The Journal of Chemical Physics

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Cite as: J. Chem. Phys. (in press) (2022); https://doi.org/10.1063/5.0112563
Submitted: 21 July 2022 • Accepted: 29 September 2022 • Accepted Manuscript Online: 04 October 2022

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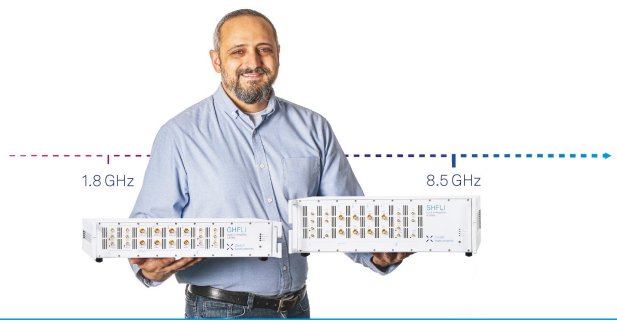


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Accepted to J. Chem. Phys. 10.1063/5.0112563



# Pivot invariance of Multiconfiguration Perturbation Theory via frame vectors

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(Dated: 20 September 2022)

Multiconfiguration perturbation theory (MCPT) is a general framework for correcting a reference function of arbitrary structure. Variants of MCPT introduced so far differ in the specification of the zero-order Hamiltonian, i.e. the partitioning. A common characteristic of MCPT variants is that no numerical procedure is invoked when handling the overlap of the reference function and determinants spanning the configuration space. This comes at the price of pinpointing a principal term in the determinantal expansion of reference, rendering the PT results dependent on this choice.

It is here shown, that pivot dependence of MCPT can be eliminated by using the over-complete set of projected determinants in the space orthogonal and complementary to the reference. Projected determinants form a so-called frame, a generalization of the notion of basis, allowing for redundancy of the set. Simple structure of the frame overlap matrix facilitates overlap treatment in closed form, a feature shared by previous MCPT variants. In particular, Moore-Penrose inverse of singular matrices appearing in frame-based MCPT can be constructed without the need of any pivoting algorithm or numerical zero threshold.

Pilot numerical studies are performed for the singlet-triplet gap of biradicaloid systems, relying on geminal based, incomplete model space reference function. Comparison with previous MCPT variants as well as illustration of pivot invariance is provided.

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## I. INTRODUCTION

As an economical trade-off between antagonistic requirements of accuracy and computational feasibility, perturbation theory (PT) is a prevailing electronic structure method to account for dynamical correlation. Low order PT correction in the Møller-Plesset (MP) partitioning is overwhelming in applications where the Hartree-Fock (HF) determinant serves as a reliable reference[1]. When the restricted HF (RHF) approximation breaks down, e.g. in so-called strongly correlated scenarios, conventional MP deteriorates as well. Damping techniques[2–5], repartitioning[6–9] and resummation ideas[10–14], scaling techniques[15] can be used to mitigate the problem whilst sticking with the RHF reference. Success of these methods often lies with extrapolation or redefinition of the zero-order Hamiltonian, achieving the removal of quasi-degeneracy affecting the ground state. Replacing the RHF determinant with a qualitatively correct, multideterminantal zero-order wavefunction represents a more involved approach for treating strong correlation. Development of this field, coined multireference PT (MR PT), has proven to be considerably more difficult than its RHF based analogue, requirement of size-extensivity and consistency as well as unitary invariance presenting additional challenge to the intruder-free character of the theory. Moreover, being applicable to ground as well as excited states, balanced account of static and dynamic correlation in MR PT is essential in order to get spacing of energy levels correct. Orientation among the multitude of MR PT approaches is assisted by general overviews by Durand and Malrieu[16] and Davidson and Jarzęcki[17], topical of their time. A more recent account focusing on excited states is due to Lischka and coworkers[18]. Reviews on particular methods or class of methods are provided e.g. on state-specific MR PT (SS-MRPT)[19] developed by Mukherjee and coworkers, complete active space PT[20,21] advocated by Roos and coworkers, multireference MP[22] developed by Nakano, Hirao and coworkers, *n*-electron valence state PT[23] initiated by Malrieu and coworkers.

The present study is concerned with the MR PT framework termed multiconfiguration perturbation theory (MCPT) that has been previously reviewed[24] and compared in numerical terms[25–27] with related PT methods, in particular with SS-MRPT[28], with generalized Van Vleck PT (GVVPT2)[29] and with a geminal based, Dyall-type[30,31] PT framework[32]. Main features of MCPT can be summarized as follows. Assume the existence of a reference function, $\Phi$ accounting for strong correlation. The reference needs not be of any special structure, it can be of complete or incomplete model space type or even a coupled-cluster wavefunction[33], provided that its expansion over determinants of the configuration interaction (CI) space is known. Excited states not

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being available along with the reference, they are constructed with the help of determinants of the CI space, $\varphi_i$. Nonunit overlap of $\Phi$ and $\varphi_i$ is treated differently in various variants of MCPT. In particular $\varphi_i$ can be Schmidt-orthogonalized to $\Phi$, giving rise to $\varphi_i'$. Working with the set $\{\Phi\} \cup \{\varphi_i' | i = 1, \dots\}$ leads to the variant termed projected MCPT (pMCPT)[34]. It is possible to omit the Schmidt-orthogonalization step, and work with the set $\{\Phi\} \cup \{\varphi_i | i = 1, \dots\}$ resulting in the flavour termed unprojected MCPT (uMCPT)[35]. Both sets mentioned above are linearly dependent. A common characteristic of projected and unprojected MCPT is lifting redundancy by pinpointing the component of largest weight in the determinantal expansion of $\Phi$, termed pivot, and omitting the corresponding element. Assuming that the pivot is indexed by $i = 1$, pMCPT thence considers $\{\varphi_i' | i = 2, \dots\}$ as excited zero-order functions while $\{\varphi_i | i = 2, \dots\}$ serve the same purpose with uMCPT. The zero-order Hamiltonian of both variants is specified in spectral form with the help of the reference and excited functions, overlap of which is positive definite, but nonunit. The situation is handled by constructing the reciprocal vectors, expressed with the help of the inverse overlap and developing the theory along the lines of biorthogonal PT[36–39]. An important characteristic of both pMCPT and uMCPT is that the overlap is invertible in closed form, reciprocal vectors consequently arise without the need of any numerical procedure. Ref. 40 provides a detailed presentation of the two formulations in parallel. Specification of the energy levels associated with excited functions governs the partitioning of pMCPT and uMCPT corrections[41]. User defined nature of the energy levels allows direct control over the intruder state problem, i.e. intruders are avoidable by appropriate tuning of the partitioning. A generalized MP partitioning has been also put forward in the framework of MCPT[42,43], the zero-order Hamiltonian defined with the help of the generalized Fockian[44]. Determinant based formulation of the theory facilitates a diagrammatic representation of the terms to be evaluated. Computational cost associated with uMCPT is proportional to $n_{\text{occ}}^2 n_{\text{virt}}^2$ while pMCPT features $M n_{\text{occ}}^2 n_{\text{virt}}^2$ scaling, where $n_{\text{occ}}$ and $n_{\text{virt}}$ stand for the number of orbitals occupied and unoccupied in the pivot, respectively and $M$ gives the length of the determinantal expansion of $\Phi$. Considering size-consistency, pMCPT violates this requirement while the second order energy of uMCPT is well behaving with appropriate choice for the excited energy levels. Applications of the MCPT methodology involve correcting antisymmetrized product of strongly orthogonal as well as nonorthogonal geminals[27,45,46]. It has been also put to use for natural orbital functional construction[47,48].

Our present concern lies with pivot dependence of the MCPT framework, generated by redundancy handling. Though eliminating the determinant of largest weight in $\Phi$ from the set of

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excited functions appears plausible, it is hard to argue in a situation where two or more determinants are of comparable weight. Furthermore a change in pivot leads to a non-analytic point on the potential energy curve. The extent of the effect depends on the particular formulation[26], e.g. it is by rule more expressed with uMCPT than with pMCPT due to the fact that $\Phi$ agrees with its reciprocal vector in pMCPT but not in uMCPT. Pivot invariance has been previously addressed by considering all determinants contributing to $\Phi$ as pivot and forming the weighted average of the corrections[40]. The resulting distinct, averaged pMCPT and uMCPT variants, both feature $Mn_{\mathrm{occ}}^2 n_{\mathrm{virt}}^2$ scaling. A shortcoming of the averaging approach is the enhancement of the intruder effect with determinants of small weight in $\Phi$ being selected as pivot. While specification of the partitioning provides a control over intruders, alternative solutions for pivot invariance deserve attention.

A novel look on the problem is provided by the concept of frames introduced in connection with signal analysis[49,50]. Frames are generalizations of basis sets, relaxing the requirement of linear independence on the constituting vectors. In our point of view, frame theory offers a way of keeping all vectors of the linearly dependent set and formulating a variant of MCPT without pinpointing any pivot. In what follows frame-based MCPT (fMCPT) is developed in Section II, adopting the projected approach. The presentation is intended to be self-contained and supposes no prior knowledge of frame theory. Basic mathematical statements utilized in course of the derivation are worked out in Appendix A in more detail.

In one way or another, all variants of MCPT profit from the special structure of the overlap. In fMCPT this manifests in the projected and unprojected approaches leading to the same expressions, as shown in Appendix A 4. Moreover the outcome of the frame-based derivation of MCPT could in effect be formulated without making any reference to frame vectors. Frame-based presentation and nomenclature is nevertheless kept here, for it contributes to having a complete picture. Pilot numerical results of fMCPT are presented along with pMCPT in Section III. Section IV concludes the work in view of formal and numerical results.

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## II. THEORY

Suppose that a reference function expanded over the orthonormal set of determinants $\varphi_i$ is given as

$$|\Phi\rangle = \sum_{i=1}^{M} |\varphi_i\rangle c_i \ , \tag{1}$$

with $\sum_{i=1}^{M} |c_i|^2 = 1$ reflecting that $\Phi$ is normalized. The sum in Eq. (1) is restricted to determinants exhibiting nonzero $c_i$, forming the model space of dimension $M$. Usually $M$ is considerably smaller than the dimension of the full configuration interaction (FCI) space, $N$. In order to develop a PT based on reference $\Phi$, a zero-order Hamiltonian is required to fulfill

$$\hat{H}^{(0)}\Phi = E_0\Phi \ . \tag{2}$$

Introduce now the one-dimensional projector corresponding to the reference

$$\hat{O} = |\Phi\rangle\langle\Phi| \tag{3}$$

and its orthogonal complement over the model space

$$\hat{P}_M = \sum_{i=1}^{M} |\varphi_i\rangle\langle\varphi_i| - \hat{O} \ .$$

A third projector

$$\hat{P}_\perp = \sum_{i=1}^{N} |\varphi_i\rangle\langle\varphi_i| - \hat{O} - \hat{P}_M = \sum_{i=M+1}^{N} |\varphi_i\rangle\langle\varphi_i|$$

describes the subspace of the FCI space orthogonal to the model space. As a consequence of Eq. (2), $\hat{H}^{(0)}$ is block diagonal respecting $\hat{O}$ and $(\hat{1}-\hat{O})$ while its effect over $\hat{P}_M$ and $\hat{P}_\perp$ is yet to be specified. Aiming at a simple representation of the zero-order on the basis of determinants, a spectral form of $\hat{H}^{(0)}$ of MCPT with $\varphi_i$ is preferred. This is straightforward to achieve for determinants corresponding to $\hat{P}_\perp$ as they form an orthonormal set of dimension $N-M$. A $P_\perp$-block of $\hat{H}^{(0)}$ is thence defined as

$$\hat{H}^{(0)}_\perp = \hat{P}_\perp\hat{H}^{(0)}\hat{P}_\perp = \sum_{i=M+1}^{N} E_i^{(0)} |\varphi_i\rangle\langle\varphi_i| \ , \tag{4}$$

and the total zero-order is specified as

$$\hat{H}^{(0)} = E_0\hat{O} + \underbrace{\hat{P}_M\hat{H}^{(0)}\hat{P}_M}_{\hat{H}^{(0)}_{PM}} + \hat{H}^{(0)}_\perp \ . \tag{5}$$

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Choice

$$E_0 = \langle \Phi | \hat{H} | \Phi \rangle \tag{6}$$

is convenient for the zero-order energy while Davidson-Kapuy (DK), Epstein-Nesbet (EN) or an alternative partitioning[41] may be adopted for $E_i^{(0)}$ in Eq. (4).

