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Near-degeneracy corrections for second-order perturbation theory: comparison of two approaches

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Abstract. We compare two approximate perturbation schemes which were developed recently to deal with the (quasi)degeneracy problem in many-body perturbation theory. We conclude that although the two methods were introduced on quite different theoretical grounds, their performances are quite similar, and present an improvement over traditional perturbation theory. Both methods are cheap in computation time, but cannot compete in accuracy with more sophisticated schemes such as complete-active-space perturbation theory or dressed particle theories.

Key words: Many-body perturbation theory (MBPT) – Second order perturbation theory – Correlation energy – Quasidegeneracy – Epstein–Nesbet partitioning

1 Introduction

Perturbation theory (PT) is an efficient tool to compute electronic correlation energies and many other kinds of weak interactions in various fields. Although this theory does not give an upper bound to the total energy, it presents numerous advantages (conceptual and practical simplicity, ability of giving size-consistent results, invariance under unitary transformations, analytical first and second derivatives), and is therefore widely used. By limiting the perturbational treatment to second order only, one has to fulfill two requirements for the applicability of nondegenerate PT: the interactions (perturbation terms) should be small and the energy difference between the reference state and the lowest excited state should not be small. When the second condition is not met, we face the quasidegenerate (or near-degeneracy) problem which is responsible, for example, for the bad behavior of low-order PT for describing molecular dissociation [1]. While the problem of exact degeneracy (zero-energy denominators) can be treated by standard techniques, quasidegenerate cases must receive particular attention [2–5].

Even if many other more sophisticated methods [coupled cluster, complete active space (CAS), CASPT, multireference (MR)PT, MR configuration interaction (CI), ...] can be free of this problem, they are far more expensive in computer time and only applicable to small molecular systems. In this article we focus our attention only on single-determinant-based second-order PT (PT2). In 1995, two different schemes were proposed independently to extend the validity of PT2 to handle the problem of quasidegeneracy. One, called degeneracy-corrected PT second order (DCPT2) [6], was first applied by Kuhler et al. [7] in the quantum theory of molecular vibrations. The second one borrowed an idea from optical spectroscopy, where damping factors are used to avoid singularities, and was named quasidegenerate PT second order (QDPT2) [8, 9]. These methods have many common features: a single determinantal Hartree–Fock reference state, uncoupled excited states, both require the calculation of the same terms as traditional PT2. Therefore, the computational cost is very similar for DCPT2, QDPT2 and traditional PT2. They are also very easily implemented in any quantum chemical package which can perform PT2 computations. Moreover, since they do not require the calculation of any other terms, gradients and Hessians can easily be reached.

The theoretical backgrounds of the two schemes are briefly summarized in the following section. We compare the performances of these two different schemes on a set of chosen molecular systems within the Møller–Plesset (MP) partitioning [10] in Sect. 3. A study on the H_2 molecule will apply the Epstein–Nesbet (EN) partitioning [11, 12] as well. The behavior of the two approaches at intermediate interatomic distances will be analyzed in some detail.

Prior to publishing the two schemes discussed earlier, in 1993, Lepetit and Malrieu [13] proposed an ingenious method, a bit more sophisticated than DCPT,

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in which the diagonal elements of the 2×2 matrices were “dressed” by incorporating higher-order effects (EPV terms). Since the dressing involves the eigenvectors of the 2×2 matrices, it requires an iterative procedure.

2 Theoretical background

The Rayleigh–Schrödinger (RS) PT2 gives the traditional formula for one contribution:

$$E_k^{(2)} = -\frac{|W_{0k}|^2}{E_k - E_0} \ , \tag{1}$$

where W_{0k} represents the matrix element of the perturbation between the ground state (referred to with the subscript 0) and an excited state (labeled with the letter k), E_0 and E_k are the zero-order energies of the two states. The structure of Eq. (1) clearly shows that as E_k approaches E_0 this term tends to infinity, thus producing an unreliable PT correction. Two simple methods for correcting this phenomenon are discussed later.

