Knowles Partitioning from a Stationary Condition: Single- and Multireference case

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Abstract

A stationary condition involving the first-order wavefunction of many-body perturbation theory (PT) is shown to lead to the partitioning introduced recently by Knowles (*J. Chem. Phys., 156, 011101 (2022)*). This facilitates direct generalization for multireference (MR) PT schemes operating with a one-body Hamiltonian at zero-order. The essence of the method is an optimization of one-body integrals in the first-order interacting subspace, thereby achieving superior performance over Møller-Plesset (MP) type approaches. The stationary condition based extension, performed in the pivot-independent variant of the multiconfiguration PT (frame MCPT, fMCPT), rectifies the shortcomings of our previous MR adaptation. The resulting PT series comes close to the stationary condition-based extension, carried out in the complete active space PT (CASPT) formalism. Numerical results demonstrate that Knowles partitioning consistently outperforms MP partitioning in fMCPT.

1 Introduction

A fundamental level of quantum chemistry is electronic structure computation, performed nowadays overwhelmingly by density functional theory (DFT)[1] based methods, as well as relatively low-order scaling wavefunction based approaches. Of the latter, second order of Møller-Plesset (MP) perturbation theory (PT) stands out as a veritable workhorse, often providing optimal cost per performance.[2,3] Reliability of Hartree-Fock (HF) based many-body approaches for weakly correlated systems is a definite advantage over DFT, which often needs calibration before trustworthy application.[4] Lower computational cost, on the other hand, favors DFT especially for large systems, posing a challenge for many-body methods to extend their applicability to comparable scales. Many efforts invested in computational cost reduction came to the benefit of wavefunction methods, e.g. local approximations,[5–7] quadrature based and stochastic evaluation strategies,[8–11] density fitting[12,13] or embedding approaches.[14,15]

Redesigning methodology to improve performance is an alternative route of progress. The MP series has been an especially popular target of inspired modifications along this line.[16–20] In PT, an immediate grab for fine-tuning the theory is offered by choosing the partitioning. Several studies addressed the idea of fixing a partitioning optimal in some sense, mostly with a HF determinantal starting point.[21–29] Recently, Knowles suggested a new partitioning in the single-determinantal context,[30] paralleling Kolmogorov PT[31] in that the splitting of $\hat{H}$ is redesigned in course of calculating terms of the series. The Knowles equations also bear kinship with a partitioning optimization suggested previously in our laboratory.[32] From the application point of view, the second order results in Knowles partitioning are of coupled-cluster (CC) singles and doubles (CCSD) quality, both regarding performance and the sixth power-scaling computational cost.[30,33] Connected nature of the many-body expressions ensure that size-extensivity is maintained in the Knowles partitioning.

From a purely pragmatical perspective, a CCSD quality outcome at the same quality investment may appear expected and not particularly noteworthy. This picture changes when stepping to the multideterminantal reference scenario, for which CC theory is considerably more difficult to extend, than PT. In fact, PT is prevalent in applications where the presence of strong correlation makes an MR approach indispensable.[34,35] Lack of straightforward generalization of HF determinant based PT led to the development of numerous MRPT methods over time.[36–50] A long standing paradigm has been to use a one-body Hamiltonian at zero-order, due to its simplicity and the success of the MP partitioning in the single reference context. Early developments and the difficulties around choosing an appropriate Fockian in the open-shell case were reviewed by Davidson and Jarzęcki.[51]

Of MRPT methods widely used today, the complete active space (CAS) based PT of Roos and coworkers[52,53] and the MRMP method of Hirao and coworkers[54] feature a one-body operator at order zero, typically the generalized Fockian built with the spin-summed, one-particle reduced density matrix (RDM) of the reference function. Including explicit two-body terms in the zero-order Hamiltonian was first advocated by Dyall,[55] pointing out feasibility when restricting indices of two-body integrals as active. Among the approaches following in the footsteps of Dyall,[50,56–60] the n-electron valence state PT (NEVPT) of Malrieu and coworkers is used most extensively in our time.[61,62]

Partitioning is a key factor determining many characteristics of a PT series. Intruder-free nature of NEVPT is thanks to the two-body term in $\hat{H}^{(0)}$, which also makes it more costly than CASPT, the latter requiring at most three-particle RDM's of the reference, while NEVPT needing up to four-particle RMD's, without any approximations. Size-consistency violation of CASPT can be traced back to the appearance of Hilbert-space projectors in the zero-order operator,[63,64] which are not used in NEVPT. At the early stage of developments it has been stressed that CASPT allows for a reference of arbitrary structure,[38,65] whereas the complete active space concept is hard to abandon with NEVPT. Restricted active space (RAS) reference based extensions led to to successful RASPT applications.[66–68] Efficient evaluation, multi-state versions[69–74] as well as gradient computation[75,76] are among current methodological developments of CASPT and/or NEVPT.

Altering the partitioning has been addressed in CASPT[77–79] and MRMP,[80] often in the form of level-shifts with the aim of mitigating the intruder problem. A simpler but well parametrized zero-order in PT can be be competitive with more convoluted constructions, as demonstrated by a recent benchmark study, finding that vertical excitation energies by CASPT with the IPEA shift[81] are comparable in performance to NEVPT.[82] Partitioning optimization attempts aiming to exploit this potential in the MR framework mostly worked with zero-order levels in the Hilbert-space,[44,83–86] with rare examples for targeting the full one-body matrix.[87] A Fock-space based approach works with less parameters in general, than energy-level optimization in the Hilbert-space. At the same time, off-diagonal Fockian elements bring about a more complex, orbital rotation effect.[33]

Our previous work aiming for a Knowles partitioning at the MR level considered the multiconfiguration PT (MCPT)[88,89] framework, developed earlier in our laboratory. Performing the extension in the projected version of the theory introduced a pivot dependence with obvious drawbacks in strongly correlated situations.[90] The present study corrects for this effect, abandoning the concept of a pivotal determinant and showing a way of easy generalization in any MRPT operating with a one-body operator at zero-order.

We start the presentation by rederiving the Knowles equations in the single-reference case, starting from a stationary condition, c.f. Section 2.1.1. Extension for the MR case, presented for CASPT in Section 2.1.2 and for the pivot independent variant of MCPT (frame MCPT, fMCPT) in Section 2.2, are found closely related. Implementation and testing, performed in the fMCPT context is reported in Section 3.

