

Many-body Perturbation Theory with Localized Orbitals: Accounting for Localization Diagrams as Integral Dressing

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Abstract

We argue that the so-called localization diagrams, originating from off-diagonal Fockian elements, do not have to be dealt with explicitly in the Davidson-Kapuy many-body perturbation theory with localized orbitals, but can be accounted for by dressed two-electron integrals.

Introduction

In developing many-body perturbation theory (MBPT) in terms of localized (or any non-canonical) orbitals, the following distinct strategies have been devised.

- Pulay advocated to preserve the Møller-Plesset partitioning,¹ i.e., to choose the Fockian $\hat{F}$ as the zero order Hamiltonian. Since $\hat{F}$ is not diagonal in a localized basis, one has to solve appropriate linear equations in course of evaluating corrections of each successive order.^{2,3}
- Based on early works by Amos and Musher⁴ and Davidson,^{5,6} Kapuy paved the way to a different approach.⁷⁻¹¹ He kept only the diagonal elements of $\hat{F}$ in the zero order Hamilto-

nian, thereby changing the partitioning. As a result, the offdiagonal Fockian elements enter the perturbation operator as one-body terms. In a diagrammatic representation, these terms introduce "localization diagrams" involving one-body Hamiltonian vertices occurring from the third order on. Examples for such localization diagrams were presented already in Ref.⁵ This type of partitioning has been named after Davidson and Kapuy¹² and this nomenclature is applied in this paper. For a review, see Ref.¹³

A common initiative of both approaches is that MBPT calculations can be performed much faster in terms of localized molecular orbitals (LMOs), since the latter permit one to neglect excitations between far-lying orbitals. Keeping the MP partitioning as advanced by Pulay usually results in better energies in the 2nd and 3rd orders at the price of some extra effort spent in solving the linear equations. Low order energies of the Davidson-Kapuy method are often less accurate, but, owing to the diagonality of the zero order Hamiltonian, easier to compute.

Subotnik and Head-Gordon recently emphasized this aspect,¹⁴ pointing out that localization diagrams are not necessary to compute when stopping at the second order in energy. They devised orthonormal occupied and virtual orbitals which were localized but the associated Fockian remained diagonally dominated, thereby achieving highly accurate second-order energies using the Davidson-Kapuy method.

The aim of this paper is to show that explicit evaluation of localization diagrams is not necessary at all. Following Davidson,⁶ one can assign the matrix elements of an arbitrary one-electron operator (that we call Davidson's A -matrix) to the one-body and two-body parts of the Hamiltonian in an appropriate manner and realize that this formulation is equivalent to turning to a new set of occupied and virtual orbitals. In particular we show that

1. elements of Davidson's A -matrix can be simply constructed from a given set of (say, localized) orbitals
2. fixing the A -matrix according to point 1. permits one to generate terms of the Davidson-Kapuy PT series with the use of canonical MBPT expressions with "dressed" two-electron

integrals. Integral dressing has to be performed only once, before the PT calculation is started, and generates negligible computational cost.

Davidson's A -matrix technique

Davidson suggested^{5,6} to rewrite the N -electron Hamiltonian

$$H = \sum_n^N h(n) + \sum_{n < m}^N g(n, m) \quad (1)$$

as

$$H = \sum_n^N \bar{h}(n) + \sum_{n < m}^N \bar{g}(n, m) \quad (2)$$

where

$$\bar{h}(n) = h(n) + A(n)$$

and

$$\bar{g}(n, m) = g(n, m) - \frac{A(n) + A(m)}{N - 1}.$$

Here A is an arbitrary hermitian one-electron operator, while indices $n, m = 1, 2, \dots, N$ label electrons. He called the attention that while Hamiltonians (1) and (2) are the same, the corresponding Fockians are not. Choosing these two Fockians as zero order Hamiltonians corresponds to different partitionings in MBPT.

To recapitulate Davidson's derivation in second quantized notation, let us denote spatial molecular orbitals by $i, j, \dots$, use σ for spin label, and put $i_\sigma^+ (i_\sigma^-)$ for creation(annihilation) operators of the corresponding spinorbitals. Then the total Hamiltonian in an orthonormal basis is written as

$$H = \sum_{ij} h_{ij} \sum_{\sigma} i_{\sigma}^+ j_{\sigma}^- + \frac{1}{2} \sum_{ikjl} [ik|jl] \sum_{\sigma\sigma'} i_{\sigma}^+ k_{\sigma'}^+ l_{\sigma'}^- j_{\sigma}^- \quad (3)$$

(note that Davidson presented his formulae for the non-orthogonal case, that we do not need here).

