Optimized quasiparticle energies in many-body perturbation theory [*]

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Abstract

For the calculation of the electron correlation energy, usual Koopmans one-electron energies (used in Møller-Plesset partitioning) are replaced by energy-optimized ones to form the denominators of many-body perturbation theory. Changing these quasiparticle energies can be interpreted as applying special level shifts to the zero-order Hamiltonian, thus it is related to the problem of partitioning in perturbation theory. The energy functional chosen to be optimized with respect to the quasiparticle energies is the Rayleigh quotient evaluated with the first-order wavefunction Ansatz, expanded up to the third order. The resulting level shifts preserve size extensivity of many-body perturbation theory.

Keywords: Many body perturbation theory (MBPT), level shifts, optimized partitioning, effective one-electron energies, quasiparticle energies

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[*] Dedicated to Professors Petr Čarsky, Ivan Hubač and Miroslav Urban on the occasion of their 60^{th} birthday

I. INTRODUCTION

Correlation in the motion of electrons in molecules is a determining factor in diverse chemical phenomena[1], and can be accounted for by various many-body techniques. The authors whom the present paper is dedicated to, Professors Petr Čársky, Ivan Hubač and Miroslav Urban, have had an exceptionally important contribution to the development and application of such theories[2–12]. Among several possibilities, many-body perturbation theory (MBPT) offers a conceptually simple, computationally economical, and practically reliable method in many cases.

In MBPT, one usually separates the entire many-body Hamiltonian into two parts

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

where F^0 is the Fockian

$$F^0 = \sum_i \varepsilon_i^0 \; a_i^\dagger a_i \tag{2}$$

with ε_i^0 being the canonical (Koopmans) quasiparticle energies satisfying the eigenvalue relation

$$F^0 \varphi_i = \varepsilon_i^0 \varphi_i . \tag{3}$$

While F^0 is considered as the zero-order Hamiltonian, W, defined formally as the difference between H and F^0, gives rise to the perturbation.

It is well know that both the convergence features of PT and the reliability of low-order estimations depend crucially on the partitioning[13–16]. The Møller-Plesset (MP) scheme[17] that corresponds to Eq. (1) is often very useful, but it requires further improvements either in quasi-degenerate situations or if high accuracy of the low-order results is desirable.

A simple way of improving a given partitioning is offered by level shifts. When repartitioning by level shifts, a diagonal operator is added to the zero-order Hamiltonian which changes the zero-order spectrum but leaves the zero-order eigenvectors unaffected[12, 18–21].

Previously[22, 23], we have derived an equation for optimal level shifts in perturbation theory. The optimization was based on the Rayleigh quotient evaluated with the first-order wavefunction Ansatz, expanded up to the third-order in PT. The resulting method showed convergence properties superior to the MP partitioning and offered highly improved second-order results. The third-order contribution was shown to be zero in the optimized partitioning, and higher-order terms turned out to contribute little, especially at odd orders. If using the Hartree-Fock determinant as the reference state, the second-order energy estimation was found to be equivalent to the CEPA-0 energy. The practical usefulness of that method, however, is quite limited as a consequence of the huge number of level shift parameters to be optimized.

In this work, we investigate a much simpler possibility: the optimization of the orbital energies ε_i, entering the PT denominators in a MP-type partitioning. The number of these parameters is quite low (just the number of basis functions), thus even if the equation determining the optimal ε_i-s are complicated, the problem remains manageable.

Modifying the one-particle energies on the basis of a variational condition, as it is done in the following chapter, is closely related to a recent work of I. Lindgren[24]. The inspiring finding of the above study is that varying the one-particle orbitals and requiring the stationarity of a PT estimate of certain order, one is led to Brueckner orbitals, and Brueckner orbital energies of that particular order. The resulting orbital energies can be interpreted as ionization potentials. This is a very interesting result, which involves much more free parameters in the optimization than we use presently.