A definition of the $P_M$-block of $\hat{H}^{(0)}$, analogous to Eq. (4) is hindered by the fact that $\varphi_i$ exhibit $O$-space component for $i = 1, \ldots, M$ and therefore that projected determinants

$$|\varphi_i'\rangle = \hat{P}_M |\varphi_i\rangle \;=\; |\varphi_i\rangle - |\Phi\rangle c_i^* \;,\; i = 1, \ldots, M \tag{7}$$

form a nonorthogonal and overcomplete set in $P_M$-space, their overlap reading as

$$S_{ij} = \langle \varphi_i' | \varphi_j' \rangle \;=\; \langle \hat{P}_M \varphi_i | \hat{P}_M \varphi_j \rangle \;=\; \langle \varphi_i | \hat{P}_M | \varphi_j \rangle \;=\; \delta_{ij} - c_i c_j^* \;. \tag{8}$$

Matrix $\boldsymbol{S}$ composed of elements $S_{ij}$ is the $M$-dimensional representation of $\hat{P}_M$ on model space determinants, its rank is therefore $(M-1)$. Redundancy of $\{\varphi_i'\}_{i=1}^M$ was circumvented in the original formulation of MCPT[34] by omitting the element corresponding to the pivotal term in Eq. (1), giving rise to a nonsingular overlap of dimension *and* rank $(M-1)$. This facilitates the construction of reciprocal vectors[34] or Löwdin-orthogonalized vectors[51,52] via the inverse or inverse square-root of the overlap, respectively. It however introduces a pivot dependence in the general case when a spectral form of $\hat{H}_{PM}^{(0)}$ is composed with the help of either of these sets.

Presently an alternative treatment is explored whereby all elements of the set $\{\varphi_i'\}_{i=1}^M$ are used to formulate $\hat{H}_{PM}^{(0)}$. To this end let us invoke that $\{\varphi_i'\}_{i=1}^M$ form a so-called frame[50] as shown in Appendix A 1. Frame theory can be put to use in our context by composing the elements of the so-called canonical dual frame as

$$\langle \widetilde{\varphi'}_i | = \sum_{j=1}^{M} R_{ij} \langle \varphi_j' | \;,\;\; i = 1, \ldots, M \;, \tag{9}$$

with matrix elements $R_{ij}$ constituting matrix $\boldsymbol{R}$, the Moore-Penrose inverse[53] of $\boldsymbol{S}$, obeying relations Eq. (A5) given in Appendix A 1. With the help of frame vectors and their duals, projector $\hat{P}_M$ can be written as

$$\hat{P}_M = \sum_{i=1}^{M} |\varphi_i'\rangle \langle \widetilde{\varphi'}_i | \tag{10}$$

as argued in Appendix A 2. The above expression can be simplified, observing that $\boldsymbol{S}$ is the representation of a projector, c.f. Eq. (8). A projector is not invertible in the regular sense in

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general, at the same time it possesses a rather trivial Moore-Penrose inverse: itself. Utilizing $\boldsymbol{S}^2 = \boldsymbol{S}$, it can be seen by substitution in Eq. (A5), that $\boldsymbol{R} = \boldsymbol{S}$ is the Moore-Penrose inverse of $\boldsymbol{S}$. It is then easy to verify, based on Eqs. (7) and (8), that

$$\langle \widetilde{\varphi'}_i| = \sum_{j=1}^{M} S_{ij} \langle \varphi'_j| \; = \; \langle \varphi'_i| \; , \tag{11}$$

i.e. elements of the frame and its canonical dual are the same. Projector $\hat{P}_M$ therefore takes the form

$$\hat{P}_M = \sum_{i=1}^{M} |\varphi'_i\rangle\langle\varphi'_i| \; . \tag{12}$$

Idempotency of the right hand side of the above can be checked based on Eqs. (7) and (11), it should however be stressed that individual terms of the sum in Eq. (12) , $|\varphi'_i\rangle\langle\varphi'_i|$ are neither idempotent nor orthogonal. This inhibits to formulate a spectral form analogous to Eq. (4) in $P_M$-space with the help of frame vectors. At the same time, it is possible to make use of Eq. (12) in writing the $P_M$-block of $\hat{H}^{(0)}$ as

$$\hat{H}^{(0)}_{PM} = \hat{P}_M \hat{H}^{(0)} \hat{P}_M \; = \; \sum_{i,j=1}^{M} |\varphi'_i\rangle\langle\varphi'_i|\hat{H}|\varphi'_j\rangle\langle\varphi'_j| \; . \tag{13}$$

Eq. (13) completes the specification of $\hat{H}^{(0)}$ of frame MCPT (fMCPT) in principle. An obvious consequence of utilizing a redundant set of frame vectors in $P_M$-space is the appearance of singular matrices. E.g. $\boldsymbol{H}'$ composed of elements $H'_{ij} = \langle\varphi'_i|\hat{H}|\varphi'_j\rangle$ appearing on the right hand side of Eq. (13) is of dimension $M$ but its rank is at most $(M-1)$, since $\hat{P}_M$ is of rank $(M-1)$. At each order of PT, this matrix (modified by a constant) figures as the coefficient matrix of the equation for the wavefunction. An essential element of manipulating frames is that singular linear equations arising from redundancy are solved by application of the Moore-Penrose inverse, and the procedure is equivalent to working with an underlying orthonormal basis. This is illustrated in Appendix A 3.

In the present context however, the special structure of $\boldsymbol{S}$ can once again be harnessed, this time in avoiding the numerical construction of the Moore-Penrose inverse when solving the PT equations. A key result in this line is due to Dalgaard[54] and Mayer[51] who gave explicit expression of $(M-1)$ orthonormal vectors in $P_M$-space. (See also Refs. 55 and 56.) Allowing for complex coefficients in Eq. (1), Dalgaard-Mayer (DM) vectors read as

$$|\psi_i^{\text{DM}}\rangle = \sum_{j=1}^{M-1} |\varphi_j\rangle \left( \delta_{ij} - c_i^* c_j \frac{1-c_M^*}{1-|c_M|^2} \right) - |\varphi_M\rangle c_i^* \; , \;\; i = 1, \ldots, M-1 \; . \tag{14}$$

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The vectors above were introduced by Dalgaard in the context of multiconfigurational self-consistent field wavefunction optimization. Mayer rederived them independently later, considering Jacobi rotations in the many-electron space. It has been shown that DM vectors are those arising upon subjecting $\{\varphi_i'\}_{i=1}^{M-1}$ to Löwdin's symmetrical orthogonalization procedure[52]. With the help of $\{\psi_i^{\mathrm{DM}}\}_{i=1}^{M-1}$ projector $\hat{P}_M$ is expressible as in Eq. (A7) and the $P_M$-block of $\hat{H}^{(0)}$ takes the form

$$\hat{H}^{(0)}_{PM} = \sum_{i,j=1}^{M-1} |\psi_i^{\mathrm{DM}}\rangle\langle\psi_i^{\mathrm{DM}}|\hat{H}|\psi_j^{\mathrm{DM}}\rangle\langle\psi_j^{\mathrm{DM}}| \,. \tag{15}$$

The advantage of Eq. (15) over Eq. (13) is that zero eigenvalue due to redundancy is not an issue any more. The matrix composed of $\langle\psi_i^{\mathrm{DM}}|\hat{H}|\psi_j^{\mathrm{DM}}\rangle$ is of dimension $(M-1)$, agreeing with its rank (pathological cases excluded). For this reason, the $(M-1)$ dimensional basis of $\psi_i^{\mathrm{DM}}$ in $P_M$-space is preferred over the $M$ dimensional frame of $\{\varphi_i'\}_{i=1}^{M}$. Note that construction of $\langle\psi_i^{\mathrm{DM}}|\hat{H}|\psi_j^{\mathrm{DM}}\rangle$ is trivial with the help of Eq. (14) and represents no computational bottleneck as far as $M$ is small compared to e.g. the dimension of the first order interacting space. Since $|\psi_i^{\mathrm{DM}}\rangle\langle\psi_i^{\mathrm{DM}}|$ are orthonormal projectors, a spectral form of $\hat{H}^{(0)}_{PM}$ analogous to Eq. (4), resorting to diagonal terms, appears a plausible alternative to Eq. (15). Preferring the full representation of $\hat{H}$ in block $P_M$ over a spectral form with $\{\varphi_i'\}_{i=1}^{M}$ at zero-order is supported by the following

(i) $M$ is thought to be small;

(ii) $\psi_i^{\mathrm{DM}}$ are not simple in the sense that they considerably differ from a single determinant in general;

(iii) Eq. (15) is invariant to unitary transformation in $P_M$-space;

(iv) Eqs. (13) and (15) are thereby equivalent;

(v) such a zero-order arises from a partitioning optimization strategy[8].

