}.
\end{aligned}
$$

This was just the functional we used in Eq.(1.10) 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 (1.22), which is clearly the same as the energy formula in the LCCD method [95, 132].

Based on the equivalence between the second order results 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 zero oder 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 formulae. This property markedly discerns the optimized partitioning from EN or MP, since the former is not orbital invariant at all, while the orbital invariant formulation of the latter [85, 86] requires the use of non-diagonal resolvents. In the optimized partitioning the same second order formula (1.17) gives the same result whatever orbitals (canonical or localized) are used.

The equivalence between $E^{(2)'}$ and the LCCD energy holds only if one uses the Hartree-Fock wave function as the reference state $|0\rangle$. The optimization of the partitioning by level shifts is, therefore, a more general procedure.

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.

Since 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 quadruples 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.

Numerical results found in the optimal partitioning are presented in Table 1.1 and Figs. 1.8–1.10, comparing them with standard MPn values and the FCI benchmark. Note the parallelity of the OPT curves with the exact results and the improvement of the convergence features.

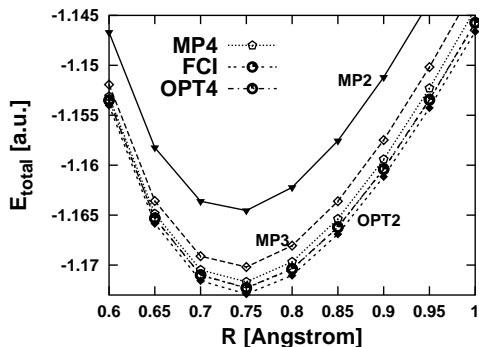| method	inversion barrier		
	STO3-G	6-31G**	6-311G**
MP2	0.05240	0.02372	0.02027
MP3	0.05306	0.02415	0.02075
MP4	0.05323	0.02436	0.02087
OPT2	0.05360	0.02425	0.02083
CCSD	0.05361	0.02414	0.02074
CCSDT	0.05339	0.02433	0.02098
QCISD(TQ)	0.05343	0.02429	0.02081
FCI	0.05341		

Table 1.1. Inversion barriers [a.u.] of the NH_3 molecule

Figure 1.8. Absolute energy at around equilibrium on the potential curve of the H_2 molecule in [3s2p1d] basis set[137], in MP and optimized partitioning
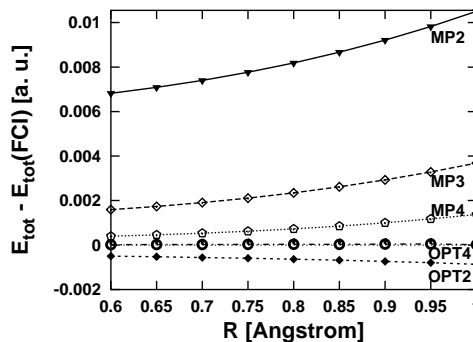
Figure 1.9. The same as in Fig. 1.8, but deviation from Full CI

8.   Using noncanoninal orbital energies in MBPT

8.1   Davidson-Kapuy partitioning

Assume that we work in an MO basis set in which $\hat{F}$ is non-diagonal, say a basis set of localized MOs (LMOs). Defining just the diagonal part of $\hat{F}$ as $\hat{H}^{(0)}$, one arrives at a partitioning, in which the off-diagonal elements of $\hat{F}$ give rise to a new kind of perturbation. This, in connection with using non-canonical MOs in MBPT, was introduced by Davidson [139, 140] and extensively used by Kapuy[141–145] (for a review, see [146]). To distinguish this second possibility from MP, we shall refer to it as the Davidson-Kapuy (DK) partitioning. In the DK partitioning the
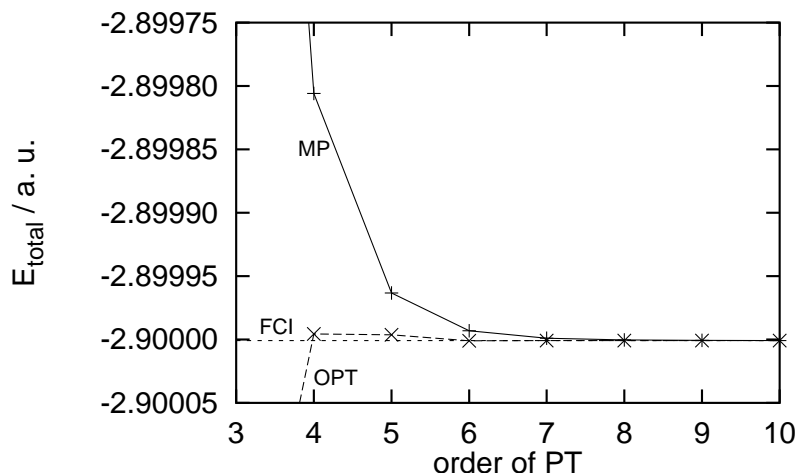
Figure 1.10. Convergence of perturbation series estimating the total energy of the
He atom in 10s2p1d basis set[138]

diagonals of the actual Fockian (say the energies of LMOs) are considered
as effective one-particle energies. The DK partitioning was reported to
provide numerical results inferior to those of MP in the single-reference
case[86], but it has the advantage of computational simplicity.

   An example where the Davidson-Kapuy partitioning comes about nat-
urally is the description of intermolecular interactions by PT. Consider
a many-body PT to describe the interaction of two subsystems in the
one-particle basis set formed by the canonical MOs of the isolated inter-
acting partners. These MOs are strictly localized on the fragments thus
they are not canonical for the dimer system. As a consequence, inter-
fragment perturbation one-electron matrix elements appear both in the
occupied and the virtual blocks, exactly like in the DK partitioning[3].

   The performance of the DK partitioning in multi-reference PT (MRPT)
theories is currently under investigation[147].

---

[3]An extra complication in the intermolecular case is that the fragment MOs are neither
orthogonal, nor satisfy the Brillouin theorem.

8.2   Dyson partitioning

One may wonder, why the MP partitioning has proved to be more reliable than any other. Its success – the reason of which has not yet been completely understood – implies that there should be some physical model behind. One may quote Koopmans' theorem [148] interpreting ε_i-s as ionization potentials or electron affinities. A straightforward modification of the partitioning emerges then by constructing the denominators from *correlated ionization potentials*. General experience shows that the difference between ionization potentials and electron affinities is overestimated at the Hartree-Fock level: Koopmans gaps are usually too large. Using better ionization potentials and/or electron affinities in Møller-Plesset type expressions may, therefore, yield better correlation energies. This modification is all the more appealing as it preserves the size-extensivity of the perturbative formulae.

A simple improvement of one-particle energies can be obtained from the second order inverse Dyson equation[95] which in its spin-orbital form reads:

$$\epsilon_i = \varepsilon_i + \frac{1}{2} \sum_{abp} \frac{[ip||ab]^2}{\epsilon_i + \varepsilon_p - \varepsilon_a - \varepsilon_b} + \frac{1}{2} \sum_{apq} \frac{[ia||pq]^2}{\epsilon_i + \varepsilon_a - \varepsilon_p - \varepsilon_q}$$

where the antisymmetrized two-electron integrals are written in [12||12] convention and orbital occupancies are restricted as mentioned before. We identify the partitioning when ϵ_i-s are used in MP-type denominators as the Dyson (DY) partitioning. The structure of the second order (MP2) formula is not affected by such a change, while diagonal corrections appear at higher orders. For example, the term

$$- \sum_{abpq} \frac{[ab||pq]^2}{(\epsilon_p + \epsilon_q - \epsilon_a - \epsilon_b)^2} (\eta_p + \eta_q - \eta_a - \eta_b) \tag{1.25}$$

has to be added to the usual third order formula, where $\eta_i = \epsilon_i - \varepsilon_i$.

