A Perspective on the CASPT2 Method

PETER PULAY

Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR

ABSTRACT: The CASPT2 method, developed by Roos and coworkers, is reviewed. The rationale for a method that can deal with arbitrary strongly correlated systems at affordable computational cost is presented, and the main milestones in the 20-year history of CASPT2 are listed. The basic features of the method are summarized. The strengths and weaknesses of CASPT2 are assessed. Its main strength is its ability to deal with arbitrary electronic states at a reasonable computational cost, and giving exact spin states. Its main limitation is that, it is not a black box method, and requires considerable experience to use. Another limitation is that, for accurate results, the active space must be generally larger than the minimum required to describe only the strong (static) correlation. Including dynamical correlation at an earlier stage may resolve some of these issues. © 2011 Wiley Periodicals, Inc. Int J Quantum Chem 111: 3273–3279, 2011

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1. Introduction

The most challenging problem in contemporary quantum chemistry is to provide an accurate and balanced description of systems with nondynamical (static) electron correlation. In such systems, electron correlation, which is usually a relatively small, although not unimportant, correction to the wavefunction, becomes qualitatively important. As a consequence, a single electron configuration, i.e., a single Slater determinant, is not a proper zeroth-order approximation. The wavefunction in such cases is a mixture of configuration state functions (CSFs), each with appreciable weight. There is no general agreement on the definition of static versus dynamic electron correlation, and the transition between the two is gradual. Most researchers would agree that static correlation generally involves a limited number of close-lying orbitals, usually the frontier orbitals near the Fermi level, with significant fractional occupation numbers (say, above 0.02 but below 1.98 in the exact wavefunction). These orbitals tend to be delocalized and often have strong bonding or antibonding character. They thus have an important effect on potential energy surfaces. In contrast, dynamical electron correlation involves a very large number of configurations,

each with a small weight. Dynamic correlation is important for the quantitative determination of energies but its effect on potential energy surfaces tends to be modest because of cancellation between the numerous individual configurations.

Examples of molecules with static correlation include systems with partially broken bonds, for instance transition states for bond breaking and/or bond formation reactions, most transition metal compounds where various occupation patterns of the d-orbitals are close in energy, compounds of the strongly electronegative first-row atoms (F,O, and to a lesser extent N and C) which have empty low-lying antibonding orbitals, large conjugated systems that approach the metallic state of vanishing HOMO–LUMO gap, and the majority of excited states. It is clear from this list that some of the most interesting chemistry and molecular spectroscopy—reactions, transition metal compounds, electronically excited states—require a balanced treatment of both static and dynamical correlation. There is still no generally accepted routine method for the accurate treatment of these systems. Density functional theory (DFT) often yields quite reasonable results at a modest computational cost. However, it is not a convergent theory, i.e., its accuracy cannot be improved without limit, and there are electronic states which cannot be treated directly by DFT, for instance low-spin open-shell states. Electron correlation methods based on a single Hartree-Fock reference determinant are unsatisfactory for systems with strong static correlation. Perturbation theory, for instance the simplest configuration-based correlation theory, second-order Møller-Plesset theory (MP2) [1], is particularly sensitive to near-degeneracy of the frontier orbitals which lead to small denominators and large unphysical correlation effects. Multireference Configuration Interaction (MRCI) can account for both dynamic and static correlation but it is expensive and not size-consistent. There are approximate size-consistent generalizations of MRCI but the ultimate solution, multireference coupled cluster theory, is still under development. All these methods are very expensive for larger systems and a larger number of strongly correlated orbitals. The Complete Active Space Second Order Perturbation Theory (CASPT2) method of Roos and coworkers [2, 3] was an important step toward a cost-effective and accurate determination of approximate wavefunctions for a wide variety of systems, including systems that cannot be treated satisfactorily at

simpler levels of theory, such as excited states with double excitation character. To date, there are almost 2,000 publications referring to the CASPT2 method. These encompass a wide variety of topics: organic radical reactions, actinide chemistry, biochemical systems, hypothetical molecules, radical, ions and intermediates, and a large number of excited state studies, including the study of conical intersections. CASPT2 has been implemented both in MOLCAS program system [4] and in MOLPRO [5].

