MCQDPT2 and XMCQDPT2

I. Introduction

Perturbation Theory (PT) is one of the most successful yet relatively inexpensive tools of quantum chemistry. In particular, the variant of PT suggested by Møller and Plesset[1] (MPn) turned out to be a very powerful tool for computational ground-state quantum chemistry already at the second order (MP2)[2-3]. However, it is well known that simple single-reference constructs, which the MPn is, work very well for electronic states dominated by a single Slater determinant, but fail severely for multi-configuration wavefunctions. Several successful generalizations of MP or MP-like approaches to the case of multi-configuration reference states (MR-PT) have been suggested during last two decades. Among them are the MR-MP2 approach by Hirao[4-7], CASPT2 approach by Andersson, Malmqvist and Roos[8-11], and NEVPT2 by Angeli *et al*[12-15]. An overview of other approaches to MR-PT can be found in Ref. 16.

Nevertheless, the single-state approaches to MR-PT assume the "diagonalize-then perturb" philosophy and require a zero-order wavefunction that is already well described by CASSCF or a similar procedure. In practice, this is more the exception than the rule; so the possibility for several reference states to mix within the MR-PT treatment is very important. The natural way to allow this mixing is to use the multi-state (MS) formulations of MR-PT approaches leading to various MS-MR-PT theories. Specifically, the MS formulation of MR-MP2 has long been known as the MCQDPT approach developed by Nakano[17-23]. The MS formulation of CASPT2 known as MS-CASPT2 was originally suggested by Finley *et al*[24] while the MS version of NEVPT2 known as QD-NEVPT2 has been developed by Angeli *et al*[25]. All of them are of the "diagonalize-then perturb-then diagonalize" type. In particular, this means that instead of perturbing the entire CASCI Hamiltonian, only several selected CI roots are perturbed and mixed i.e., these methods employ the so-called partial contraction in the space of CI expansion coefficients. These approaches are more or less directly related to the formal theory of the effective Hamiltonians and Quasi-Degenerate Perturbation Theories (QDPT) that have been well established for a long time[26-37]. Essentially, all three theories define approximations to the exact effective Hamiltonian acting within a model space[33,37] – i.e., a subspace spanned by the selected CI roots. Energies of perturbed states are then obtained as eigenvalues of effective Hamiltonian while projections of perturbed states onto zero-order states are defined by the corresponding eigenvectors.

Besides direct mixing of target states, effective Hamiltonians technique allows indirect relaxation via interaction with higher-energy CASCI states. When entering effective Hamiltonians, higher-energy states admix with target states thus allowing relaxation of low-lying states within CASCI space and improving their overall description. Indeed, CASSCF usually tends to converge to solutions that are too delocalized in the space of CI coefficients, so additional states in the model space are often needed to eliminate this deficiency at MS-MR-PT level.

The most important distinctions in formulation of various MS-MR-PT schemes are the selection of zero-order Hamiltonian and of so called "perturbers" – i.e., zero-order states allowed to interact with zero-order wavefunctions in PT treatment. In the case of MCQDPT2, "perturbers" are simply all possible individual CSFs or Slater determinants not belonging to CASCI space and obtained applying single and double excitations individually to every CSF (determinant) entering reference states. In contrary, both MS-CASPT2 and QD-NEVPT2 are formulated using state-specific and more sophisticated "perturbers" defined as specific linear combinations of some selected classes of CSFs or determinants. Depending on the particular scheme in use, the latter approach is known as either internal[8,9,38] or external[39,40] contraction. For instance, most of CASPT2 variants can be considered as internally contracted approximations to the MR-MP2, while MS-CASPT2 theories are internally contracted approximation to the MCQDPT2.

Both MR-MP2 and CASPT2 approaches apply one-particle Fock-like zero-order Hamiltonian. In contrast, NEVPT2 scheme adopts partially bi-electronic zero-order Hamiltonian initially suggested by Dyall[41]. The situation is more complicated for the MS-MR-PT counterparts of these approaches.

II. Overview of MCQDPT

The MCQDPT (Multi-Configuration Quasi-Degenerate Perturbation Theory) approach was suggested by Nakano[17] as a multi-state generalization of the MR-MP2 theory by Hirao[4]. Here we review the basics of MCQDPT. Additional details can be found in the original papers on this theory[17-23].

MCQDPT is the multi-state multi-reference Van-Vleck-type perturbation theory of partially contracted type that employs isometric (i.e., unitary through any PT order) normalization[42-44]. More precisely, a model space is spanned by several CI vectors (i.e the partial contraction is used) that are typically obtained as a result of the state-averaged CASSCF procedure (the **P** subspace), while the secondary, first-order interacting space is formed by the individual CSFs or determinants and thus is not contracted (the **S** subspace). It is also helpful to define the **O** subspace as a subspace of the CASCI vectors that are complementary to **P**, with **P⊕O** forming the entire CASCI subspace **R**, and **O⊕S** forming the subspace **Q,** as shown in Fig. 1.

MCQDPT applies $\boldsymbol{H^0}$ which is constructed using a diagonal model Fock operator $\hat{F}$. More precisely, MCQDPT applies individual blocks of $\boldsymbol{H^0}$ that are defined via expectation values of $\hat{F}$ using projectors onto individual CI vectors and perturbers. The particular choice of interacting space and zero-order Hamiltonian in MCQDPT theory results in a $\boldsymbol{H^0}$ that is fully diagonal in **P**, **O**, and **S** subspaces. The attractive consequence of this feature is a very simple expression for the Resolvent that eliminates any need to solve large systems of linear equations.