To illustrate its effect, we present a potential curve of the H_2 molecule in a 8s/5s basis set augmented with 2p 1d ($\zeta_{p1} = 0.46$, $\zeta_{p2} = 1.39$, $\zeta_d = 1.0$) [149] in Fig. 1.11. It can be seen that DY2 and DY3 remove the quasidegeneracy-induced divergence of the MP series, permitting a rough estimation of the dissociation energy. At the long range limit DY2 covers at about 30% and DY3 55% of the correlation energy.

As a second process we selected the dissociation of methane to a CH_3 radical and a H atom in 6-311G** basis (Fig. 1.12). For comparison, the potential curve calculated by a 2 electron-3 orbital CAS-SCF is also shown. The second and third order level shifted curves do not show
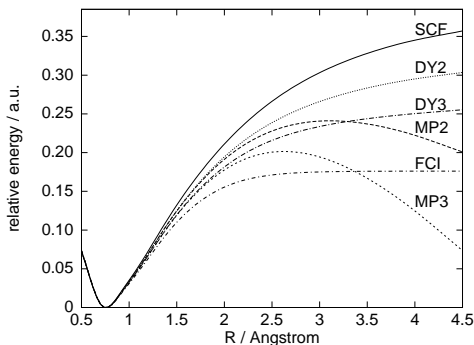
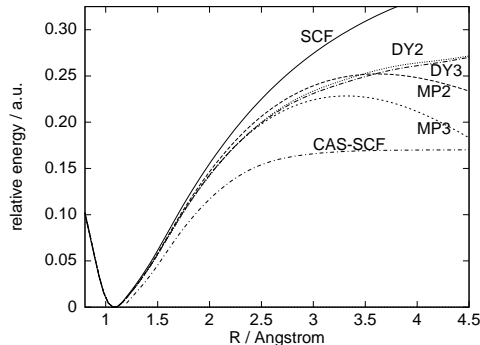*Figure 1.11.* Potential curve of H_2 in Dyson and Møller-Plesset partitionings in comparison with full CI

Figure 1.12. CH4→CH3...H dissociation in Dyson and Møller-Plesset partitionings in comparison with a CAS-SCF curve

considerable deviation from each other, they both yield a non-negligible part of the static correlation energy at long distance, and show the same effect as MPn at around equilibrium.

The performance of the Dyson-partitioning for quantitative details of potential curves, such as geometries and spectroscopic constants, has not yet been investigated in sufficient detail.

8.3   Optimized orbital energies in MBPT

The standard MP, the Davidson-Kapuy and the Dyson partitionings all deal with some kind of effective one-particle energies, their differences being used in the energy denominators. In the spirit of the optimized partitioning, one may attempt to define effective orbital energies that are optimal in some sense. The most straightforward choice is again to minimize the third order energy with respect to the orbital energies.

To develop the necessary formalism, we write

$$\hat{H} = \hat{F} + \hat{V} \tag{1.26}$$

where $\hat{F}$ is the shifted Fockian

$$\hat{F} = \sum_i \epsilon_i \, a_i^\dagger a_i = \sum_i (\varepsilon_i + \eta_i) \, a_i^\dagger a_i$$

with the shifted quasiparticle energies $\epsilon_i = \varepsilon_i + \eta_i$. The relation between perturbation operators $\hat{W}$ and $\hat{V}$ is simply

$$\hat{V} = \hat{W} - \sum_i \eta_i \, a_i^\dagger a_i. \tag{1.27}$$

The unknown parameters of the theory are the level shifts η_i or, equivalently, the shifted quasiparticle energies ϵ_i. One of them can be kept fixed to prevent an immaterial constant shift of the zero-order spectrum, the number of free parameters is therefore $(N_{\text{basis}} - 1)$. Following the philosophy of the optimized partitioning method[68, 150], we determine the level shifts from the equation

$$\frac{\partial[E^{(2)} + E^{(3)}]}{\partial\epsilon_i} = 0. \tag{1.28}$$

Actual expression for $E^{(2)}$ agrees with the standard MP2 formula, while $E^{(3)}$ differs from MP3 as a consequence of the diagonal perturbation in Eq.(1.27), giving rise to the term in Eq.(1.25).

Having obtained the explicit functional, partial derivatives occurring in Eq.(1.28) can be derived in a lengthy but straightforward manner. The analytical solution of the resulting equations is formidable. We obtained numerical solutions using analytical gradients and diagonal Hessians to initiate a BFGS procedure.

Quasiparticle energies determined in this way have the property that, given two noninteracting subsystems A and B, each ϵ_i belongs either to system A or B. This follows from the extensivity of the functional $[E^{(2)} + E^{(3)}]$ and ensures that repartitioning by the corresponding level shifts does not spoil size extensivity of the MBPT scheme. Of course, the dissociation behavior with a closed shell (RHF) reference state will not be correct, thus the results in this sense are not *size-consistent*. To achieve the latter, an unrestricted (UMP-type) formulation would be necessary.

As an example, we show the effect of ε-optimization on the correlation energy of the Be atom (Table 1.2). It seems that for this system the correlation energies drastically improve upon optimization, but the optimized results go somewhat below the FCI limit.

Based on a model study of a two-state problem, Finley[151] suggested to define one-particle energies in an MP type scheme that maximize the radius of convergence of PT. The numerical performance and feasibility of this approach is yet to be investigated.

Note that optimization of one-particle energies in MP-type PT is a special case of a more general theory introduced by Davidson[139]. In this latter, one adds an arbitrary, general one-body operator and subtracts its two-electron counterpart regrouping in these manner the terms of the total Hamiltonian entirely. Eqs.(1.26-1.27) correspond to the special case when this one-body operator is diagonal.

basis	MP2	MP3	ε-OPT2	ε-OPT3	FCI
6-311G**	-41.555	-52.881	-64.718	-64.865	-61.502
10s5p1d	-57.120	-72.673	-80.433	-80.868	-78.109

Table 1.2. Correlation energy of the Be atom in mH. Second and third order PT results are shown in two partitionings. Abbreviation ε-OPT refers to the partitioning optimized with respect to orbital energies. FCI is indicated for reference.

Optimized orbitals in MBPT: Lindgren's approach. In a recent paper[152], Lindgren discussed an interesting possibility. He proposed to optimize the n-th order energy with respect to the orbitals themselves, not only just orbital energies. He argued that with increasing n the optimal orbitals will converge to Brueckner orbitals[153, 154], and the energies of these orbitals will be ionization potentials. The significance of these arguments is still under discussion, but it is evident that the idea has lead to a new kind of 'optimal' partitioning in PT.

9.   Zero order Hamiltonians with two-body terms

The case we have considered so far is that of a zero order wave function consisting of a single Slater determinant, when $\hat{H}^{(0)}$ is naturally a one-body operator. If one aims to improve a multi-configurational wave function via PT, one may define a zero order Hamiltonian possessing multi-configurational eigenfunctions. Such a Hamiltonian is either formally defined by means of appropriate projectors[24, 29] or it should contain explicit two-body terms of type $\sum_{i<j} h_{ij}$ or $\frac{1}{2}\sum[\mu\nu|\lambda\sigma]a_\mu^+ a_\nu^+ a_\lambda a_\sigma$. The pioneering work in this direction by Dyall[155] was followed in Malrieu's [76, 156] and Mukherjee's[157, 158] laboratories. In our group, we have developed[159–163] a specific PT to perturb the antisymmetrized product of strongly orthogonal geminal[164] (APSG) wave function, where the geminals are eigenfunctions of an effective two-body Hamiltonian. Inclusion of explicit two-body terms is conceptually an appealing feature, but complicates the formalism significantly. Very recently, a promising idea has been expressed by Rassolov[165] who suggested to keep only certain terms of a two-body operator to form $\hat{H}^{(0)}$, leading to a much more effective construction of zero order excited states.