As previously mentioned, DCPT2 originated from the quantum theory of molecular vibration and was also applied to electronic structure calculations. The idea behind it is simple: given a two-level system, the RS perturbation series can be exactly summed leading to the infinite-order result for level k:

$$E_k^{\mathrm{DCPT2}} = \frac{1}{2}\left(E_{k0} - \sqrt{E_{k0}^2 + 4|W_{0k}|^2}\right) \ , \tag{2}$$

where E_{k0} is the energy difference between the two states, which does not contain any energy denominator and is thus clearly applicable in a quasidegenerate situation as well. Applying this formula for a multilevel system, one simply sums over all states,

$$E_{\mathrm{DCPT2}}^{(2)} = \frac{1}{2}\sum_k \left(E_{k0} - \sqrt{E_{k0}^2 + 4|W_{0k}|^2}\right) \ , \tag{3}$$

which evidently involves the approximation that the interaction of the ground state with various excited states is treated independently, i.e., no coupling between excited states is accounted for. This approximation is in agreement with the general spirit of a second-order theory.

In the QDPT2 method, one also starts from a two-level model system, for which a complex level shift parameter is introduced,

$$E_k^{(2)} = -\frac{|W_{0k}|^2}{E_{k0} + i\Gamma_k} \ , \tag{4}$$

where k refers to the excited state. With the aim of having real corrections for any Γ_k, we take the absolute value of Eq. (4):

$$E_k^{\mathrm{QDPT2}} = -\frac{|W_{0k}|^2}{\sqrt{E_{k0}^2 + \Gamma_k^2}} \ . \tag{5}$$

The determination of the parameter Γ_k can be made either by requiring that Eq. (5) be exact for the fully degenerate limit, $E_k = E_0$, or by demanding that an expansion of the square root in Eq. (5) produce the fourth-order contribution with the same coefficient as would emerge in fourth-order RSPT [14]. The resulting parameter is $\Gamma_k = W_{0k}$ in the former case, while it is $\Gamma_k = 2W_{0k}$ if the latter criterion is applied.

Previous numerical studies [14, 15] suggest that the choice $\Gamma_k = 2W_{0k}$ is more appropriate for many cases, but then, of course, the formula will not be exact in the completely degenerate limit. By choosing $\Gamma_k = W_{0k}$, the QDPT2 and the DCPT2 methods go to the same degenerate limit.

Going to multilevel systems, one keeps the structure of the previous equation and simply sums to all excited levels:

$$E_{\mathrm{QDPT2}}^{(2)} = -\sum_k \frac{|W_{0k}|^2}{\sqrt{(E_k - E_0)^2 + \Gamma_k^2}} \ . \tag{6}$$

In a multilevel system, an apparent disadvantage of Eq. (6) is that it is not invariant to unitary transformations within degenerate subsets of excited states. This problem can, in principle, be avoided by using averaged Γ values for degenerate subsets. In practice, however, we have found it more appropriate to fix the degenerate vectors in a unique manner. For example, in the orbital form of Eq. (6), we apply a localization transformation for degenerate subsets of molecular orbitals (MOs), which then keeps the size extensivity of the results.[1]

An advantage of the damping procedure described here is that it is not restricted to second-order effects: third-order correlation energies can also be evaluated in a straightforward manner [8, 9]. If it is not the lowest state that is accounted for perturbatively, the two methods outlined earlier still apply. The only difference is that one should take care which root of the 2×2 matrix is chosen in the case of DCPT2. As for the QDPT2 expression, the sign of each term should be kept from the original formula.

