

# A Note on Perturbation-Adapted Perturbation Theory

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The partitioning introduced recently by Knowles (J. Chem. Phys., 156:011101, 2022) is analyzed and its connections with the Adams partitioning and the Davidson-Kapuy partitioning are discussed. Davidson's partitioning is reformulated using second quantized formalism. A relation is pointed out between Knowles' condition for the MBPT zero order Hamiltonian and the CEPA0 equations.

## I. INTRODUCTION

Perturbation theory (PT) is a standard and useful method in many-body theory<sup>1,2</sup>. In the most often used partitioning, i.e., the separation of the total Hamiltonian  $\hat{H} = \hat{H}^0 + \hat{W}$  of many-body PT (MBPT), one chooses the Fockian as the zero order Hamiltonian  $\hat{H}^0 = \hat{F}$  making the two-electron part of  $\hat{H}$  as the perturbation (Møller-Plesset partitioning<sup>3</sup>, MP). For a review on several other types of partitioning, see e.g. Ref.<sup>4</sup>

Application of PT may be plagued by convergence problems. Especially prone to this phenomenon are chemical systems far from their equilibrium structure and for those treated in large basis sets<sup>5</sup>. Olsen and coworkers have undertaken a series of studies<sup>6-8</sup> exhaustively documenting divergences and explaining their mathematical backgrounds. A similar sound study has recently been published by Marie et al.<sup>9</sup>

An important tool for improving the convergence properties of PT is to change the partitioning. The aim of this Note is to discuss the relation of a recently reported new type of partitioning to two earlier technics.

## II. PERTURBATION-ADAPTED PT<sup>10</sup>

Very recently, an interesting paper was published in this Journal by Peter Knowles<sup>10</sup>. He observed that leaving the MP partitioning, superior convergence properties of the perturbation series can be obtained. He introduced a new zero-order Hamiltonian  $\hat{\Lambda}$  containing a set of parameters that are determined by a set of auxiliary conditions aiming to get  $\hat{\Lambda}$  as close to  $\hat{H}$  as possible, without destroying the solubility of the zero-order problem. The approach based on the new partitioning was termed perturbation-adapted PT (PAPT).

The general formula from which operator  $\hat{\Lambda}$  emerges is a momentum-like condition

$$\langle 0 | \hat{\Theta}_p^\dagger (\hat{\Lambda} - \hat{H}) | 1 \rangle = 0, \quad (1)$$

where  $|i\rangle$  is the  $i$ -th order wave function obtained from the original ("root") partitioning,  $\hat{\Theta}_p$ -s form a set of suitable operators, depending on the problem in question. We note that this formula shows some formal analogy to the single-reference CEPA0 equations<sup>11</sup> formulated for the first-order wave function<sup>4,12</sup>

$$\langle \phi_{ab}^{pq} | \hat{H} - H_{00} | 1 \rangle = 0, \quad (2)$$

where  $\phi_{ab}^{pq}$  is a doubly excited determinant.

Two examples for determining the partitioning are treated in Ref<sup>10</sup>: an anharmonic oscillator and the MBPT for electronic systems, showing the success of Eq.(1).

## III. ADAMS PARTITIONING

Another standard partitioning is that of Epstein<sup>13</sup> and Nesbet<sup>14</sup> (EN). In the EN partitioning the zero order Hamiltonian matrix consists of the diagonal elements of  $\hat{H}$ . Adams<sup>15</sup> has generalized this idea to assign larger blocks of  $\hat{H}$  to  $\hat{H}^0$ , in operator notations:

$$\hat{H}_{\text{Adams}}^{(0)} = \hat{P}\hat{H}\hat{P} + \hat{O}\hat{H}\hat{O}, \quad (3)$$

where  $\hat{O}$  and  $\hat{P}$  are two appropriately chosen complementary projectors with  $\hat{O} + \hat{P} = 1$ .

In the Adams partitioning, the zero order problem is not diagonal, thus equations have to be solved in course of evaluating the perturbation. A similar task occurs in MBPT if one keeps the MP partitioning but works with localized molecular orbitals, as advocated by Pulay<sup>16,17</sup>.

The zero order Hamiltonian according to Eq.(5) from Ref.<sup>10</sup> for the anharmonic oscillator,

$$\hat{\Lambda} = \hat{P}\hat{H}_{\text{root}}^{(0)}\hat{P} + \hat{O}\hat{H}\hat{O}, \quad (4)$$

clearly matches Eq.(2) above when

$$\hat{P}\hat{H}_{\text{root}}^{(0)}\hat{P} = \hat{P}\hat{H}\hat{P}$$

where  $\hat{H}_{\text{root}}^{(0)}$  corresponds to the partitioning we depart from. Though  $\hat{P}\hat{H}_{\text{root}}^{(0)}\hat{P}$  is not  $\hat{P}\hat{H}\hat{P}$  in Ref.<sup>10</sup>, deviation of the two quantities affects only the zero and first order energies leaving their sum, as well as higher order corrections invariant, as  $\hat{P}$  is one-dimensional.