10. Optimized partitioning with multi-configurational zero order

10.1 Multi-configurational perturbation theory

For the perturbation of wave functions consisting of several Slater-determinants various MRPT approaches have been proposed[21–33]. We discuss here the one developed in our laboratory[147] which was termed multi-configurational perturbation theory (MCPT). Consider a normalized, multiconfigurational reference state $|0\rangle$ and the associated projector $\hat{O} = |0\rangle\langle0|$. The projector to the orthogonal complement space is $\hat{P} = 1 - \hat{O}$. Let us further introduce a set of determinants, denoted by $|K\rangle$, generated by applying single, double, etc. excitation operators on a Hartree-Fock-like determinant $|HF\rangle$, chosen as the 'principal' component of $|0\rangle$:

$$|0\rangle = d_0 |HF\rangle + \sum_{K=1} d_K |K\rangle.$$

Coefficient d_0 needs not be close to 1, merely the singular case $d_0 \sim 0$ is excluded.

The set of vectors $|0\rangle$ and $|K\rangle$ $(K = 1, 2, \ldots)$ forms a basis in the full M-dimensional vector space. Since vectors $|K\rangle$ form an orthonormal basis in the $M - 1$ dimensional subspace, and the reference function does not lie in this subspace for $d_0 \neq 0$, $|0\rangle$ and $|K\rangle$-s together span the full space.

One finds that $|0\rangle$ and $|K\rangle$ overlap. Projected determinants $|K'\rangle = \hat{P}|K\rangle = (1 - \hat{O})|K\rangle$ are orthogonal to the reference state, but overlap among themselves. The block structure of the full overlap matrix reads

$$\mathcal{S} = \begin{bmatrix} \langle 0|0\rangle & \langle 0|\hat{P}|L\rangle \\ \langle K|\hat{P}|0\rangle & \langle K|\hat{P}|L\rangle \end{bmatrix} = \begin{bmatrix} 1 & \mathbf{0} \\ \mathbf{0} & \mathbf{S} \end{bmatrix}$$

with the overlap matrix $\mathbf{S}$ of the projected excited determinants

$$S_{KL} = \langle K'|L'\rangle = \langle K|\hat{P}|L\rangle = \delta_{KL} - \langle K|0\rangle\langle 0|L\rangle = \delta_{KL} - d_K d_L.$$

where we used the Hermiticity and idempotency of $\hat{P}$.

The inverse of matrix $\mathbf{S}$ can be found analytically as

$$(S^{-1})_{KL} = \delta_{KL} + \frac{d_K d_L}{1 - \sum_{J=1} d_J^2} = \delta_{KL} + \frac{d_K d_L}{d_0^2},$$

facilitating a bi-orthogonal formulation through the reciprocal vectors $\langle \tilde{K}'|$:

$$\langle \tilde{K}'| = \sum_{J=1} (S^{-1})_{KJ}\langle J'| = \langle K'| + \frac{d_K}{d_0^2} \sum_{J=1} d_J \langle J'|,$$

and the definition of a non-Hermitian zero order Hamiltonian:

$$\hat{H}^{(0)} = E_0^{(0)} \, \hat{O} + \sum_{K=1} E_K^{(0)} \, |K'\rangle\langle\tilde{K}'|,$$

where $E_0^{(0)} = \langle 0|\hat{H}|0\rangle$ is the energy of the reference state. The zero order excited state energies $E_K^{(0)}$ are the parameters of the theory.

This definition of $\hat{H}^{(0)}$ possesses the properties $\hat{H}^{(0)}|0\rangle = E_0^{(0)}|0\rangle$ and $\hat{H}^{(0)}|K'\rangle = E_K^{(0)}|K'\rangle$. One can also see that the left eigenvectors are the reciprocal projected determinants $\langle\tilde{K}'|$, and the bra reference state $\langle 0|$.

The lowest order energy corrections, following standard bi-orthogonal perturbation theory, can be given as

$$E^{(1)} = \langle 0|\hat{W}|0\rangle \; = \; 0$$

with the perturbation operator $\hat{W} = \hat{H} - \hat{H}^{(0)}$,

$$E^{(2)} = -\langle 0|\hat{W}\hat{R}\hat{W}|0\rangle = -\sum_{K=1} \frac{\langle 0|\hat{W}|K'\rangle\langle\tilde{K}'|\hat{W}|0\rangle}{E_K^{(0)} - E_0^{(0)}}$$

$$
\begin{aligned}
E^{(3)} \;&=\; \langle 0|\hat{W}\hat{R}(\hat{W} - \langle\hat{W}\rangle)\hat{R}\hat{W}|0\rangle \\
&=\; \sum_{K,L=1} \frac{\langle 0|\hat{W}|K'\rangle\langle\tilde{K}'|\hat{W} - \langle\hat{W}\rangle|L'\rangle\langle\tilde{L}'|\hat{W}|0\rangle}{(E_K^{(0)} - E_0^{(0)})(E_L^{(0)} - E_0^{(0)})},
\end{aligned}
$$

etc.

Accuracy of low-order approximations as well as the convergence properties of the PT depend on how we choose the parameters $E_K^{(0)}$. Several possibilities for choosing these parameters will be listed below.

10.1.1   Generalized MP partitioning.   Following a Møller-Plesset-like philosophy one may specify $E_K^{(0)}$-s as

$$E_K^{(0)} = E_0^{(0)} + \Delta\varepsilon_K \qquad K = 1, 2, 3, \dots \tag{1.29}$$

where $\Delta\varepsilon_K$ are differences of suitably chosen one-particle energies:

$$\Delta\varepsilon_K = \begin{cases} \varepsilon_p - \varepsilon_a \\ \varepsilon_p + \varepsilon_q - \varepsilon_a - \varepsilon_b \\ \dots \end{cases}$$

for singles, doubles, etc. Several authors have applied such excitation energies in their formulations of MP-type MRPT[23–25, 27, 28, 30, 72, 74, 155, 166–170].

One-electron energies may be obtained as eigenvalues of a one-electron operator called multiconfiguration Fockian, which can be defined in two alternative forms[171]:

$$F_{ij}^1 = \langle 0|a_j^\dagger \left[a_i, \hat{H}\right]_- |0\rangle = \sum_k h_{ik}P_{kj} + \sum_{klm}[ik|lm]\Gamma_{lm,jk} \qquad (1.30)$$

or

$$F_{ij}^2 = \langle 0| \left[a_j^\dagger, \left[a_i, \hat{H}\right]_-\right]_+ |0\rangle = h_{ij} + \sum_{kl} P_{kl}[ik||jl] \qquad (1.31)$$

where subscripts $\pm$ indicate commutator $(-)$ or anticommutator $(+)$, P and Γ denote the first- and second-order density matrices. The usual notations are used for the one-electron integrals h_{ij}. The two expressions are not equivalent in general.

Both F^1 and F^2 have their own significance. Matrix F^1, called also the (negative) Koopmans matrix[171], is non-symmetric in general, its antisymmetric part giving rise to orbital gradients in MC-SCF theory [57, 171]. Matrix F^2 is always symmetric and can be considered as the generalization of the usual Fockian built up by the actual (correlated) density matrix P. The eigenvalues of both matrices can be interpreted as approximate ionization potentials[171]. Using the eigenvalues, we may speak about a generalized MP partitioning.

10.1.2   Generalized DK partitioning.   While the usual Fockian is diagonal in the MO basis set in HF theory, neither F^1 nor F^2 are diagonal in the multi-configurational case. It is hence also possible to use the diagonal elements of either F^1 or F^2 as one-particle energies. Defining just the diagonal elements as ε_i-s, one arrives at a partitioning, which resembles the DK partitioning discussed in Sect.1.8.1 To identify this possibility, we shall refer to it as the generalized Davidson-Kapuy (GDK) partitioning.

The advantage of the GDK partitioning from the computational point of view in the MC case is obvious. Namely, if using the eigenvalues of the Fockian (1.30) or (1.31), one has either to rewrite the reference state to the one-particle basis which diagonalizes these matrices, or deal with a non-diagonal $\hat{H}^{(0)}$, both of which is quite impractical.