Instead, the second-order effective Hamiltonian is expressed as the direct sum of different contributions corresponding to each particular class of diagrams, with energy denominators of a very simple structure. This opens a way to a very efficient implementation of MCQDPT2 as was shown in[45-46] and implemented within Firefly. In particular, the so-called Resolvent-fitting (a.k.a. table-driven) approach is very computationally efficient[45]. The current implementation allows MCQDPT2 calculations of systems with active spaces up to several millions of CSFs and with the overall number of molecular orbitals up to 2000-3000 to be routinely performed on a standalone single-CPU workstation or desktop computer.

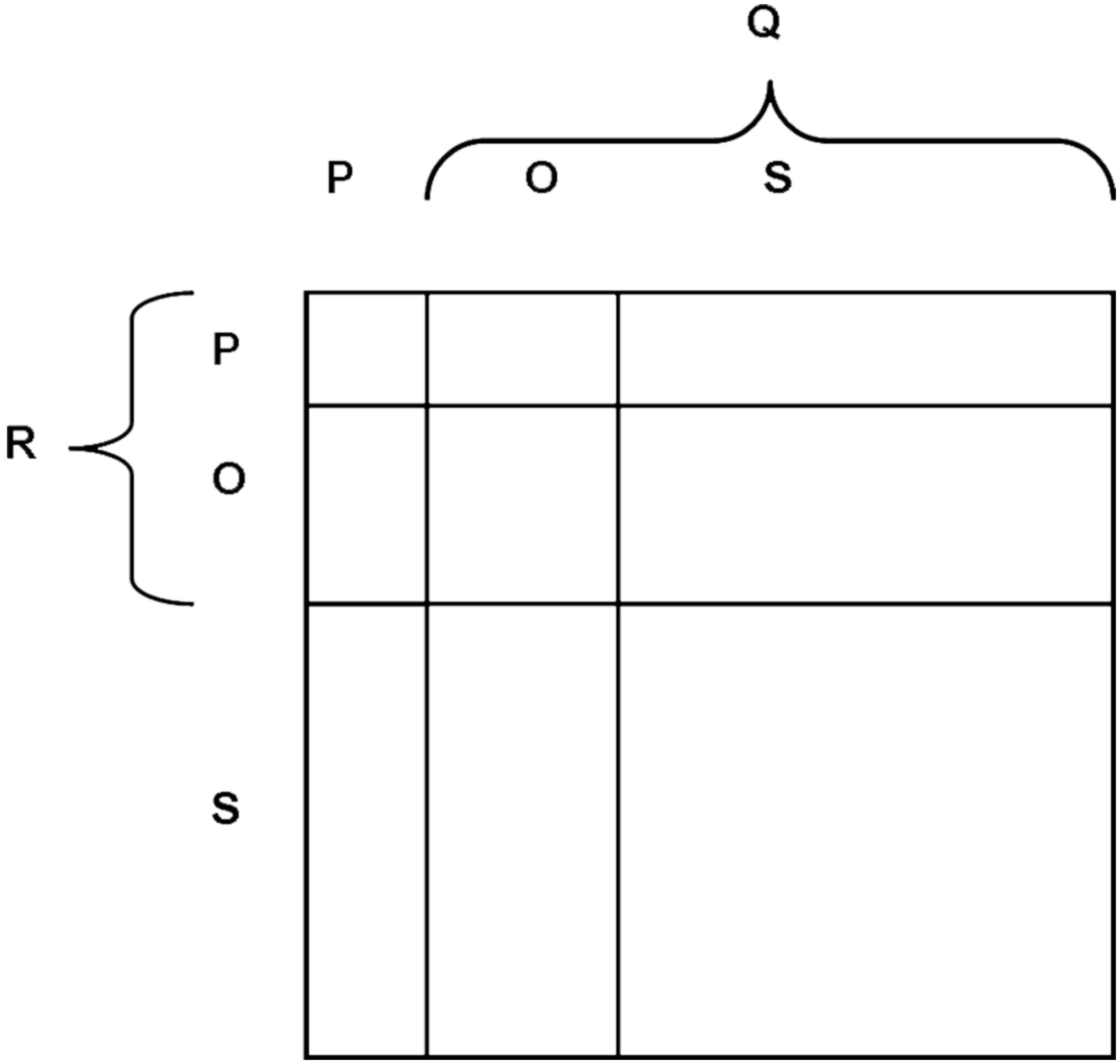

Fig. 1. Schematic illustration on various subspaces.

However, H^0_{mcqdpt} does not have any well-defined algebraic transformation properties with respect to transformations of basis within the model space. Moreover, for any non-trivial model space H^0_{mcqdpt} is actually a many-particle operator; and hence, the perturbation is also artificially made to be a many-particle operator rather than the two-particle one as would naturally expect. These two points apply equally to MS-CASPT2 and QD-NEVPT2 theories. More precisely, MCQDPT results in perturbation being a many-particle operator in the **R** subspace, MS-CASPT2 results in perturbation being a many-particle operator in both **R** and **S** subspaces, while QD-NEVPT2 results in perturbation being a many-particle operator in the **S** subspace. It is worth noting that both original MS-CASPT2 and QD-NEVPT2 apply internal contraction and a multi-partitioning scheme by Zaitsevskii and Malrieu[47] which introduce an additional source of non-invariance into these theories.

For instance, let us assume one holds fixed the number of CI roots and values of their corresponding weights in computing the averaged one-particle density matrix that is used to define the model Fock operator $\hat{F}$. In this case, the effective second-order MCQDPT2 Hamiltonians of progressively decreasing dimension form the trivial sequence with the $n \times n$ effective operator being exactly equal to the $(n+1) \times (n+1)$ operator with the row and column, corresponding to the $(n+1)^{th}$ extra CI root, being removed. Evidently, there is no any explicit dependence of the effective Hamiltonian on the dimension of model space in this approach, as the $n \times n$ effective operator is simply enclosed into $(n+1) \times (n+1)$ one.

