

# Fermi-vacuum invariance in multiconfiguration perturbation theory

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**Abstract** We investigate the dependence of multiconfigurational perturbation theory framework on the choice of the Fermi-vacuum. A new formulation, based on a-posteriori averaging is suggested. The averaged theory is invariant with respect to Fermi-vacuum choice but enhances the intruder effect. The performance of the averaged formulation is illustrated on the ethylene rotational potential curve.

## 1 Introduction

Dissociation of covalent bonds in molecules, description of electronic excited states or transition metal compounds belong to current problems of theoretical chemistry, usually addressed as "multiconfiguration cases". Basic quantum chemical paradigms, such as configuration interaction, coupled-cluster (CC) and perturbation theory (PT) have lived diverse multireference (MR) extensions of the single-reference approach, in order to treat the above systems. Among multireference theories one may distinguish genuine MR methods[1, 2, 3, 4, 5] as well as essentially single-reference type multiconfiguration (MC) approaches[6, 7, 8]. This categorization – which has been most used in CC methodology – is of relevance from the point of view of the present PT study. Purely single-reference CC methods, called completely renormalized CC approaches, which do not use any MR or MC concepts, also have the potential to describe bond breaking and biradicals[9, 10]. A common characteristics of purely single-reference and essentially single-reference type MC methods is the presence of a formal reference determinant in the theory,

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which facilitates the particle/hole orbital assignment and involves one well-defined excitation amplitude set. As opposed to this, genuine MRCC methods consider all determinants present in a complete or incomplete model space as Fermi-vacua, and consequently involve multiple amplitude sets to parametrize the exact wavefunction. We adopt the convention of referring to this latter strategy as Jeziorski-Monkhorst parametrization.

Multiple amplitude sets have been applied in PT methodology as well. Perturbative approximations of the Jeziorski-Monkhorst parametrized SS-MRCC[11] show outstanding properties: size-consistency, size-extensivity and the potential to be intruder free at the same time. It is however not wide-spread to consider multiple amplitude sets within a PT framework for the electron-correlation problem. A usual categorization of MRPT frameworks is the distinction of effective Hamiltonian strategies[12, 13, 14] and single-but-multi philosophies[15, 16]. The former can target many electronic states of a system while the latter focuses on just one state at a time. Both approaches have their own advantages and shortcomings. In rough terms effective Hamiltonian theories are good candidates for fulfilling the size-extensivity requirement they however struggle with serious intruder state problem[17]. Single-but-multi approaches like CASPT[18, 19] or MRMP[20] usually violate size-consistency but the sensitivity to intruders may be less severe. There are several exceptions to the above rule. The intermediate Hamiltonian theory developed by Malrieu et al.[21] e.g. is size extensive and avoids intruders via the application of multiple partitionings when building the effective Hamiltonian matrix.

Multiconfiguration perturbation theory (MCPT)[22] is another exception to the above categorization, since it can provide rigorously size-consistent energy at second order[23] although it applies a single-but-multi framework. In MCPT there appears a Fermi-vacuum which can be any of the determinants of nonzero weight in the multiconfiguration zero-order function. The necessity to pinpoint a Fermi-vacuum is a common feature of MCPT and single-reference type MRCC approaches. Neither MCPT nor affected MRCC theories show invariance with respect to the Fermi-vacuum choice. Switching from one Fermi-vacuum to another when following a potential energy surface has been shown to cause discontinuities. Though the error due to this effect has been shown to be small in MRCC[24], the non-invariance can become a qualitative problem when causing symmetry breaking. This issue has been addressed recently in the context of XCASCCSD and cured by symmetry-adaptation at a suitable step of the algorithm[25].