10.1.3   Generalized Dyson partitioning.   A further possibility is to substitute Koopmans-type orbital energies in the PT denominators by correlation-corrected ionization potentials coming from, e.g., the Dyson equation in the MR case as well, in the same manner as described in section 1.8.2 for single reference PT. This interesting possibility has not yet been tested numerically.

Table 1.3. MCPT total energies of the Be atom in atomic units with various parti-
tionings. Basis set: 6-311G**, reference state: APSG[164]

HF	-14.57187		
APSG reference state	-14.59095		
	Epstein-Nesbet	GDK	MCPT-Opt
MCPT2	-14.61384	-14.62346	-14.63458
MCPT3	-14.60565	-14.62993	-14.63458
∞ (FCI)	-14.63337		

10.1.4 Generalized EN partitioning.

Instead of following a MP-type philosophy, one may also specify $E_K^{(0)}$ in the Epstein-Nesbet spirit[66, 67]. Several authors have investigated this possibility[70, 72, 73, 172–178]. Then, an alternative to Eq.(1.29) is

$$E_K^{(0)} = \langle K|\hat{H}|K\rangle.$$

However, in the spirit of the bi-orthogonal formulation of MCPT, it is more natural to define

$$E_K^{(0)} = \langle \tilde{K}'|\hat{H}|K'\rangle$$

which can be characterized as the generalized EN partitioning.

10.2 Optimized partitioning in multi-reference theories

10.2.1 Optimized partitioning in MCPT.

The zero order excitation energies $E_K^{(0)}$, which are parameters in MCPT, can also be determined variationally by Eq.(1.10), as it was discussed in Section 1.6.1. Alternatively, optimal $E_K^{(0)}$-s can be resulted from setting $E_K^{(3)'}$-s of (1.14) zero. These two conditions were shown to be equivalent for reference states constructed from a single configuration, while they give slightly different results in MCPT. The results of the partitioning optimization are illustrated in Table 1.3, where the latter condition was used.

10.2.2 Witek-Nakano-Hirao approach.

Witek et al.[179, 180] have also presented an optimally partitioned PT applied to Hirao's MRPT formalism. They have also used the equation $E_K^{(3)'} = 0$ as the condition of optimization, and noted that this is equivalent to setting $\Psi^{(2)} = 0$ in the new partitioning. They have shown that the second order result becomes identical to the multireference linearized coupled-cluster

(MR-LCCD) energy introduced by Laidig and Bartlett[181, 182]. This can be considered as the generalization of the theorem on the equivalence between optimal partitioning second order results and LCCD, shown in Section 1.7, to the MR case. It is worth to recall in this context that Davidson's Hylleraas variational MRPT[183] was also shown to be nearly equivalent to MR-LCCD.

10.2.3   Freed's otimization approach.   A simple and practical way of optimizing energy denominators in single- and multi-reference PT has been advocated by Freed and coworkers[184–186]. The essence of this approach is to consider a few low-lying states, solve the FCI problem in the basis formed by them, and select optimal zero order energies that minimze

$$|E_{\text{FCI}} - E^{(3)}| + |E_{\text{FCI}} - E^{(4)}|$$

where all quantities $E^{(4)}, E^{(3)}$ and E_{FCI} refer to the small model problem of low-lying states mentioned above. In a subsequent large calculation, the zero order energies corresponding to the small model space are selected as the optimized ones, while others, falling out of the model space, may correspond e.g. to the EN partitioning. This approach has been shown to work very well.

A different philosophy of selecting an appropriate partitioning was followed by Davidson and coworkers in their OPTn schemes[72, 187]. In these works, the partitioning was tuned by selecting an appropriate orbital basis.

Selecting suitable one-particle energies in an MP-type MRPT was also studied in Freed's group[188]. In their effective Hamiltonian method [21, 189–191], which belongs to the *'perturb then diagonalize'* type approaches[4], they have shown that high-preciosity results can be obtained starting from a MP type partitioning but introducing a democratic average of valence orbital energies obtained from V^{N-1} potentials[192–194]. The effective Hamiltonian method has been compared[188] to another *'perturb then diagonalize'* scheme, the so called intermediate Hamiltonian method[195], in which the proper choice of zero order energies is also an important issue[196–200].

---

[4]The term *'perturb then diagonalize'* expresses that one first forms an effective Hamiltonian of relatively low dimension by some perturbative approximation to Löwdin's partitioning technique, then diagonalizes this effective Hamiltonian to yield several eigenvalues. This approach can be contrasted to the *'diagonalize then perturb'* schemes, which the CASPT-type methods belong to. The latter methods set up first an active space and solve the FCI problem in it, then consider PT corrections to account for the effect of external states. Both type of methods are markedly different from the *'single but multi'* approach (a single reference state of multi-configurational character), such as MCPT.

11.   Minimizing the norm of RW

When repartitioning some original splitting of the Hamiltonian, one may think about utilizing the parameter for accelerating the convergence of the PT series. In fact, several repartitioning schemes have grown out of this idea, like that of Feenberg[105], Dietz et al.[128], or Goodson [121]. Here we present the idea emerged recently in our laboratory[60].

11.1   On the convergence of the PT series

The theory of Green functions provides a sufficient condition for the convergence of the PT series[20]. To recall this, consider the operator called the resolvent or the Green function (GF):

$$\hat{G}(z) = (z - \hat{H})^{-1}$$

where z is a complex scalar variable. The GF is an analytical function of z except for points where z coincides with an eigenvalue of $\hat{H}$, where it has a simple pole. Eigenvalues of $\hat{H}$ can be extracted from $\hat{G}(z)$ by a contour integration:

$$E_K^{(0)} = \frac{1}{2\pi i} \oint z \, \mathrm{Tr} \, \hat{G}(z) \, \mathrm{d}z \tag{1.32}$$

where the integration has to be performed on a path which contains exclusively the K-th (isolated) eigenvalue. This statement can be proved by inserting the spectral resolution of $\hat{H}$ and performing the integration via Cauchy's theorem for contour integrals.

If one splits the Hamiltonian to a zero-order part and a perturbation and defines

$$\hat{G}^{(0)}(z) = (z - \hat{H}^{(0)})^{-1}$$

as the GF of $\hat{H}^{(0)}$, than $\hat{G}(z)$ fulfills the relation

$$\hat{G}(z) = \hat{G}^{(0)}(z) + \hat{G}^{(0)}(z)\hat{W} \, \hat{G}(z) \tag{1.33}$$

which is called the (simple form of) Dyson equation[5]. This result is easily proved by multiplying Eq.(1.33) by the inverse of $\hat{G}^{(0)}(z)$ (from the left) and the inverse of $\hat{G}(z)$ (from the right), when simply the definition of the partitioning $\hat{H} = \hat{H}^{(0)} + \hat{W}$ is recovered.

---

[5]The true Dyson equation emerges after projecting Eq.(1.33) into a subspace; after this projection the simple perturbation operator $\hat{W}$ has to be replaced by a much more complicated self-energy operator[201].

The formal solution of Eq.(1.33)

$$\hat{G} = \left(1 - \hat{G}^{(0)}\hat{W}\right)^{-1}\hat{G}^{(0)}$$

can be expanded into a Taylor series to yield

$$\hat{G} = \hat{G}^{(0)} + \hat{G}^{(0)}\hat{W}\hat{G}^{(0)} + \hat{G}^{(0)}\hat{W}\hat{G}^{(0)}\hat{W}\hat{G}^{(0)} + \ldots \qquad (1.34)$$

Upon integrating this equation according to Eq.(1.32) on an appropriate contour term by term, one gets:

$$E_K = E_K^{(0)} + E_K^{(1)} + E_K^{(2)} + \ldots$$

Accordingly, the convergence of this series depends upon the validity of expansion (1.34) for all z values touched during the integration[6]. At a given z value, the convergence of Eq.(1.34) is known to depend on the norm of operator $\hat{G}^{(0)}\hat{W}$: if and only if $||\hat{G}^{(0)}(z)\hat{W}|| < 1$, the series is convergent. However, there is an infinite number of ways how an 'appropriate' contour can be set up, and finding the necessary and sufficient condition for convergence assumes that one has specified the most suitable path for the integration, which is usually unknown. Therefore, in practice, this observation yields only sufficient but not necessary criteria for the convergence of the PT series. The exact convergence conditions, necessary and sufficient, therefore, still remain unknown in the Rayleigh-Schrödinger perturbation theory.