II. THEORY

Instead of the standard MP partitioning expressed by Eq.(1), we propose

$$H = F + V \tag{4}$$

where F is the shifted Fockian

$$F = \sum_i \varepsilon_i \; a_i^\dagger a_i \tag{5}$$

with the shifted quasiparticle energies

$$\varepsilon_i = \varepsilon_i^0 + \lambda_i . \tag{6}$$

The relation between perturbation operators W and V is simply

$$V = W - \sum_i \; \lambda_i \; a_i^\dagger a_i . \tag{7}$$

The unknown parameters of the theory are the level shifts λ_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[22, 23], we determine the level shifts from the equation

$$\frac{\partial[E^2 + E^3]}{\partial\varepsilon_i} = 0 \tag{8}$$

where E^p denotes the p-th order contribution to PT. Note that in the numerator on the left-hand side of Eq.(8), one can equally put $[E^0 + E^1 + E^2 + E^3]$, which is just the Rayleigh quotient evaluated by the first-order wave function written out up to the 3rd order. This holds simply because the sum $[E^0 + E^1]$, the expectation value of the total Hamiltonian, is independent of the level shifts.

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.(7), giving rise to the term[25]:

$$-\sum_{abrs} \frac{[rs||ab]^2}{(\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b)^2}(\lambda_r + \lambda_s - \lambda_a - \lambda_b) \ , \tag{9}$$

written in spin orbitals. Indices a, b label occupied orbitals, r, s refer to virtual ones, and the $[12|12]$ integral convention is used. The double bar denotes an antisymmetrized integral, $[rs||ab] = [rs|ab] - [rs|ba]$.

Having obtained the explicit functional, partial derivatives occurring in Eq.(8) can be given in a somewhat lengthy but straightforward manner. However, the analytical solution of the resulting equations is formidable. Therefore, we have performed an iterative numerical solution using the gradient technique with the diagonal Hessian approximation:

$$\varepsilon_i^{[n+1]} = \varepsilon_i^{[n]} - \frac{g_i}{h_i} \tag{10}$$

with the gradients

$$g_i = \frac{\partial[E^2 + E^3]}{\partial\varepsilon_i} \tag{11}$$

and diagonal Hessians

$$h_i = \frac{\partial^2[E^2 + E^3]}{\partial\varepsilon_i^2}. \tag{12}$$

We used the analytical first derivatives while the second ones were evaluated numerically and updated at each iteration.

Quasiparticle energies determined in this way have the property that, given two noninteracting subsystems A and B, each of them belongs either to system A or B. This follows from the size 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 to the cost of the optimization procedure, the CPU-determining step is the evaluation of orbital gradients. It has practically the same cost as that of the evaluation of the MP3 correction.

III. EXAMPLES

The present paper reports merely a few preliminary numerical results testing the effect of using optimized quasiparticle energies on the correlation energies of few-electron systems. The helium and neon atoms, the water molecule near equilibrium, and the hydrogen molecule potential curve serve as examples. Further numerical studies will be published in a forthcoming paper.

The He atom was computed in the 10s2p1d basis set of Huzinaga[26]. Correlation energies obtained in the Møller-Plesset partitioning are compared with those with optimized orbital energies in Table 1. Here the exact basis set (full CI) energy is indicated as a reference. The improvement upon optimization is dramatic: the error of the second-order result is decreased to 0.14 mE_h. For comparison, the error of MP2 is 6.09, that of MP3 is 1.06 mE_h. Note that there is no difference between orders 2 and 3 in this system, if the optimized quasiparticle energies are used. This remounts to the theorem[22] that $E^3 = 0$ if all denominators corresponding to levels that interact with the ground state are optimized, not just the orbital energies.

The results for the Ne atom are presented in Table 2. This system behaves quite differently since MP2 strongly overestimates the correlation energy coming from doubles. Trying to correct for this, MP3 predicts smaller correlation energy than MP2. Optimization of orbital energies does not push the 2nd- and 3rd-order toward CID, rather to CCD. The small difference between the optimized second and third-order results is again noteworthy.