The formulae are quite general in the sense that they can be applied to any given partitioning of the Hamiltonian. The most straightforward is to use the MP partitioning, where the perturbation operator, W, is the difference between the Hamiltonian and the Fockian. Most of the numerical calculations presented here were done with the MP scheme. We have to emphasize, however, that the exactness of the DCPT2 formula for two-level systems holds only if one applies the EN partitioning, where the diagonals of the CI matrix define the zero-order energies and the offdiagonals constitute the perturbation. Therefore, in the case study on the H_2 molecule, we also performed comparative calculations for the EN scheme. For many-electron systems, however, the EN partitioning is ill defined: it leads to quite different results in a determinantal basis or if configuration state functions (CSFs) are used; in addition, the results of different spin-adapta-

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[1] Violation of orbital invariance is quite unfortunate also from the point of view of size extensivity, since one set of MOs may fulfill this latter requirement while another set may violate it.

tion schemes are also not the same. This well-known deficiency of the EN partitioning [16, 17] is a consequence of the violation of unitary invariance of this scheme. Therefore, many-electron systems are studied here only within the MP partitioning. For the H_2 molecule, EN calculations are performed using a spin-adapted basis, which is unique in the special case of a two-electron system.

The idea of complex damping of quasidegenerate perturbation formulae was also investigated by Forsberg and Malmqvist [18], who, instead of taking the modulus of the complex expression, considered the real part of Eq. (4). They performed MRPT calculations with a generalization of this damped formula by selecting the magnitude of the damping factor empirically.

3 Results and discussion

This section presents a numerical comparison of second-order correlation energies as obtained from the DCPT2 and QDPT2 formulae. As a basis of the comparison, we take some of the model systems considered by Assfeld et al. [6]. Then, prototype potential curves for single-bond dissociation of H_2 and F_2 are presented.

The energies of several molecules in the 6-311G** basis set [19] using a Cartesian (6-) d set as polarization functions on heavy atoms are listed in Table 1. The equilibrium geometries are taken from the work of Assfeld et al. [6]. In the first column, the total energies are presented at the second-order MP (MP2) equilibrium geometry, while the second and third columns show energy differences relative to the equilibrium energy at somewhat increased bond lengths. Accordingly, the level of quasidegeneracy increases from the left to the right in the table: there is no such effect around equilibrium but as a single bond length increases the corresponding bonding and antibonding MOs tend to become degenerate. Among the selected methods, we include standard MP2 values (i.e., without any degeneracy correction) and the CC with doubles (CCD) for comparison. Although the latter method, being a single-reference scheme, does not dissociate properly in the general case, for single bond rupture it yields much better potential-energy curves than MP2. The QDPT2 results were obtained using $\Gamma_k = 2W_{0k}$ (cf. Eq. 6).

The conclusions we can draw from Table 1 are as follows. At equilibrium, neither DCPT2 nor QDPT2 differs significantly from MP2, the differences being typically in the fourth to fifth digit (in atomic units). At partial dissociation (third column), these differences appear already in the second or third digits, emphasizing that the uncorrected MP2 values are unrealistic and the importance of quasidegeneracy corrections. The differences between DCPT2 and QDPT2, however, are still smaller than their deviation from MP2, especially at large distances. This indicates that both methods account for the same effect in a similar manner.

On the basis of the data reported in Table 1 it is not possible to describe either DCPT2 or QDPT2 as being better than the other. There are cases, such as that of the HOF molecule, where QDPT2 is astonishingly close to CCD, but for the F_2 molecule, for example, DCPT2 is in better agreement. A third type of case is represented by the N_2 molecule, where both QDPT2 and DCPT2 are quite far from CCD, indicating that this electronic system cannot be described by a simple perturbative account of electron correlation with no coupling between excitations. By comparing the perturbation schemes presented here (DCPT2, QDPT2) to that of Lepetit and Malrieu (SC2) on the example of the F_2 molecule in Table 1, the effect of higher-order corrections incorporated in this latter method is apparent. Thus, the deviation of the two former schemes from each other is negligible if compared to the difference taken with SC2, both at the equilibrium distance and at partially dissociated arrangements.

Stronger degeneracy appears at longer bond lengths. We studied this effect on the dissociation profiles of H_2 and F_2 molecules (Figs. 1, 2). Two different partitionings (MP and EN) were addressed for H_2. The H_2 results are compared with full CI (FCI) values, while CCD was chosen for F_2 as a reference.