The zero-order being specified by Eqs. (4), (5) and (15), we step to formulating fMCPT corrections to $E_0$ and $\Phi$. At first order $E^{(1)} = 0$ is a consequence of Eq. (6). Coefficients $c_i^{(1)}$ in the expansion of the first-order wavefunction

$$|\Psi^{(1)}\rangle = \sum_{i=1}^{M-1} |\psi_i^{\mathrm{DM}}\rangle c_i^{(1)} + \sum_{i=M+1}^{N} |\varphi_i\rangle c_i^{(1)} \tag{16}$$

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are determined from

$$(E_0 - \hat{H}^{(0)})|\Psi^{(1)}\rangle = (\hat{H} - \hat{H}^{(0)})|\Phi\rangle \ . \tag{17}$$

Projecting Eq. (17) by $\langle\varphi_i|$

$$c_i^{(1)} = -\frac{\langle\varphi_i|\hat{H}|\Phi\rangle}{E_i^{(0)} - E_0} \ , \ \ i = M+1,\ldots,N \tag{18}$$

is obtained while multiplication by $\langle\psi_i^{\rm DM}|$ leads to

$$\sum_{j=1}^{M-1} \underbrace{\langle\psi_i^{\rm DM}|E_0 - \hat{H}|\psi_j^{\rm DM}\rangle}_{A_{ij}} c_j^{(1)} \ = \ \langle\psi_i^{\rm DM}|\hat{H}|\Phi\rangle \tag{19}$$

when making use of Eq. (15). Provided that $E_0$ is well separated from the spectrum of $\hat{H}^{(0)}_{PM}$, matrix $\boldsymbol{A}$ composed of elements $A_{ij}$ introduced in Eq. (19) is invertible. Using $Q_{ij}$ to refer to the elements of the inverse of $\boldsymbol{A}$, $c_i^{(1)}$ is expressible from Eq. (19) as

$$c_i^{(1)} \ = \ \sum_{j=1}^{M-1} Q_{ij}\langle\psi_j^{\rm DM}|\hat{H}|\Phi\rangle \ , \ \ i = 1,\ldots,M-1 \ . \tag{20}$$

From $E^{(2)} = \langle\Phi|\hat{H}|\Psi^{(1)}\rangle$ via Eqs. (16), (18) and (20) the second order energy is obtained as

$$E^{(2)}_{\rm fMCPT} = \sum_{i,j=1}^{M-1} \langle\Phi|\hat{H}|\psi_i^{\rm DM}\rangle Q_{ij} \langle\psi_j^{\rm DM}|\hat{H}|\Phi\rangle \ - \ \sum_{i=M+1}^{N} \frac{|\langle\Phi|\hat{H}|\varphi_i\rangle|^2}{E_i^{(0)} - E_0} \ . \tag{21}$$

Eq. (21) is the working formula tested in the present study. Its characteristic feature, pivot invariance is not immediately obvious based on Eq. (14), where $\varphi_M$ apparently plays a role different from other model space determinants. Pivot invariance of fMCPT however simply rests on $\hat{H}^{(0)}_{PM}$ being formulated with pivot invariant operators $\hat{P}_M$ and $\hat{H}$. Note, that $E_i^{(0)}$ in Eq. (4) also need to be specified in a pivot invariant manner in order not to spoil this property of $E^{(2)}_{\rm fMCPT}$. Provided that $M$ is small, computational cost of the second order energy of fMCPT is determined by the second term on the right hand side of Eq. (21), generating an $Mn^2_{\rm occ}n^2_{\rm virt}$ scaling, similarly to pMCPT.

Since fMCPT results are contested with pMCPT in Section III, the relevant formulae are summarized here for completeness. As mentioned in Section I, pMCPT considers the linearly independent set of $\{\varphi'_i\}_{i=2}^{M}$ in $P_M$-space and its reciprocal vectors reading as

$$\langle\widetilde{\varphi}'_i| = \langle\varphi_i| - \frac{c_i}{c_1}\langle\varphi_1| \ , \ \ i = 2,\ldots,M \ . \tag{22}$$

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Note, that $\widetilde{\widetilde{\varphi}}'_i$ differ from $\widetilde{\varphi}'_i$ in Eq. (9) since redundancy in pMCPT is eliminated by discarding the element with index $i = 1$. Comparing the second order correction of pMCPT

$$E^{(2)}_{\mathrm{pMCPT}} = -\sum_{i=2}^{M} \frac{\langle\Phi|\hat{H}|\varphi'_i\rangle\langle\widetilde{\widetilde{\varphi}}'_i|\hat{H}|\Phi\rangle}{E^{(0)}_i - E_0} - \sum_{i=M+1}^{N} \frac{|\langle\Phi|\hat{H}|\varphi_i\rangle|^2}{E^{(0)}_i - E_0} \tag{23}$$

with Eq. (21), $P_\perp$-space terms of the two expressions manifestly agree. It also deserves mention that $P_M$-space terms, stemming from relaxation of model space coefficients in the first order wavefunction are zero in both theories whenever $\Phi$ is an eigenvector of $(\hat{O}+\hat{P}_M)\hat{H}(\hat{O}+\hat{P}_M)$, since integrals in the numerators are trivially zero in this case. This holds for a complete active space reference.

Regarding size-consistency[57], fMCPT lines up with pMCPT in violating this condition. Unprojected version of MCPT[35], lacking the Gram-Schmidt orthogonalization step of Eq. (7) deserves a remark at this point. Unprojected MCPT was developed with the aim of fulfilling size-consistency and the goal was achieved at second order in energy. As shown in Appendix A 4, it is possible to introduce frame vectors in uMCPT, the resulting equations however do not mitigate size-inconsistency, them matching the equations derived based on the pMCPT concept.

## III. APPLICATION

### A. Reference functions

As demonstrated in Section II, it is the model space term that makes the difference between fMCPT and pMCPT, the variants we wish to compare presently. For this reason the numerical assessment applies incomplete model space type reference functions, based on geminals.

The Ansatz termed strictly localized geminals (SLG) for a system of $N_e$ electrons reads as

$$|\mathrm{SLG}\rangle = \prod_{\mu=1}^{N_e/2} \phi^\dagger_\mu |\mathrm{vac}\rangle \ , \tag{24}$$

where $\phi_\mu$ is an $M_S = 0$ two-electron fragment, termed geminal, expressed as

$$\phi^\dagger_\mu = \sum_{p,q\in\mu} C_{pq}\, a^\dagger_{p\alpha} a^\dagger_{q\beta} \tag{25}$$

and $N_e$ is assumed to be even. Geminals entering Eq. (24) are strongly orthogonal, meaning that spatial orbitals indexed by $p,q$ are distributed disjointly among geminals, as indicated by $p,q \in \mu$

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in Eq. (25). Orbitals assigned to geminal $\mu$ form the so-called geminal subspace. Variational optimization of the SLG Ansatz implies setting the expectation value of $\hat{H}$ stationary with respect to geminal coefficients $C_{pq}$ and geminal subsets, i.e. the orbitals. The Generalized Valence Bond (GVB)[58] wavefunction in its simplest formulation represents a prototype of the Ansatz in Eq. (24) with the restrictions that (i) geminal subsets are two-dimensional and (ii) the geminal coefficient matrix is symmetric. The latter requirement ensures singlet nature of the geminals as well as their antisymmetrized product, Eq. (24). The wavefunction class allowing for geminal subspace dimension larger than two but keeping them singlet has been introduced under the names Antisymmetrized Product of Strongly Orthogonal Geminals (APSG)[59,60] and Restricted Singlet-type Strongly Orthogonal Geminals (RSSG)[61]. Relaxing the symmetric nature of the coefficient matrix leads to the appearance of triplet geminal components. Fully optimized models of this latter type involve Unrestricted Singlet-type Strongly Orthogonal Geminals (USSG)[61], Restricted Unrestricted Singlet-type Strongly Orthogonal Geminals (RUSSG)[62] as well as Unrestriction within Active Pairs (UAP)[63]. The wavefunction termed USLG below is also built with singlet-triplet mixed geminals. It however arises by optimizing only the geminal coefficient matrix and fixing two-dimensional geminal subspaces with the help of Löwdin-paired orbitals[64,65] of the Unrestricted HF (UHF) wavefunction.

Singlet-triplet mixing at the level of geminals results in violation of spin-symmetry of the product wavefunction, Eq. (24) in general. Spin purification represents a remedy which however induces size-inconsistency[66]. As a middle ground between spin contamination and size-consistency violation, half-projection (HP)[67], operating with

$$\hat{\mathscr{A}}_S = \frac{1}{2}\left[1 + (-1)^{N_e/2-S}\hat{\mathscr{P}}\right] , \tag{26}$$

has been adopted for USLG[68]. In Eq. (26) $\hat{\mathscr{P}}$ is a spin-flip operator interchanging spin labels $\alpha$ and $\beta$ and $S$ stands for the desired spin quantum number. Operator $\hat{\mathscr{A}}_S$ does not remove all spin contaminants but results in partial purification and nonzero but reduced size-consistency violation when compared to full spin-projection. The HPSLG acronym refers to the Ansatz[68]

$$|\mathrm{HPSLG}\rangle = \frac{\hat{\mathscr{A}}_S|\mathrm{SLG}\rangle}{\sqrt{\langle \mathrm{SLG}|\hat{\mathscr{A}}_S\mathrm{SLG}\rangle}} \tag{27}$$

and implies setting the expectation value of $\hat{H}$ with $|\mathrm{HPSLG}\rangle$ stationary respecting geminal coefficients $C_{pq}$, while orbitals are fixed as UHF natural orbitals (UNO), similarly to USLG.

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### B. Computational details

The performance of second-order fMCPT correction of Eq. (21) and pMCPT correction of Eq. (23) is evaluated below in terms of energetic data, focusing on the spacing of the lowest singlet and triplet levels of biradical systems. We also demonstrate the pivot dependence of pMCPT vis-à-vis fMCPT on a suitable reaction profile. Finally, size-inconsistency of both variants is evaluated on the example of two noninteracting water molecules.

Reference functions USLG and HPSLG are both invariant to the unitary transformation of core orbitals while the perturbative corrections do not show such invariance regarding neither the core, nor the virtual orbital subspace. (In geminal parlance core orbitals constitute HF-type, one-dimensional geminal subspaces.) In order to avoid ambiguities, core and virtual orbitals are fixed by the so-called pseudo canonical requirement, i.e. by setting the core-core and virtual-virtual block of the generalized Fockian[44] diagonal. Excited state energies $E_i^{(0)}$ in Eqs.(21) and (23) are of EN type, in particular $E_i^{(0)} = \langle \varphi_i | \hat{H} | \varphi_i \rangle$ is taken for $i = M+1, \ldots$ Regarding the model space contribution of pMCPT, $E_i^{(0)} = \langle \widetilde{\varphi'}_i | \hat{H} | \varphi'_i \rangle$, $i = 2, \ldots, M$ is applied for the para-benzyne and ozone test cases and $E_i^{(0)} = \langle \varphi_i | \hat{H} | \varphi_i \rangle$, $i = 2, \ldots, M$ is taken for the 1,4-hexadiene and the water molecule(s).

Reference functions USLG and HPSLG were generated by the Budapest version[69] of the MUNGAUSS program package[70], PT corrections were obtained by an in-house implementation, interfaced to it.