Applying Davidson's transformation one writes

$$H = \sum_{ij} (h_{ij} + A_{ij}) \sum_{\sigma} i_{\sigma}^{+} j_{\sigma}^{-} + \frac{1}{2} \sum_{ikjl} [ik|jl] \sum_{\sigma\sigma'} i_{\sigma}^{+} k_{\sigma'}^{+} l_{\sigma'}^{-} j_{\sigma}^{-} - \sum_{ij} A_{ij} \sum_{\sigma} i_{\sigma}^{+} j_{\sigma}^{-}$$

where A_{ij} correspond to the matrix elements of an arbitrary hermitian one-electron operator. The last term can be identically transformed as

$$\begin{aligned} - \sum_{ij} A_{ij} \sum_{\sigma} i_{\sigma}^{+} j_{\sigma}^{-} &= - \sum_{ijk} \frac{A_{ij}}{N-1} \sum_{\sigma\sigma'} i_{\sigma}^{+} k_{\sigma'}^{+} k_{\sigma'}^{-} j_{\sigma}^{-} \\ &= - \sum_{ijkl} \frac{A_{ij} \delta_{kl}}{N-1} \sum_{\sigma\sigma'} i_{\sigma}^{+} k_{\sigma'}^{+} l_{\sigma'}^{-} j_{\sigma}^{-} \\ &= - \frac{1}{2} \frac{1}{N-1} \sum_{ijkl} (A_{ij} \delta_{kl} + A_{kl} \delta_{ij}) \sum_{\sigma\sigma'} i_{\sigma}^{+} k_{\sigma'}^{+} l_{\sigma'}^{-} j_{\sigma}^{-} \end{aligned} \quad (4)$$

where the one-body Hamiltonian was first diluted^{15,16} to a two-electron form, then it was symmetrized to exhibit the usual symmetry of two-electron integrals. With this transformation, the original Hamiltonian reads

$$H = \sum_{ij} \bar{h}_{ij} \sum_{\sigma} i_{\sigma}^{+} j_{\sigma}^{-} + \frac{1}{2} \sum_{ikjl} \overline{[ik|jl]} \sum_{\sigma\sigma'} i_{\sigma}^{+} k_{\sigma'}^{+} l_{\sigma'}^{-} j_{\sigma}^{-} \quad (5)$$

where

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

and

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

Integrals with overlines are dressed by the extra terms indicated at the rhs of Eqs. (6) and (7), with $i, j, \dots$ being molecular orbitals. The Fockians associated to the two forms of H , Eqs.(3) and (5),

assuming a closed-shell system for simplicity, read

$$F_{ij} = h_{ij} + \sum_k^{\text{occ}} (2[ik|jk] - [ik|kj]) \quad (8)$$

and

$$\bar{F}_{ij} = \bar{h}_{ij} + \sum_k^{\text{occ}} \left(2\overline{[ik|jk]} - \overline{[ik|kj]} \right) \quad (9)$$

Their difference is evaluated as

$$\bar{F}_{ij} - F_{ij} = A_{ij} \left(1 - \frac{N}{N-1} + \frac{n_i + n_j}{N-1} \right) - \frac{2\delta_{ij}}{N-1} \text{Tr}_{\text{occ}}(A) \quad (10)$$

where $n_i = 1$ if i is an occupied orbital, otherwise $n_i = 0$, Tr_{occ} refers to the partial trace of matrix A the summation extending to the occupied orbitals only.

One realizes that if $n_i = 1$ and $n_j = 0$, i.e., i corresponds to an occupied and j to a virtual orbital, and the original Fockian satisfies the Brillouin theorem $F_{ij} = 0$, then from Eq.(10)

$$\bar{F}_{ij} = A_{ij} \left(1 - \frac{N}{N-1} + \frac{1}{N-1} \right) = 0 \quad \text{for } n_i = 1, n_j = 0 \quad (11)$$

since $\delta_{ij} = 0$. This means that Davidson's transformation keeps the occ-virt block of the Fockian zero. The interpretation is, therefore, that matrix A generates an orbital transformation, which mixes occupied (virtual) orbitals among themselves, but does not generate any occ-virt mixing.