The H_2 curves in MP and EN partitionings are presented in Fig. 1a and b, respectively. One can see that the three perturbation-based methods are quite similar up to approximately twice the equilibrium distance. On further increasing the bond lengths, MP2 diverges, while the corrected curves remain regular. The DCPT2 results tend to approach the CI ones at large distances, but they show an unphysical maximum at around 3 Å. The QDPT2 curve does not have this maximum; it has a nice shape, but it exaggerates the dissociation energy compared to FCI. Nevertheless, it represents a dramatic improvement over the self-consistent field (SCF), which fails to describe dissociation, and was not even plotted in Fig. 1.

The situation is quite similar for F_2 plotted in Fig. 2, where, for the reasons discussed earlier, only MP results are included. The MP2 curve breaks down even more rapidly, and DCPT2 tends to a limit smaller than CCD for large distances, in better agreement with experimental data [20].

Regarding the results for H_2 in the EN partitioning, we observe that standard second-order EN data are useless above about 1.5 Å, while the second-order DCEN (DCEN2) ones are quite close to FCI in a wide range of interatomic distance. This could be connected to the fact that DCEN2 is strictly equivalent to FCI for a two-electron system in a minimal basis, and the difference between these two curves in Fig. 1b arise from coupling between excitation pairs. Therefore, the unphysical maximum on the DCEN2 profile has been strongly reduced. The second-order QDEN results in the EN partitioning are similar to those in MP.

In conclusion, we may say that the simple degeneracy-correction schemes investigated in this article work rather well for the weakly quasidegenerate situations reported in Table 1. For the full dissociation problem they offer a method, that although not qualitatively accurate, eliminates the inapplicability of single-reference PT2 for quasidegenerate situations.

Since both correction schemes are quite cheap, maybe the method they have to compare with is the one by

Table 1. Total energies and energy differences taken with total energy at equilibrium geometry for several molecules in the 6-311G** basis. Besides the perturbation theory (*PT*) results, coupled cluster with doubles (*CCD*) and multireference self-consistent field (SCF) (CASSCF + PT2) results are shown as references. $\Delta E_a = E_{tot}(R_a) - E_{tot}(R)$, $\Delta E_b = E_{tot}(R_b) - E_{tot}(R)$