In the present study we consider the same problem in the framework of MCPT and propose a modification which restores the invariance to the choice of Fermi-vacuum. This involves calculating the perturbed quantities by all possible choices and constructing a weighted average. The number of parameters in the theory agrees with that of a Jeziorski-Monkhorst type MRCC parametrization. The redundancy of a Jeziorski-Monkhorst parametrization however does not show up in the present approach due to the fact that perturbational amplitudes corresponding to different Fermi-vacua are determined separately. The linear combination of thus produced

functions is constructed a-posteriori, the weights taken from the unrelaxed zero-order wavefunction.

In this account we first briefly summarize MCPT followed by an analysis on the extent of Fermi-vacuum non-invariance in different versions of the theory. We continue by presenting the approach to ensure Fermi-vacuum invariance and close with a numerical illustration.

## 2 Theory

### 2.1 Zero-order Hamiltonians

The perturbational framework designated as MCPT has been developed in two variants: the original formulation, hereafter called projected-MCPT[22] (p-MCPT) and a version which can give size-consistent correction at second order, hereafter called unprojected-MCPT[23] (u-MCPT). Both variants start with a multiconfiguration zero-order function written as

$$|0\rangle = c_{\text{HF}}|\text{HF}\rangle + \sum_{K \in R \setminus \{\text{HF}\}} c_K |K\rangle \quad (1)$$

where  $|\text{HF}\rangle$  and  $|K\rangle$  denote determinants. Determinant  $|\text{HF}\rangle$  is used as Fermi-vacuum. It can be any determinant which appears with nonzero weight in  $|0\rangle$ , practically it is the one associated with the largest coefficient squared. Determinants appearing in the zero-order reference function form a subspace in the configuration space, denoted by  $R$ . The sum for  $K$  in Eq.(1) runs over elements of subspace  $R$ , except the pinpointed Fermi-vacuum.

In MCPT theories a zero-order Hamiltonian is constructed in spectral form, taking  $|0\rangle$  as ground state zero-order eigenvector and determinants different from  $|\text{HF}\rangle$  as excited state zero-order eigenvectors. These functions represent a non-orthogonal basis in the FCI space which necessitates the treatment of overlap. It is at this stage where p-MCPT and u-MCPT versions deviate. In p-MCPT

1. excited vectors  $|K\rangle$  are first Schmidt-orthogonalized to  $|0\rangle$  to get  $|K'\rangle$ ;
2. a reciprocal set is constructed to  $|K'\rangle$ , denoted by  $\langle \tilde{K}'|$ .

In u-MCPT version step 1. is missing, reciprocal vectors to the set  $|0\rangle$  and  $|K\rangle$ 's are directly constructed, giving  $\langle \tilde{0}|$  and  $\langle \tilde{K}|$ . The spectral form of the zero-order Hamiltonian is non-symmetric in both formulations, due to the use of bi-orthogonal vector sets:

$$\hat{H}_{\text{p-MCPT}}^{(0)} = E_0 |0\rangle \langle 0| + \sum_{K \in R \setminus \{\text{HF}\}} E_K |K'\rangle \langle \tilde{K}'| \quad (2)$$

$$\hat{H}_{\text{u-MCPT}}^{(0)} = \eta_0 |0\rangle \langle \tilde{0}| + \sum_{K \in R \setminus \{\text{HF}\}} \eta_K |K\rangle \langle \tilde{K}|. \quad (3)$$

Comparing zero-order operators of Eq.(2) and Eq.(3) one may observe, that an advantage of Schmidt-orthogonalization is getting the zero-order Hamiltonian symmetric at least in the one-dimensional reference space spanned by  $|0\rangle$ . Left and right hand zero-order eigenvectors expressed in terms of determinants  $|\text{HF}\rangle$ ,  $|K\rangle$  and MR function  $|0\rangle$  are listed in Table 1 for completeness. Detailed derivation of the reciprocal vectors has been shown in an earlier report[23].