CASPT2 has been reviewed in several articles and book chapters. A book chapter by Anderssen and Roos [6] is the best technical introduction to the method. A more general review of multiconfiguration techniques is provided in Ref. [7]. Applications of CASPT2 to excited states are reviewed in Refs. [8–10] and more recently in Ref. [11]. Applications to heavy element [12, 13] and actinide [14] chemistry has been described in detail. CASPT2 has been compared with other methods, in particular density functional theory, for redoxactive enzymes [15]. Its applications in photobiology are reviewed in Ref. [16].

The first attempt to develop a multireference analogue of the widely used [17] single-reference Møller-Plesset second-order perturbation theory (MP2) [1] was made in 1982 [18]. This formulation did not include the important semi-internal substitutions, and the results were not encouraging. Efficient methods for matrix element evaluation allowed the inclusion of the full first order interactive space in the current versions of CASPT2 [2, 3], in the spirit of the internally contracted multireference CI, introduced by Meyer [19] and implemented by Werner and Reinsch, and Werner and Knowles (see Ref. [20]).

While CASPT2 is the most widely used method of its kind, several similar methods have been proposed. Wolinski et al. has developed a second-order perturbation theory method, GMP2 [21] which, according to Ref. [6], is identical to the second version of CASPT2 [3]. However, it was implemented only for a two-configuration reference function [22]. This was the first use of a non-diagonal reference Fock matrix, and it used internal contraction [19]. The formulations of Murphy and Messmer [23, 24], the MR-MP method of Hirao [25, 26] and the method suggested by Kozlowski and Davidson [27] do not make use of internal contractions. Of these methods, only the MR-MP method of Hirao is still in general use; it is included in the GAMESS program system [28].

2. The CASPT2 Method

2.1. THE REFERENCE WAVEFUNCTION

The most widely used method of dealing with strongly correlated systems is to determine first a multiconfigurational (MC) reference wavefunction that includes all static correlation effects, and add dynamical correlation to this in a second step. The multiconfigurational wavefunction plays the role of the Hartree-Fock reference function for systems with only dynamic correlation. In this method, the total orbital space (in a finite basis representation) is partitioned in three sets. Inactive orbitals are doubly occupied in all configurations. Active orbitals may have different occupancy in different configurations. Virtual orbitals are unoccupied in all configurations. In general, orbital energy increases in the order inactive, active, virtual. Comments on this generally used approach will be made at the end of this article.

For both practical and theoretical reasons, it is best to include in the reference space all possible (symmetry allowed) configuration functions (CSFs) from the active (variably occupied) orbital subspace. The coefficients of the configurations in the reference wavefunction are determined by the CI procedure, i.e., by optimizing the energy. This is the complete active space (CAS) concept [29]. A CAS wavefunction is invariant against orbital rotations in the active space, greatly simplifying the definition of the wavefunction. If the orbitals are also optimized, the CASSCF wavefunction is obtained. In a somewhat different context, this was first introduced as the Full Optimized Reaction Space (FORS) wavefunction [30]. The CAS concept also improves very much the often difficult process of converging the CASSCF wavefunction. The number of configurations in the CAS wavefunction increases exponentially as the number of active orbitals and active electrons increases. This limits the CAS wavefunction to less than 20 active orbitals in the usual case when the number of active electrons and orbitals is about the same. A generalization of the CAS idea that allows larger active spaces is the Restricted Active Space (RAS) wavefunction [31]. Here, the active space is partitioned in three parts, and the number of holes in the first part and the number of electrons in the second part is restricted. The CASPT2 method has been generalized to RAS reference functions [32].