11.2   The norm of RW

Apart from the problem of finding the most appropriate integration path, i.e. the appropriate z values, it is evident that quantity $||\hat{G}^{(0)}\hat{W}||$ plays a determining role in the problem of convergence.

Instead of $\hat{G}^{(0)}$, let us focus here on a related quantity, the reduced resolvent $\hat{R}$. This is defined for the ground state as

$$\hat{R}(E_0^{(0)} - \hat{H}^{(0)}) = 1 - |\Psi_0^{(0)}\rangle\langle\Psi_0^{(0)}|.$$

or can be given in spectral resolution as used in previous sections. Unlike $\hat{G}^{(0)}(z)$, $\hat{R}$ is regular if the ground state is non-degenerate in the zero-order spectrum. The role of the reduced resolvent in PT can be summarized by recalling the compact PT energy formulae at the lowest orders[202]:

$$E^{(2)} = \langle\hat{W}\hat{R}\hat{W}\rangle$$

---

[6]This contour should embed the K-th pole of both $\hat{G}$ and $\hat{G}^{(0)}$

$$E^{(3)} = \langle \hat{W}\hat{R}(\hat{W} - \langle\hat{W}\rangle)\hat{R}\hat{W}\rangle$$

etc. The PT corrections are constructed from the powers of operator $\hat{R}\hat{W}$. A natural idea appears therefore to minimize the square norm of this operator, $||\hat{R}\hat{W}||^2$ with respect to any free parameters that are at our disposal.

As free level shift parameters can always be introduced in PT, these can be utilized to minimize $||\hat{R}\hat{W}||^2$. For this purpose one first has to choose a norm in the operator space. Let us define the norm of operator A as

$$||A||^2 = \mathrm{Tr}\ (AA^\dagger),$$

expanding in a basis set representation

$$||A||^2 = \sum_{IK} A_{IK}A_{IK}^* = \sum_{IK} |A_{IK}|^2,$$

which is the two-norm or Frobenius norm in matrix theory.

Evaluating $||\hat{R}\hat{W}||^2$ with this definition, we get:

$$
\begin{aligned}
||\hat{R}\hat{W}||^2 &= \sum_{IK}\langle I|\hat{R}\hat{W}|K\rangle\langle K|\hat{W}\hat{R}|I\rangle = \sum_I \langle I|\hat{R}\hat{W}^2\hat{R}|I\rangle \\
&= \sum_{I\neq 0} \frac{\langle I|\hat{W}^2|I\rangle}{(E_I^{(0)} - E_0^{(0)})^2},
\end{aligned}
$$

where the resolution of identity was used to get rid of the summation over K. Applying level shifts (1.4) we get

$$||\hat{R}\hat{W}'||^2 = \sum_{I\neq 0} \frac{\langle I|\hat{W}^2|I\rangle - 2\eta_I\langle I|\hat{W}|I\rangle + \eta_I^2}{(E_I^{(0)} - E_0^{(0)} + \eta_I)^2}$$

where the level shift of the ground state, η_0, was set zero to fix the energy origin.

To determine η_I values that are optimal in this sense, we require

$$\frac{\partial}{\partial\eta_K}||\hat{R}\hat{W}'||^2 = 0,$$

which yields

$$\eta_K = \frac{\langle K|\hat{W}^2|K\rangle + \langle K|\hat{W}|K\rangle(E_K^{(0)} - E_0^{(0)})}{\langle K|\hat{W}|K\rangle + (E_K^{(0)} - E_0^{(0)})}. \qquad (1.35)$$

In what follows, level shifts obtained from this relation will be identified as RW-optimized ones. Similarly, the partitioning defined by them will be referred to as RW-optimized (shortly: RW-opt) partitioning.

Figures 1.13 and 1.14 illustrate the effect of RW-optimization on the anharmonic oscillator. Note that the PT is divergent both in the standard and EN partitionings, while it turns out to be nicely convergent in the RW-opt case.
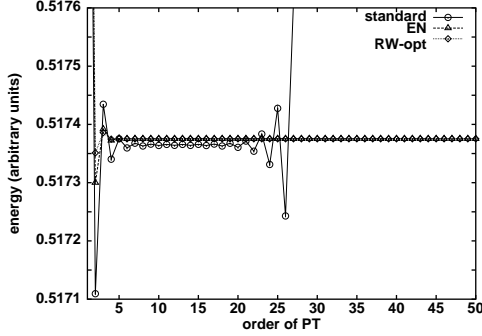

Figure 1.13. Convergence of the perturbed energies of the quartic anharmonic oscillator up to the 50th order for weak coupling constant $\lambda = 0.025$
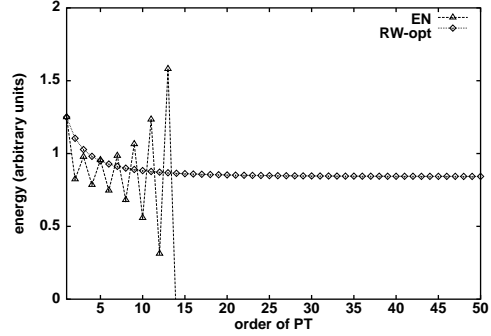
Figure 1.14. The same as for Fig.1.13, but with a larger value $\lambda = 1.0$

11.3 Properties of the RW-optimized partitioning

11.3.1 Uniqueness. The RW-opt partitioning is unique, i.e., the resulting shifted denominators do not depend on the initial partitioning. To see this, evaluate the shifted denominators

$$
\begin{aligned}
\Delta_K + \eta_K &= \Delta_K + \frac{W_{KK}^2 + W_{KK}\Delta_K}{W_{KK} + \Delta_K} \\
&= \frac{\Delta_K^2 + W_{KK}^2 + 2W_{KK}\Delta_K}{W_{KK} + \Delta_K} \\
&= \frac{(W_{KK} + \Delta_K)^2 - (W_{KK})^2 + W_{KK}^2}{W_{KK} + \Delta_K} \\
&= W_{KK} + \Delta_K + \frac{\langle W_{KK}^2 \rangle_c}{W_{KK} + \Delta_K}
\end{aligned}
$$

where the abbreviation $W_{KK}^2 = \langle K|\hat{W}^2|K \rangle$ and the second connected moments of the perturbation operator,

$$
\langle W_{KK}^2 \rangle_c = W_{KK}^2 - (W_{KK})^2
$$

are introduced. To arrive at our final formula for the shifted denominators, we observe that

$$W_{KK} + \Delta_K = H_{KK} - E_0^{(0)},$$

by which the shifted energy denominators become

$$\Delta_K + \eta_K = H_{KK} - E_0^{(0)} + \frac{\langle W_{KK}^2 \rangle_c}{H_{KK} - E_0^{(0)}}. \qquad (1.36)$$

Here both $H_{KK} - E_0^{(0)}$ and the connected moments $\langle W_{KK}^2 \rangle_c$ are independent of the initial partitioning[7]. Therefore we see that the RW-optimization results uniquely defined energy denominators.

11.3.2   Uncoupled nature.   A second property of the RW-opt partitioning can be inferred from (1.35) or (1.36) observing that these formulae do not present explicit coupling between the states K. (There is, however, an implicit coupling expressed by the presence of the square of $\hat{W}$ in the connected moments.) This uncoupled nature of RW-optimization makes it markedly different from the energy-optimized partitionings discussed in Sections 1.6-1.10, where the coupling between different states represents a serious computational difficulty. The simplicity exhibited by Eqs. (1.35) or (1.36) is a great advantage from the computational point of view, but gives a warning that the power of this simple optimization might not be strong enough.