III. The XMCQDPT theory

The XMCQDPT (Extended Multi-Configuration Quasi-Degenerate Perturbation Theory) theory[46] is a novel multistate formulation of MR-MP2 employing invariant zero-order

Hamiltonian. Being the alternative to MCQDPT2, it is superior to MCQDPT2 and is free of multiple drawbacks of the latter and obeys several important physical and mathematical properties that are desirable for any partially contracted MS-MR-PT-based approach. These properties are discussed below and can be considered as an attempt to bring various formulations of MS-MR-PT into better accordance with the formal theory of Effective Hamiltonians.

In practical applications, various MR-PT and especially MS-MR-PT theories can be plagued by the so-called "intruder state problem"[48,49] causing appearance of very small energy denominators in PT series and leading to spurious results of the entire PT calculation. The persistence of this problem varies with particular theory. For instance, it has been demonstrated that NEVPT2 is inherently less prone to this problem as compared with MR-MP2 and CASPT2[50,51]. However, the problem still persists in the QD version of NEVPT2 approach on the par with other MS-MR-PT schemes. For simplicity, we assume below that intruder states are either irrelevant, or that they were successfully eliminated using, for instance, intruder state avoidance[52] (ISA) or similar techniques.

First, we assume that ***the effective Hamiltonian should be explicitly dependent on the dimension of the model space in any nontrivial order of PT***. Evidently, this dependence should not be just the trivial one caused by the simple extension of the model space. It also should not be related only to the variations of orbital energies, orbitals, or both, caused by the averaging of one-particle density matrices over varying number of CI roots, and hence, should not be related only to the implicit dependence of the effective Fock operator(s) and zero-order Hamiltonian on the dimension of the model space. Indeed, exact effective Hamiltonians depend explicitly on the model space dimension[46]. Hence, approximations to the exact effective Hamiltonian should approximate this explicit dependence on the model space size as well. It should be realized that, in general, the restriction of an effective Hamiltonian to a subspace of the model space is not a new effective Hamiltonian associated with this smaller subspace.

Second, the very important property is ***the convergence of energies as well as other observable properties with respect to model space extension at any fixed order of PT*** provided that the active space used in underlying MCSCF calculations is well-balanced and accurately designed so that there are no spurious zero-order states (i.e., solutions of non-linear MCSCF equations which do not describe real excited states[53-55]). This property is evidently mandatory for the low-lying electronic states that are typically of interest and is desirable for other states as well.

The third property is that ***the effective Hamiltonian should be a function of the subspace spanned by the selected CI vectors, rather than a function of any particular choice of basis in this subspace***. In particular this means that the effective Hamiltonian should be the same regardless of whether the initial CI vectors, or any alternative vectors obtained as their arbitrary orthogonal transformation, were used for MS-MR-PT computations. Indeed, as many-body perturbation theory (MBPT) is a purely algebraic approach, it has well-defined algebraic invariance properties. Hence, it is natural to impose the same restriction on the MS-MR-PT. The very important consequence of this property is that ***the correctly formulated partially-contracted theory should be exactly equivalent to the corresponding uncontracted theory provided that the dimension of the model space is equal to the dimension of the CI space*** (i.e., the overall number of CSFs or determinants spanning the CI space).

Finally, the most important and physically evident requirement is that ***the computed energies must be uniquely defined, continuous and smooth functions of the molecular geometry and any other external parameters***, with possible exceptions at the manifolds of their accidental degeneracy such as conical intersections.

In modeling of many-electron molecular systems, the correct dependence of computed energies and other properties on the number of electrons in the correlation treatment plays crucial role. This requirement is related to such features of the underlying theories as exact or approximate size-consistency[56] and separability[57-60]. It is often believed that the exact size-consistency is very desirable for any high-level computational approach designed to describe large systems. However, we do not consider small deviations from the exact size-consistency as a serious deficiency of MS-MR-PT theories, provided that these deviations are more or less constant regardless of the model space dimension and do not cause any significant unphysical effects even for large systems. It seems that the exact or approximate core-separability[60] is the most important requirement, while small deviations from the strict separability are quite acceptable. In particular, the possibility of applying the correctly formulated MS-MR-PT-based methods to the calculation of vertical electronic excitation energies should not be affected by these deviations.

The difference between MCQDPT and XMCQDPT is the choice of the $\boldsymbol{H^0}$ operator. Namely, XMCQDPT employs $\boldsymbol{H^0}$ that is much closer to the one-particle Fock operator $\hat{F}$. More precisely, unlike MCQDPT, the **PP** and **OO** blocks of $\boldsymbol{H^0}$ is non-diagonal in the basis of CASCI eigenvectors and is formed by the entire projection of $\hat{F}$ onto **P** and **O** subspaces.

It can be easily shown that any unitary transformation of the basis set in the model space transforms second-order effective Hamiltonian $\boldsymbol{H^{(2)}_{eff}}$ of XMCQDPT according to the usual law of transformation of an arbitrary linear operator so that XMCQDPT2 (XMCQDPT at the second order of PT) satisfies the invariance property above. Hence, the XMCQDPT2 theory is evidently equivalent to the fully uncontracted approach provided that the dimension of the model space is equal to the dimension of the CI space. The "explicit dependence on the model space extension" property is also satisfied taking into account the non-diagonal nature of the **PP** block of $\boldsymbol{H^0}$ in the basis of CI vectors forming the model space.

As has been mentioned above, MCQDPT, MS-CASPT, and QD-NEVPT2 theories assume the **PP** block of $\boldsymbol{H^0}$ that is defined using projectors onto individual CI vectors and does not have well-defined transformation properties with respect to the unitary transformation of the model space. This results in the non-invariant perturbation theories and introduces an artificial many-particle nature into the perturbation. In contrast, XMCQDPT applies $\boldsymbol{H^0}$ resulting in the invariant theory with balanced perturbation being approximation to the true two-particle operator in the **R** subspace and the true two-particle operator in the **S** space. A discussion on the importance of balanced perturbation in PT treatment can be found in Ref. 13 in the context of NEVPT approach.