When defining zero-order ground-state eigenvalues, projection of the Schrödinger-equation is taken either with  $\langle 0|$  or with  $\langle \tilde{0}|$  to get

$$E_{\text{p-MCPT}}^{(0)} = E_0 = \langle 0|\hat{H}|0\rangle \quad (4)$$

or

$$E_{\text{u-MCPT}}^{(0)} = \eta_0 = \langle \tilde{0}|\hat{H}|0\rangle, \quad (5)$$

respectively. By this definition, the first order energy correction is zero in both versions. It is to be mentioned at this point, that the symmetric and non-symmetric energy formulae (4) and (5) are equivalent if the zero-order function  $|0\rangle$  is obtained from a variational solution of the Schrödinger-equation. This is the case e.g. if  $|0\rangle$  is a complete-active space wavefunction or stems from a configuration-interaction procedure.

Zero-order excited state energies can be chosen in both variants e.g. in the spirit of Davidson and Kapuy (DK)[26, 27, 28, 29]

$$E_K = E_0 + \Delta\varepsilon_K$$

or

$$\eta_K = \eta_0 + \Delta\varepsilon_K$$

where  $\Delta\varepsilon_K$  is formed as sums and differences of one-particle energies defined as diagonals of a generalized Fockian. This partitioning is different from Møller–Plesset, since the generalized Fockian is not necessarily diagonal.

Alternatively, excited state energies may be chosen to obtain a generalized Epstein-Nesbet (EN) partitioning

$$E_K = \eta_K = \langle K|\hat{H}|K\rangle. \quad (6)$$

A non-symmetric generalization of EN partitioning is also conceivable in the form  $E_K = \langle \tilde{K}'|\hat{H}|\tilde{K}'\rangle$  or  $\eta_K = \langle \tilde{K}|\hat{H}|K\rangle$ . For our present purpose the definition of Eq.(6) is more appealing because it avoids any reference to the Fermi-vacuum. A detailed discussion on partitionings in MCPT can be found in Ref.[30].

## 2.2 Non-invariance to the choice of Fermi-vacuum

The first-order wavefunction in p-MCPT as obtained by bi-orthogonal Rayleigh-Schrödinger theory looks

$$\Psi_{\text{p-MCPT}}^{(1)}(\text{HF}) = - \sum_{K \in R \setminus \{\text{HF}\}} |K'\rangle \frac{\langle \tilde{K}' | \hat{H} | 0 \rangle}{E_K - E_0}$$

while the second-order energy is given by

$$\begin{aligned} E_{\text{p-MCPT}}^{(2)}(\text{HF}) &= - \sum_{K \in R \setminus \{\text{HF}\}} \frac{\langle 0 | \hat{H} | K' \rangle \langle \tilde{K}' | \hat{H} | 0 \rangle}{E_K - E_0} \\ &= - \sum_{K \in R \setminus \{\text{HF}\}} \frac{(\langle 0 | \hat{H} | K \rangle - c_K E_0) (\langle K | \hat{H} | 0 \rangle - c_K \eta_0)}{E_K - E_0}. \end{aligned} \quad (7)$$

Notation HF in round braces on the left-hand-side refer to the dependence of the quantities on the Fermi-vacuum choice. Examining the second-order energy, dependence on |HF⟩ is least severe in EN partitioning if  $E_0 = \eta_0$ . In this case neither the numerator nor the denominator of the energy expression is affected by changing the choice for |HF⟩. Dependence on the Fermi-vacuum only stems from the restriction on the sum  $K \neq \text{HF}$ . At contrast to this, denominators show explicit dependence on |HF⟩ in DK partitioning, because particle/hole assignment is based on |HF⟩. This means that changing |HF⟩ may change the actual orbital indices which contribute to a  $\Delta \varepsilon_K$ . Whether the value  $\varepsilon_i$  itself is affected or not, depends on the definition. One may use the diagonals of the generalized Fockian appearing in multi-configurational self-consistent field (MCSCF) theories[31]

$$\varepsilon_i = h_i + \sum_{jk} P_{jk} (\langle ij | ik \rangle - \langle ij | ki \rangle) \quad (8)$$