The same conclusion is supported by the observation that the RW-opt denominators lie quite close to the EN denominators. The reason is that if $W_{00} = 0$, the EN partitioning results from Eq.(1.36) simply by neglecting the (usually quite small) second connected moments of $\hat{W}$. The results obtained in the RW-opt partitioning for modest perturbations will thus be close to those of the EN partitioning. Moreover, since the correction term $\langle W_{KK}^2 \rangle_c / (H_{KK} - E_0^{(0)})$ is always positive, the RW-opt denominators are slightly larger than the EN ones. Thus, low-order corrections are expected to be in absolute value smaller in RW-opt partitioning as compared with EN corrections. The difference between the EN and RW-opt partitionings is therefore expected to be major if the perturbation is strong, i.e., if $\langle \hat{W}_{KK}^2 \rangle_c$-s are large. In these cases RW-optimization appears to be a promising tool.

---

[7]With no loss of generality, one can choose $W_{00} = 0$. This can always be achieved – without affecting the partitioning – by a simple shift of the origin of the energy scale. Then, $E_0^{(0)} = H_{00}$ which clearly expresses a partitioning independence of Eq.(1.36).

11.3.3 Degeneracy elimination. An interesting property of the RW-opt partitioning is associated with the fact that all shifted denominators are definitely positive. This is because $(H_{KK} - E_0^{(0)}) \geq 0$ by definition and the second connected moments $\langle W_{KK}^2 \rangle_c$ are always positive quantities (these moments are zero if and only if evaluated with an exact eigenfunction of H, when all PT corrections are zero anyway). Accordingly, any possible degeneracy of the zero-order spectrum will be lifted upon RW-optimization. To have a closer look into the degeneracy problem, let us evaluate the limit of the second-order RW-opt correction when a state K becomes degenerate with the ground state, i.e., when $\Delta_K = E_K^{(0)} - E_0^{(0)} = 0$ for some K. This leads to the shifted denominator (c.f (1.35)):

$$W_{KK}^2/(W_{KK})^2,$$

which is a regular expression for nonzero W_{KK}.

In the special case when the initial partitioning is the EN one, i.e. $W_{KK} = 0$, the shifted denominator diverges thereby eliminating the contribution of level K. This is not the accurate result that would be obtained from degenerate PT, but it is certainly a better estimate than the divergent energy of non-degenerate PT. The result of RW-opt partitioning in such a degenerate limit will be the elimination of the effect of degenerate levels, a damping of quasi-degeneracies, while summing up slightly modified EN-type contributions from non-degenerate states. To see how it works in practice, numerical studies will be necessary.

12. Constant denominator PT

12.1 Unsøld approximation

With the aim to extract PT formulae in the so called Unsøld approximation that uses averaged energy denominators, let us define a zero order Hamiltonian[203]

$$\hat{H}^{(0)} = E^{(0)}\hat{O} + \nu\hat{P}. \tag{1.37}$$

Here ν stands for a constant or 'averaged' value of excited energy levels, thus $\nu - E^{(0)}$ is an Unsøld type excitation energy. The reduced resolvent has therefore the form

$$\hat{R} = -\frac{\hat{P}}{\nu - E^{(0)}}$$

leading to the second and third order PT corrections

$$E_{\text{Unsøld}}^{(2)} = -\frac{\langle 0|\hat{W}\hat{P}\hat{W}|0\rangle}{\nu - E^{(0)}} = -\frac{\langle \hat{W}^2 \rangle_c}{\omega} = -\frac{\langle \hat{H}^2 \rangle_c}{\omega}$$

$$E_{\mathrm{Unsøld}}^{(3)} = \frac{\langle 0|\hat{W}\hat{P}(\hat{W} - W_{00})\hat{P}\hat{W}|0\rangle}{(\nu - E^{(0)})^2} = \frac{\langle \hat{W}^3\rangle_c}{\omega^2} = -\frac{\langle \hat{H}^2\rangle_c}{\omega} + \frac{\langle \hat{H}^3\rangle_c}{\omega^2}$$

where $\omega = \nu - E^{(0)}$ is the averaged excitation energy, and $\langle \hat{H}^n\rangle_c$ is the n-th connected moment of the Hamiltonian[204] defined recursively

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

Similar formulae can be put down at the higher orders.

12.2   Optimized Unsøld approximation: CMX2

Among numerous possible ways to determine ν, here we choose the one that makes use of the concept of optimized partitioning. We may consider ν as a level shift parameter, as it can be seen if regrouping the terms of the Hamiltonian as

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

where both the zero order operator Eq.(1.37) 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.

Parameter ν is now state-independent, which represents a substantial simplification. Zeroing th derivative of $(E_{\mathrm{Unsøld}}^{(2)} + E_{\mathrm{Unsøld}}^{(3)})$ with respect to ν, one arrives at[205]

$$\nu = E^{(0)} + \frac{\langle \hat{H}^3\rangle_c}{\langle \hat{H}^2\rangle_c} \tag{1.38}$$

This optimized averaged energy is now to be substituted into the PT correction formulae to yield

$$E_{opt}^{(2)} = -\frac{\langle \hat{H}^2\rangle_c^2}{\langle \hat{H}^3\rangle_c} \tag{1.39}$$

$$E_{opt}^{(3)} = 0 \tag{1.40}$$

That is, the third order energy correction in the optimized partitioning is zero, in agreement with the general result[150].

Determination of parameter ν 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[206]. 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.

The second and third order Unsøld formulae (1.39) and (1.40) can be compared to those resulting from the connected moment expansion (CMX)[207]. The CMX expansion is a non-perturbative technique to approach the exact energy. The lowest order corrections read[207]

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

It is apparent that the second order optimized Unsøld approximation coincides with the CMX2 energy, the latter can therefore be considered as a constant denominator PT result with optimized partitioning. The
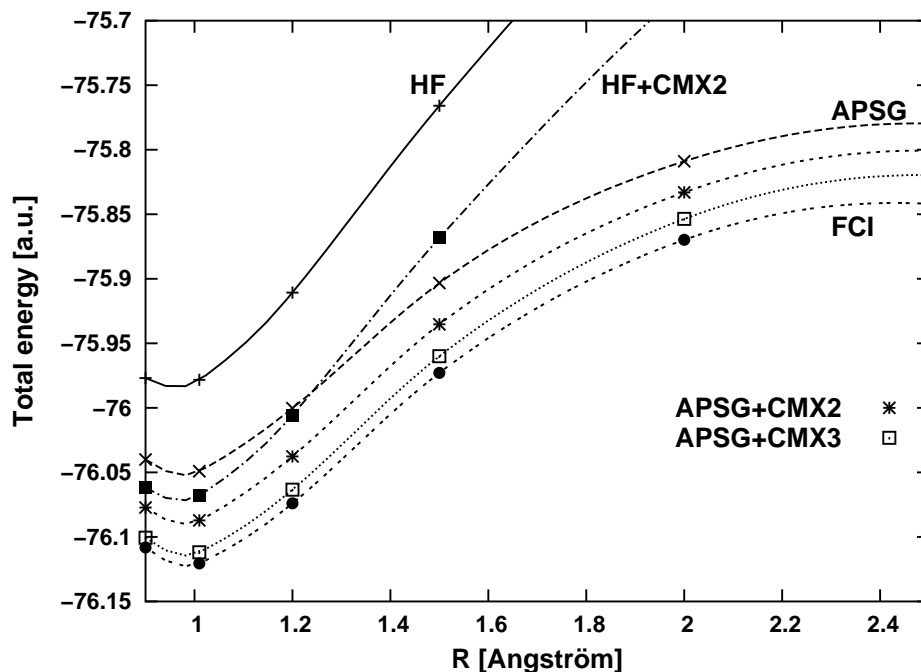

Figure 1.15. Potential curve of H_2O in comparison with FCI

third order CMX correction, however, is not zero, and it often represents a considerable improvement. This is illustrated on the example of the symmetric dissociation curve of the water molecule in 6-31G basis set, where the CMX correction is shown as applied to the Hartree-Fock (HF) and the antisymmetrized product of strongly orthogonal geminal[164] (APSG) approximations.