The water molecule provides a similar example. Here, upon optimization, the third-order energy differs from the CCD results merely by 0.95 mH.

The tendency of simulating CCD results by OPT2 and OPT3 can also be understood by the theorem found for the case of optimized partitioning, when not only ε_i-s, but all denominators interacting with the ground state are optimized[22]. Then, if the Hartree-Fock determinant is used as the zero-order ground state, the second-order energy coincides with the CEPA-0 result, known also as LCCD.

The potential curve of the H_2 molecule is plotted in Figs. 1-3. At around equilibrium (Fig.1), the second and third-order results with optimized ε_i-s can hardly be distinguished form the full-CI curve. To gain a better insight, the figure is redrawn to present the deviations from full-CI (Fig. 2.) The parallelism of OPT3 with the exact results is remarkable, showing that practically exact force constants emerge when performing a third-order PT calculation with optimized ε_i-s for this simple system.

It is interesting to have a look on the entire potential curve plotted in Fig. 3. Here MP2 and MP3 show the well-known divergence due to the dissociation catastrophe[1]. The optimized PT results, interestingly, do not diverge but get saturated at some limit. While OPT2 strongly overestimates the dissociation energy, OPT3 underestimates it by ca. 30 %. Altogether, they provide a rough estimation giving rise to the hope that single-reference MBPT with optimized quasiparticle energies may become convergent even for highly stretched geometries. To check this, one has to evaluate higher-order corrections which has not yet been done, but is in progress in our laboratory.

Another interesting point to investigate is whether optimizing the quasiparticle energies in unrestricted theory improves the UMP potential curves. We do hope this is the case.

Before closing this paper, we must add a warning statement about the convergence features of the numerical procedure by which optimized ε_i-s were produced. At present, we have not applied any acceleration procedure, yet we were able to obtain converged results without too many difficulties. We have noticed, however, that – while the 3rd-order results are numerically quite stable – it is often difficult to get the second-order energies converged. This might be associated with the problem that the variational condition we use, Eq.(8), could be satisfied with more than one set of ε_i-s providing the same $E^2 + E^3$ but different E^2. Therefore, the second-order-optimized results shown in this paper have to handled with some care, one may rather rely on third-order energies.

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TABLE I: Correlation energy of He and Ne atoms and the water molecule in milihartrees as obtained by the MP and the present optimized (OPT) partitioning in PT. For comparison, configuration interaction (CI) and coupled cluster (CC) results are indicated, counting for double excitations in both methods. Full CI is also included for He and Ne. The geometry of H_2O is $r_{\rm OH} = 1.01$Å and $\alpha_{\rm HOH} = 104^o$.