In some applications of MBPT, one does not want to start from true Hartree-Fock orbitals which minimize the energy of zero order determinantal wave function. In such a case the Brillouin theorem is not satisfied, i.e., $F_{ij} \neq 0$ for occupied i and virtual j . One has then to apply the so-called generalized MBPT¹⁷ that takes also single substitutions into account. In the present context, this means that, using Eqs.(10) and (11), one has

$$\bar{F}_{ij} = F_{ij} \quad (12)$$

for occ-virt elements. The violation of the Brillouin theorem, therefore, is inherited by the Davidson-transformed Fockian, while the occ-occ and virt-virt blocks of $\bar{F}$ will become diagonal as a result of the transformation. The latter, therefore manifests a so-called semicanonical transformation,^{17,18} used often in generalized MBPT.¹⁹

Matrix A corresponding to a set of orbitals: integral dressing

Since Fockians (8) and (9) are different, so are their eigenvectors. Assume that in the original partitioning the canonical orbitals ψ_i are eigenvectors of F . The eigenvectors of $\bar{F}$, φ_i , constitute another set of orbitals, which can be e.g., localized, at the same time, they are "canonical" with respect to operator $\bar{F}$. Such orbitals φ_i were denoted "proper canonical orbitals" by Davidson.⁶

Matrix A is, so far, arbitrary. Now one may ask the question: Given a set of non-canonical orbitals, say a set of LMOs, φ_i , what is the formula for matrix A such that the transformed Fockian matrix $\bar{F}$ is diagonal in this basis.

The answer is clear from Eq(10). If one wants to have matrix $\bar{F}$ diagonal, one chooses two orbital labels $i \neq j$, sets $\bar{F}_{ij} = 0$, and solves this equation for A_{ij} . Diagonal matrix elements A_{ii} can set be zero, if one wants to conserve the diagonal elements of F as those of $\bar{F}$. Eliminating the offdiagonal $\bar{F}$ elements determines A as follows:

$$A_{ij} = \pm(N - 1)F_{ij} \quad \text{for } i \neq j \quad (13)$$

with the negative sign to be chosen for occupied orbitals, while the positive sign being valid for virtual ones, keeping $A_{ii} = 0$.

In summary, for a set of orbitals φ_i which are not canonical in the original sense, i.e., the Fockian F is not diagonal in their basis, there exists a matrix A defined by Eq.(13), so that the associated Fockian $\bar{F}$ of Eq. (9) is diagonal.

Substituting Eq.(13) into Eq.(7) one gets the "dressed" two-electron integrals as

$$\overline{[ik|jl]} = [ik|jl] - (\pm F_{ij}\delta_{kl}(1 - \delta_{ij}) \pm F_{kl}\delta_{ij}(1 - \delta_{kl}),) . \quad (14)$$

where the sign $\pm$ for both terms is chosen so that it is + if the labels of the Fockian in that term are occupied, and – if they are virtuals.

Discussion

As shown above, if the integrals are dressed via Eq. (14), the Fockian $\overline{F}$ becomes diagonal even if the MOs are not canonical as of F . If the dressing (14) is carried out before an MBPT procedure, then a standard canonical MPn program can deal with the noncanonical orbitals φ_i without any need to consider one-electron perturbations (localization diagrams). This offers an automatic way to calculate MBPT corrections in terms of localized orbitals. Since integral dressing by Eq.(14) simply reproduces the results obtained by localization diagrams, there is no reason to perform any numerical assessment in this study.

One may mention two further important points.

First, mainly localized orbitals were discussed throughout this paper. However, the formulae presented above are equally valid for any set of noncanonical orbitals, including the optimally balanced orbitals of Subotnik and Head-Gordon,¹⁴ or the "maximum delocalized" MOs by Pipek,²⁰ to any order of MBPT.

Second, while off-diagonal elements of matrix A are defined above in a unique manner, diagonal elements remained arbitrary. These elements were set to zero in the equations above. However, changing the one-electron energies that enter PT denominators also changes the partitioning, and as was shown before,²¹ their "optimization" may improve MBPT corrections. Whether such an approach is useful in connection with the A -matrix technique, requires further studies.

Finally we mention that to our knowledge (F. Bogár, private communication) the higher order localization corrections presented in Ref.¹³ for Davidson-Kapuy partitioning, were also obtained by some kind of effective integrals constructed from diagrammatic considerations.

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TOC Graphic

$$\begin{aligned} \overline{[ik|jl]} &= [ik|jl] \\ &\quad - \left(\pm F_{ij} \delta_{kl} (1 - \delta_{ij}) \right. \\ &\quad \quad \left. \pm F_{kl} \delta_{ij} (1 - \delta_{kl}) \right) \\ &\quad \text{— integral dressing —} \end{aligned}$$