The preference for a CAS type wavefunction originates from the difficulty of predicting which configurations will be important in the final wavefunction. In addition, the importance of a given configuration can vary widely across the potential surface. Nevertheless, certain well-defined incomplete active space multiconfigurational wavefunctions, in particular the Generalized Valence Bond (GVB) method [33], offer a useful alternative to the more expensive CAS method. The CAS-PT2 concept is sufficiently general to accommodate incomplete active spaces, for instance RAS or GVB [34]. In addition, an analog of the CASPT2 wavefunction and energy can be defined for a reference wavefunction, where the orbitals are not fully optimized. Indeed, this is necessary for a state-averaged calculation where the goal is to provide uniform accuracy to a set of states [35]. Another potential application is an unrestricted natural orbital—complete active space (UNO-CAS) reference function [36]. UNO-CAS avoids the often problematic and expensive orbital optimization step of MC-SCF and yields potential surfaces that are generally close and almost parallel to the corresponding MC-SCF surface.

2.2. THE ZEROTH-ORDER HAMILTONIAN

In the single-configuration case, the almost universal choice of the zeroth-order Hamiltonian (an n-electron operator) is the sum of the one-electron Fock operators, introduced by Møller and Plesset [1]:

$$\mathbf{H}_0 = \mathbf{F} = \sum_i \mathbf{f}(i). \tag{1}$$

It is usually used in a canonical orbital basis that makes the Fock operators diagonal. However, this is not strictly necessary, and Møller-Plesset perturbation theory can be expressed exactly in noncanonical, for instance localized basis [37].

It is highly desirable to generalize this to the multiconfigurational case in such a way that in the limit when the multireference (MR) wavefunction becomes the Hartree-Fock determinant, the zeroth-order Hamiltonian goes over smoothly to the Møller-Plesset operator, Eq. (1). This has proved to be surprisingly difficult. First, the definition of the Fock operator is not unique in the MR case. Most formulations, including CASPT2, use the Fock operator of the spin-averaged first order density matrix of the reference wavefunction as the Fock operator. This is well defined and has the important advantage that it preserves

spin symmetry. However, it is somewhat biased between open-shell and closed-shell orbital occupancies and shows systematic errors for bond formation and excitation energies (both too small) [38]. A modified Fock operator was proposed [39] but it is not applicable in all cases. The current standard technique is to introduce a small level shift (≈ 0.25 E_h or less) which depends on the occupation number of the active orbital, and whether the orbital is excited into or excited from [40]. A theoretically more satisfactory solution is to introduce two-electron terms in $\mathbf{H}_0$ [41]. For a while, this was considered too complicated for practical use but it was applied successfully lately by Malrieu and coworkers under the acronym NEVPT2 [42, 43], who also explored the relaxation of the internal contraction scheme. One potential problem with the Dyall [41] Hamiltonian is that it treats orbitals differently, based on their formal assignment to the inactive or active space, giving different results for the same reference function depending on the labeling of the orbitals [44]. Of course, methods based on an alternative zeroth-order Hamiltonian, like NEVPT2 [42] cannot be properly called CASPT2.

In the MR case, the reference wavefunction is not necessarily an eigenfunction of the n-electron Fock operator $\mathbf{F}$, and thus the latter is not a proper zeroth-order Hamiltonian. To restore this property, $\mathbf{H}_0$ is defined using the projection operator $\mathbf{P}$ to the reference function and its orthogonal complement $\mathbf{Q} = \mathbf{1} - \mathbf{P}$:

$$\mathbf{H}_0 = \mathbf{PFP} + \mathbf{QFQ} \qquad (2)$$

Unlike in the single-reference case, the MR one-electron Fock operator $\mathbf{f}$ may have off-diagonal matrix elements that cannot be entirely eliminated by an orbital transformation that leaves the wavefunction unchanged. Unitary transformations within the inactive, within the active, and within the virtual orbital spaces can remove non-diagonal matrix elements within these subspaces but not between the subspaces. They were neglected in the first version of CASPT2 [2], and this has significant computational advantages. However, energies may change discontinuously if an orbital is transferred, e.g., from the inactive to the active space, even if it is fully occupied in both cases. Later versions of CASPT2 [3] include these terms; they are also included in the MOLPRO implementation [5], and in the early GMP2 program [22].