where  $h_i$  denotes a one-electron integral incorporating kinetic energy and nuclear-electron attraction, and the two-electron integral  $\langle ij | ik \rangle$  is written in the  $\langle 12 | 12 \rangle$  convention. Ordinarily the one-particle density matrix is defined as

$$P_{jk} = \langle 0 | a_k^\dagger a_j | 0 \rangle. \quad (9)$$

Using Eq.(9) in the expression for  $\varepsilon_i$ , orbital energies are independent from the Fermi-vacuum choice. It may be however appealing to substitute the Hartree-Fock density matrix

$$P_{jk} = \langle \text{HF} | a_k^\dagger a_j | \text{HF} \rangle \quad (10)$$

into Eq.(8), because  $\varepsilon_i$ 's obtained this way do not show degeneracies which may stem from the spatial symmetry of the system and may lead to zero excitation en-

ergy denominators in the PT expressions. Substituting Eq.(10) into Eq.(8) has the consequence that  $\varepsilon_i$ 's become Fermi-vacuum dependent.

Turning our attention to u-MCPT formulation, the first order wavefunction can be written as

$$\Psi_{\text{u-MCPT}}^{(1)}(\text{HF}) = - \sum_{K \in R \setminus \{\text{HF}\}} |K\rangle \frac{\langle \tilde{K} | \hat{H} | 0 \rangle}{\eta_K - \eta_0}$$

while the second order energy looks

$$\begin{aligned} E_{\text{u-MCPT}}^{(2)}(\text{HF}) &= - \sum_{K \in R \setminus \{\text{HF}\}} \frac{\langle \tilde{0} | \hat{H} | K \rangle \langle \tilde{K} | \hat{H} | 0 \rangle}{\eta_K - \eta_0} \\ &= - \frac{1}{c_{\text{HF}}} \sum_{K \in R \setminus \{\text{HF}\}} \frac{\langle \text{HF} | \hat{H} | K \rangle (\langle K | \hat{H} | 0 \rangle - c_K \eta_0)}{\eta_K - \eta_0}. \end{aligned} \quad (11)$$

In contrast to the p-MCPT version, second-order u-MCPT energy shows explicit dependence on the Fermi-vacuum in the numerator. As illustrated in Section 3, dependence of second-order u-MCPT on the choice of  $|\text{HF}\rangle$  is more expressed in numerical terms than  $E^{(2)}$  of p-MCPT.

### 2.3 A Fermi-vacuum invariant treatment

A simple way to remove dependence of the PT expressions on the Fermi-vacuum is to deliberately make every possible choice and form an average of the quantities obtained. Theoretical formulation may start by a linearized Jeziorski-Monkhorst type parametrization of the wavefunction

$$\Psi = |0\rangle + \sum_{K \in R} \hat{T}_K |K\rangle c_K \quad (12)$$

with

$$\hat{T}_K = \sum_{L \neq K} t_K^L |L\rangle \langle K|, \quad K \in R,$$

if working with the vector set of p-MCPT. Substitution of the excitation operator  $\hat{T}_K$  into the wavefunction Eq.(12) reveals that the number of parameters associated with an excited determinant  $L$  not present in  $|0\rangle$ , equals the number of determinants appearing in  $|0\rangle$ . This parametrization is redundant, since it is not possible to determine the amplitudes by the usual projection of the  $n$ th order Schrödinger-equation by excited functions.