It is natural to expect that non-invariance should lead to significant erratic behavior of the non-invariant theories in the regions of the molecular geometries where the corresponding CI vectors undergo rapid change or are not uniquely defined at all. More precisely, all non-invariant theories are not defined at the geometries corresponding to conical intersections at the underlying MCSCF level, and behave badly in the vicinities of the avoided crossings.

In multi-reference electronic structure calculations for mixed electronic states, the relative contributions of different reference configurations tend to differ substantially between the reference SA-CASSCF wavefunctions and the final correlated wavefunction. For instance, the position of avoided crossing point between neutral and ionic PECs of $^1\Sigma^+$ states of LiF molecule differs by ca. 3 Bohr between SA-CASSCF and MRSDCI calculations. Obviously, in the region between SA-CASSCF and correlated crossing points, the quality of zero-order wavefunctions obtained using SA-CASSCF procedure degrades. This can be a serious issue for non-invariant MS-MR-PT approaches defined using projectors that can result in incorrect description of interstate mixing and PESs. In contrast, situation is much better for invariant theories such as XMCQDPT2. Indeed, the final correlated states depend only on the subspace spanned by zero-order wavefunctions (i.e., on the model space) rather than on the zero-order wavefunctions themselves. Therefore, if the number of physically important CSFs shared by zero-order SA-CASSCF states is less or equal to the dimension of model space, one can *a priori* expect better and more balanced description of the interstate mixing and PESs by invariant MS-MR-PT theories as compared with non-invariant formulations.

MCQDPT2 is neither size-consistent nor core-separable. In contrast, different variants of CASPT2 as well as NEVPT2 are exactly core-separable; moreover, NEVPT2 is exactly size consistent and strictly separable. While analysis of their MS counterparts is more complicated, both theories are at least exactly core-separable.

In the special case of a one-dimensional model space, XMCQDPT2 is completely equivalent to the MR-MP2 approach[4]. Due to the structure of its energy denominators, MR-MP2 is neither exactly size-consistent, nor core-separable. This can be easily verified by performing test computations on simple model systems like the Be_2 molecule at large internuclear distances. However, the deviations from exact size-consistency are typically small.

Keeping these properties of MR-MP2 in mind, it is logical to expect that XMCQDPT2 should not be in general exactly size-consistent or core-separable as well. This is indeed the case. However, we mention as an important fact that the fully uncontracted limit of XMCQDPT is an exactly size-consistent and separable theory through the fourth order of Van-Vleck PT expansion[61]. Assuming that the convergence of energies with increase of the dimension of model space is reasonably fast, XMCQDPT2 should be approximately size-consistent and core-separable for low-lying states even for the quite modest dimensions of effective Hamiltonians, with size-inconsistency errors rapidly decreasing upon the extension of the model space.

Let XMCQDPT2' and MCQDPT2' denote the modified (and thus approximate) XMCQDPT2 and MCQDPT2 calculations that apply the MP2-like expression for double excitations from double occupied inactive orbitals to external MOs. This approximation eliminates the dominant contribution violating exact core-separability and makes both theories almost exactly core-consistent. While MCQDPT2' is typically an improvement over MCQDPT2, XMCQDPT2' is not usually an improvement over XMCQDPT2 as XMCQDPT2' introduce approximations not needed by the parent theory while does not significant improve the core-separability properties of computed XMCQDPT2 energies.

MCQDPT2 and MS-CASPT2 tend to overestimate off-diagonal elements of effective Hamiltonians[62-70]. This is true, although to a lesser extent, for MCQDPT2' as well. Indeed, one can consider MCQDPT2 as the approximation to XMCQDPT2 which completely neglects the off-diagonal elements of $\boldsymbol{H^0}$ in the CASCI space. The quality of this approximation depends on the magnitude of the neglected off-diagonal elements. If the zero-order interaction of states forming the model space is small, these two theories should be in the close agreement. However, as soon as zero-order interaction increases, MCQDPT2 performance starts to degrade. For instance, one can *a priori* expect large zero-order interactions in situations when two or more CI roots share a common set of leading CSFs, resulting in questionable applicability of MCQDPT2 as well as of all other non-invariant theories formulated using projectors onto the model space. The neglect of off-diagonal terms introduces inaccuracy into both diagonal and off-diagonal elements of effective Hamiltonians.

In the case of MCQDPT2', the leading MP2-like contribution to the correlation energy is treated differently so it results only in the equal shift of all diagonal elements of $\boldsymbol{H^{(2)}_{eff}}$. Hence, this reduces the accumulated errors in off-diagonal elements of $\boldsymbol{H^{(2)}_{eff,\ mcqdpt}}$. However, this does not eliminate errors entirely.

IV. XMCQDPT vs. XMS-CASPT2

Soon after the paper on XMCQDPT theory was published, the XMS-CASPT2 theory (i.e. the Extended Multi-State Second Order Complete Active Space Perturbation Theory) has been suggested by Shiozaki, Győrffy, Celani and Werner (Ref 71) who based their work on the ideas of the XMCQDPT paper (Ref. 46). The XMS-CASPT2 theory is the improvement over standard MS-CASPT2 and can be considered as an internally-contracted approximation to XMCQDPT2. Typically one may expect similar results from MS-CASPT2 and XMCQDPT2. However, the Resolvent fitting technique cannot be applied to XMS-CASPT2 as this theory does not allow direct summation of PT series. This makes XMCQDPT2 much more computationally efficient as compared with XMS-CASPT2, especially for large molecular systems.