### C. Singlet-triplet splittings

Excitation energies for the adiabatic singlet-triplet transition of para-benzyne computed in the 6-31G* basis are collected in Table I. Spin-flip orbital-optimized equation of motion coupled-cluster doubles (SF-OD) values of Krylov et al.[71], obtained in the same basis serve as benchmark for the PT results. Energetic data in Table I make the impression that USLG is superior to HPSLG since the former predicts the singlet-triplet gap rather accurately, while HPSLG results are poor in comparison. This picture is however deceptive. Seemingly correct transition energy of USLG masks a considerable spin-contamination of the singlet state, the expectation value of $\hat{S}^2$ being 1.05 instead of the correct, zero value. Failure of USLG based PT corrections in improving the gap is manifest in Table I: neither the sign, nor the magnitude of the energy gaps are correct

frame MCPT

TABLE I: Total energies in $E_h$ for the $^1A_{1g}$ singlet and $^3B_{1u}$ triplet state and adiabatic singlet-triplet gap, $\Delta E = E_T - E_S$ in eV for para-benzyne in 6-31G* basis. Optimal geometries for the singlet and triplet are taken from Ref. 71. (There is a manifest typo in the carbon-carbon distance of 1.4186 Å for the triplet state in Ref. 71. Based on the nuclear repulsion data, this parameter is corrected for 1.367 Å.) Reference functions USLG and HPSLG are corrected by second order MCPT in the projected and frame-based variant, SF-OD serves as benchmark.

| | $E_S$ / $E_h$ | $E_T$ / $E_h$ | $\Delta E$ / eV |
|---|---|---|---|
| USLG | -229.4226 | -229.4175 | 0.140 |
| USLG-pMCPT | -230.2088 | -230.2236 | −0.403 |
| USLG-fMCPT | -230.2180 | -230.2236 | −0.154 |
| HPSLG | -229.4389 | -229.4391 | −0.004 |
| HPSLG-pMCPT | -230.1997 | -230.1924 | 0.200 |
| HPSLG-fMCPT | -230.2003 | -230.1932 | 0.193 |
| SF-OD[a] | -230.1542 | -230.1478 | 0.174 |

[a] Based on Ref. 71.

by USLG-pMCPT and USLG-fMCPT. This breakdown can be attributed to the flaw in the USLG reference for the singlet state. Defect of the reference is resolved at the qualitative level by HPSLG, spin-expectation value of the singlet getting reduced to 0.25. In parallel with this, and in spite of the incorrect sign of the HPSLG gap, HPSLG based PT corrections are well behaving and bring considerable improvement. Both HPSLG-pMCPT and HPSLG-fMCPT results collected in Table I are rather close to the SF-OD benchmark value, fMCPT slightly outperforming pMCPT. Decomposition of the PT correction for $P_\perp$-space and $P_M$-space components is as follows. Large majority of the rough $-761$ m$E_h$ correction for the singlet, specifically $-755$ m$E_h$ arises from the second term on the right hand side of Eq. (21) or Eq. (23). First term of these expressions amount to $-6$ m$E_h$, difference between fMCPT and pMCPT being even smaller by an order of magnitude, on the level of 0.6 m$E_h$, as can be inferred from Table I. A similar picture is obtained when considering the triplet state or the energy gap.

Vertical singlet-triplet transition of ozone presented in Table II, calculated in cc-pCVDZ basis provides a further example. Here the linear-response coupled-cluster singles, doubled and full

frame MCPT

TABLE II: Total energies in $E_h$ for the $^1A_1$ singlet and $^3B_2$ triplet state and vertical singlet-triplet transition energy, $\Delta E = E_T - E_S$ in eV for ozone in cc-pCVDZ basis. Symmetry of the molecule is $C_{2v}$ with parameters taken from Ref. 72 as $R_{\mathrm{O–O}} = 1.2569$ Å and $\angle(\mathrm{OOO}) = 116.54°$. Reference functions USLG and HPSLG are corrected by second order MCPT in the projected and frame-based variant, CCSDT-LR serves as benchmark.

| | $E_S$ / $E_h$ | $E_T$ / $E_h$ | $\Delta E$ / eV |
|---|---|---|---|
| USLG | -224.3653 | -224.3294 | 0.977 |
| USLG-pMCPT | -225.0389 | -224.9758 | 1.718 |
| USLG-fMCPT | -225.0408 | -224.9758 | 1.769 |
| HPSLG | -224.3746 | -224.3402 | 0.937 |
| HPSLG-pMCPT | -225.0299 | -224.9660 | 1.739 |
| HPSLG-fMCPT | -225.0292 | -224.9661 | 1.716 |
| CCSDT-LR[a] | -225.0311 | -224.9680 | 1.716 |

[a] Based on Ref. 72.

triples (CCSDT-LR) results of Jagau and Gauss are regarded as benchmark[72]. At difference with the case of para-benzyne, both USLG and HPSLG based PT is acceptable for ozone, as reflected in Table II. This is in accordance with the observation that spin is not contaminated significantly by USLG, expectation value of $\hat{S}^2$ being on the order of 0.01 for the singlet state. Compared with the benchmark CCSDT-LR value of $\sim 1.7$ eV, the singlet-triplet gap is off almost by a factor of two when considering either of the zero-order approximations, USLG or HPSLG. Dynamical correlation by MCPT establishes the correct order of magnitude for the gap, deviation from the benchmark value reduced to the level of $\sim 10^{-2}$ eV. Contesting pMCPT and fMCPT gaps, the former is closer to the benchmark with USLG reference, while the latter is right on top of the benchmark when applied with HPSLG as reference. Model space contribution of the PT correction for individual states is somewhat larger in this example than for para-benzyne. Taking the singlet state and HPSLG reference, the cca. $-655$ m$E_h$ PT correction decomposes for a $P_\perp$-space contribution of $-642$ m$E_h$ and a model space contribution of $-13$ m$E_h$, difference between pMCPT and fMCPT being again on the order of 0.7 m$E_h$.

Accepted to J. Chem. Phys. 10.1063/5.0112563

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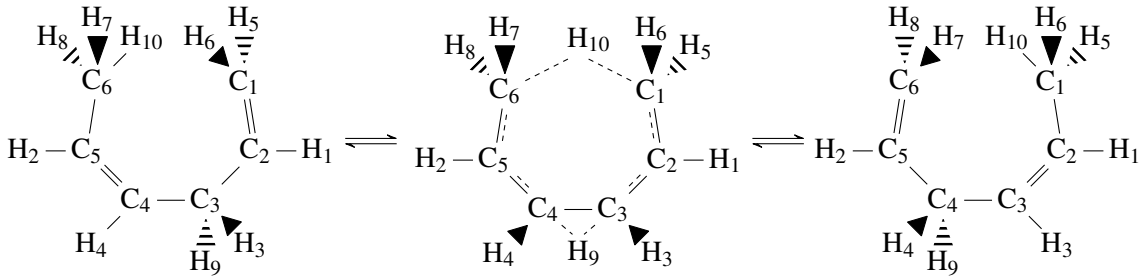


FIG. 1: Isomerization process of 1,4-hexadiene producing 1,4-hexadiene involving CC double bond and CH single bond rearrangement.

### D. Pivot invariance

Given the rather similar performance of fMCPT and pMCPT seen above, one might wonder whether pivot dependence of pMCPT ever leads to a non-negligible effect. In the following application the ambiguity associated with the pivot choice emerges naturally, allowing to highlight its consequence in pMCPT. We monitor the isomerization reaction profile of the 1,4-hexadiene molecule ($C_6H_{10}$), as depicted in Fig. 1. The process involves rearrangement of hydrogen atoms 9 and 10, involving carbon atoms 3-4 and 1-6, respectively. Rearrangement of $\pi$-bonds occurs simultaneously. Entries of the Z-matrix parametrizing the process are given in the supplementary material. Molecular geometry exhibits no symmetry element along the reaction coordinate, apart from the structure at the mid point, belonging to group $C_s$. The formula in the middle of Fig. 1 represents this transition structure.

The calculation is performed in 6-31G* basis, reference function is provided by HPSLG. Of the 23 geminals constituting the overall wavefunction, 19 geminals are one-dimensional and 4 geminal subsets are two-dimensional at around the mid point of the reaction path. Geminal coefficient matrix mostly affected by correlation is geminal No. 23, UNOs No. 23 and 24 forming its subspace. Starting from a weakly correlated pair, geminal No. 23 gradually becomes strongly correlated along the process, and evolves back to a weakly correlated fragment. Strong correlation is most pronounced at the transition structure, where UNOs 23 and 24 are mirror images of each other, as shown in Fig. 2. The weight of closed shell determinants in geminal No. 23 become equal at the mid point, as reflected in Fig. 3.

Moving to the left or right from the mid point along the reaction path, either this or that determinant becomes of larger weight in geminal No. 23, generating a change in the most dominant determinant in the HPSLG wavefunction. The consequence on the energy contribution of the model

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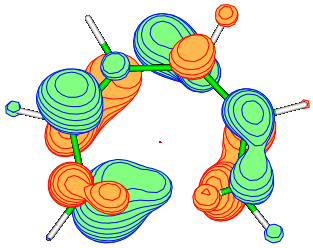
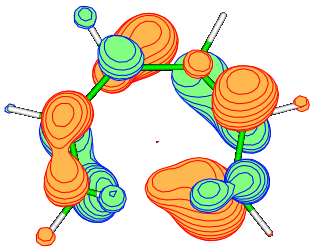


(a)



(b)

FIG. 2: Contour plot of UNOs constituting geminal No. 23 of 1,4-hexadiene at the mid point of the reaction path depicted in Fig. 1. Pictures (a) and (b) reflect UNOs No. 23 and 24, respectively. Occupation number at the UHF level is 1.000 for both orbitals shown. The plots are generated by package Molden[73].

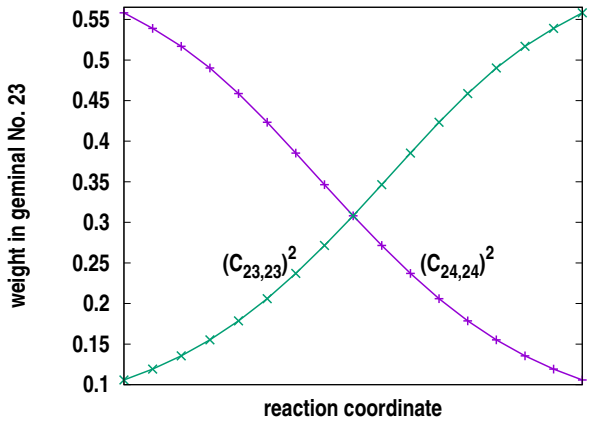



FIG. 3: Weight of closed shell determinants in geminal No. 23 at around the mid point of the reaction path depicted in Fig. 1 for 1,4-hexadiene. The HPSLG calculation is performed in 6-31G* basis, number of electrons is $N_e = 46$. Orbitals No. 23 and 24 are assigned to geminal No. 23, that is most affected by correlation. Geminal coefficients $C_{pq}$ are introduced in Eq. (25).