	E_{tot}	E_{tot}	ΔE_a	E_{tot}	ΔE_b
C_2H_2	$R_{CC} = 1.2143$ Å	$R_a = 1.8$ Å		$R_b = 2.4$ Å	
DCMP2	−77.151483	−76.940363	0.211120	−76.851925	0.299558
QDMP2	−77.151310	−76.937816	0.213494	−76.834809	0.316501
MP2	−77.151658	−76.943033	0.208625	−76.871231	0.280427
CCD	−77.164133	−76.906767	0.257366	−76.754897	0.409236
C_2H_4	$R_{CC} = 1.3355$ Å	$R_a = 2.0$ Å		$R_b = 2.7$ Å	
DCMP2	−78.385776	−78.219458	0.166318	−78.115638	0.270138
QDMP2	−78.385678	−78.218257	0.167421	−78.107094	0.278584
MP2	−78.385876	−78.220741	0.165135	−78.125611	0.260265
CCD	−78.412231	−78.234226	0.178005	−78.098770	0.313461
HOF	$R_{OF} = 1.4221$ Å	$R_a = 2.1$ Å		$R_b = 2.8$ Å	
DCMP2	−175.252332	−175.169071	0.083261	−175.123339	0.128993
QDMP2	−175.252244	−175.165218	0.087026	−175.106806	0.145438
MP2	−175.252421	−175.173461	0.07896	−175.146996	0.105425
CCD	−175.255141	−175.166059	0.089082	−175.101837	0.153304
C_2H_6	$R_{CC} = 1.5263$ Å	$R_a = 2.3$ Å		$R_b = 3.0$ Å	
DCMP2	−79.612519	−79.500722	0.111797	−79.419376	0.193143
QDMP2	−79.612505	−79.500621	0.111884	−79.418101	0.194404
MP2	−79.612533	−79.500823	0.11171	−79.420767	0.191766
CCD	−79.646759	−79.537279	0.109480	−79.455049	0.191710
Li_2	$R_{LiLi} = 2.7357$ Å	$R_a = 4.1$ Å		$R_b = 5.5$ Å	
DCMP2	−14.915605	−14.893001	0.022604	−14.870186	0.045419
QDMP2	−14.915582	−14.892933	0.022649	−14.869746	0.045836
MP2	−14.915629	−14.893070	0.022559	−14.870664	0.044965
CCD	−14.930758	−14.907811	0.022947	−14.891875	0.038883
LiH	$R_{LiH} = 1.5939$ Å	$R_a = 2.4$ Å		$R_b = 3.1$ Å	
DCMP2	−8.022020	−7.985659	0.036361	−7.947411	0.074609
QDMP2	−8.022007	−7.985641	0.036366	−7.947388	0.074619
MP2	−8.022032	−7.985676	0.036356	−7.947434	0.074598
CCD	−8.031879	−7.996980	0.034899	−7.961602	0.070277
HF	$R_{FH} = 0.9184$ Å	$R_a = 1.4$ Å		$R_b = 1.8$ Å	
DCMP2	−100.294235	−100.191897	0.102338	−100.109905	0.18433
QDMP2	−100.294168	−100.191695	0.102473	−100.108730	0.185438
MP2	−100.294303	−100.192101	0.102202	−100.111160	0.183143
CCD	−100.295672	−100.193523	0.102149	−100.111293	0.184379
CASSCF(4,4) + PT2	−100.291824	−100.185318	0.106506	−100.118319	0.173505
F_2	$R_{FF} = 1.4068$ Å	$R_a = 2.1$ Å		$R_b = 2.8$ Å	
DCMP2	−199.210102	−199.135813	0.074289	−199.118463	0.091639
QDMP2	−199.209451	−199.126116	0.083335	−199.082771	0.12668
SC2	−199.290242	−199.232593	0.057649	−199.201845	0.088397
MP2	−199.210775	−199.147860	0.062915	−199.179902	0.030873
CCD	−199.209813	−199.138739	0.071074	−199.113241	0.096572
CASSCF(4,4) + PT2	−199.175060	−199.152854	0.022206	−199.147042	0.028018
HOOF	$R_{OO} = 1.3663$ Å	$R_a = 2.0$ Å		$R_b = 2.7$ Å	
DCMP2	−250.265731	−250.193113	0.072618	−250.147319	0.118412
QDMP2	−250.265674	−250.191144	0.07453	−250.135223	0.130451
MP2	−250.265787	−250.195246	0.070541	−250.163488	0.102299
CCD	−250.264823	−250.186896	0.077927	−250.162438	0.136412
N_2	$R_{NN} = 1.1108$ Å	$R_a = 1.7$ Å		$R_b = 2.2$ Å	
DCMP2	−109.341613	−109.187672	0.153941	−109.274372	0.067241
QDMP2	−109.341215	−109.179055	0.16216	−109.227993	0.113222
MP2	−109.342016	−109.196895	0.145121	−109.329171	0.012845
CCD	−109.336030	−109.040736	0.295294	−108.951017	0.385013
CASSCF(4,4) + PT2	−109.337036	−109.037248	0.299788	−108.926857	0.410179