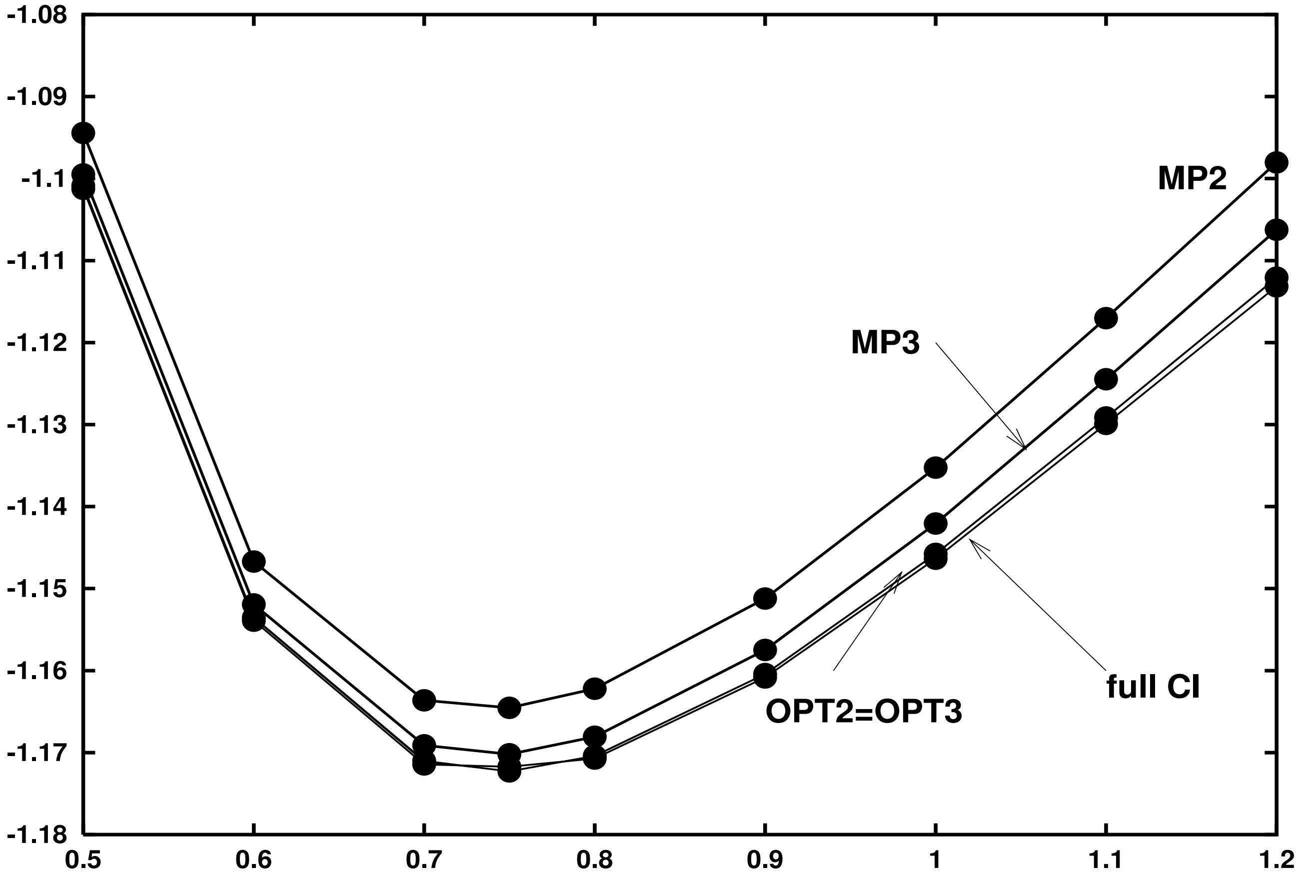
Method	He atom	Ne atom		H_2O
	10s2p1d	6-31G**	6-311G**	6-311G**
MP2	-32.24	-151.77	-227.94	-239.80
MP3	-37.27	-151.62	-227.72	-243.88
OPT2	-38.47	-151.68	-228.12	-244.88
OPT3	-38.47	-151.89	-228.11	-245.15
CID	-38.31	-149.22	-223.57	-235.97
CCD	”	-152.94	-228.82	-246.10
FCI	-38.33	-155.55	-231.79	

Figure legends

Fig.1 Potential curve of the hydrogen molecule near equilibrium in Dunning's cc-pVTZ basis set[27]. Distances (horizontal axis) in Å, total energies (vertical axis) in atomic units. Labels MPn refer to standard *n*-th order Møller Plesset theory, OPTn identify the optimized results proposed in this paper.

Fig.2 Deviation of perturbative estimates from full CI. (Hydrogen molecule, cc-pVTZ basis[27].) For units and notations, see Fig. 1.