2 Theory

2.1 Knowles equations in many-body PT

2.1.1 Single reference case

Assuming a closed shell HF determinant as reference Φ, the normal-ordered molecular Hamiltonian, $\hat{H}_N = \hat{H} - \langle\Phi|\hat{H}|\Phi\rangle$ is written in spin-orbital basis as

$$\hat{H}_N = \sum_{pq} f_{pq} \left\{p^+ q^-\right\} + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \left\{p^+ q^+ s^- r^-\right\}$$

where curly braces refer to normal-ordering of the second quantized operator string, f_{pq} are Fockian matrix elements and Coulomb-integrals are antisymmetrized as $\langle pq||rs\rangle = \langle pq|rs\rangle - \langle pq|sr\rangle$.

Many-body PT in MP partitioning starts with

$$\hat{F} = \sum_{p} \varepsilon_p \left\{p^+ p^-\right\} \tag{1}$$

as zero-order Hamiltonian, written on the canonical molecular orbital (MO) basis, leading to the first-order wavefunction

$$\Psi^{(1)} = \frac{1}{4}\sum_{ij}^{occ}\sum_{ab}^{virt} \left\{a^+ b^+ j^- i^-\right\} |\Phi\rangle\, c_{ab}^{ij} \, , \tag{2}$$

with $c_{ab}^{ij} = -\langle ij||ab\rangle/(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)$ obtained by ordinary Rayleigh-Schrödinger theory. Unless otherwise noted, indices $i, j, \ldots$ label occupied, $a, b, \ldots$ virtual and $p, q, \ldots$ generic MOs.

Knowles replaces the Fockian of Eq.(1) with a more general one-body zero-order Hamiltonian of the form

$$\hat{\Lambda} = \sum_{pq}^{\mathrm{oo}\,\vee\,\mathrm{vv}} \Lambda_{pq} \left\{p^+ q^-\right\} \tag{3}$$

with the aim of using it as zero-order operator in many-body PT. Parameters Λ_{pq} in Eq.(3) are set such that $\hat{\Lambda}$ should be possibly close to $\hat{H}_N$. This is expressed by the equation

$$\left(\hat{H}_N - \hat{\Lambda}\right)|\Psi^{(1)}\rangle = 0 \ . \tag{4}$$

To ensure Hermiticity of $\hat{\Lambda}$, $\Lambda_{pq} = \Lambda^*_{qp}$ is required. Note, that $\hat{\Lambda}$ takes Φ as its eigenfunction, due to the restriction of summation indices in $\hat{\Lambda}$ as $p, q \in occ$ or $p, q \in virt$. Shorthand notation "oo $\vee$ vv" refers to this in Eq.(3).

To generate equations for Λ_{pq}, projections of Eq.(4) were taken in Ref.[30] Instead of this, we proceed by minimization of a squared norm, according to

$$\frac{\partial}{\partial \Lambda_{pq}} \langle\Psi^{(1)}| \left(\hat{H}_N - \hat{\Lambda}\right) \hat{P}_1 \left(\hat{H}_N - \hat{\Lambda}\right)|\Psi^{(1)}\rangle = 0 \ , \tag{5}$$

for $p \leq q$ and both occupied or virtual. In the above, $\hat{P}_1$ projects onto the first-order interacting subspace of the configuration interaction space (FOCI), i.e. the space of functions contributing to $\Psi^{(1)}$. When Φ is the HF wavefunction, $\hat{P}_1$ is the projector of doubly excited determinants. Performing the derivation in Eq.(5) leads to

$$\langle\Psi^{(1)}| \left\{p^+q^- + q^+p^-\right\} \hat{P}_1 \left(\hat{H}_N - \hat{\Lambda}\right)|\Psi^{(1)}\rangle + c.c. = 0 \ \ , \ p < q \tag{6a}$$

$$\langle\Psi^{(1)}| \left\{p^+p^-\right\} \hat{P}_1 \left(\hat{H}_N - \hat{\Lambda}\right)|\Psi^{(1)}\rangle + c.c. = 0 \ . \tag{6b}$$

Substituting Eq.(2) in Eq.(6) and using the generalized Wick's theorem[91] yields the following many-body formulae, in the real case

$$0 = \langle\Theta^+_{de}|\hat{H}_N - \hat{\Lambda}|\Psi^{(1)}\rangle \ , \tag{7a}$$

$$0 = \langle\Theta^+_{kl}|\hat{H}_N - \hat{\Lambda}|\Psi^{(1)}\rangle \ , \tag{7b}$$

with

$$|\Theta^+_{de}\rangle = \sum_{ij}^{occ}\sum_{a}^{virt}\Big(\big\{d^+a^+j^-i^-\big\}\,|\Phi\rangle\,c^{ij}_{ea} \;+\; \big\{e^+a^+j^-i^-\big\}\,|\Phi\rangle\,c^{ij}_{da}\Big) \ , \tag{8a}$$

$$|\Theta^+_{kl}\rangle = -\;\sum_{i}^{occ}\sum_{ab}^{virt}\Big(\big\{a^+b^+i^-k^-\big\}\,|\Phi\rangle\,c^{li}_{ab} \;+\; \big\{a^+b^+i^-l^-\big\}\,|\Phi\rangle\,c^{ki}_{ab}\Big) \ , \tag{8b}$$

for $d < e$ virtual and $k < l$ occupied and

$$|\Theta^+_{dd}\rangle = \sum_{ij}^{occ}\sum_{a}^{virt}\big\{d^+a^+j^-i^-\big\}\,|\Phi\rangle\,c^{ij}_{da} \ , \tag{9a}$$

$$|\Theta^+_{kk}\rangle = -\;\sum_{i}^{occ}\sum_{ab}^{virt}\big\{a^+b^+i^-k^-\big\}\,|\Phi\rangle\,c^{ki}_{ab} \ , \tag{9b}$$

when outer indices are equal .