13.   Perturbation corrections to ionization energies

The optimized partitioning elaborated above can also be used when calculating ionization potentials perturbatively[8]. Energy differences like excitation energies and ionization potentials (IPs) can be obtained from the equation-of-motion[209, 210]

$$[\hat{H},\hat{\Omega}] \; = \; \omega\hat{\Omega} \qquad\qquad (1.41)$$

that holds for the ionization (excitation) operator $\hat{\Omega}$ connecting two eigenstates of $\hat{H}$, Ψ_0 and Ψ_K, by

$$\hat{\Omega}\Psi_0 \; = \; \Psi_K \; .$$

The ionization energy is $\omega = E_K - E_0$. Introducing the "super" Hamiltonian or Liouvillean $\mathcal{H}$ defined by its action on any operator $\hat{A}$ being $\mathcal{H}\hat{A} \; = \; [\hat{H},\hat{A}]$, one may rewrite Eq.(1.41) as [211–213]

$$\mathcal{H}\hat{\Omega} \; = \; \omega\hat{\Omega} \; . \qquad\qquad (1.42)$$

Ionization operators are thus eigenfunctions of a superoperator defined over ordinary operators, and one gets the corresponding ionization energy as an eigenvalue.

To apply standard approximations to the solution of this eigenvalue problem, one needs a scalar product $(.|.)$ among the operators that constitute the domain of $\mathcal{H}$. Accordingly, bra- and ket vectors of the operator space are identified as $(.|$ and $|.)$.

To obtain a perturbative series for ω, the super Hamiltonian is split for a zero order superoperator and a perturbation

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{W}$$

and it is supposed that the solutions of the zero order problem

$$\mathcal{H}^{(0)}|\hat{\Omega}^{(0)}) \; = \; \omega^{(0)}|\hat{\Omega}^{(0)})$$

---

[8]An early, substantial paper on the perturbative calculation of ionization potentials was written bu Hubač and Urban[208].

are known. Expanding the exact ionization energy ω to a Brillouin-Wigner perturbation series one gets the "super" counterpart of the well known sequence[2]:

$$\omega = \omega^{(0)} + (\hat{\Omega}^{(0)}|\mathcal{W}|\hat{\Omega}^{(0)}) + (\hat{\Omega}^{(0)}|\mathcal{W}\mathcal{R}^{(0)}(\omega)\mathcal{W}|\hat{\Omega}^{(0)}) + \dots \quad (1.43)$$

where the reduced resolvent is defined so that

$$\mathcal{R}^{(0)}\left(\omega^{(0)} - \mathcal{H}^{(0)}\right) = I - O$$

with

$$O = |\hat{\Omega}^{(0)})(\hat{\Omega}^{(0)}|$$

and the unity superoperator acting as

$$I\hat{A} = \hat{A} \ .$$

A suitable approximation to the IPs is given by the Koopmans approximation[148], which is recovered at zero order if specifying the zero order superoperator as

$$\mathcal{H}^{(0)} = \mathcal{F} .$$

Here $\mathcal{F}$ is defined by $\mathcal{F}\hat{A} = [\hat{F}, \hat{A}]$, and $\hat{F}$ denotes the Fockian of the neutral molecule.

Since any product of second quantized creation and annihilation operators (corresponding to the MOs of the neutral molecule) is an eigenoperator of $\mathcal{F}$, the zero order solution for the ionization from the ith canonical orbital looks:

$$\mathcal{F}|a_i) = -\varepsilon_i|a_i) \ .$$

The above specification of $\mathcal{H}^{(0)}$ therefore involves $\omega^{(0)} = -\varepsilon_i$ and $O = |a_i)(a_i| \ .$

13.1   The ionization operators' subspace

To proceed further the scalar product and the superoperator of unity has to be specified more in detail.

For any operator describing single ionization like

$$a_p, \quad a_p^\dagger a_q a_r, \quad a_p^\dagger a_q^\dagger a_r a_s a_t, \quad \text{etc.} \quad (1.44)$$

the binary product can most simply be [212, 214]

$$(\hat{A}|\hat{B}) = \langle HF|[\hat{A}^\dagger, \hat{B}]_+|HF\rangle \quad (1.45)$$

where $|HF\rangle$ corresponds to the neutral system[9]. In order that the product of Eq.(1.45) becomes a scalar product in the strict sense, the operators having zero norm have to be excluded from those listed in (1.44). Furthermore, it is useful to select an orthonormal set with respect to (1.45) among the operators in (1.44). This is usually achieved by devising the following subset of (1.44)[214]:

$$
\{a_j\} \cup \{a_b\} \cup \{a_j^\dagger\, a_b\, a_c | b > c\} \cup \{a_b^\dagger\, a_j\, a_k | j > k\}
$$

$$
\cup\ \{a_j^\dagger a_k^\dagger\, a_b\, a_c\, a_d | j{>}k,\ b{>}c{>}d\} \cup \{a_b^\dagger a_c^\dagger\, a_j\, a_k\, a_l | b{>}c,\ j{>}k{>}l\} \cup \ldots \quad (1.46)
$$

Having an orthonormal set of single ionization operators, the spectral resolution of the identity superoperator can be put down as:

$$
\begin{aligned}
I \;=\;& \sum_p |a_p)(a_p|\ +\ \sum_{\substack{pqr \\ (q>r)}} N_{p,qr}^+ |a_{p,qr})(a_{p,qr}| \\
&+\ \sum_{\substack{pqrst \\ (p>q,r>s>t)}} N_{pq,rst}^+ |a_{pq,rst})(a_{pq,rst}|\ +\ \ldots
\end{aligned}
$$

with the shorthands

$$
a_{p,qr} = a_p^\dagger\, a_q a_r\ , \qquad\qquad a_{pq,rst} = a_p^\dagger a_q^\dagger\, a_r a_s a_t\ ,
$$

$$
N_{p,qr}^+ = \left(n_p\, \overline{n}_q \overline{n}_r + \overline{n}_p\, n_q n_r \right)\ ,
$$

$$
N_{pq,rst}^+ = \left(n_p n_q\, \overline{n}_r \overline{n}_s \overline{n}_t + \overline{n}_p \overline{n}_q\, n_r n_s n_t \right)\ ,
$$

n_p denoting the occupation number, and $\overline{n}_p = 1 - n_p$.

13.2 PT formulae for single ionization

The fact that basis vectors in (1.46) are eigenvectors of $\mathcal{F}$, permits to compose the spectral form of superoperators $\mathcal{F}$ and $\mathcal{R}^{(0)}(z)$ as:

$$
\mathcal{F} \;=\; \sum_p (-\epsilon_p)|a_p)(a_p| + \sum_{\substack{pqr \\ (q>r)}} (\epsilon_p - \epsilon_q - \epsilon_r)|a_{p,qr})(a_{p,qr}| N_{p,qr}^+ + \ldots \quad (1.47)
$$

and

$$
\mathcal{R}^{(0)}(z) \;=\; \sum_{p \ne i} \frac{|a_p)(a_p|}{z + \epsilon_p} + \sum_{\substack{pqr \\ (q>r)}} \frac{|a_{p,qr})(a_{p,qr}|}{z - \epsilon_p + \epsilon_q + \epsilon_r} N_{p,qr}^+ + \ldots \quad (1.48)
$$

---

[9]In this section the orbital labeling follows the convention: $a, b, \ldots$ virtual, $i, j, \ldots$ occupied, $p, q, \ldots$ generic.