Fig.3 Long-range potential curve of the hydrogen molecule in Dunning's cc-pVTZ basis set[27]. For units and notations, see Fig. 1.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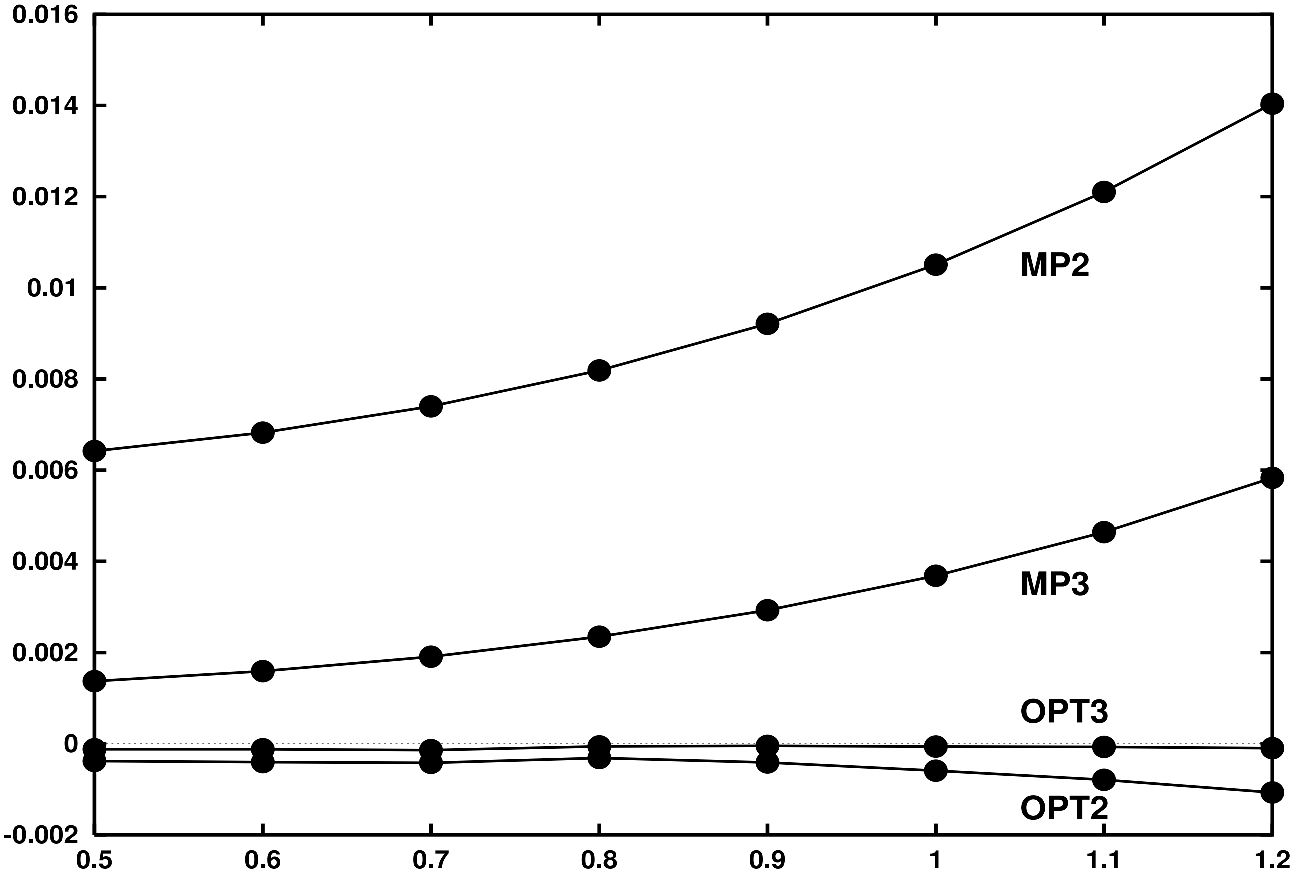
-1.11
-1.12
-1.13
-1.14
-1.15
-1.16
-1.17
-1.18
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
MP2
MP3
OPT2=OPT3
full CI

Fig.1.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-0.002
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MP2
MP3
OPT3
OPT2

Fig.2.