Comparison with Ref.[30] shows, that Eq.(7) is essentially the system of equations set by Knowles, differing in trivial numerical factors which do not affect the solution. Introducing the above theta functions in the ket of Eq.(7) by noting that

$$\hat{P}_1\hat{\Lambda}|\Psi^{(1)}\rangle \;=\; \sum_{p\leq q}^{oo\vee vv}|\Theta^+_{pq}\rangle\,\Lambda_{pq} \ ,$$

one arrives at the condensed form

$$\sum_{r\leq s}^{oo\vee vv} T_{pq,rs}\,\Lambda_{rs} \;=\; Y_{pq} \tag{10}$$

with a symmetric coefficient matrix

$$T_{pq,rs} \;=\; \langle\Theta^+_{pq}|\Theta^+_{rs}\rangle \tag{11}$$

and the inhomogeneous term

$$Y_{pq} \;=\; \langle\Theta^+_{pq}|\hat{H}_N|\Psi^{(1)}\rangle \tag{12}$$

for $p \leq q$, both being either occupied or virtual. The fact, that $\mathbf{T}$ composed with elements in Eq.(11) is symmetric simplifies the analysis of the underdetermined nature of Eq.(10). While the original form of the Knowles equations necessitated to rely on singular value decomposition and to identify the left and right singular vectors corresponding to the zero singular value,[33] one presently arrives at the same conclusion by simply noting that $\mathbf{T}$ is an overlap matrix with one zero eigenvalue, generated by the identity

$$\sum_{d}^{virt} \Theta^{+}_{dd} \; + \; \sum_{k}^{occ} \Theta^{+}_{kk} \; = \; 0 \; ,$$

following from the definition in Eq.(9)

Recalling that the third order energy can be expressed as $\langle \Psi^{(1)} | \hat{H}_N - \hat{\Lambda} | \Psi^{(1)} \rangle$, Eq.(6) can be interpreted as setting terms of the third order energy zero. In fact, when the Knowles procedure is iterated till self consistency (i.e. $\Psi^{(1)}$ stems from $\hat{H}_N - \hat{\Lambda}$ as perturbation), the third-order PT correction vanishes.[30,33]

2.1.2 Multireference case

A previous attempt[90] of extending the partitioning of Knowles for the MR case has been based on Eq.(7) with the many-body form of theta functions in Eqs.(8)-(9). The occ, virt categorization of indices in Eqs.(8)-(9) necessitated a Fermi vacuum even in the case where identification of one determinant as pivotal could not be justified based on the associated weights in Φ. This resulted a deterioration in the performance in parallel with the increase in the multireference character of Φ.

A solution to the problem is offered by Eq.(6) since theta functions deducible as

$$|\Theta^{+}_{pq}\rangle = \hat{P}_1 \left\{ p^{+} q^{-} + q^{+} p^{-} \right\} |\Psi^{(1)}\rangle \quad , \; p < q \tag{13a}$$

$$|\Theta^{+}_{pp}\rangle = \hat{P}_1 \left\{ p^{+} p^{-} \right\} |\Psi^{(1)}\rangle \tag{13b}$$

are free from occ, virt categorization of the indices. Any restriction on p, q in Eq.(13) stems from the expression of $\hat{\Lambda}$ in Eq.(3). Such constraints are governed by the nature of the reference, vide infra, and do not require a Fermi vacuum in the general case. In principle, indices in Eq.(3) can be completely unconstrained in the MR case, though pilot tests warn to be cautious in applying the Knowles condition for all index pairs.[90]

The main message of the present study is that Eqs.(10), (11) and (12) together with Eq.(13) offer a direct way of adapting the Knowles partitioning in any MRPT framework operating with an effective one-body Hamiltonian at zero-order. The formulae relevant for CASPT are outlined below.

The difficulty about extending HF based many-body PT for the single-but-multi scenario is that several important characteristics of the single-determinantal starting point, e.g.

1. Φ is the eigenfunction of a Fockian,
2. excited determinants are also eigenfunctions of the same Fockian,
3. excited determinants provide an orthonormal basis in the Hilbert-space for constructing wavefunction corrections,

cease to be valid when Φ is multideterminantal. Wolinsky and Pulay suggested to compose a zero-order Hamiltonian with the help of projectors in the Hilbert-space, to alleviate problems 1, 2 above.[37,92] Taking $\hat{P}_0 = |\Phi\rangle\langle\Phi|$ as the projector corresponding to the reference, and $\hat{P}_\perp = \hat{1} - \hat{P}_0$ its orthogonal complement, the most simple form of the Wolinsky-Pulay zero-order can be cast as

$$\hat{H}^{(0)}_{WP} \;=\; \hat{P}_0 \hat{F} \hat{P}_0 \;+\; \hat{P}_\perp \hat{F} \hat{P}_\perp \;. \tag{14}$$

Addressing problem 3 above, Wolinsky and Pulay applied internally contracted (IC) single, double, etc. substitutions of the reference and treated the overlap among excitation subspaces by successive Gram-Schmidt orthogonalization. Nonorthogonality within a given excitation level has been handled by various techniques.[38,63,66] Roos and coworkers[34,52,53] and Werner and coworkers[66,93] became significant developers of the theory, giving rise to a method established in quantum chemical practice under the acronym CASPT.

The aspect of CASPT, important for our present purpose is operator $\hat{F}$ in Eq.(14), which is typically the generalized Fockian, possibly modified by level-shifts for treating the intruder-problem.[81] In the spirit of Knowles, one would rewrite Eq.(14) as

$$\hat{H}^{(0)}_{WPK} \;=\; \hat{P}_0\hat{\Lambda}\hat{P}_0 \;+\; \hat{P}_\perp\hat{\Lambda}\hat{P}_\perp \;, \tag{15}$$

with

$$\hat{\Lambda} \;=\; {\sum_{pq}}' \Lambda_{pq} \left\{p^+q^-\right\} \;, \tag{16}$$

where $\{p^+q^-\} = p^+q^- \;-\; \langle\Phi|p^+q^-|\Phi\rangle$ can be considered a generalized normal-ordered operator string[94,95] when Φ is multideterminantal and prime on the sum refers to possible restriction of the orbital indices. Assuming a complete active space (CAS) reference, Roos et al. e.g. allowed only the doubly occupied (docc), active (act) and virtual (virt) block of the generalized Fockian to enter the zero-order in one of their early works.[38] They later extended the approach, admitting the docc-act and act-virt block, and keeping the docc-virt block zero, in agreement with the generalized Brillouin theorem for a CAS function.[65]