2.3. THE CASPT2 WAVEFUNCTION

The CASPT2 configuration space is generated by applying single and double substitution operators (also called, pedagogically incorrectly, excitation operators) on the reference wavefunction Ψ_0. As pointed out in Ref. [6], single substitutions do not have to be explicitly considered, they can be included with the much more numerous doubles. The first-order wavefunction,

$$\Psi^1 = \sum_{pqrs} T_{pr}^{qs} \mathbf{E}_{pq} \mathbf{E}_{rs} \Psi^0, \qquad (3)$$

is formally the same as in the single-reference case, and the number of amplitudes is also the same. An $\mathbf{E}$ operator, say $\mathbf{E}_{pq}$, removes an electron from orbital q and places it in orbital p. Obviously, q must be an occupied (inactive or active) orbital, and p must be an active or virtual orbital. The configuration functions generated from Ψ^0 span exactly the first-order interacting subspace, i.e., the set of CSFs that have a non-zero Hamiltonian matrix element with Ψ^0. This is the internally contracted form of the configuration expansion [19, 20]. Its advantage is that the number of amplitudes T is dramatically less than in a general expansion, where the substitution operators act on each component of Ψ^0, the number of which may be very large. Thus for larger active spaces, some sort of contraction of the wavefunction is indispensable. The disadvantage of internal contraction is twofold. First, the formulas for the matrix elements become involved, and require higher order density matrices in the active space (up to third order for CASSCF, up to fourth order in the general case). Second, the CSFs do not form an orthogonal set, and are often linearly dependent. Orthogonalization and removal of redundant functions requires significant computational overhead, particularly if it is done by diagonalizing large overlap matrices. Internal contraction also restricts the flexibility of the wavefunction and thus raises the energy. No tests for larger cases have been carried out but for smaller systems this error is small [6].

The first order wavefunction is determined by solving the equation below for Ψ^1 in CSF basis:

$$(\mathbf{H}^0 - E^0)\Psi^1 = (\mathbf{H}^0 - \mathbf{H})\Psi^0. \qquad (4)$$

This is a large linear system of equations, and in general has to be solved iteratively, unless the zeroth-order Hamiltonian $\mathbf{H}^0$ is truncated to

diagonal form. The energy is obtained using the standard perturbation theory second order energy formula.

2.4. EXTENSIONS OF THE CASPT2 METHOD

The CASPT2 method has been extended in several ways from the original form, both by Roos and coworkers and others. The zeroth-order Hamiltonian has been modified to remove most of the systematic errors in electron pair forming and breaking reactions [40]. It has been generalized to state-averaged calculations [35]. Level shifts have been introduced, both real [45] and imaginary [46]. These eliminate the troublesome singularities in the calculated energies which are caused by intruder states (see below). The limitations in the size of the active space can be alleviated by using a Restricted Active Space [31] reference in a CASPT2-like approach [32]. The formulation of Celani and Werner [32] also removes some of the complications caused by the internal contraction formalism, by treating some subspaces uncontracted, while the largest subspaces retain the internally contracted form. This, of course, gives a slightly different wavefunction than the original CASPT2.

Other extensions include calculation of the third-order energy [47], analytical gradients [48], a combination of MRCI and CASPT2 [49], and the use of explicit R_{12}-dependent correlation functions for dynamical correlation [50].