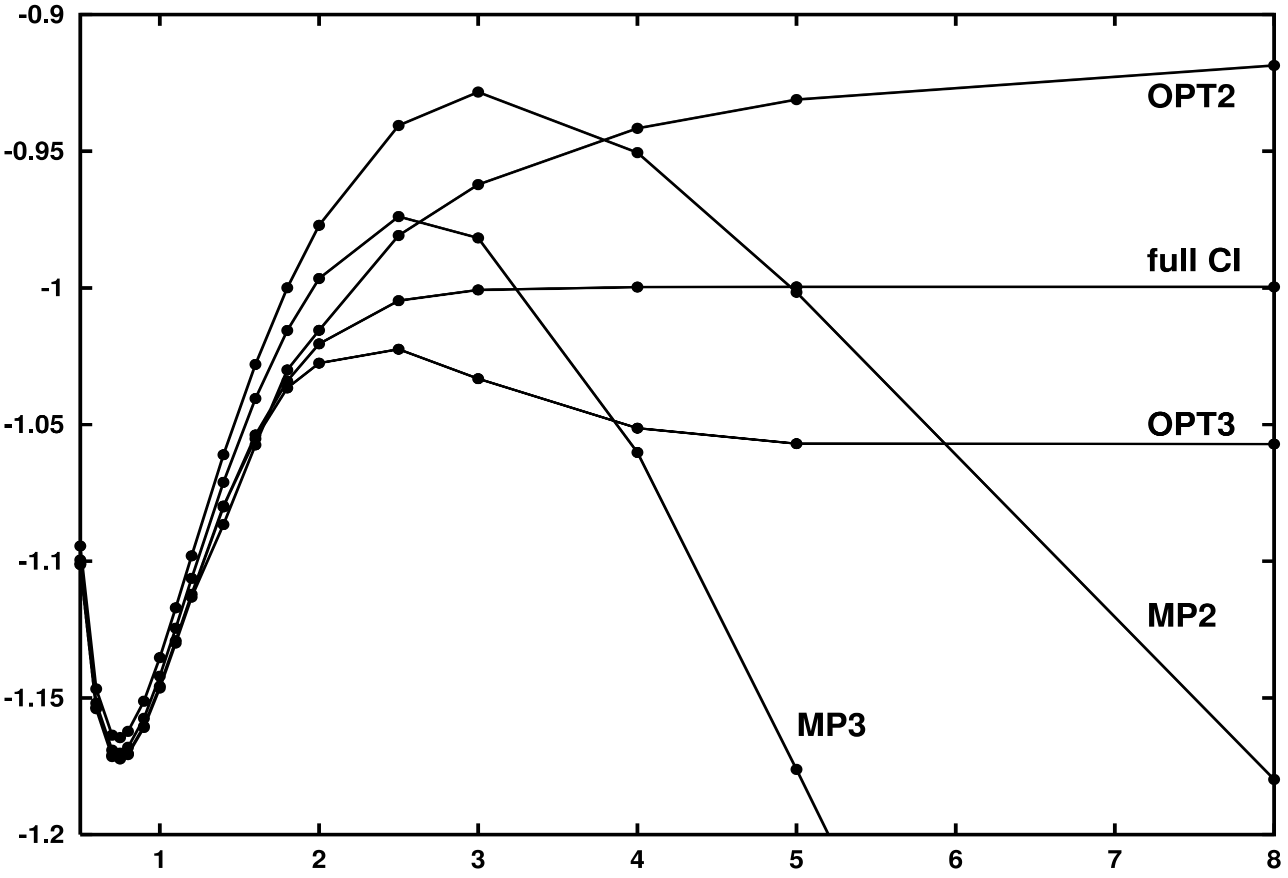

Fig.3.