To set up the equations for parameters Λ_{pq}, the first-order CASPT wavefunction

$$|\Psi^{(1)}\rangle \;=\; \sum_{K}^{\mathrm{FOCI}} |\Phi_K\rangle\, c_K \tag{17}$$

is to be computed first, with Φ_K standing for orthogonalized IC functions belonging to the FOCI. First-order coefficients c_K are the MR analogue of c^{ij}_{ab} in Eq.(2), arising from

$$\sum_{K}^{\mathrm{FOCI}} \langle\Phi_L|\hat{F} - E^{(0)}|\Phi_K\rangle\, c_K \;=\; -\,\langle\Phi_L|\hat{H}_N - \hat{H}^{(0)}_{WP}|\Phi\rangle \;, \tag{18}$$

with $E^{(0)} = \langle\Phi|\hat{F}|\Phi\rangle$.

In the next step, theta functions are composed as

$$|\Theta^{+}_{pq}\rangle = \sum_{K,L}^{\text{FOCI}} |\Phi_L\rangle\langle\Phi_L| \left\{p^+q^- + q^+p^-\right\} |\Phi_K\rangle\, c_K \quad ,\; p < q \tag{19a}$$

$$|\Theta^{+}_{pp}\rangle = \sum_{K,L}^{\text{FOCI}} |\Phi_L\rangle\langle\Phi_L| \left\{p^+p^-\right\} |\Phi_K\rangle\, c_K \; . \tag{19b}$$

Using the above, Eqs.(11)-(12) can be evaluated and Eq.(10) solved for parameters Λ_{pq}, $p \leq q$ restricted in agreement with Eq.(16). The first order CASPT equation can now be written in the Knowles partitioning as

$$\sum_{K}^{\text{FOCI}} \langle\Phi_L|\hat{\Lambda} - E^{(0)}|\Phi_K\rangle\, c_K \;=\; -\,\langle\Phi_L|\hat{H}_N - \hat{H}^{(0)}_{WPK}|\Phi\rangle \;, \tag{20}$$

with $E^{(0)} = \langle\Phi|\hat{\Lambda}|\Phi\rangle$. The CASPT2 energy either in the original or in the Knowles partitioning is obtained as

$$E^{(2)} \;=\; \sum_{K}^{\text{FOCI}} \langle\Phi|\hat{H}_N|\Phi_K\rangle\, c_K \; . \tag{21}$$

Calculation of Eq.(12) is the time determining step of solving the Knowles equations in the single reference setting, featuring sixth power scaling with the number of basis functions. Calculation of Y_{pq} in the CASPT context is based on

$$Y_{pq} \;=\; \sum_{K,L,M}^{\text{FOCI}} c_K\, \langle\Phi_K| \left\{p^+q^- + q^+p^-\right\} |\Phi_L\rangle\langle\Phi_L|\hat{H}_N|\Phi_M\rangle\, c_M \quad ,\; p < q \tag{22}$$

and remains the bottleneck of the procedure. Efficient methods worked out within the MRCI framework for matrix element computation with IC functions,[96,97] facilitate an implementation scaling with the number of IC states but not with the length of the determinantal expansion of the reference.[66] Relying on this approach, the cost of the Knowles equations in the CASPT framework essentially agrees with that of CASPT3.[93,98] Computation of $\mathbf{T}$ in Eq.(11) is less demanding than that of $\mathbf{Y}$, as it involves only one-body couplings in the place of $\hat{H}_N$ in Eq.(22).

Before stepping on, let us briefly comment on further two MRPT methods, available in broadly used quantum chemistry program systems. One is the MRMP[41] method of Hirao and coworkers, working with a diagonal zero-order, written in spectral form in the Hilbert-space with the help of determinants or configuration state functions. The role of the MR Fockian, the key point in the Knowles partitioning, is somewhat different in MRMP from what have we considered so far, since it is used to generate zero-order eigenvalues only. This diagonal assumption on the zero-order is the origin of non-invariance of the method to unitary transformation of CI space vectors used to build the zero-order. An energy level optimization strategy, working in the Hilbert-space is therefore more suitable in the context of MRMP, than the idea of Knowles. This has been designed and tested previously.[84,85] The extension of Granovsky[73] stepped in the direction of restoring unitary invariance by assuming a block-diagonal form of the zero-order Hamiltonian over model and secondary subspaces. Relying on the full, generalized Fockian within the blocks, Granovsky's extension provides a suitable framework for adapting the Knowles partitioning in the multi-state realm of MRPT.

The NEVPT introduced by Malrieu and coworkers[45,61] is also amenable to the partitioning optimization idea of Knowles. It carries over in a straightforward manner to the core and virtual orbitals involving term of the Dyall-Hamiltonian used to compose the zero-order. The active orbitals' term, involving two-body integrals, calls for an extension of the Knowles partitioning, which is out of scope of the present study.

2.2 Frame-based Multiconfiguration perturbation theory (fMCPT)

The MCPT family of methods[88,89] was devised in our laboratory with the aim of correcting a wave function of arbitrary structure by PT. In its original formulation, the zero-order MCPT Hamiltonian is composed in spectral form, relying on projected determinants in the space complementary to the reference. A characteristic feature of the theory is the treatment of the (inverse) overlap of projected determinants in closed form, without the need of invoking any numerical orthogonalization procedure. Within the MCPT framework, definition of a specific method requires fixing the partitioning, for which several options have been tested, e.g. Davidson-Kapuy or Epstein-Nesbet.[86] Optimization of the zero-order energy levels has been also considered both in the Fock-space and in the Hilbert-space.[86,99] The latter relates to the MR generalization of the simplest coupled electron pair approximation, CEPA0.[100,101]

The present focus being on the use of effective one-body operators at zero-order, we briefly recapitulate the MP variant of the theory. This abandons the spectral form of the zero-order and uses projectors to satisfy the zero-order equations, in the spirit of Wolinsky and Pulay. The MP partitioning of MCPT was first developed with an antisymmetric product of singlet coupled, strongly orthogonal geminals reference[102] and later got extended for the open-shell case.[103] The geminal structure does not affect essential elements of MP-MCPT, its role is merely to keep the determinantal expansion of the first order wavefunction relatively short and simplify matrix element calculation. Below we leave the geminal restriction and consider an arbitrary zero-order function.