V. Useful hints and best practices

A. Understanding basic steps of MCQDPT2 and XMCQDPT2 execution flow with Firefly

To activate one of XMCQDPT2 or MCQDPT2, one needs to use $contrl mplevl=2 together with scftyp=mcscf. The choice between XMCQDPT2 and MCQDPT2 theories is controlled by the presence of the corresponding input groups. If the $mcqdpt group is given in the input, Firefly will perform MCQDPT2 computations. Otherwise, if $xmcqdpt or $qdpt group is given in input file, XMCQDPT2 computations will be performed. All three groups share the common set of the input variables; and, as explained in details in Ref. 46, the XMCQDPT2 and MCQDPT2 computations with Firefly share the same common code. In the following we use (X)MCQDPT2 to term either of two. There are three flags and one extra input group that significantly affect execution flow of (X)MCQDPT2 computations.

First, (X)MCQDPT2 can be preceded by the MCSCF computations. This is the most typically used scenario. However, there is a possibility to skip the MCSCF part. To do this, one needs to provide a complete $VEC group with converged orbitals, read in orbitals using $guess guess=moread with norb= variable equal to the overall number of MOs, and set the inorb variable of $(x)mcqdpt group to 2 (default is inorb=0) to indicate that MCSCF stage should not be performed. It is recommended to use orbitals saved with extra high precision i.e. with $contrl wide= flag set to .true. (default is wide=.false.).

Second, (X)MCQDPT2 code performs canonicalization of input or previously computed MOs by default. This requires some additional computations i.e. the extra CASCI-type integral transformation (performed by routine MQTRMC), CAS CI computations (routine MQCACI), first order state-averaged density matrix construction, Fock matrix construction and its block-diagonalization (routine MQFORB). Note, the WSTATE array is used in computing weights of roots for state-averaged density matrix calculation at this stage.

However, input orbitals or orbitals generated by the preceding MCSCF procedure can already be in semi-canonical form, so that user can request Firefly to skip canonicalization. This can be done by setting the iforb variable of $(x)mcqdpt group to 0 (default is iforb=1 i.e. not to skip canonicalization).

Third, one can either request the exact (X)MCQDPT2 (the default setting) or the approximate (X)MCQDPT2'. The latter option is activated by setting the irot variable of $(x)mcqdpt group to 1 (default is 0). Computationally, (X)MCQDPT2' is a bit cheaper than (X)MCQDPT2. As was discussed above, (X)MCQDPT2' theories also have better properties if the approximate core-separability is of concern. However, one should realize that (X)MCQDPT2' theories are the approximations to the exact second-order answer given by the (X)MCQDPT2 theories.

Finally, the presence of $mcqfit group triggers the use of Resolvent fitting (a.k.a. table-driven) code[45]. Additional options can be specified in $mcqfit group allowing fine control over Resolvent fitting code.

Regardless of the variables described above, the rest of computations is organized as follows. First, the MP2-type integral transformation is performed by routine MQTRF. This can be disk-based or semi-direct transformation, the latter is selected by the $trans dirtrf=.true. flag and is highly recommended. Then, molecular integrals are rearranged and a CAS CI procedure in the basis of semi-canonical Fock orbitals is performed (MQCACI). Next, provided the optional CSF selection option is turned on, the number of CSFs entering PT computations is reduced based on user-specified criteria, and the final CI procedure is performed in this reduced subspace. Note that CSF selection is disabled by default. Finally, the one-particle state-averaged density matrix is recomputed using the AVECOE array, then the Fock matrix and the effective orbital energies are constructed by the routine MQORB2, and some additional setup is performed by routines MQLPR1 and MQLPR2 (alternatively by MQLPR1, MQLPRB and MQLPRC). At this point, the code is ready for summation of PT series, which is performed for contributions of different types by routines MQLMB1, MQLMB2, MQLMB3 and MQLMBR/ MQLMBR0/MQLMBR1/MQLMBR2 called in a big loop over all CI states forming the model space.

(Footnote: Note both WSTATE and AVECOE arrays are used to define the state's weights used to compute state-averaged density matrices. Technically, the averaging used to define semi-canonical orbitals and to define orbital energies of these orbitals, can be different. If both WSTATE and AVECOE are given in the input file, the first one defines the averaging used to compute orbitals while the second is used for energies. If only one of them is given in input, then the second one will be set to be identical with the first one. The latter option should be used almost exclusively unless one has really good reasons why to use different averaging for different stages.)

At the very end, routine MQGETE (which is preceded by the routine MQVSML in the case of PT with CSF selection) is called and prints computed energies and zero-order QDPT properties: dipole moments, transition moments, and so on.

B. Planning (X)MCQDPT2 computations

1. Use XMCQDPT2 rather than MCQDPT2
2. When absolutely in need to use MCQDPT2, use MCQDPT2'
3. Use Intruder State Avoidance (ISA) denominator shift. The default shift is zero. To set ISA shift to 0.02 Hartree (the recommended value) use: $(x)mcqdpt edshft=0.02
4. For reliable results, use at least triple zeta + polarization functions basis sets e.g. cc-pvtz or better.

5. Use the same averaging in SA-CASSCF (defined by the wstate array of $det or $gugdm2), and in (X)MCQDPT2 (defined by the wstate and avecoe arrays of $(x)mcqdpt) unless there are strong reasons for opposite. Use all weights equal to unity, once again unless there are strong reasons for opposite.
6. Add some extra CASCI states to a model space i.e. use NSTATE that is larger than the number of states in SA-CASSCF averaging.