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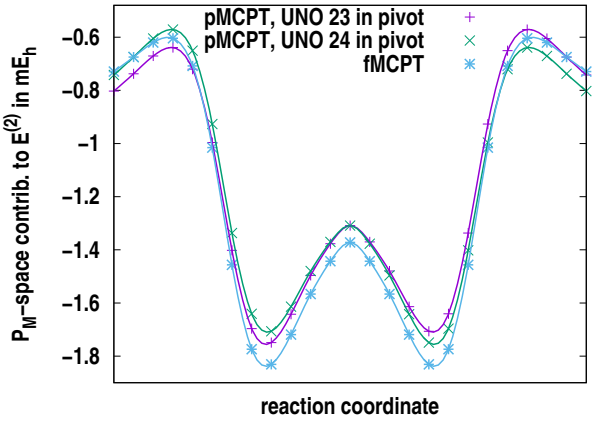
space at second order in PT is illustrated in Fig. 4(a), in the vicinity of the transition structure. In pMCPT one has the option of selecting one of the two determinants, and sticking to it along the process, even when it is not of the largest weight in the reference function. Colour codes in Fig. 4, matched with those in Fig. 3, indicate this strategy. The corresponding potential energy curves (PEC) are apparently nonsymmetric, predicting different pMCPT energies for equivalent isomers, which is clearly nonphysical. The effect is enhanced in Fig. 4(b), showing the difference of pivot dependent pMCPT and pivot invariant fMCPT model space contributions. As Fig. 4(b) reflects, deviation of fMCPT from pMCPT-s lies on the 0.1 m$E_h$ scale, and fMCPT does not interpolate between the two pMCPT curves.

Another option with pMCPT is to use the determinant of largest weight in the reference as pivot all along the reaction coordinate, thereby arriving at a symmetric curve and predicting the same energy for equivalent isomers. The drawback of this approach is that a non-analytic point is generated on the PEC at the transition structure, where the change in the pivotal determinant takes place. The reason behind is that analytic continuation of the curves at the mid point in Fig 4(b) are those in matching colour. Patching together two pieces of different colours, there necessarily arises a discontinuity in a derivative at some order at the mid point (even if the first derivatives observably match), otherwise there would be a contradiction with the unicity theorem of Taylor series. As a closing remark of this test case, we reiterate that the effect is small in comparison to the full second order correction, that is of a rough -920 m$E_h$ in the geometry range plotted.

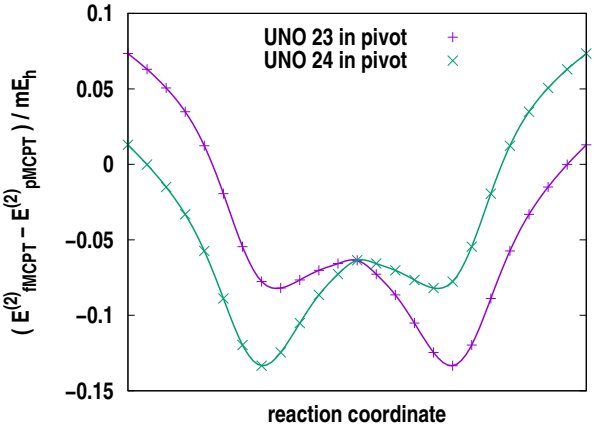
### E. Size-inconsistency

In a final example, size-inconsistency is assessed for pMCPT and fMCPT juxtaposing the case of a single $H_2O$ molecule with the results for two molecules with the same geometry, set infinitely apart. Table III collects MCPT results based on the size-consistent USLG reference as well as considering the size-consistency violating HPSLG reference. A glance at Table III reveals that size-inconsistency induced by second order MCPT is in the order of 10 m$E_h$ while the second order correction amounts to hundreds of m$E_h$ for this system. Size-consistency violation of HPSLG indicated in the last column of Table III is in the range of the violation by second order MCPTs. Comparing MCPT variants in Table III, fMCPT is seen to profit from an error cancellation. With USLG reference, size-inconsistency of the $P_M$-space contribution partly compensates the same effect of the $P_\perp$-space in the case of fMCPT, while the two effects are of the same sign and thence

frame MCPT




(a)




(b)

FIG. 4: Model space contribution of the second order PT correction to HPSLG for the isomerization process of 1,4-hexadiene in 6-31G* basis. Panel (a) shows the first term of Eqs.(21) and (23) by fMCPT and pMCPT, respectively. Two pivot choices with pMCPT correspond to the two closed shell determinants becoming of equal weight at the transition structure. Panel (b) depicts the deviation of pivot dependent pMCPT from pivot invariant fMCPT.

accumulate for pMCPT. Considering HPSLG as zero-order, it is size-inconsistency of the reference, that is largely compensated by the consistency violation contribution of the $P_M$-space for fMCPT and less so for pMCPT. It is certainly immature to draw conclusions on size-inconsistency based on the single example in Table III. It appears fair to state that the test case of Table III is thought provoking, requiring further inspection to decide whether the error compensation taking

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TABLE III: Total energies in $E_h$ for a single $H_2O$ molecule ($E_{mon}$) of $C_{2v}$ symmetry in 6-31G* basis at geometry $R_{O\text{–}H} = 1.5$ Å and $\angle(HOH) = 104.5°$. Two molecules of the same geometry, set infinitely apart, are tabulated under $E_{dim}$. Size-inconsistency, $\Delta E = E_{dim} - 2E_{mon}$ is indicated in the last column. Reference functions are provided by USLG and HPSLG. Second order MCPT energies arise by adding the $P_M$-space and $P_\perp$-space contribution to the reference value, c.f. Eqs.(21) and (23).

| | $E_{mon}$ / $E_h$ | $E_{dim}$ / $E_h$ | $\Delta E$ / $E_h$ |
|---|---|---|---|
| USLG | −75.83944 | −151.67887 | 0.000 |
| USLG-MCPT | | | |
| pMCPT, $P_M$ contr. | −0.03037 | −0.05180 | 0.009 |
| fMCPT, $P_M$ contr. | −0.03873 | −0.09723 | −0.020 |
| $P_\perp$ contr. | −0.22273 | −0.41579 | 0.030 |
| pMCPT, total | −76.09254 | −152.14647 | 0.039 |
| fMCPT, total | −76.10090 | −152.19189 | 0.010 |
| HPSLG | −75.86032 | −151.69995 | 0.021 |
| HPSLG-MCPT | | | |
| pMCPT, $P_M$ contr. | −0.01630 | −0.03676 | −0.004 |
| fMCPT, $P_M$ contr. | −0.01400 | −0.05500 | −0.027 |
| $P_\perp$ contr. | −0.19212 | −0.38420 | 0.000 |
| pMCPT, total | −76.06875 | −152.12091 | 0.017 |
| fMCPT, total | −76.06645 | −152.13916 | −0.006 |

place at the second order of fMCPT is fortuitous or can be reasoned out. Considerations along this line are deferred to follow-up studies.

## IV. CONCLUSION

The above examined, frame-based formulation represents a novel variant in the family of MCPT methods applicable for describing weak (dynamic) correlation on top of strong correlation. The second order energy correction formula of fMCPT bears most kinship with the previously

Accepted to J. Chem. Phys. 10.1063/5.0112563



introduced, projected MCPT variant. In particular, the two variants differ only in the relaxation of model space coefficients, while contributions from the orthogonal complement of the model space are the same. Relaxation effect in the model space being zero for complete model space reference functions, numerical assessment is performed with incomplete model space type zero-order functions. Test calculations show a minor difference between pMCPT and fMCPT, the former producing slightly more accurate absolute energies, while fMCPT yielding somewhat better energy differences. Size-consistency violation of pMCPT and fMCPT is on the same order of magnitude, fMCPT outperforming pMCPT by a factor of $2-4$ in the examples studied.

Frame based formulation results in fMCPT being pivot invariant, a feature that makes it superior to pMCPT when the reference is of incomplete model space type. Pivot invariance becomes an issue whenever the determinant of largest weight in the reference changes in the explored range of the PES. Keeping to the determinant of largest weight as pivot is a usual practice, which however introduces non-analiticity on the PES at the point of change. Averaging over pivot choices is an alternative route of establishing pivot invariance in MCPT. Since pivot averaging requires careful selection of the partitioning in order to avoid intruders, fMCPT certainly represents a more black box solution of the problem.

We finally mention, that when treating overcompleteness of projected determinants in MCPT, that formalism of frames could be sidestepped by using the linearly independent set of vectors, provided in closed form by Dalgaard and Mayer. We nevertheless believe that the equivalence of the frame-based and DM vectors based formulation is a valuable contribution in complementing the picture. Frame-based derivation presented here also provides a working example of redundancy treatment without the dimension reduction characteristic of Löwdin's canonical procedure. This is a general scheme that may find application in various situations in quantum chemical methodology.

## SUPPLEMENTARY MATERIAL

See supplementary material for the entries of the Z-matrix providing parametrized geometry points along the isomerization process of of the 1,4-hexadiene molecule ($C_6H_{10}$).

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## ACKNOWLEDGMENTS

The authors are grateful to prof. Tamás Geszti (ELTE, Budapest, Hungary) and Dr. András Bodor (University of Pécs, Hungary) for calling their attention to frame theory and for discussions. Discussions with János Wołosz on algorithmic developments are greatly appreciated.

The work has been supported by the ÚNKP-21-4 New National Excellence Program of the Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund.

## DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are essentially provided within the article and its supplementary material file. Further data are available from the authors upon reasonable request.

## Appendix A: Considerations on frames

### 1. Frame attribute of $\varphi_i$

Vectors $\{\varphi_i'\}_{i=1}^{M}$ introduced in Section II fulfill the inequalities defining a frame as[50]

$$A\boldsymbol{P}_M \leq \boldsymbol{F}\boldsymbol{F}^{\dagger} \leq B\boldsymbol{P}_M \ , \tag{A1}$$

with the $(M-1)\times M$ rectangular matrix $\boldsymbol{F}$ composed of elements $F_{ij} = \sigma_i (V^{\dagger})_{ij}$ and $\boldsymbol{S} = \boldsymbol{F}^{\dagger}\boldsymbol{F}$. Note, that $\sigma_i$ are the square-root of the nonzero eigenvalues of $\boldsymbol{S}$, in decreasing order, while $\boldsymbol{V}$ collects the corresponding eigenvectors in columns. Index $i$ of $\sigma_i$ ranges from 1 to $M-1$. One eigenvalue of matrix $\boldsymbol{S}$ is zero, corresponding to $i = M$. In Eq. (A1) $\boldsymbol{P}_M$ is the $(M-1)$-dimensional unit matrix and scalars $A$ and $B$ are given by the smallest and largest $\sigma_i^2$ for $i = 1,\ldots,M-1$.