3. Assessment and Perspectives

The CASPT2 method, if applied carefully, affords an accurate treatment of strongly correlated systems: bond breaking and forming reactions, transition metals, and in particular excited states with less computational effort than multireference CI and coupled cluster theory. Its impact was the largest for excited states. Unlike its computationally less expensive and more routine competitors, in particular time-dependent density functional theory, CASPT2 can treat in principle any system, including excited states with doubly excited character. Density functional theory is often surprisingly accurate for the ground or low-lying states of transition metal compounds but it is limited by its single-reference nature. Low-spin open-shell systems, which are inherently multiconfigurational, are difficult or impossible to han-

dle directly by DFT. Unlike most DFT methods, CASPT2 generates pure spin states.

CASPT2 has, however, its own problems. To a certain extent, these are also shared by higher level internally contracted methods, like MRCI and MRCC (Multireference Coupled Cluster) theories. Computational expense is one of these problems but perhaps not the worst. In the opinion of this writer, the most important problem is the strong effect the selection of the active space has on the results. Because of this, CASPT2 is very far from a black-box method, and requires much experience and a deep understanding of electronic structure to obtain reliable results. Ideally, one would like to include in the active space only the orbitals that exhibit genuine, strong nondynamical correlation, for instance two π-type orbitals (a_2 and b_1) in the ground state of ozone, or the four π-type frontier orbitals in the ground state of porphine [51]. A minimum active space is not very difficult to identify, see, e.g., [52]. Using the smallest necessary active space improves the convergence of the CASSCF procedure; convergence is understandably poor and multiple minima occur if the active space contains orbitals with very low ($\sim$0) or very high ($\sim$2) occupation numbers which properly belong to the virtual or inactive subspaces. Unfortunately, a CASPT2 wavefunction based on a minimum CAS reference is often quite poor. Most likely, the root of the problem is that that the starting minimal CAS wavefunction gives an unbalanced description of the molecular electronic structure, for two reasons. First, static correlation is exaggerated in a minimum CAS because only the valence-like active orbitals are available for correlation. Second, occupation numbers of the active orbitals are distorted because of differential dynamical correlation effects [11]. For instance, dynamical correlation energy is very different for configurations with covalent and an ionic, a paired electron and a diradical, or a valence and a Rydberg character. Omitting dynamical correlation increases the zeroth-order energy of configurations with large dynamical correlation energy relative to the other configurations, and incorrectly reduces their participation in the zeroth-order wavefunction. This error cannot be removed by the CASPT2 procedure because the orthogonal complement of Ψ_0 in the active space is not part of the first-order interacting space. In multireference CI, it is possible to include the fully internal substitutions iteratively, improving the reference state.

The solution generally employed to alleviate this problem is to enlarge the active space beyond the minimum required for strong correlation. The extra orbitals add some (essentially dynamic) correlation, and improve the zeroth-order wavefunction. Unfortunately, they also increase the computational effort greatly, and make the active space selection less straightforward and therefore the wavefunction less well defined. For instance, in calculations on transition metals, it is important to include a second set of d orbitals in the active space [53] to describe the radial correlation of the d electrons. Rules have been formulated for selecting the appropriate active space in difficult cases [8], but CASPT2 is still far from a black box method.

Besides the general problem of treating strongly correlated systems, most multireference perturbation theories suffer from the "intruder state problem," particularly when applied to excited states (methods based on the Dyall Hamiltonian [41] like NEVPT2 [42] are claimed to be immune to this problem). Intruder states are configurations that are weakly coupled to the state of interest, often states with Rydberg-type diffuse orbitals, and have energies which make $(\mathbf{H}_0 - \mathbf{E}_0)$ in Eq. (4) singular. For a diagonal zeroth-order Hamiltonian, this means that an energy denominator vanishes, causing the perturbation theory to blow up. Including the offending orbitals in the active space removes the problem but increases the computational cost, and may generate other intruder states. It is generally undesirable to include orbitals in the active space that do not contribute to static correlation. Small level shifts [45, 46] are often effective in removing singularities caused by intruder states, or shifting them to areas of the potential surface which are not important. However, level shifts can in some cases reverse the energy ordering of close-lying states [54].