Expansion of the reference on the set of orthonormal determinants is written as

$$|\Phi\rangle = \sum_{K=1}^{M} |K\rangle\, d_K \ , \tag{23}$$

where determinants with nonzero d_K are considered to form the M-dimensional model space. We seek a set of simple functions to compose projector $\hat{P}_\perp = \hat{1} - \hat{P}_0$, orthogonal and complementary to $\hat{P}_0 = |\Phi\rangle\langle\Phi|$. For this end, Slater-determinants $|K\rangle$ are orthogonalized to $|\Phi\rangle$ as

$$|K'\rangle = \hat{P}_\perp |K\rangle = |K\rangle \ - \ |\Phi\rangle\, d_K .$$

While $|K'\rangle = |K\rangle$ for $d_K = 0$, we keep using $|K'\rangle$ for $K > M$, for notational simplicity.

The overlap matrix

$$S_{KL} = \langle K'|L'\rangle$$

features a full block corresponding to projected model space determinants and it is diagonal otherwise. Due to the Schmidt-orthogonalization, the model space block of $\mathbf{S}$ built with S_{KL} above has a rank of $M-1$. This renders $\mathbf{S}$ singular, hindering any overlap treatment working with the ordinary inverse, e.g. Löwdin's symmetrical orthogonalization[104] or biorthogonalization. A workaround applied initially was excluding one element of the model space, practically the determinant of pivotal role in Φ.[86,88,89] The Fermi vacuum dependence, introduced this way, was overcome in two subsequent studies,[105,106] of which the approach based on the theory of frames, abbreviated as fMCPT is pursued below.

The essence of fMCPT[106] is to compose $\hat{P}_\perp$ with the help of the redundant set of functions $|K'\rangle$ as

$$\hat{P}_\perp = \sum_{KL} |K'\rangle\, R_{KL}\, \langle L'|$$

where matrix $\mathbf{R}$ is the inverse of $\mathbf{S}$ in the generalized, Moore-Penrose[107] sense. Since $\mathbf{S}$ is the representation of a projector, $\mathbf{R} = \mathbf{S}$ and $\sum_L S_{KL}\langle L'| = \langle K'|$, leading to

$$\hat{P}_\perp = \sum_K |K'\rangle\langle K'| \;, \tag{24}$$

with the sum in Eq.(24) running for all determinants of the Hilbert-space.

The zero-order Hamiltonian of MP-fMCPT is given by Eq.(14) with $P_\perp$ taken from Eq.(24) and $\hat{F}$ written as

$$\hat{F} \;=\; \sum_{pq} f_{pq} \left\{ p^+ q^- \right\} \;, \tag{25}$$

with $f_{pq} = h_{pq} + \sum_{rs} \gamma_{sr} \langle pr||qs\rangle$ and $\gamma_{sr} = \langle\Phi|r^+ s^-|\Phi\rangle$. The spin-summed one-body RDM appears in a trivial manner for a singlet wavefunction, when rewriting $\hat{F}$ in terms of spatial orbitals. In the general case, the spin-averaged $f_{PQ} = 0.5(f^\alpha_{PQ} + f^\beta_{PQ})$ is used to achieve this.

Expansion of the first order wavefunction in MP-fMCPT takes the form analogous to Eq.(17)

$$|\Psi^{(1)}\rangle \;=\; \sum_K^{\mathrm{FOCI}} |K'\rangle\, c_K \tag{26}$$

with the sum running for projected determinants of the FOCI. The first order equation is an analogue of Eq.(18) , reading as

$$\sum_{K}^{\mathrm{FOCI}} \langle L'|\hat{F}|K'\rangle\, c_K \;=\; -\,\langle L'|\hat{H}_N - \hat{H}^{(0)}_{WP}|\Phi\rangle \;, \tag{27}$$

where $E^{(0)} = \langle\Phi|\hat{F}|\Phi\rangle = 0$ was utilized, in accordance with Eq.(25).

At this point it is apparent that the MP-fMCPT version presented here basically agrees with the version of CASPT, where the complementary space term in Eq.(14) is kept as a full block.[63] Representation of the complementary space projector, $P_\perp$ is determinant based in fMCPT and IC function based in CASPT, which is a formal difference and should have no effect on the PT terms. A technical difference affecting the first-order equation is that IC excitation types giving rise to Φ_L in Eq.(17) are those, potentially contributing to $\Psi^{(1)}$, e.g. internal excitations are excluded for a CAS reference. Preparing for a reference of arbitrary structure, such a selection is not performed when setting up Eq.(26) for fMCPT. All determinants related by single or double replacement to any determinant of Φ contribute as $\langle L'|$ to Eq.(26).

Methods of intruder avoidance, worked out in the context of CASPT[79] carry over to the determinantal based formulation of MP-fMCPT in a trivial manner. The applications presented in Section 3 are not challenging from this respect as seen by the correct behaviour of MP partitioning results. For this reason, neither level-shifts, nor regularization techniques are applied in this study.

Turning to our present interest, adaptation of the Knowles partitioning, Eqs.(15)-(16) of Section 2.1.2 apply in fMCPT also. Equations (19)-(21) necessary for the Knowles partitioning are rewritten for fMCPT as seen above, orthogonalized IC functions $|\Phi_K\rangle$ getting substituted for $|K'\rangle$ and the same for index L.

3 Assessment

The pilot tests presented in this section were conducted using the determinant-based fMCPT approach described in Section 2.2. For clarity of terminology, we refer to the methods in general with prefix MP- and K- indicating Møller-Plesset and Knowles partitioning, respectively. The results of the fMCPT-based variants are presented in comparison with the previously introduced Fermi-vacuum-dependent projected MCPT-based (pMCPT) variants[90] taking Full-CI (FCI) as reference.

Apart from CAS, perfect pairing generalized valence bond (GVB) functions are also investigated as reference. The latter offers an economic means of accounting for static correlation and works well at around equilibrium and in single bond breaking processes. If the geminals are singlet coupled, multiple bond breaking is qualitatively correct only for isolated single bonds. Breaking multiple bonds or adjacent single bonds calls for an extension of GVB which is possible e.g. by involving triplet components mixed to singlets at the two-electron level. This leads to a spin contaminated two-electron function aka. geminal.