A rationale behind Eq. (A1) can be given as follows. Taking an orthonormal basis in space $P_M$, denoted by $\{e_i\}_{i=1}^{M-1}$ and an arbitrary function $\xi$ expanded as

$$\xi = \sum_{i=1}^{M-1} |e_i\rangle x_i \ ,$$

it follows from $\langle e_i|e_j\rangle = \delta_{ij}$ that

$$\sum_{i=1}^{M-1} \langle \xi|e_i\rangle\langle e_i|\xi\rangle = \sum_{i=1}^{M-1} x_i^* x_i \ . \tag{A2}$$

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Next compose the analogue of Eq. (A2) with the overcomplete set $\{\varphi_i'\}_{i=1}^M$ instead of the ON basis as

$$\sum_{i=1}^{M} \langle \xi | \varphi_i' \rangle \langle \varphi_i' | \xi \rangle \ . \tag{A3}$$

Introduce now the orthonormal basis in $P_M$-space according to Löwdin's canonical scheme[56,74], the ON vectors reading as

$$|\psi_i^L\rangle = \sum_{j=1}^{M} |\varphi_j'\rangle G_{ji} \ , \ \ i = 1, \ldots, M-1 \tag{A4}$$

where the $M \times (M-1)$ rectangular matrix $\boldsymbol{G}$ is built of elements $G_{ji} = V_{ji}\sigma_i^{-1}$. Matrix $\boldsymbol{G}$ is the Moore-Penrose inverse of $\boldsymbol{F}$ fulfilling the basic properties

$$\boldsymbol{FGF} = \boldsymbol{F} \ , \tag{A5a}$$

$$\boldsymbol{GFG} = \boldsymbol{G} \ , \tag{A5b}$$

$$(\boldsymbol{FG})^\dagger = \boldsymbol{FG} \ , \tag{A5c}$$

$$(\boldsymbol{GF})^\dagger = \boldsymbol{GF} \ . \tag{A5d}$$

Substituting

$$|\xi\rangle = \sum_{i=1}^{M-1} |\psi_i^L\rangle x_i \ = \ \sum_{i=1}^{M-1} \sum_{j=1}^{M} |\varphi_j'\rangle G_{ji} x_i$$

in Eq. (A3) and making use of $\langle \varphi_i' | \varphi_j' \rangle = S_{ij}$, $\boldsymbol{S} = \boldsymbol{F}^\dagger \boldsymbol{F}$ and Eq. (A5) one arrives at

$$\sum_{i=1}^{M} \langle \xi | \varphi_i' \rangle \langle \varphi_i' | \xi \rangle = \sum_{i,j=1}^{M-1} x_i^* \, (\boldsymbol{FF}^\dagger)_{ij} x_j \ . \tag{A6}$$

Instead of the squared norm of vector $\boldsymbol{x}$, obtained on the right hand side of Eq. (A3), the expression in Eq. (A6) yields the squared norm of $\boldsymbol{F}^\dagger \boldsymbol{x}$. Well behaving nature[75] of the expansion of function $\xi$ in terms of $\{\varphi_i'\}_{i=1}^M$ requires the squared norm of $\boldsymbol{F}^\dagger \boldsymbol{x}$ to be bounded, i.e.

$$0 < \boldsymbol{x}^\dagger \boldsymbol{FF}^\dagger \boldsymbol{x} < \infty \ .$$

Since function $\xi$ is arbitrary, boundedness can be required for $\boldsymbol{FF}^\dagger$, according to Eq. (A1). The significance of Eq. (A1) is that scalars $A, B$ are positive and finite.

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### 2. Identity built with frame vectors

We here wish to justify that frame vectors and their canonical duals composed according to Eq. (9) can be used to represent the identity of $P_M$-space, spanned by $\{\varphi'_i\}_{i=1}^{M}$. To this end let us compose projector $\hat{P}_M$ with the help of Löwdin vectors of Eq. (A4) as

$$\hat{P}_M = \sum_{i=1}^{M-1} |\psi_i^L\rangle\langle\psi_i^L| \, . \tag{A7}$$

Substituting Eq. (A4) in the above, one arrives at

$$\hat{P}_M = \sum_{i,j=1}^{M} |\varphi'_i\rangle(\boldsymbol{G}\boldsymbol{G}^\dagger)_{ij}\langle\varphi'_j| \;=\; \sum_{i=1}^{M} |\varphi'_i\rangle\langle\widetilde{\varphi'}_i| \, , \tag{A8}$$

where $\langle\widetilde{\varphi'}_j|$ are defined in Eq. (9) and $\boldsymbol{R} = \boldsymbol{G}\boldsymbol{G}^\dagger$ has been utilized. That $\boldsymbol{G}\boldsymbol{G}^\dagger$ is the Moore-Penrose inverse of $\boldsymbol{S}$ is a consequence of $\boldsymbol{S} = \boldsymbol{F}^\dagger\boldsymbol{F}$ and the relation between $\boldsymbol{F}$ and $\boldsymbol{G}$, c.f. Eq. (A5). The right hand side of Eq. (A8) forms the starting point of the considerations in Section II, c.f. Eq. (10).

The use of an alternative generalized inverse, due to Drazin[76] deserves a brief note at this point. While it is different from the Moore-Penrose definition, Eq. (A5) in general, they coincide for hermitian matrices, which holds true for the overlap, $\boldsymbol{S}$. Though the same does not apply to $\boldsymbol{F}$, the key relation to be used below is Eq. (A8), which involves the generalized inverse of $\boldsymbol{S}$.

### 3. Linear equation solved with frame vectors

We here wish to show that the $P_M$-space component of the first order wavefunction, $\Psi^{(1)}$ is the same when working with redundant frame vectors $\{\varphi'_i\}_{i=1}^{M}$ and Eq. (13) or with orthonormal Löwdin-vectors of Eq. (A4) and the counterpart of Eq. (15), composed with $\{\psi_i^L\}_{i=1}^{M-1}$ as

$$\hat{H}^{(0)}_{PM} = \sum_{i,j=1}^{M-1} |\psi_i^L\rangle\langle\psi_i^L|\hat{H}|\psi_j^L\rangle\langle\psi_j^L| \, . \tag{A9}$$

Starting with a frame-based consideration, the $P_M$-space component of $\Psi^{(1)}$ is expanded as

$$\hat{P}_M|\Psi^{(1)}\rangle = \sum_{i=1}^{M} |\varphi'_i\rangle d_i \, . \tag{A10}$$

Note, that coefficients $d_i$ are not unique due to $\{\varphi'_i\}_{i=1}^{M}$ forming an overcomplete set. Eq. (A10) substituted in Eq. (17) and the equation projected by $\langle\varphi'_i|$ results

$$\sum_{j=1}^{M} \langle\varphi'_i|E_0 - \hat{H}|\varphi'_j\rangle d_j \;=\; \langle\varphi'_i|\hat{H}|\Phi\rangle \;\; . \tag{A11}$$

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We now need the reverse relation of Eq. (A4), expressing $\varphi'_i$ with the help of $\psi^L_i$. This is obtained by acting with $\hat{P}_M$ of Eq. (A7) on $\varphi'_i$ yielding

$$|\varphi'_i\rangle = \sum_{j=1}^{M-1} |\psi^L_j\rangle F_{ji} \ , \quad i = 1,\ldots,M \tag{A12}$$

when making use of Eqs. (A4), (A5) and $\boldsymbol{S} = \boldsymbol{F}^\dagger \boldsymbol{F}$, c.f. Appendix A 1. Let us now append an $M$th row to rectangular matrix $\boldsymbol{F}$, resulting in the $M$-dimensional square matrix $\overline{\boldsymbol{F}}$ with elements

$$\overline{F}_{ji} = \begin{cases} F_{ji} = \sigma_j (V^\dagger)_{ji} & \text{for } \ j = 1,\ldots,M-1 \ \text{ and } \ i = 1,\ldots,M \\ \eta (V^\dagger)_{Mi} & \text{for } \ j = M \qquad\quad \text{and } \ i = 1,\ldots,M \end{cases}$$

with $\eta$ being an arbitrary, nonzero scalar. Let us also append the $M$th eigenvector of $\boldsymbol{S}$ to the set of Löwdin's canonical vectors according to

$$\psi_i = \begin{cases} \psi^L_i = \sum\limits_{j=1}^{M} |\varphi'_j\rangle V_{ji} \sigma_i^{-1} & \text{for } \ i = 1,\ldots,M-1 \\ \sum\limits_{j=1}^{M} |\varphi'_j\rangle V_{jM} & \text{for } \ i = M \end{cases} \tag{A13}$$

It is important to realize, that $\psi_M$ is a vector of zero norm

$$\langle \psi_M | \psi_M \rangle = (\boldsymbol{V}^\dagger \boldsymbol{S} \boldsymbol{V})_{MM} \ = \ 0$$

since the $M$th eigenvalue of $\boldsymbol{S}$ is zero. Therefore Eq. (A12) can be equivalently written as

$$|\varphi'_i\rangle = \sum_{j=1}^{M} |\psi_j\rangle \overline{F}_{ji} \ , \quad i = 1,\ldots,M \tag{A14}$$

The advantage of Eq. (A14) over Eq. (A12) is that $\overline{\boldsymbol{F}}$ appearing in Eq. (A14) is invertible, as ensured by the frame inequality Eq. (A1). We shall need the inverse of $\overline{\boldsymbol{F}}$ shortly.

Substituting Eq. (A14) in Eq. (A11) we obtain

$$\overline{\boldsymbol{F}}^\dagger \boldsymbol{A} \overline{\boldsymbol{F}} \boldsymbol{d} = \overline{\boldsymbol{F}}^\dagger \boldsymbol{b} \tag{A15}$$

with column vector $\boldsymbol{d}$ collecting coefficients $d_i$, column vector $\boldsymbol{b}$ collecting $b_i = \langle \psi_i | \hat{H} | \Phi \rangle$ and matrix $\boldsymbol{A}$ composed of elements $A_{ij} = \langle \psi_i | E_0 - \hat{H} | \psi_j \rangle$. Since $\psi_M$ is of zero norm, the corresponding entries of vector $\boldsymbol{b}$ and matrix $\boldsymbol{A}$ are zero. In particular

$$\boldsymbol{b} = \begin{pmatrix} \boldsymbol{b}^L \\ 0 \end{pmatrix}$$

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and

$$\boldsymbol{A} = \begin{pmatrix} \boldsymbol{A}^L & 0 \\ 0 & 0 \end{pmatrix}$$

with column vector $\boldsymbol{b}^L$ collecting $b_i^L = \langle \psi_i^L | \hat{H} | \Phi \rangle$ and matrix $\boldsymbol{A}^L$ composed of elements $A_{ij}^L = \langle \psi_i^L | E_0 - \hat{H} | \psi_j^L \rangle$.

Express now vector $\boldsymbol{d}$ from Eq. (A15) by (i) left multiplying by the inverse of $\overline{\boldsymbol{F}}^\dagger$; (ii) then left multiplying by the Moore-Penrose inverse of $\boldsymbol{A}$; (iii) then left multiplying by the inverse of $\overline{\boldsymbol{F}}$ resulting

$$\boldsymbol{d} = \overline{\boldsymbol{F}}^{-1} \begin{pmatrix} \boldsymbol{Q}^L & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \boldsymbol{b}^L \\ 0 \end{pmatrix} = \overline{\boldsymbol{F}}^{-1} \begin{pmatrix} \boldsymbol{c}^{(1)L} \\ 0 \end{pmatrix} \tag{A16}$$

where $\boldsymbol{Q}^L$ is the inverse of $\boldsymbol{A}^L$ and $\boldsymbol{c}^{(1)L}$ is the column vector collecting expansion coefficients of $\Psi^{(1)}$ on the Löwdin basis according to

$$\hat{P}_M |\Psi^{(1)}\rangle = \sum_{i=1}^{M-1} |\psi_i^L\rangle c_i^{(1)L} \,. \tag{A17}$$

In the second equality in Eq. (A16) we made use of $\boldsymbol{c}^{(1)L} = \boldsymbol{Q}^L \boldsymbol{b}^L$, which is the counterpart of Eq. (20), written with Löwdin vectors.