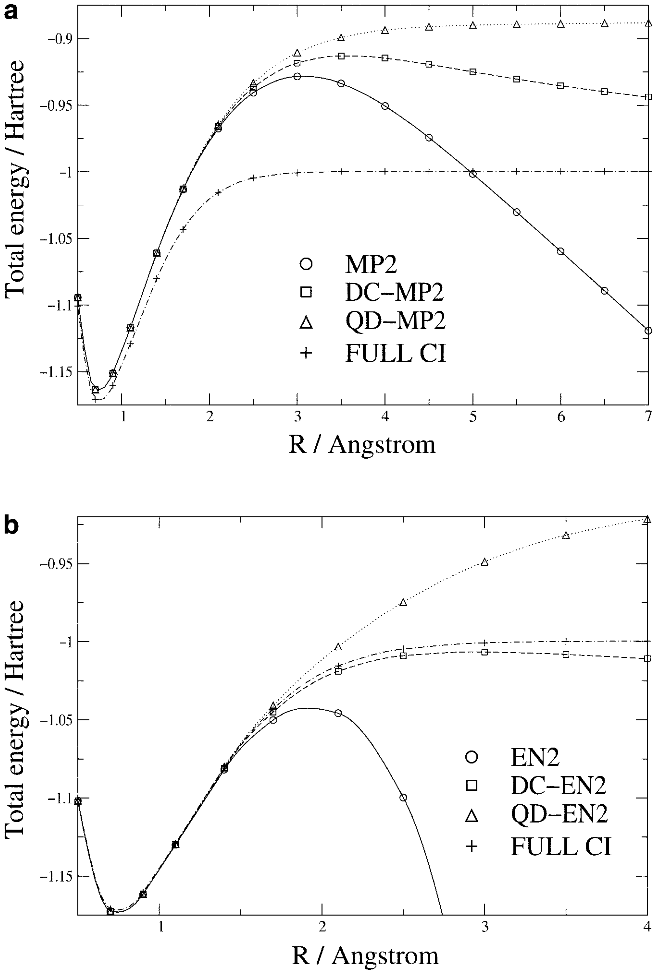

Fig. 1. Potential-energy curves for the H_2 molecule in the (311/11/1) basis set [23]. The results obtained using perturbation theory based on Møller–Plesset (*MP*) partitioning are plotted in **a**; those computed with Epstein–Nesbet (*EN*) partitioning are shown in **b**. Full line: second-order PT (*PT2*); *dashed line*: degeneracy-corrected PT2 (*DCPT2*); *dotted line*: quasidegenerate (*QDPT2*); *dot-dashed line*: full configuration interaction (*CI*)

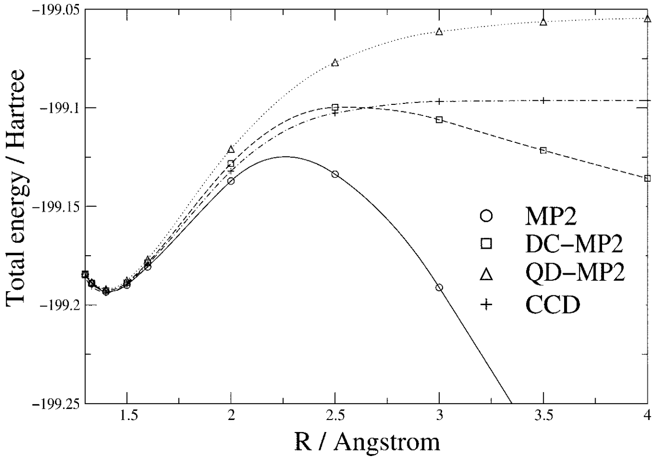

Fig. 2. Dissociation curve for the F_2 molecule in the 6-311G** basis set [19], computed with second-order PT schemes (MP2, DCMP2 and QDMP2) and the coupled cluster with doubles (*CCD*) method

Lepetit and Malrieu [13] mentioned in the Introduction. That method, suming up all EPV terms, gives very low total energies but quite accurate potential curves. The essential difference is that in the simpler schemes (QDPT and DCPT), we do not want to affect MP2 results appreciably where the single-determinant reference state is qualitatively appropriate. The dressed Hamiltonian of Lepetit and Malrieu yields a larger fraction of dynamical correlation energy, even in the vicinity of equilibrium distances.

Acknowledgements. The CC and MRSCF results were obtained using the Gaussian94 program package [21]. Some of the PT results were also computed using a modified version of this program, into which DCPT2 and QDPT2 formulae were coded. Calculation of the rest of the PT results was performed using the MUNGAUSS program [22] to which supplementary routines were added. This work was partly supported by grants OTKA T23052 and FKFP 165/99 and by the MTA/CNRS 6472 cooperation project.

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