How can a CASPT2 type procedure limited to the minimum active space improved? In my opinion, one should start the opposite way: instead of using "naked" configurations and including dynamical correlation later, we should include dynamical correlation from the outset, similar in spirit to the externally contracted CI [55]. However, formulating a multiconfiguration method using "dressed" (dynamically correlated) configurations is not simple, except for the simplest approximation, adding level shifts (corresponding to the dynamical correlation energy of the configuration) to the diagonal elements of the Hamiltonian [56–58]. A viable method beyond this approximation has yet to be proposed. Perhaps an new look at quasi-degenerate perturbation theory (QDPT) [59–66] is warranted. For all the theoretical effort expended, QDPT had virtually no relevant chemical applications. However, computing is now fundamentally different from the 60s and 70s when most of QDPT theory was developed. Computer price/performance ratios improved eight or nine orders of magnitudes, and memory capacities improved close to a millionfold since 1970. This means that techniques that were deemed not practical in the past may be feasible now.

4. Conclusions

The CASPT2 method, created in the research group of B. O. Roos, is a valuable and widely used technique to study strongly correlated system, and in particular excited states that cannot be described by routine techniques. It has contributed greatly to our understanding of molecular electronic spectra and other properties. It would be desirable to make it more black box like, and to limit the active space to orbitals that strongly participate in nondynamical correlation.

References

1. Møller, C.; Plesset, M. S. Phys Rev 1934, 46, 618.

2. Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. J. Phys Chem 1990, 94, 5477.

3. Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. J Chem Phys 1992, 96, 1218.

4. Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P.-O.; Cossi, M.; Schimmelpfennig, B.; Neogrady, P.; Seijo, L. Comput Mater Sci 2003, 28, 222.

5. Werner, H.-J.; Knowles, P. J.; Manby, F. R.; Schütz, M.; Celani, P.; Knizia, G.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hesselmann, A.; Hetzer, G.; Hrenar, T.; Jansen, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Shiozaki, T.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. MOLPRO, a package of ab initio programs.

6. Andersson, K.; Roos, B. O. In Modern Electronic Structure Theory; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; Vol. 2, p 55.

7. Roos, B. O. In Theory and Applications of Computational Chemistry: The First Forty Years; Dykstra, C. E., Frenking, G., Kim, K., Scuseria, G., Eds.; Elsevier: Amsterdam, 2005; p 725.

8. Roos, B. O.; Andersson, K.; Fülscher, M. P.; Malmqvist, P.-Å.; Andres, L. S.; Pierloot, K.; Merchan, M. Adv Chem Phys 1996, 93, 219.

9. Roos, B. O. Acc Chem Res 1999, 32, 137.

10. Merchan, M.; Serrano-Andres, L.; Fülscher, M. P.; Roos, B. O. Recent Adv Comput Chem 1999, 4, 161.

11. Serrano-Andres, L.; Merchan, M. J Mol Struct THEOCHEM 2005, 729, 99.

12. Roos, B. O. In Computational Inorganic and Bioinorganic Chemistry; Solomon, E. I., Scott, R. A., King, B., Eds.; Wiley: Chichester, 2009; p 147.

13. Roos, B. O.; Malmqvist, P.-Å.; Gagliardi, L. In Fundamental World of Quantum Chemistry; Brändas, E. J.; Kryachko, E. S., Eds.; Springer: Berlin, 2003; Vol. 2, p 435.

14. Gagliardi, L.; Roos, B. O. Chem Soc Rev 2007, 36, 893.

15. Siegbahn, Per. E. M. Faraday Discuss 2003, 124, 289.

16. Schapiro, I.; Ryazantsev, M. N.; Ding, W. J.; Huntress, M. M.; Melaccio, F.; Andruniow, T.; Olivucci, M. Aust J Chem 2010, 63, 413.