Coefficients $d_i$ from Eq. (A16) substituted in Eq. (A10) also gives gives $\hat{P}_M |\Psi^{(1)}\rangle$ that we now wish to relate with Eq. (A17). For this end expression Eq. (A14) of the projected vectors is also substituted in Eq. (A10) to get

$$\hat{P}_M |\Psi^{(1)}\rangle = \sum_{i,j=1}^{M} \sum_{k=1}^{M-1} |\psi_i\rangle \overline{F}_{ij} \overline{F}^{-1}_{jk} c_k^{(1)L} = \sum_{k=1}^{M-1} |\psi_k^L\rangle c_k^{(1)L} \tag{A18}$$

making use of Eq. (A13). The frame-based expansion of Eq. (A10) with $\boldsymbol{d}$ from Eq. (A16) therefore matches the orthonormal vectors based expansion Eq. (A17) with $\boldsymbol{c}^{(1)L}$ determined according to Section II. Expansion coefficients $d_i$ of the frame depend on scalar $\eta$, c.f. Eq. (A16), in accordance with their non unique nature. As expected, $\eta$ drops from the expression of quantities unaffected by redundancy, i.e. $\hat{P}_M |\Psi^{(1)}\rangle$ and $\boldsymbol{c}^{(1)L}$.

### 4. Unprojected MCPT with frame vectors

Taking the normalized reference in Eq. (1), let us now consider the set $\{\Phi\} \cup \{\varphi_i\}_{i=1}^M$ as our starting point in composing a zero-order Hamiltonian. In this Section symbols $\boldsymbol{S}, \boldsymbol{F}, \boldsymbol{R}, \ldots$ are

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used in analogy with the previous, upper index $u$ referring to the uMCPT variant of the given quantity. Vectors $\{\Phi\}\cup\{\varphi_i\}_{i=1}^{M}$ constitute an $(M+1)$ dimensional frame, the overlap reading as

$$\boldsymbol{S}^u = \boldsymbol{F}^{u\dagger}\boldsymbol{F}^u$$

with the rectangular $M\times(M+1)$ matrix $\boldsymbol{F}^u$ given by

$$\boldsymbol{F}^u = \begin{pmatrix} c_1 & 1 & 0 & \dots & 0 \\ c_2 & 0 & 1 & \dots & 0 \\ \vdots & 0 & 0 & \ddots & 0 \\ c_M & 0 & 0 & \dots & 1 \end{pmatrix} = \left( \boldsymbol{c} \middle| \boldsymbol{I}_M \right) ,$$

where $\boldsymbol{c}$ is the column vector collecting elements $c_i$ and $\boldsymbol{I}_M$ stands for the $M$-dimensional unit matrix. Vectors constituting the canonical dual frame are expressed as

$$\langle\widetilde{\Phi}| = R^u_{1,1}\langle\Phi| + \sum_{j=1}^{M} R^u_{1,(j+1)}\langle\varphi_j| \tag{A19a}$$

$$\langle\widetilde{\varphi}_i| = R^u_{(i+1),1}\langle\Phi| + \sum_{j=1}^{M} R^u_{(i+1),(j+1)}\langle\varphi_j| \ , \quad i=1,\dots,M \tag{A19b}$$

with $\boldsymbol{R}^u$ standing for the Moore-Penrose inverse of $\boldsymbol{S}^u$, obeying the relation

$$\boldsymbol{R}^u = \boldsymbol{F}^{u\dagger}(\boldsymbol{F}^{u\dagger}\boldsymbol{F}^u)^{-2}\boldsymbol{F}^u \ .$$

By some algebraic manipulation $\boldsymbol{R}^u$ is found to be expressed with $\boldsymbol{c}$ as

$$\boldsymbol{R}^u = \frac{1}{4}\left(\begin{array}{c|c} 1 & \boldsymbol{c}^\dagger \\ \hline \boldsymbol{c} & 4\boldsymbol{I}_M \end{array}\right) - \frac{3}{4}\left(\begin{array}{c|c} 0 & \boldsymbol{0}^\dagger \\ \hline \boldsymbol{0} & \boldsymbol{c}\boldsymbol{c}^\dagger \end{array}\right) ,$$

$\boldsymbol{0}$ denoting the column vector built of $M$ zeroes. Substituting $\boldsymbol{R}^u$ in Eq. (A19) we find

$$\langle\widetilde{\Phi}| = \frac{1}{2}\langle\Phi| \ , \tag{A20a}$$

$$\langle\widetilde{\varphi}_i| = \langle\varphi_i| - \frac{c_i}{2}\langle\Phi| \ . \tag{A20b}$$

With the help of the vectors in Eq. (A20), projector of the entire model space can be formulated as

$$\hat{O} + \hat{P}_M = |\Phi\rangle\langle\widetilde{\Phi}| + \sum_{i=1}^{M} |\varphi_i\rangle\langle\widetilde{\varphi}_i| \ , \tag{A21}$$

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while for our purpose orthogonal projectors corresponding to the reference and its complement would be needed. The former is provided by simple normalization of $|\Phi\rangle\langle\widetilde{\Phi}|$, leading to the expression

$$\hat{O} = |\Phi\rangle \langle\widetilde{\Phi}|\Phi\rangle^{-1} \langle\widetilde{\Phi}| \;=\; |\Phi\rangle\langle\Phi|$$

matching Eq. (3). The second term on the right hand side of Eq. (A21) can be orthogonalized to $\hat{O}$, yielding

$$\hat{P}_M = \sum_{i=1}^{M} (1-\hat{O})|\varphi_i\rangle\langle\widetilde{\varphi}_i|(1-\hat{O}) \;=\; \sum_{i=1}^{M} |\varphi_i'\rangle\langle\varphi_i'| \; .$$

The above expression again matches that obtained in Section II, c.f. Eq. (12). We therefore find that the projected and unprojected approaches in MCPT collapse onto the same formulation when using the concept of frames.

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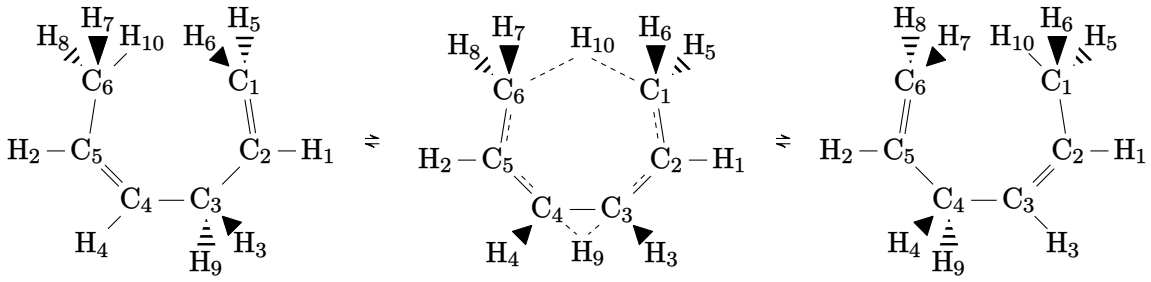

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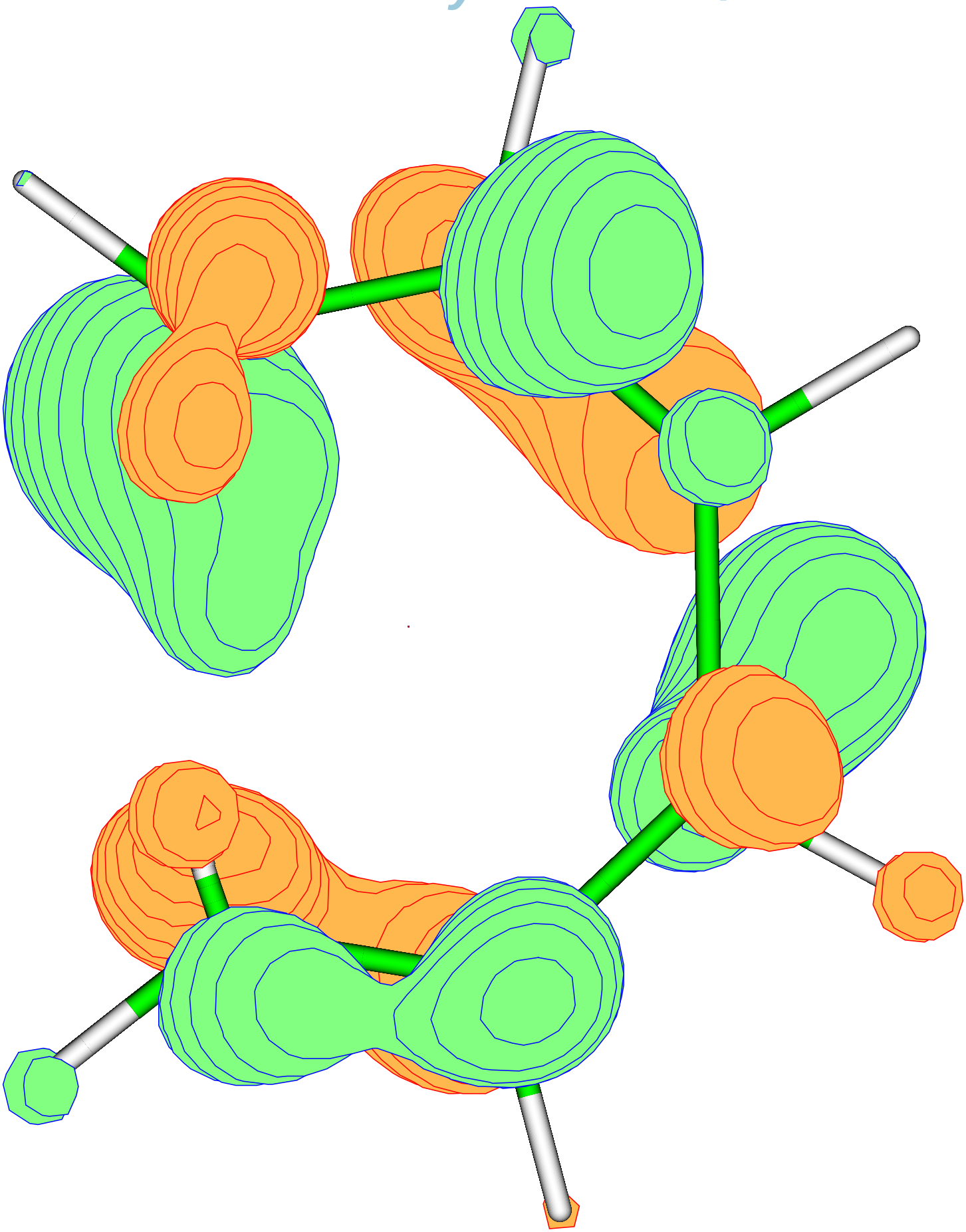