An anti-symmetrized product of strongly orthogonal, spin-contaminated geminal (APSG) wavefunction is a suitable reference when overall spin is just slightly spoiled.[108] When spin is seriously violated by the geminal product, a partial restoration can be of help, achieved by the so-called half-projection yielding half-projected APSG, HPAPSG.

Previously, we have successfully applied the variationally optimized HPAPSG wavefunction as reference for describing the lowest singlet and triplet states of biradical systems both relying on UHF orbitals[60,109] as well as those corresponding to the HPAPSG energy minimum.[110] The Dyall-type zero order PT scheme, exploiting the geminal structure of the reference is here used as benchmark, under acronym SAPT2, referring to symmetry-adapted PT.[111] Of the symmetry adaptation variants discussed in Ref.,[60] the so-called weak forcing scheme is adopted. It is stressed that spin is purified both at the level of HPAPSG and SAPT2. A partial spin adaptation is built in HPAPSG at zero-order, while SAPT2 incorporates the effect perturbatively, in a Dyall-type framework.

3.1 Bond dissociation curve of LiH

First, the potential curve for a bond dissociation is monitored on a test system of the heteronuclear diatomic lithium-hydride molecule. The system starts to exhibit correlated characteristics of medium strength as the weight of the first doubly excited determinant, lowest in energy, becomes comparable to that of the Hartree-Fock determinant during the bond dissociation.

In Fig. 1 the influence of the pivot can be observed by comparing pMCPT to fMCPT. It also serves to demonstrate the performance of the Knowles partitioning relative to its MP counterpart. Potential energy curves were computed using a CAS(2,2) reference function to capture static correlation.

Comparing with MP-pMCPT2, the pivot-dependent previous formulation of the Knowles partitioning (K-pMCPT) had been observed to bring significant improvement, lowering the 6-8 mE$_h$ deviations from FCI of MP-pMCPT2 under 1 mE$_h$ at around equilibrium distance.[90] However, the error curve of K-pMCPT2 is not balanced showing a significant increase during the dissociation, as the single determinant dominated description deteriorates. By contrast, the recent pivot-independent variant of the Knowles partitioning (K-fMCPT2) maintains an error below 1 mE$_h$ along the entire potential curve, significantly outperforming the other methods both regarding mean error and non-parallelity. The slight hump around 3 Å indicates remaining imbalance in the description of static and dynamic correlation. Note that this is a range of avoided crossing with the first excited singlet state.

Fig. 1 also serves to compare the Knowles partitioning in MCPT with more established methodologies. The MRMP curve, obtained by the GAMESS program suite[112] and shown in Fig. 1 closely overlaps with MP-fMCPT2, which in turn can be regarded a CASPT2, without any level-shifts, as discussed below Eq.(27) in Section 2.2. It is apparent in Fig. 1 that both MRMP2 and CASPT2 exhibit a deficit in dynamical correlation, more at around equilibrium and somewhat less in the dissociated regime, bringing a significant non-parallelity in addition to the overall deviation from FCI. Both effects are spectacularly reduced by switching to the

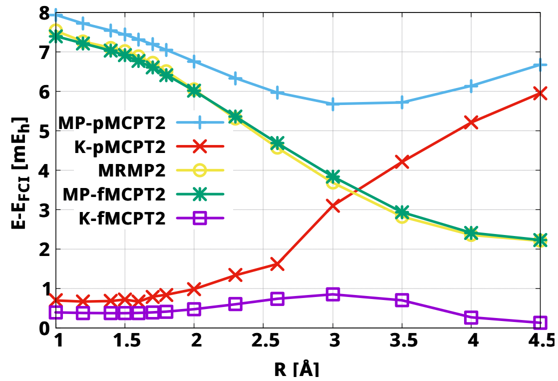


Figure 1: Second-order energy deviations from Full-CI as a function of interatomic distance R in LiH in cc-pVTZ basis set. A CAS(2,2) reference function is implied. Prefix K- refers to the Knowles partitioning. See text for more on labels.

Knowles partitioning, i.e. K-fMCPT, which is essentially a Knowles partitioning in CASPT2.

3.2 Size-consistency test on non-interacting LiH dimer

Extensivity is a key property of many-body methods and warrants careful investigation. Here we test the related concept of size-consistency, defined as the strict additive separability of the energy of two non-interacting subsystems. In the single reference case, the Knowles partitioning was shown to be extensive by construction.[30] The MCPT family of methods was shown to be slightly size-inconsistent.[89] This is exemplified on a test system of two non-interacting LiH molecules in Table 1.

Focusing on MP, the errors are roughly in the 0.01 mE_h range for the double zeta (DZ) quality basis and in the 0.1 mE_h range for the correlation consistent polarized DZ basis. The fMCPT results are more favourable than pMCPT in both basis sets.

Addressing the effect of Knowles partitioning, the error is increased approximately by a factor of three in pMCPT2, while it is considerably reduced in fMCPT2, dropping to the level of numerical convergence threshold in the 6-31G basis test. Improvement of K-fMCPT over K-pMCPT in Table 1 is a clear sign of the superiority of the present, pivot independent extension over the previous approach.

Table 1: Size-consistency errors, $(E_{\text{dimer}} - 2E_{\text{monomer}})$, for the LiH dimer in m$E_h$. The reference state is a CAS(2,2) on the monomer, and their direct product for the dimer. Bond lengths of the monomer units are 2.00 Å. Core electrons are correlated in calculations in 6-31G basis and are frozen in cc-pVDZ basis.

basis set	6-31G	cc-pVDZ
MP-pMCPT2	0.1193	0.5415
K-pMCPT2	0.3178	1.0726
MP-fMCPT2	−0.0561	−0.1512
K-fMCPT2	−0.0003	−0.0853

In line with the observations of Van Dam et al.[63] on size-inconsistency getting reduced with enhancing the block-diagonal structure of the matrix of $\hat{H}^{(0)}$ in the Hilbert-space, the error of K-pMCPT2 is only cca. twice that of MP-pMCPT2 when only double excitations are allowed to contribute.