Presently we do not attempt to take down sufficient conditions for determining all the amplitudes from a coupled set of equations. Instead, we apply an a-posteriori

procedure and determine amplitudes so that the  $n$ th order wavefunction becomes

$$\bar{\Psi}^{(n)} = \sum_{K \in R} c_K^2 \Psi^{(n)}(K), \quad n \geq 1, \quad (13)$$

a weighted average of separately determined  $n$ th order corrections, obtained by a given choice for the Fermi-vacuum,  $K$ . To reach this goal,  $t_K^L$ 's are to be evaluated as

$$t_K^{L(1)} = -c_K \frac{\langle \tilde{L}' | H | 0 \rangle}{E_L - E_0}, \quad K \in R \quad (14)$$

where  $\langle \tilde{L}' | = \langle L | - c_L / c_K \langle K |$  is the reciprocal vector to  $|L\rangle$ , constructed while  $K$  plays the role of the principal determinant.

Terms of the energy may be obtained either by averaging according to

$$\bar{E}_{\text{p-MCPT}}^{(n)} = \sum_{K \in R} c_K^2 E_{\text{p-MCPT}}^{(n)}(K),$$

or by calculating the usual projection

$$\bar{E}_{\text{p-MCPT}}^{(n)} = \langle 0 | \hat{H} - \hat{H}_{\text{p-MCPT}}^{(0)} | \bar{\Psi}^{(n-1)} \rangle,$$

with  $n \geq 2$ . By either formula one arrives at the second-order energy

$$\bar{E}_{\text{p-MCPT}}^{(2)} = - \sum_{K \in R} c_K^2 \sum_{L \neq K} \frac{\langle 0 | \hat{H} | L' \rangle \langle \tilde{L}' | \hat{H} | 0 \rangle}{E_L - E_0}. \quad (15)$$

Note, that  $\langle \tilde{L}' |$  depends on  $K$ , and  $E_L - E_0$  may also be  $K$  dependent (e.g. in DK partitioning). For this reason the outer sum on  $K$  can not be evaluated irrespective of  $L$ . Equation (15) is one of our working formulae, which ensures Fermi-vacuum independence of the energy, within the p-MCPT framework.

It is worthwhile to examine a Fermi-vacuum invariant formulation with the use of basis vectors of u-MCPT also, e.g. to obtain a size-consistent second-order energy. This variant of the theory does not alter form (12) of the exact wavefunction, it only affects the expression of the excitation operator:

$$\hat{T}_K = \sum_{L \neq K} t_K^L |L\rangle \langle K|, \quad K \in R. \quad (16)$$

Parameters  $t_K^L$  at first order, fulfilling criterion Eq.(13) in u-MCPT look

$$t_K^{L(1)} = -c_K \frac{\langle \tilde{L}' | H | 0 \rangle}{\eta_L - \eta_0}, \quad K \in R,$$

which equals Eq.(14) if the excitation energy denominators are the same.

At difference with p-MCPT, energy terms obtained by averaging or by projection with  $\langle 0|$  are different, since the reciprocal function to  $|0\rangle$  varies with the Fermi-vacuum choice. In this work we investigate the averaging procedure defined by

$$\bar{E}_{\text{u-MCPT}}^{(n)} = \sum_{K \in R} c_K^2 E_{\text{u-MCPT}}^{(n)}(K),$$

which now applies to  $n = 0$  as well, to give

$$\bar{E}_{\text{u-MCPT}}^{(0)} = \sum_{K \in R} c_K^2 \langle \tilde{K} | \hat{H} | 0 \rangle = \langle 0 | \hat{H} | 0 \rangle = E_{\text{p-MCPT}}^{(0)}.$$

The second order energy obtained by averaging looks

$$\bar{E}_{\text{u-MCPT}}^{(2)} = - \sum_{K \in R} c_K \sum_{L \neq K} \frac{\langle K | \hat{H} | L \rangle \langle \tilde{L} | \hat{H} | 0 \rangle}{\eta_L - \eta_0}. \quad (17)$$

where  $c_K$  appears in the first power since the reciprocal counterpart of  $|0\rangle$  is  $c_K^{-1} \langle K|$  when  $K$  plays the role of the Fermi-vacuum. This latter expression is the second working formula of this study which is tested in Section 3.