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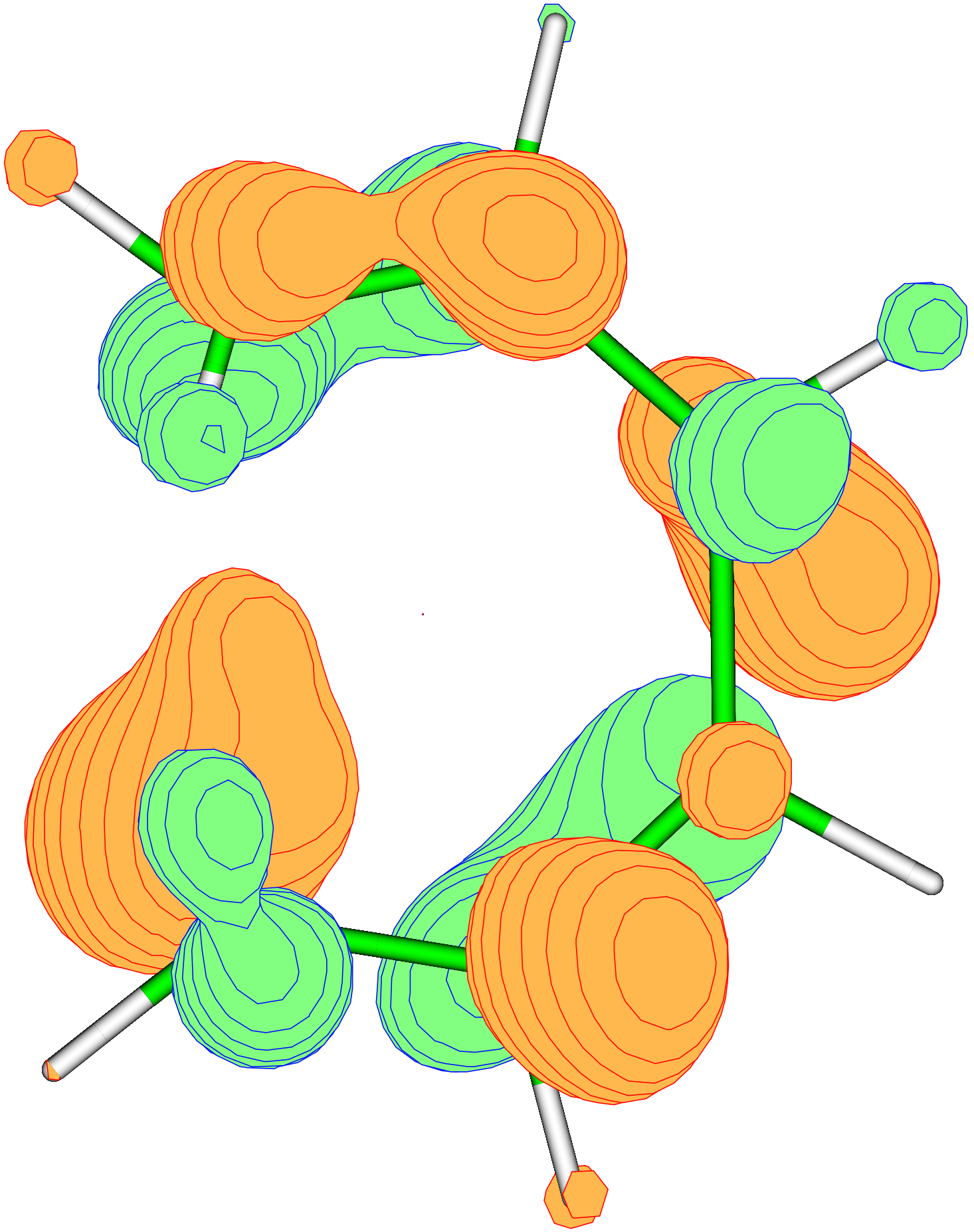

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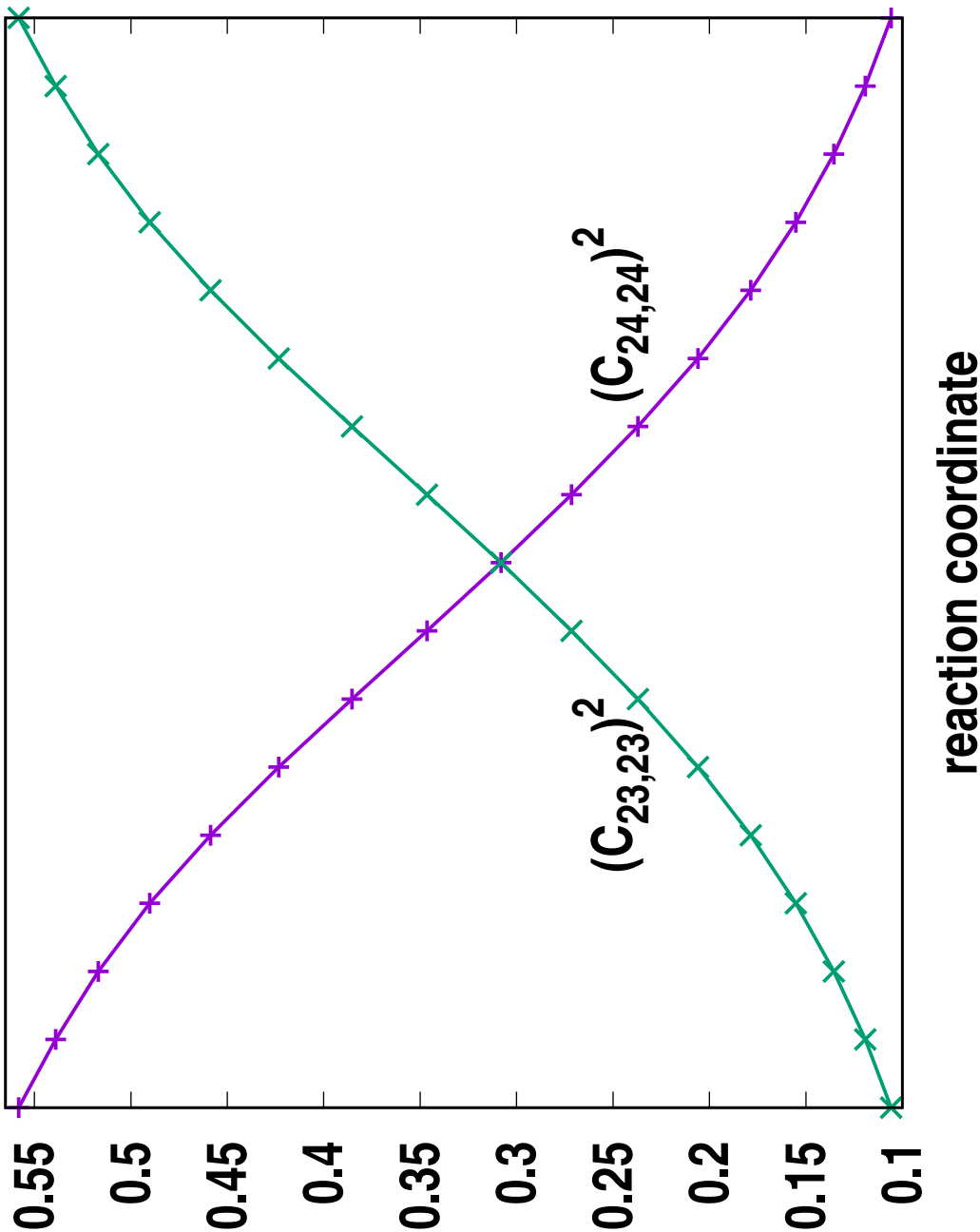

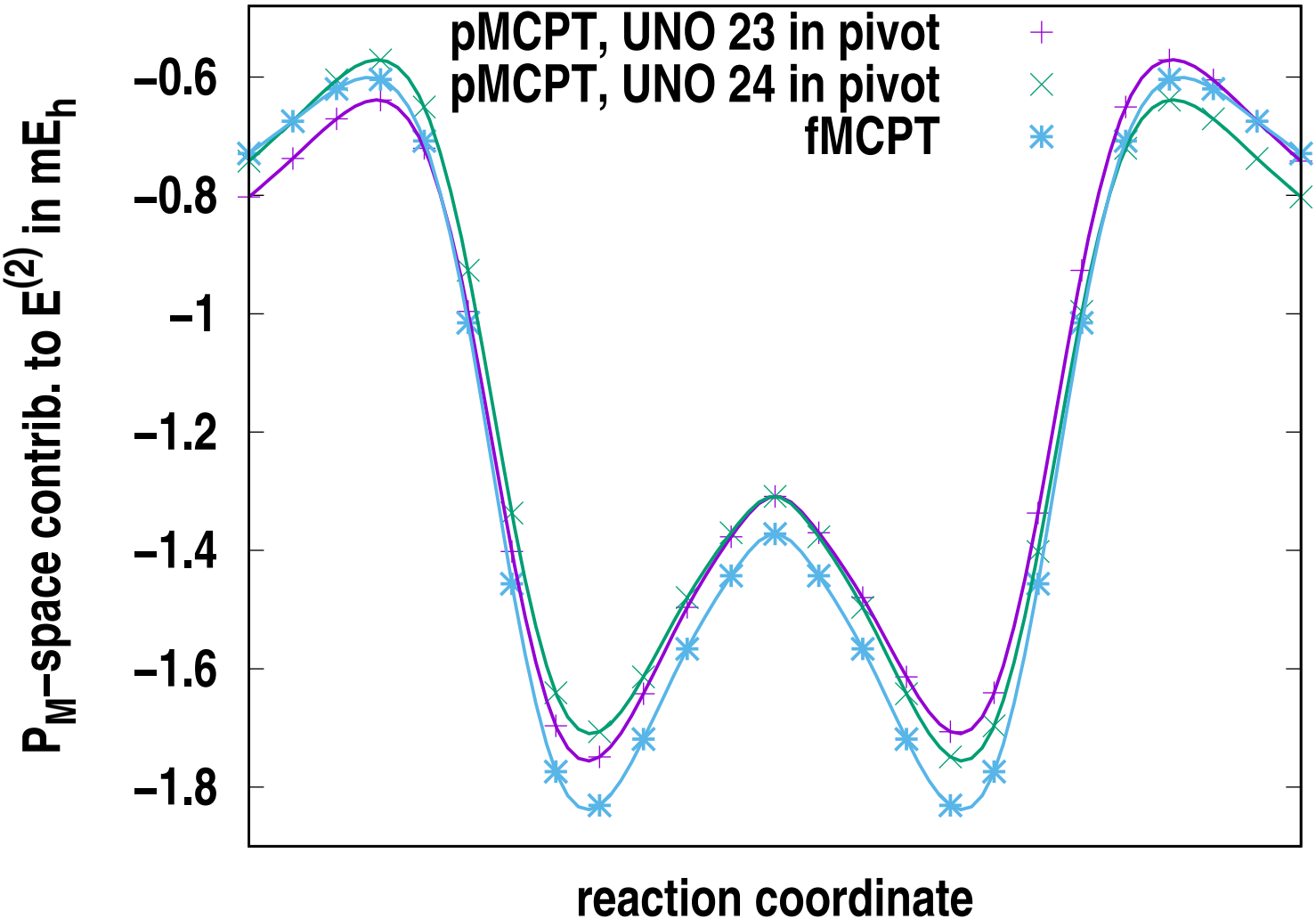


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