3.3 Potential curve of BeH_2

A more challenging bond cleavage and formation process to be monitored is provided by the C_{2v} insertion of a Be atom into a H_2 molecule at nine standardized geometry points of Purvis and Bartlett along a theoretical reaction pathway.[113]

The reference function is chosen as valence GVB. Natural molecular orbitals of the system vary significantly along the potential energy curve. They are delocalized in the middle, at point E, and gradually localize on Be-H bonds towards points D-A, while they correspond to an H-H bond and a separated Be towards points F-I, in line with chemical intuition.

The strongly correlated characteristics of the system in points D-F stem from the complete deterioration of the single-determinantal picture as two determinants become equal in weight then switch dominance of the CI expansion along the path. As a consequence, it can be observed in Fig. 2 that methods based on projected MCPT yield significantly larger errors in the D-F range, reaching a maximum deviation from FCI of 20-25 mE_h in point E. Knowles partitioning in pMCPT reduces the error of MP-pMCPT but cannot mitigate the large non-parallelity of the curve. The MP-fMCPT results are much improved, showing no sudden

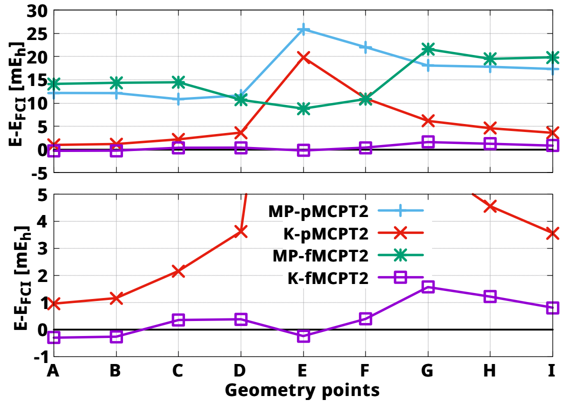
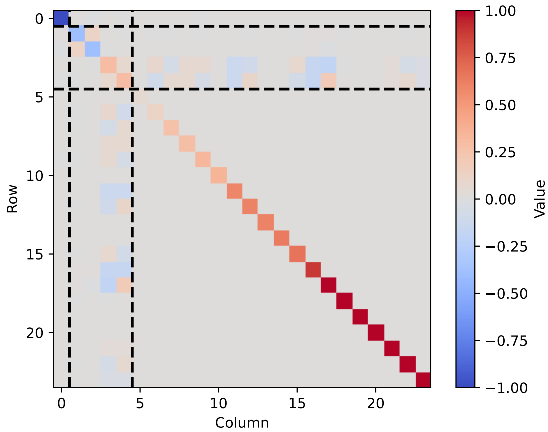


Figure 2: Second-order energy deviations from Full-CI at standardized geometry points of BeH_2.[113] Calculations were performed with a GVB reference function in cc-pVDZ basis set. The lower panel is a zoom into the -1 to 5 mE$_h$ energy range.

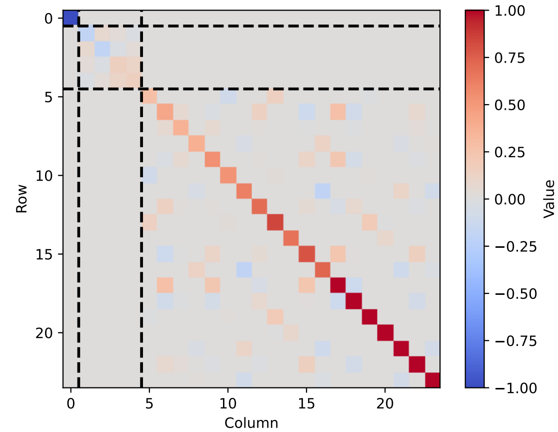
increase in error at point E. The success of the Knowles partitioning with the fMCPT-based variant is spectacular in Fig. 2 staying below 2 mE$_h$ in all points. The absence of pronounced error trends and the overall lower deviations indicate that Knowles partitioning in fMCPT consistently outperforms MP, similarly to the experience in single-reference theory.[30]

The effect of partitioning optimization on the value of parameters is shown in Fig. 3, on the example of geometry D, exhibiting matrices $\mathbf{F}$, $\mathbf{\Lambda}$ and their difference as colormaps. The scale of color codes in panels (a) and (b) focus on a ± 1 E$_h$ window around the Fermi-level, facilitating comparison of offdiagonal and active index involved elements. (Diagonals of both $\mathbf{F}$ and $\mathbf{\Lambda}$ fall in the range of [-4.8,2.4] E$_h$.) The block structure of matrices in panel (a) and (b) indicate that the full Fockian was considered in MP-fMCPT while a block-diagonal assumption was applied on the effective one-body operator of K-fMCPT. This means that only the diagonal blocks in panel (c) can be regarded as resulting from parameter optimization. The active-virtual block of panel (c) is simply the negative of panel (a), shown on a finer scale.

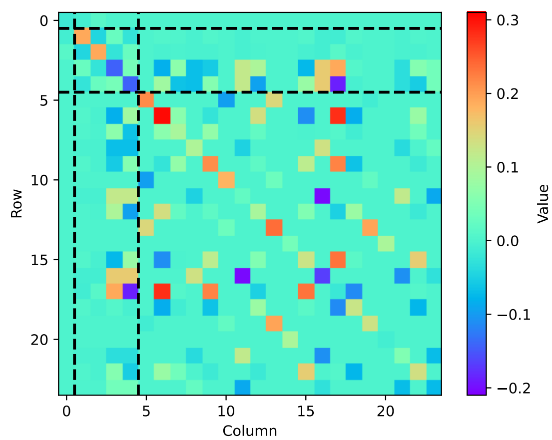
The most significant change in the active block is closing of the gap, as deducible from Fig. 3. Setting the Knowles-condition has a more pronounced effect on offdiagonal elements in the virtual block, amply scattering it with elements on the order of 0.1 mE$_h$, of both positive



(a) Matrix $\mathbf{F}$, with scale zoomed in around the Fermi-level.



(b) Matrix $\mathbf{\Lambda}$, with scale zoomed in around the Fermi-level.