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#### IV. DAVIDSON-KAPUY PARTITIONING

After an early initiative by Amos and Musher<sup>18</sup>, but independently from it, Davidson elaborated a powerful theory<sup>19</sup>, the essence of which is to repartition the total Hamiltonian by adding and subtracting an arbitrary one-body operator  $\hat{A}$ , and absorbing the subtracted  $\hat{A}$  into the two-body part by an appropriate transformation. Here we reformulate Davidson's transformation using second quantized notations.

Let  $i, j, k, l$  denote molecular spinorbitals, and  $i^+, i^-$  creation/annihilation operators. Then, in the spirit of Davidson<sup>19</sup>, the Hamiltonian is transformed as

$$\begin{aligned}\hat{H} &= \sum_{ij} h_{ij} i^+ j^- + \frac{1}{2} \sum_{ijkl} [ik|jl] i^+ k^+ l^- j^- \quad (5) \\ &\equiv \sum_{ij} (h_{ij} + A_{ij}) i^+ j^- \\ &\quad + \frac{1}{2} \sum_{ijkl} [ik|jl] i^+ k^+ l^- j^- \\ &\quad - \underbrace{\sum_{ij} A_{ij} i^+ j^-}_{\text{absorbed}} \\ &\quad - \sum_{ijkl} \frac{A_{ij} \delta_{kl}}{N-1} i^+ k^+ l^- j^- \\ &= \sum_{ij} \bar{h}_{ij} i^+ j^- + \frac{1}{2} \sum_{ijkl} [\bar{ik}|\bar{j}l] i^+ k^+ l^- j^- \end{aligned}$$

where

$$\bar{h}_{ij} = h_{ij} + A_{ij} \quad (6)$$

and

$$[\bar{ik}|\bar{j}l] = [ik|jl] - \left( \frac{A_{ij} \delta_{kl} + A_{kl} \delta_{ij}}{N-1} \right). \quad (7)$$

Here we diluted the second occurrence of the one-electron operator  $\hat{A}$  to get a two-electron shape, and symmetrized it to exhibit the symmetry of two-electron integrals explicitly (this way of transforming a one-electron operator to a two-electron one was extensively used by Valdemoro and coworkers<sup>20,21</sup>).

It is worth noting here that transformation (7) is specific to an  $N$ -electron Hilbert space. Once it is introduced, one no longer has a common second quantized Fock operator in all sectors of Fock space.

Although the entire Hamiltonian remains intact, their associated Fockians

$$F_{ij} = h_{ij} + \sum_k^{\text{occ}} [ik||jk] \quad (8)$$

and

$$\bar{F}_{ij} = \bar{h}_{ij} + \sum_k^{\text{occ}} [\bar{ik}||\bar{j}k] \quad (9)$$

are different. (The double bar  $||$  indicates antisymmetrized integrals.)

While the Fockian  $F$  is diagonal in terms of canonical orbitals,  $\bar{F}$  has nonzero occupied-occupied and virtual-virtual blocks. Its occ-virt interaction block remains zero maintaining the Brillouin theorem.

Davidson used this transformation to account for the effects of orbitals different from canonical ones, say some types of localized orbitals. This feature was utilized by Kapuy<sup>22-26</sup> when performing PT in terms of localized orbitals, hence the name "Davidson-Kapuy partitioning". More recently, Head-Gordon emphasized its advantages and applied this partitioning up to the second order<sup>27</sup>. Knowles, when applying PAPT to the many-electron problem, approached the problem of repartitioning from the reverse side. His equation (7) in Ref.<sup>10</sup>, apart from a constant, can be written as

$$\hat{\Lambda} = \sum_{ab} \Lambda_{ab} a^+ b^- + \sum_{ij} \Lambda_{ij} i^+ j^- \quad (10)$$

in terms of occupied (i,j) and virtual (a,b) spinorbitals. This indicates that the applied one-electron zero order Hamiltonian  $\hat{\Lambda}$  has off-diagonal occ-occ and virt-virt matrix elements, just like the Fockian in a non-canonical basis. Accordingly, the partitioning he introduced corresponds to changing the molecular orbitals by a unitary transformation without any occ-virt mixing. A smart idea in paper<sup>10</sup> is to determine the off-diagonal matrix elements of  $\hat{\Lambda}$  (i.e., that of the Fockian) by the momentum-like formula (1) using a special contraction of the terms of the first order PT wave function, e.g.:

$$|\Theta_{ij}\rangle \sim \sum_{abk} c_{ab}^{ik} a^+ b^+ k^- j^- |0\rangle \quad (11)$$

and an analogous formula for virtuals (cf. Eqs (10-11) in Ref.<sup>10</sup>). Thereby, the number of unknowns (matrix elements of  $\hat{\Lambda}$ ) is the same as that of the equations. The full CEPA0 type conditions (see Eqs. (1) and (2)) are thus simplified, leading to an economical computational procedure. Applications of the resulting partitioning on the CH<sub>2</sub> radical and the Ne atom are impressive, even if divergences are not completely eliminated for Ne.