Comparing averaged energy formulae one may observe that relative simplicity of u-MCPT expressions with respect to p-MCPT is diminished. Averaged zero-order in u-MCPT becomes exactly equal to  $E_{\text{p-MCPT}}^{(0)}$ , which is unaffected by averaging. At second order, determinants interacting with any determinant in  $|0\rangle$  contribute to Eq.(17). This is not the case in the original formulation, where only determinants interacting with the Fermi-vacuum may appear when summing for  $K$  in Eq.(11).

Before proceeding to applications, let us discuss another important aspect of averaged second-order energies Eq.(15) and Eq.(17). Both formulae are of multi-partitioning nature: the zero-order operator varies with principal determinant  $|K\rangle$ . This affects not only the bi-orthogonal vector set, but also the zero-order excitation energies. The latter fact may become a disadvantage, since it may enhance sensitivity to intruders. If there is just one pair of determinants appearing in  $|0\rangle$  which are close in energy at zero-order, it is going to produce an almost zero denominator, when either of them is taken as  $|\text{HF}\rangle$ . An extreme example is a pair of open shell determinants e.g.  $|K_1\rangle = |j_\beta i_\alpha \dots\rangle$  and  $|K_2\rangle = |j_\alpha i_\beta \dots\rangle$  which are exactly degenerate in DK partitioning. This particular problem may be solved by turning to a spin-adapted formulation, but it does not provide a solution if there are two or more spin-functions belonging to a given multiplicity.

To suppress intruders, one may e.g. turn to intermediate Hamiltonian theory, where multi-partitioning has been applied successfully as a remedy[21]. Quasi-degeneracy may also be handled by partial averaging, i.e. omitting the problematic determinant pair from the summation for  $K$  in Eqs.(15) and (17). As long as the affected determinants do not become of principal weight in the problem considered, partial averaging may be acceptable. However, to apply the theory in the general case, further considerations on intruder avoidance are necessary. We do not



address this question in the present work. Our aim is only to illustrate the usefulness of averaging, when intruder states do not influence the situation. For this end we restrict ourselves to two-determinantal multiconfiguration reference function, built exclusively of closed shell determinants.

### 3 Numerical illustration

A test case showing spectacular failure of MCPT is provided by the torsional potential curve of the ethylene molecule. In equilibrium the system possesses  $D_{2h}$  symmetry. Upon rotating the  $\text{CH}_2$  groups with respect to each other, the symmetry reduces to  $D_2$ . At the top of the barrier (at  $90^\circ$  dihedral angle) the point group becomes  $D_{2d}$ , non-Abelian.

The system is computed in Dunning's double-zeta polarized basis[32]. A multiconfigurational reference function is provided by a complete active space (CAS) function with 2-electrons on two orbitals. The Full-CI solution being exclusive due to the large system size, state selective MRCCSDT[2+2] method[8] was computed. Since this method incorporates full triples, it is highly superior to the second-order PT methods we wish to evaluate, and serves as a good benchmark. Notation 2+2 refers to active indices (two-hole, two-particle) which define a reference space for MRCC.

Inspecting the coefficients squared of the two-determinantal CAS wavefunction as a function of the dihedral angle (Fig.1), one can see that the two determinants exchange the principal role for dihedral angles smaller and larger than  $90^\circ$ . At  $90^\circ$  the weights of the two determinants become of opposite value, and orbital degeneracies build up in the spectrum of the generalized Fockian (Eq.(8) and (9)), in accordance with the non-Abelian symmetry. In Fig.2 we present rotational barriers obtained by either p-MCPT or u-MCPT in both EN and DK partitioning. Due to the degeneracy problem, Eq.(10) was applied when computing the generalized Fockian to produce orbital energies for DK partitioning. In Fig.2 the Fermi-vacuum choice follows the principal determinant, hence it is changed at  $90^\circ$ . Fig.2 does not indicate ill-behaviour of p-MCPT neither in EN nor in DK partitioning. The same holds for MRCCSDT[2+2] which – in principle – also depends on the Fermi-vacuum choice. In contrast to the above, u-MCPT shows a completely erroneous, cusp-like barrier top. The source of this phenomenon is the crossing of two continuous energy curves obtained by one or the other determinant taken as Fermi-vacuum. The crossing occurs in p-MCPT as well, but in u-MCPT the crossing angle is considerably sharp as the derivatives with respect to the dihedral angle differ a lot from zero at  $90^\circ$ . In p-MCPT, the crossing at  $90^\circ$  remains unnoticed in Fig.2.