C. Running (X)MCQDPT2 computations

1. Use Firefly's efficient and fast SOSCF or FOCAS convergers for MCSCF stage of job.
2. Use Resolvent fitting-based code for large (X)MCQDPT2 jobs as it is much faster than the default code. The use of Resolvent fitting-based code is triggered by the presence of the $mcqfit group in the input file. In most cases, it is sufficient to just specify $mcqfit $end without altering any parameters of the $mcqfit group - the default parameters are selected so that the errors introduced in the computed energies are typically less than 10^{-8} Hartree. There are three adjustable parameters in the $mcqfit group:
    a. DELTAE - double precision, default is zero. If nonzero, this variable is used to define step of the interpolation grid.
    b. NPOINT - integer, default is 400. Together with DELTAE this variable is used to define step size and number of points of the interpolation grid. Actual grid size will be the least of the two, the number specified using NPOINT variable and the number of points computed based on the value of DELTAE. Increasing NPOINT will result in increase of required CPU time while reducing errors in computed energy.

    c. IORDER - integer variable. Available values are 3, 5, and 7. Defines the order of the polynomial to use in interpolation. The default value is 7.

3. Use efficient direct and semi-direct integral transformation code for large (X)MCQDPT2 jobs i.e. specify $trans dirtrf=.true. in the input file. One can control large (MP2-style) integral transformation code (MQTRF stage) using appropriate variables of $MP2 group. In addition, use Firefly's specific large-scale efficient CASCI/CASSCF integral transformation code during MQTRMC stage by setting the dedicated keyword in the $trans group as follows: $trans mptran=2 dirtrf=.true. $end. Other variables that could be useful are $trans altpar= mode= cuttrf= These variables are documented elsewhere in the manual.
4. The PT series summation in Firefly's (X)MCQDPT2 code does not run in parallel at present but is efficiently threaded. To speed up computations, use SMP and/or multi-core systems and allow Firefly to use extra compute threads. One can do this by specifying the overall number of threads to use via ether the $system np= or $smp np= variables (these two variables are basically synonyms). Note, the $smp httnp= variable which can be either 1 or 2 and which is described elsewhere affects the actual number of threads if running on the processors and in the environment that support hyper-threading.
5. The preceding CASSCF stage and the semidirect MQTRF/ALTTRF integral transformation stage of (X)MCQDPT2 are allowed to run in parallel so if one runs (X)MCQDPT2 job in parallel, these stages will be executed in parallel. The summation of PT series will however be executed in serial by the master Firefly's process. To speed up this serial stage, use threading as described above. In addition, one needs to set the $smp smppar= variable to .true. indicating that created additional working threads should only be used during execution of serial parts of code i.e. indicating the use of the specific type of a mixed parallel/threaded model of execution. Note this requires (the low-level) P2P protocol and dynamic load balancing.

6. Numerical gradient based code and all runtypes involving numerical gradients are allowed to execute all stages of (X)MCQDPT2 in parallel using XP and Extended XP models of execution, which are described elsewhere. In addition, running in the Extended XP mode, one can still set $smp smppar=.true. to allow the mixed parallel/threaded model of execution within each separate group of processes.
7. Use the masmem keyword of $system group to alter the amount of memory used by the master process (or XP local master processes). The PT summation stage of (X)MCQDPT2 code typically requires more memory than the preceding CASSCF and MQTRF integral transformation stages. With this option, one can allow a master Firefly process to use more memory than other Firefly's instances. E.g. the following line in the input file **$system mwords=100 masmem=200 $end** would allow master to use 200 mwords with regular instances of parallel Firefly process still consuming 100 mwords each. While using masmem, it is a good idea to perform exetyp=check run in parallel mode. Otherwise. one can run it twice in serial (for mwords without explicit masmem and for mwords with desired masmem).
8. If (X)MCQDPT2 run is running out of memory, one can consider:
    a. decreasing the value of the $(x)mcqdpt mxbase= variable (the dimension of subspace in Davidson diagonalization, affects the amount of memory used by routine MQCACI)
    b. decreasing the number of threads used during PT summation stage and disabling the use of additional HTT threads (i.e. setting $smp httnp= to 1) (affects MQLMB1, MQLMB2, MQLMB3, and MQLMBR/R0/R1/R2)
    c. limiting the amount of stack allotted to Firefly (Linux specific, ulimit -s 2048 should normally work)
    d. allowing Firefly to use additional memory in its heap : $(x)mcqdpt HAlloc=.t.

e. allowing selection of most prominent CSFs i.e. $(x)mcqdpt iselct(1)=(one of 1, 2, 3, 4, -1, 2, -3, -4) thrwgt="the smallest CSF's weight (i.e. the squared coefficient of CSF in CI expansion) to keep". The default value of thrwgt is 10^{-6}. One can try smaller values e.g. 10^{-8}. By default, iselct(1) is equal to 0 i.e. no selection is allowed. The values of 1, 2, 3, and 4 selects slightly different schemes of CSFs selection. The least advanced and most plain method of selection is method # 1. The most advanced and recommended scheme is the method # 4, although the difference between different methods is rather subtle. Values of 2, 3, and 4 allows the use of the second element of the iselct() array i.e. iselct(2). The value of iselct(2), if given, is interpreted as the maximum allowed number of CSFs to select. If iselct(2) is in effect, the actual threshold used in selection procedure may exceed thrwgt. The values of -1, -2, -3, and -4 for iselct(1) are the counterparts of their positive analogs which in addition perform the rotation of CI roots computed in the incomplete space after CSFs selection. This rotation is within the space spanned by these CI roots and is constructed to maximize the overlap of rotated states with the initial CASCI states before CSFs selection. This option can be important for MCQDPT2 but is ignored for XMCQDPT2 as results of XMCQDPT2 depends only on the on the subspace spanned by the CI vectors rather than on the particular basis in this subspace (i.e. CI vectors).

D. Analyzing results

1. Check the resulting second-order Effective Hamiltonian (search the output for "*** EFFECTIVE HAMILTONIAN (0-2) ***") for unusually large off-diagonal elements (say 0.05 Hartree or above). In the case there are some, one may need to reexamine the appropriateness of the underlying (SA-)CASSCF procedure, esp. active orbitals, the entire active space, state-averaging protocol, etc...