(c) Di erence matrix $\mathbf{\Lambda} - \mathbf{F}$.

Figure 3: Matrices of effective one-body operators corresponding to MP-fMCPT (panel a), K-fMCPT (panel b) and their difference (panel c) on the example of the BeH_2 molecule in cc-pVDZ basis at geometry point D. Dashed lines mark the separation of doubly occupied, active and virtual orbital sets of the GVB reference.

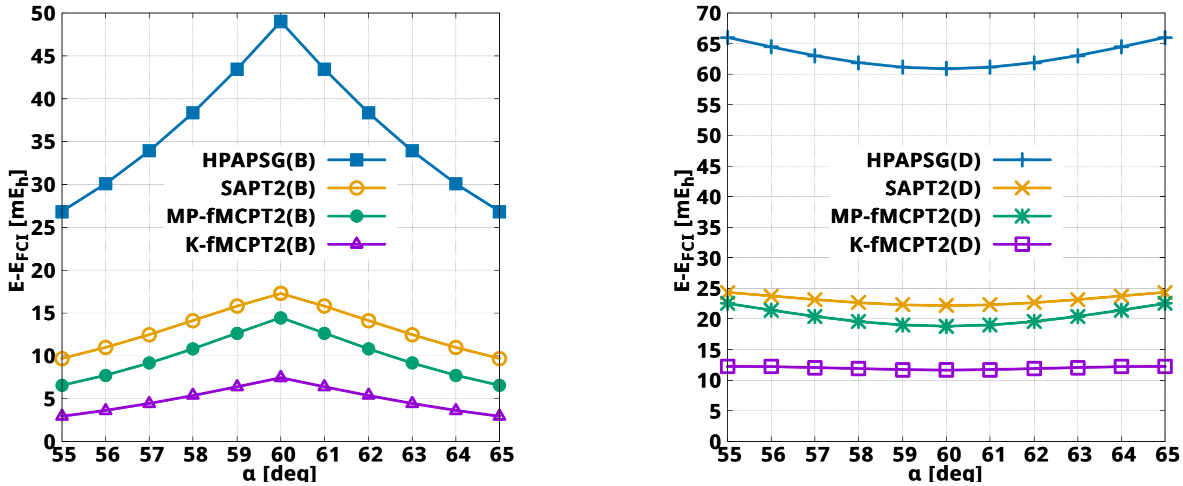
and negative sign, and indicating a non-negligible orbital transformation if one wished to turn to Knowles-optimized virtuals from pseudo-canonicals. These observations are valid all along the reaction path considered for BeH_2. Though plots of $\mathbf{\Lambda} - \mathbf{F}$ differ at each geometry, they exhibit no tendency that would justify to show them all.

3.4 Distortion of H_6 from D_{6h} to D_{3h}

A typical example for the breakdown of GVB is the D_{6h} to D_{3h} distortion of H_6, with a ring of adjacent bonds being broken and formed simultaneously. For this system, the HPAPSG wavefunction is taken as zero order and SAPT2 serves as an example for a Dyall-type dynamic correlation method.

Full variational optimum corresponds to localized bonds (B) between pairs of atoms. This introduces an artefactual cusp at the hexagonal symmetry, arising from the crossing of the two Kekulé-like bonding arrangements as the curve HPAPSG(B) in Fig. 4a shows. Though higher in energy by cca. 10 to 35 mE_h in Fig. 4b HPAPSG(D) based on delocalized UHF natural orbitals yields significantly reduced error variation along the reaction path and exhibits zero derivative at the hexagonal structure, $\alpha = 60°$.

Comparing the perturbative results obtained with the one-electron and two-electron type zero-order Hamiltonians, MP-fMCPT2 is observed to have a slight advance over SAPT2 and the remaining space for correlation is, in this case too, well-exploited by the Knowles partitioning (K-fMCPT2). The order in energy of the two orbital sets is preserved upon PT, but the energy difference is considerably diminished. With localized orbitals, all PT methods diminish the cusp of the reference at 60 degrees. Knowles partitioning exhibits the smallest error, below 10 mE_h, and the cusp of K-fMCPT2 is slightly reduced in comparison with MP-fMCPT2.



(a) HPAPSG(B) indicates variationally optimized localized orbitals for the half-projected geminal reference.

(b) HPAPSG(D) indicates delocalized UHF natural orbitals for the half-projected geminal reference.

Figure 4: Second-order energy deviations from Full-CI of H_6 transition from D_{6h} to D_{3h} at different central angles, α (between neighbouring H atoms alternating with $120° - \alpha$). Calculations were performed with HPAPSG reference functions in minimal H6S3S basis set.

4 Conclusions

Knowles partitioning gets the effect of a one-body zero-order closer to that of the full Hamiltonian. The zero-order obtained from the Knowles condition remarkably improves upon MP2 in the single reference framework. Driven by this success we have been seeking an extension to the MR case, with similar performance.

The stationary condition based reformulation of the Knowles equations, reported in this work, facilitates adaptation of the theory in the context of MRPT's, based on a one-body zero-order Hamiltonian.

In the present, proof of concept study we adapted the theory in frame MCPT. The equations being closely parallel, MP-fMCPT can be considered a CASPT variant and an implementation of the Knowles partitioning in CASPT can be expected to give results similar to K-fMCPT, shown here.

Pilot numerical results are encouraging in showing significant improvement over the MP partitioning in scenarios including single bond breaking as well as bond rearrangement reactions exhibiting strong correlation pattern. The Knowles partitioning was found to perform equally reliably with reference functions ranging from CAS, through GVB till the more intricate spin-mixed and half-projected geminal product, HPAPSG. Size-inconsistency of fMCPT in the MP partitioning is also shown to get beneficially reduced by the Knowles partitioning.

The results of this study are stimulating for a broader range of numerical tests, including intruder prone examples as well as energy differences, representing an important field of application of MRPT. Unfortunately, such calculations are out of the reach of our transparent but inefficient, pilot implementation. A more extensive test is especially warranted with a focus on the intruder effect since there is no guarantee from the theoretical side that the Knowles partitioning would circumvent it. Inclusion of the Knowles equations in gradient calculation by Lagrange-multipliers as well as extension to multistate theory can be envisaged as future lines of development.

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