To show the improvement in averaged theories, difference with MRCCSDT[2+2] energy is plotted in Fig.3. The straight curves obtained for all averaged theories indicate the removal of the cusp-like crossing at  $90^\circ$ . The usual behaviour of EN partitioning overshooting the exact energy is also probable in this case, based on Fig.3.

Comparing the values for the rotational barrier collected in Table 2, one sees that neither of averaged MCPT methods manage to improve the barrier of CAS(2,2), which fortuitously shows extraordinary accuracy. It is only u-MCPT in DK partitioning which gives a barrier of same accuracy at second-order. However, MCPT also improves cca. 250 milliHartree in total energy error, according to Fig.3. This altogether means, that averaged u-MCPT in DK partitioning at second order does represent an improvement over the CAS(2,2) wavefunction in this system.

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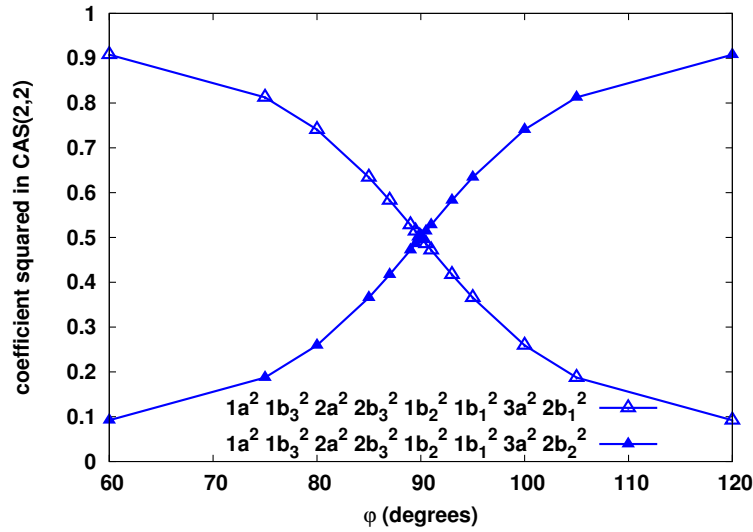
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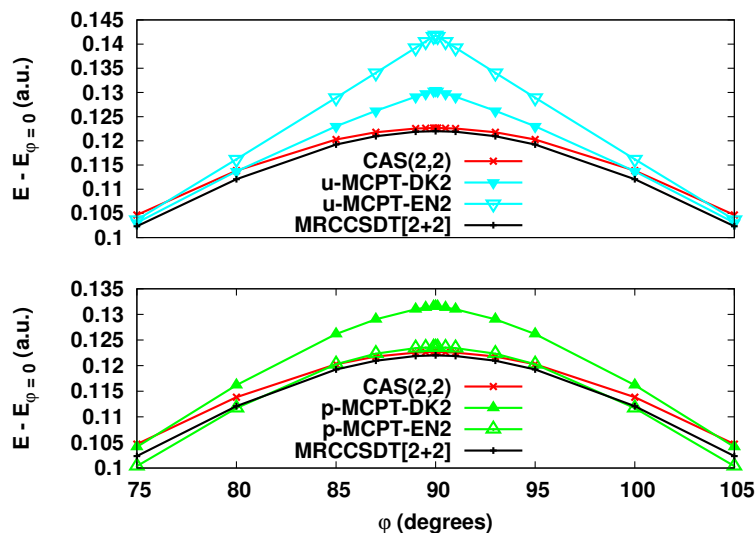
**Table 1** Left and right hand eigenvectors of zero-order Hamiltonians in p-MCPT and u-MCPT.