2. Check the numbers labeled by "E(MP2)=" (these are the energies of states within the (X)MCQDPT2 theory) for sense. This table is labeled as "*** (X)MC-QDPT2 ENERGIES ***"
3. Check the table containing "EIGENVECTORS OF THE EFFECTIVE HAMILTONIAN" for the unexpectedly strong/unphysical mixing of the zero-order CASCI states. Is this exactly what could be expected? If it is not, strong may indicate deficiencies of the underlying CASSCF description of the zero-order states. Is there any considerable admixture of higher-energy roots to the target states? One may need to consider including higher-energy states into SA-CASSCF state-averaging procedure, if so.
4. Check that the target "EIGENVALUES OF THE NON-SYMMETRIC EFFECTIVE HAMILTONIAN" are all real and are all close to the eigenvalues of the symmetric Effective Hamiltonian i.e. numbers labeled by "E(MP2)=" as mentioned above. Large deviations and large imaginary contributions indicate deficiencies of the PT treatment.
5. Check that the "OVERLAP NORM MATRIX OF NON-ORTHOGONAL EIGENVECTORS" does not contain large off-diagonal values e.g. values larger than 0.1 or 0.2. If the off-diagonal overlap is large this typically means that the target states are extremely poorly described by the model space and that they have a (very) large norm of projection on the secondary subspace i.e. they are living outside the CASCI space.
6. Check that the energies of states (or at least the transition energies) are stable with respect to the extension of a model space.
7. Analyzing molecular properties printed at the end of (X)MCQDPT2 run, take in mind that the computed values are the zero-order QDPT properties. This means that they include only a part of all effects due to interaction with the secondary space. Namely, they correctly include effects causing rotation and intermixing of zero order states (i.e. CASCI vectors) within the model space but do not include the first order correction to the wavefunction (i.e. the part of perturbed states which belongs to the secondary space).

Thus the printed properties should be considered as approximations to the "true" (X)MCQDPT2 properties.

E. Citing MCQDPT2 and XMCQDPT2

One should cite Firefly as explained in this manual and on the Firefly homepage. In addition, one need to cite XMCQDPT2 as follows: **A. A. Granovsky, J. Chem. Phys. 134, 214113 (2011).** For MCQDPT2, the proper reference is: **H. Nakano, J. Chem. Phys. 99, 7983 (1993).**

VI. References

[1] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[2] J. A. Pople, J. S. Binkley, and R. Seeger, Int. J. Quantum Chem., Quantum Chem. Symp. **S10**, 1 (1976).

[3] M.J.Frisch, M.Head-Gordon, J.A.Pople, Chem. Phys. Lett. **166**, 275 (1990).

[4] K. Hirao, Chem. Phys. Lett. **190**, 374 (1992).

[5] K. Hirao, Chem. Phys. Lett. **196**, 397 (1992).

[6] K. Hirao, Int. J. Quant. Chem. **S26**, 517 (1992).

[7] K. Hirao, Chem. Phys. Lett. **201**, 59 (1993).

[8] K. Andersson, P-Å. Malmqvist, B. O. Roos, A. J. Sadlej, K. Wolinski, J. Phys. Chem. **94**, 5483 (1990).

[9] K. Andersson, P.-Å. Malmqvist, and B. O. Roos, J. Chem. Phys. **96**, 1218 (1992).

[10] K. Andersson, B. O. Roos, Int. J. Quant. Chem. **45**, 591 (1993).

[11] B. O. Roos, K. Andersson, M. P. Fülscher, P.-Å. Malmqvist, L. Serrano-Andrés, K. Pierloot, and M. Merchán, in Advances in Chemical Physics: New Methods in Computational Quantum Mechanics edited by I. Prigogine, S. A. Rice (Wiley, New York, 1996) Vol. XCIII, p. 219.

[12] C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, and J.-P. Malrieu, J. Chem. Phys. **114**, 10252 (2001).

[13] C. Angeli, R. Cimiraglia, and J.-P. Malrieu, J. Chem. Phys. **117**, 9138 (2002).

[14] C. Angeli, R. Cimiraglia, and J.-P. Malrieu, Chem. Phys. Lett. **350**, 297 (2001).

[15] C. Angeli, S. Borini, and R. Cimiraglia, Theor. Chem. Acc. **111**, 352 (2004).

[16] R. K. Chaudhuri, K. F. Freed, and G. Hose, P. Piecuch, K. Kowalski, and M. Włoch, S. Chattopadhyay and D. Mukherjee, Z. Rolik, Á. Szabados, G. Tóth, and P. R. Surján, J. Chem. Phys. **122**, 134105 (2005)

[17] H. Nakano, J. Chem. Phys. **99**, 7983 (1993).

[18] H. Nakano, Chem. Phys. Lett. **207**, 372 (1993).

[19] H. Nakano, K. Nakayama, K. Hirao, M. Dupuis, J. Chem. Phys. **106**, 4912 (1997).

[20] T. Hashimoto, H. Nakano, K. Hirao, J. Mol. Struct. (THEOCHEM) **451**, 25 (1998).

[21] H. Nakano, R. Uchiyama, K. Hirao, J. Comput. Chem. **23**, 1166 (2002).

[22] M. Miyajima, Y. Watanabe, H. Nakano, J. Chem. Phys. **124**, 044101 (2006).

[23] R. Ebisuzaki, Y. Watanabe, H. Nakano, Chem. Phys. Lett. **442**, 164 (2007).

[24] J. Finley, P.-Å. Malmqvist, B. O. Roos, and L. Serrano-Andrés, Chem. Phys. Lett. **288**, 299 (1998).

[25] C. Angeli, S. Borini, M. Cestari, and R. Cimiraglia, J. Chem. Phys., 121, 4043 (2004)

[26] C. Bloch, Nucl. Phys. **6**, 329 (1958).

[27] B. H. Brandow, Rev. Mod. Phys. **39**, 771 (1967).