Since a choice for parameters  $\Lambda_{ab}, \Lambda_{ij}$  can be uniquely related to a choice of  $A_{ij}$ , the partition introduced by Knowles<sup>10</sup> in MBPT can be originated from Davidson's  $A$ -matrix technique, with the successful CEPA0-like condition (1) and (11) for obtaining the free parameters. Note, however, that the method of Ref.<sup>10</sup> can be

formulated without referring to this connection, since all that matters there is that operator  $\hat{\Lambda}$  does not couple the Hartree-Fock occupied and virtual orbitals.

The alternative of optimizing the *energy levels* of many-electron eigenstates of the zero order Hamiltonian deserves mention here. Parameters introduced this way are generally more numerous than those in Davidson's  $A$ . When optimized by a Feenberg<sup>28,29</sup> type condition, i.e. setting  $E^{(3)} = 0$ , the method becomes equivalent to CEPA0 (see Ref.<sup>12</sup>). This was termed as "optimal partitioning" in our laboratory<sup>12,30-32</sup>. Due to their equivalence, the cost of this method is the same as that of CEPA0, which is determined by solving a linear equation in the first-order interacting subspace<sup>12</sup>.

The analogy of Eq. (1) (the condition used by Knowles) and Eq. (2) (the CEPA0 equation) deserves a remark at this point. While the two expressions parallel, differences are also noteworthy. There figures a zero order Hamiltonian in Eq. (1) that seems to have no counterpart in Eq. (2). The purpose of the two equations can be thought to be different in the sense, that Eq. (1) determines matrix elements of  $\Lambda$  while Eq. (2) is used for finding  $|1\rangle$ , the wavefunction correct up to first order. The relation is however more complex than that. There do exists a perturbational standpoint leading to the CEPA0 equation. This is the level shift optimization technique, alluded to above. In this view, Eq. (2) can be recast in a form exhibiting the level shift parameters to be set<sup>12</sup> (see also Ref.<sup>2</sup>), hence it implies a determination of zero-order Hamiltonian. The second order energy of the resulting partitioning matches the CEPA0 energy and the associated wavefunction is recovered at first order of this PT scheme. The form of Eq. (2) reflects this latter point. Thus, Eqs.(1) and (2) share a common motif, while they are by no means equivalent.

A much cheaper alternative is to optimize only the diagonals of the Fockian entering the PT denominators<sup>33</sup>. This works also fine for small systems, but since the number of parameters is too few, it does not lead to appreciable corrections for larger molecules.

We have investigated formerly a quite different condition for determining the elements of Davidson's matrix  $A$ , the minimization of the square norm of residual

$$|r\rangle = (\hat{H} - E)|1\rangle. \quad (12)$$

where  $E = \langle 1|\hat{H}|1\rangle$ . Since performance was not found to justify the increase in numerical cost, this work remained unpublished<sup>34</sup>. Owing to its relevance to the present question, we quote some result in Table I. from Ref.<sup>34</sup>. One has to realize that minimizing the square norm of Eq.(12) can only be considered as an interesting theoretical study, but does not lead to any viable quantum chemical method. Evaluation of the residual leads to lengthy equations (not even presented in Ref.<sup>34</sup>),

TABLE I. Total energies in a.u. for some small systems obtained in various perturbational methods. "OPTn" stands for the n-th order result with optimized  $A$  matrix elements, taken from Ref.<sup>34</sup>

system	H <sub>2</sub>	HeH <sub>2</sub>	H <sub>2</sub> O
basis set	pVTZ	3-21G	STO-6G
MP2	-1.16464	-3.82031	-75.71484
MP3	-1.17026	-3.82865	-75.72462
OPT2	-1.17209	-3.83037	-75.72513
OPT3	-1.17290	-3.83238	-73.72830
FCI	-1.17233	-3.83224	-75.72913

and minimization through numerical gradients and hessian elements by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) procedure<sup>35</sup> is time-consuming. Apart from its cost, an  $A$ -matrix optimized this way may lead to violation of the extensivity condition. On the contrary, conditions (1) and (11) used by Knowles<sup>10</sup>, in our opinion, offer a powerful shortcut in defining the partitioning.

## V. CONCLUSION

Of many possible partitionings in MBPT, those by Adams and by Davidson are recollected. We point out that Knowles in his recent paper<sup>10</sup> has given a unified formulation, which reduces to the previous ones by choosing operator  $\hat{\Lambda}$  appropriately. We think that the success of Knowles' procedure is connected to the fact that the condition he used for determining elements of  $\hat{\Lambda}$  is related to a compactified form the the CEPA0 equations.

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