	ground state		excited state	
	right hand	left hand	right hand	left hand
$\hat{H}_{\text{p-MCPT}}^{(0)}$	$ 0\rangle$	$\langle 0 $	$ K'\rangle =  K\rangle - c_K 0\rangle$	$\langle \tilde{K}'  = \langle K  - \frac{c_K}{c_{\text{HF}}} \langle \text{HF} $
$\hat{H}_{\text{u-MCPT}}^{(0)}$	$ 0\rangle$	$\langle \tilde{0}  = \frac{1}{c_{\text{HF}}} \langle \text{HF} $	$ K\rangle$	$\langle \tilde{K}  = \langle K  - \frac{c_K}{c_{\text{HF}}} \langle \text{HF} $

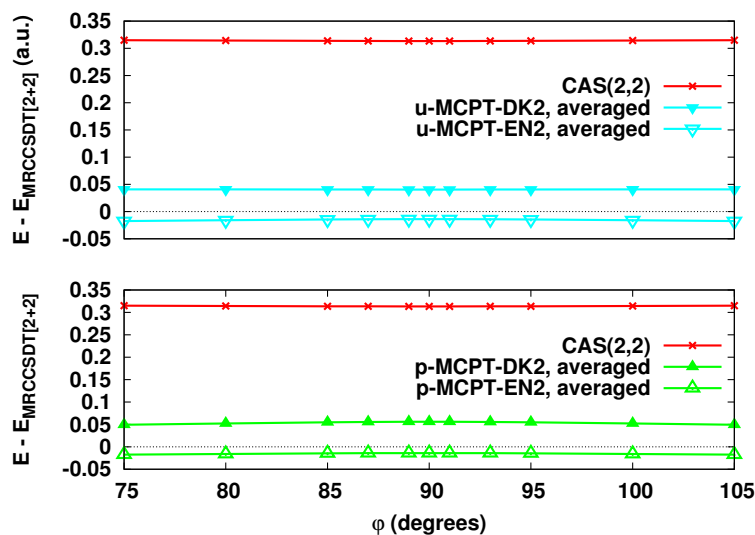
**Table 2** Barrier height of the ethylene molecule in DZP basis, obtained by the CAS(2,2) method and subsequent Fermi-vacuum dependent perturbative corrections, averaged according to Eq.(15) or Eq.(17). Abbreviations DK and EN refer to the partitioning. Method MRCCSDT[2+2] serves as a basis of comparison.

	barrier (Hartree)
CAS(2,2)	0.1226
p-MCPT-DK2, averaged	0.1387
p-MCPT-EN2, averaged	0.1313
u-MCPT-DK2, averaged	0.1226
u-MCPT-EN2, averaged	0.1313
MRCCSDT[2+2]	0.1220

**Fig. 1** Coefficient squared of the determinants constituting the CAS(2,2) function, for the  $\text{C}_2\text{H}_4$  molecule, in double zeta polarized basis set.



**Fig. 2** Rotational barrier top as the  $\text{CH}_2$  moieties are twisted in the ethylene molecule. Methods applied are CAS(2,2) and subsequent Fermi-vacuum dependent perturbative corrections Eq.(11) or Eq.(7), in two partitionings. The curve by MRCCSDT[2+2] is shown for reference.



**Fig. 3** Energy difference taken with MRCCSDT[2+2] around  $90^\circ$  dihedral angle of the ethylene molecule. Methods applied are CAS(2,2) and subsequent Fermi-vacuum dependent perturbative corrections, averaged according to Eq.(15) or Eq.(17). Abbreviations DK and EN refer to the partitioning (see text).