[28] B. H. Brandow, Int. J. Quant. Chem. **15**, 207 (1979);

[29] I. Lindgren, J. Phys. B **7**, 2441 (1974).

[30] I. Lindgren, Int. J. Quant. Chem. **14** (S12), 33 (1978).

[31] G. Hose and U. Kaldor, J. Phys. B **12**, 3827 (1981).

[32] J.-P. Daudey and J.-P. Malrieu, in Current Aspects of Quantum Chemistry 1981 (Ed R. Carbó) , p. 35 (Elsevier 1982).

[33] Ph. Durand, J.-P. Malrieu, in Adv. Chem. Phys. **67**, (Ed. K. P. Lawley), p. 321 (Wiley 1987).

[34] K. F. Freed and M. G. Sheppard, J. Chem. Phys. 75, 4507 (1981)

[35] K. F. Freed and M. G. Sheppard, J. Chem. Phys. 75, 4525 (1981).

[36] V. Hurtubise and K. F. Freed, in Adv. Chem. Phys., **83** (Eds. I. Prigogine and S. A. Rice), p. 465 (Wiley 1993).

[37] J.-P. Malrieu, J.-L. Heully, and A. Zaitsevskii, Theor. Chim. Acta **90**, 167 (1995).

[38] H.-J. Werner and P. J. Knowles, J. Chem. Phys. **89**, 5803 (1988).

[39] P. E. M. Siegbahn, Chem. Phys. **25**, 197 (1977).

[40] H. Zhang, J.-P. Malrieu, P. Reinhardt, and J. Ma, J. Chem. Phys. **132**, 034108 (2010).

[41] K. G. Dyall, J. Chem. Phys. **102**, 4909 (1995).

[42] B. Kirtman, J. Chem. Phys. **49**, 3890 (1968).

[43] B. Kirtman, J. Chem. Phys. **75**, 798 (1981).

[44] I. Shavitt and L. R. Redmon, J. Chem. Phys. **73**, 5711 (1980).

[45] a) A. A. Granovsky; URL: http://classic.chem.msu.su/gran/gamess/qdpt2.pdf, b) A. A. Granovsky; URL: http://classic.chem.msu.su/gran/gamess/table_qdpt2.pdf

[46] A. A. Granovsky, J. Chem. Phys. **134**, 214113 (2011).

[47] A. Zaitsevskii and J.-P. Malrieu, Chem. Phys. Lett. **223**, 597 (1995)

[48] T. H. Schucan, H. Weidenmüller, Ann Phys NY, **73**, 108 (1972).

[49] T. H. Schucan, H. Weidenmüller, Ann Phys NY, **76**, 483 (1973).

[50] C. Camacho, R. Cimiraglia and H. A. Witek, Phys. Chem. Chem. Phys., **12**, 5058 (2010).

[51] C. Camacho, H. A. Witek, and R. Cimiraglia J. Chem. Phys. **132**, 244306 (2010).

[52] H. A. Witek, Y.-K. Choe, J. P. Finley, K. Hirao, J. Comput. Chem. **23**, 957-965 (2002).

[53] M. Lewin, Arch. Ration. Mech. Anal **171**, 83 (2004)

[54] É. Cancès, H. Galicher, and M. Lewin, J. Comp. Phys. **212**, 73 (2006).

[55] M. Lewin, J. Math. Chem. **44**, 967 (2008).

[56] J. A. Pople, J. S. Binkley, R. Seeger, Int. J. Quantum Chem. Symp. **10,** 1 (1976).

[57] K. A. Brueckner, Phys. Rev. **100,** 36 (1955).

[58] A. Hugenholtz, Physica **23,** 481 (1957).

[59] R. J. Bartlett, Ann. Rev. Phys. Chem. **32,** 359 (1981).

[60] M. Hanrath, Chem. Phys. **356**, 31 (2009).

[61] P. Ghosh, S. Chattopadhyay, D. Jana and D. Mukherjee, Int. J. Mol. Sci. **3**, 733 (2002)

[62] A. V. Nemukhin, A. V. Bochenkova, K. B. Bravaya, and A. A. Granovsky, Proc. SPIE, **6449**, 64490N (2007).

[63] K. Bravaya, A. Bochenkova, A. Granovsky, and A. Nemukhin, J. Am. Chem. Soc., **129** (43), 13035 (2007)

[64] L. Kessel, I. B. Nielsen, A. V. Bochenkova, K. B. Bravaya, and L. H. Andersen, J. Phys. Chem. A, **111** (42), 10537 (2007)

[65] K. B. Bravaya, A. V. Bochenkova, A. A. Granovsky, A. P. Savitsky, and A. V. Nemukhin, J. Phys. Chem. A, **112** (37), 8804 (2008).

[66] K. Bravaya, A. Bochenkova, A. Granovsky, A. Nemukhin, Russian Journal of Physical Chemistry B, Focus on Physics, **2**, 671 (2008).

[67] T. Rocha-Rinza, O. Christiansen, J. Rajput, A. Gopalan, D. B. Rahbek, L. H. Andersen, A. V. Bochenkova, A. A. Granovsky, K. B. Bravaya, A. V. Nemukhin, K. L. Christiansen and M. B. Nielsen, J. Phys. Chem. A, **113** (34), 9442 (2009)

[68] M. G. Khrenova, A. V. Bochenkova, and A. V. Nemukhin, Proteins: Structure, Function, and Bioinformatics **78**, 614 (2010).

[69] A. A. Granovsky; URL: http://classic.chem.msu.su/gran/gamess/xmcqdpt.pdf

[70] L. Serrano-Andrés, M. Merchán, and R. Lindh, J. Chem. Phys. **122**, 104107 (2005).

[71] T. Shiozaki, W. Győrffy, P. Celani and H.-J. Werner, J. Chem. Phys. **135**, 081106 (2011)