where $P = I - |a_i)(a_i|$ was utilized for getting the latter expression. Substituting Eq.(1.47) and Eq.(1.48) into the PT correction terms of Eq.(1.43) one finds:

$$\omega_i^{(2)} = (a_i|\mathcal{W}\mathcal{R}^{(0)}(\omega_i)\mathcal{W}|a_i) = \sum_{\substack{pqr \\ (q>r)}} \frac{(a_i|\mathcal{W}a_{p,qr})(a_{p,qr}|\mathcal{W}a_i)}{\omega_i - \epsilon_p + \epsilon_q + \epsilon_r} N_{p,qr}^+ \quad (1.49)$$

for the second order term, and

$$
\begin{aligned}
\omega_i^{(3)} &= (a_i|\mathcal{W}\mathcal{R}^{(0)}(\omega_i)\mathcal{W}\mathcal{R}^{(0)}(\omega_i)\mathcal{W}|a_i) \\
&= \sum_{\substack{pqr \\ (q>r)}} \left[\sum_{\substack{stu \\ (t>u)}} \frac{(a_i|\mathcal{W}a_{s,tu})(a_{s,tu}|\mathcal{W}a_{p,qr})}{\omega_i - \epsilon_s + \epsilon_t + \epsilon_u} N_{s,tu}^+ \right. \\
&\quad \left. + \sum_{\substack{stuvx \\ (s>t,\ u>v>x)}} \frac{(a_i|\mathcal{W}a_{st,uvx})(a_{st,uvx}|\mathcal{W}a_{p,qr})}{\omega_i - \epsilon_s - \epsilon_t + \epsilon_u + \epsilon_v + \epsilon_x} N_{st,uvx}^+ \right] \times \\
&\quad \times \frac{(a_{p,qr}|\mathcal{W}a_i)}{\omega_i - \epsilon_p + \epsilon_q + \epsilon_r} N_{p,qr}^+ \quad (1.50)
\end{aligned}
$$

for the third order term.

Formulae (1.49) and (1.50) are relatively simple since only three operators' product contribute at maximum to the second order expression, while only five operators' product to the third order correction. No higher operators' product from (1.48) appear, due to the rank reducing nature of the commutator, which has the effect that matrix elements like $(a_{pq,rst}|\mathcal{W}a_i)$ or $(a_{stu,vxyz}|\mathcal{W}a_{p,qr})$ are all zero. Interestingly $(a_{p,qr}|\mathcal{W}a_{st,uvx})$ is also zero, but not $(a_{st,uvx}|\mathcal{W}a_{p,qr})$, showing that $\mathcal{W}$ is a non-hermitian operator if the scalar product is defined as above.

Utilizing the basic anticommutation rules, the second order correction of Eq.(1.49) is found to be identical with the ordinary second order Dyson correction or Born collision[95, 212, 215] for the IPs.

It may also be simply verified that

$$(a_p|\mathcal{W}a_q) = 0$$

in the canonical basis, consequently the first order correction in Eq.(1.43) vanishes. The fact that

$$\omega_i = -\epsilon_i + \mathcal{O}(2)$$

may be interpreted as the formulation of Koopmans' theorem[148] in this framework.

13.3   Optimal level shifts for the ionization potential

The second order Dyson correction to the ionization potential, Eq.(1.49) is known to perform poorly[216, 217], and a great deal of effort has been put into going beyond this approximation. Some studies proposed to include at least certain terms of the third order[218, 219], others applied a wave function corrected for electron correlation in Eq.(1.45), instead of the Fermi vacuum indicated there. The idea of modifying the expression of the binary product was investigated[220–223]. Level shifts have also been used to affect the convergence, and consequently alter the performance of low order approximations[215].

Another way to step beyond Eq.(1.49) is to apply a strategy different from a simple PT. For example, Green's functions techniques that use non-diagonal approximation of the self energy matrix fall into this category[217, 222–224].

In this section we apply a simple level shift of the form

$$
\mathcal{H}^{0'} = \mathcal{F} - \sum_{\substack{pqr \\ (q>r)}} \lambda_{p,qr} |a_{p,qr})(a_{p,qr}| N^+_{p,qr}
$$

$$
\mathcal{W}' = \mathcal{W} + \sum_{\substack{pqr \\ (q>r)}} \lambda_{p,qr} |a_{p,qr})(a_{p,qr}| N^+_{p,qr}
$$

and determine $\lambda_{p,qr}$ in the spirit of the optimized partitioning. Rewriting Eq.(1.50) for the primed partitioning, and equating it zero term by term, one is lead to:

$$
\sum_{\substack{stu \\ (t>u)}} \frac{(a_i|\mathcal{W}a_{s,tu})(a_{s,tu}|\mathcal{W}'a_{p,qr})}{-\epsilon_i - \epsilon_s + \epsilon_t + \epsilon_u + \lambda_{s,tu}} N^+_{s,tu}
$$

$$
+ \sum_{\substack{stuvx \\ (s>t,\ u>v>x)}} \frac{(a_i|\mathcal{W}a_{st,uvx})(a_{st,uvx}|\mathcal{W}a_{p,qr})}{-\epsilon_i - \epsilon_s - \epsilon_t + \epsilon_u + \epsilon_v + \epsilon_x} N^+_{st,uvx} = 0 \quad (1.51)
$$

for each pqr, $q > r$, $((p \in occ) \wedge (q, r \in virt)) \vee ((p \in virt) \wedge (q, r \in occ))$. Rearranging Eq.(1.51) and neglecting the term arising from five operators' product one gets:

$$
\sum_{\substack{stu \\ (t>u)}} \frac{\left[\delta_{sp}\delta_{tq}\delta_{ur}\Delta^{ip}_{qr} - \frac{(a_i|\mathcal{W}a_{s,tu})(a_{s,tu}|\mathcal{W}a_{p,qr})}{(a_i|\mathcal{W}a_{p,qr})}\right] N^+_{s,tu}}{\Delta^{is}_{tu} + \lambda_{s,tu}} = N^+_{p,qr} \quad (1.52)
$$

which is a linear inhomogeneous system of equations for $1/(\Delta^{is}_{tu} + \lambda_{s,tu})$ with $\Delta^{is}_{tu} = -\epsilon_i - \epsilon_s + \epsilon_t + \epsilon_u$. Note, that level shifts defined by the

criterion (1.51) depend on index i. This means that to each ionization potential there is a different set of level shift parameters that set the third order correction to zero.

Table 1.4. The first ionization potentials in atomic units for the H_2O molecule, at geometry R_{OH}=0.96 Å, $\alpha(HOH) = 105^o$ and for the N_2 molecule at R_{NN}=1.1 Å. Koopmans values and perturbative approximations, such as second order Dyson correction (DY2), shifted Born collision (SBC), and shifted second order Dyson correction with shifts got from Eq.(1.52) (OPTDY2) are tabulated. The so-called EOMIP results, got with using the CCSD wave function are given for comparison.

basis	FCI	EOMIP	Koopmans	DY2	SBC	OPTDY2
			H_2O molecule			
STO-3G	.317	.308	.391	.303	.282	.299
6-31G	.436	.427	.501	.398	.387	.417
6-311G**		.442	.499	.410	.404	.429
			N_2 molecule			
6-31G		.544	.629	.529	.498	.545
6-31G**		.562	.630	.545	.522	.557

To illustrate the effect of these shift parameters, a few numbers are collected into Table 1.4 relating the first ionization potentials of the water and nitrogen molecules computed by various methods. Acronym SBC in the table refers to the so-called shifted Born collision approximation [215], that is obtained if neglecting of diagonal matrix elements of superoperator $\mathcal{W}$, which gives just the EN partitioning in this framework. On the basis of the numbers presented, one can conclude that level-shift optimization does improve upon the second order Dyson approximation and also on SBC values. However, more thorough studies should be carried out to investigate the reliability of the optimized second order correction for IPs.

Finally, let's mention that the electron attachment can be dealt with in a very similar manner. Carrying out the derivation one is led to just the same structure for the PT corrections as Eq.(1.49), Eq.(1.50) with signs reversed. The same holds for the PT terms of the level shifted partitioning, if shift parameters are introduced with proper signs.

Acknowledgments

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