17. Pople, J. A.; Binkley, J. S.; Seeger, R. Int J Quantum Chem Symp 1976, 10, 1.

18. Roos, B. O.; Linse, P.; Siegbahn, P. E. M.; Blomberg, M. R. A. Chem Phys 1982, 66, 197.

19. Meyer, W. In Methods of Electronic Structure Theory; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 4, p 413.

20. Werner, H. J. In Ab Initio Methods in Quantum Chemistry II; Lawley, K. P., Ed.; Wiley: New York, 1987; p 1.

21. Wolinski, K.; Sellers, H. L.; Pulay, P. Chem Phys Lett 1987, 140, 225.

22. Wolinski, K.; Pulay, P. J Chem Phys 1989, 90, 3647.

23. Murphy, R. B.; Messmer, R. P. Chem Phys Lett 1991, 183, 443.

24. Murphy, R. B.; Messmer, R. P. J Chem Phys 1992, 97, 4170.

25. Hirao, K. Chem Phys Lett 1992, 190, 374.

26. Hirao, K. Chem Phys Lett 1993, 201, 59.

27. Kozlowski, P. M.; Davidson, E. R. J Chem Phys 1994, 100, 3672.

28. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. J Comput Chem 1993, 14, 1347.

29. Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. Chem Phys 1980, 48, 157.

30. Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. Chem Phys 1982, 71, 41.

31. Malmqvist, P.-Å.; Rendell, A.; Roos, B. O. J Phys Chem 1990, 95, 5477.

32. Celani, P.; Werner, H.-J. J Chem Phys 2000, 112, 5546.

33. Bobrowicz, F. W.; Goddard, W. A., III. In Methods of Electronic Structure Theory; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 4, p 79.

34. Sejpal, M.; Messmer, R. P. J Chem Phys 2001, 114, 4796.

35. Finley, J.; Malmqvist, P.-Å.; Roos, B. O.; Serrano-Andres, L. Chem Phys Lett 1998, 288, 299.

36. Bofill, J. M.; Pulay, P. J Chem Phys 1989, 90, 3637.

37. Pulay, P.; Saebo, S. Theor Chem Acta 1986, 69, 357.

38. Andersson, K.; Roos, B. O. Int J Quantum Chem 1993, 45, 591.

39. Andersson, K. Theor Chim Acta 1995, 91, 31.

40. Ghigo, G.; Roos, B. O.; Malmqvist, P.-Å. Chem Phys Lett 2004, 396, 142.

41. Dyall, K. J Chem Phys 1995, 102, 4909.

42. Angeli, C.; Cimiraglia, R.; Evangelisti, S.; Leininger, T.; Malrieu, J.-P. J Chem Phys 2001, 114, 10252.

43. Angeli, C.; Cimiraglia, R.; Malrieu, J.-P. J Chem Phys 2002, 117, 297.

44. Havenith, R. W. A.; Taylor, P. R.; Angeli, C.; Cimiraglia, R.; Ruud, K. J Chem Phys 2004, 120, 4619.

45. Roos, B. O.; Andersson, K. Chem Phys Lett 1995, 245, 215.

46. Forsberg, N.; Malmqvist, P.-Å. Chem Phys Lett 1997, 274, 196.

47. Werner, H.-J. Mol Phys 1996, 89, 645.

48. Celani, P.; Werner, H.-J. J Chem Phys 2003, 119, 5044.

49. Celani, P.; Stoll, H.; Werner, H.-J.; Knowles, P. J Mol Phys 2004, 102, 2369.

50. Shiozaki, T.; Werner, H.-J. J Chem Phys 2010, 133, 141103.

51. Gouterman, M. J Mol Spectrosc 1961, 6, 138.

52. Pulay, P.; Hamilton, T. P. J Chem Phys 1988, 88, 4926.

53. Roos, B. O. Collect Czech Chem Commun 2003, 68, 265.

54. Camacho, C.; Cimiraglia, R.; Witek, H. A. Phys Chem Chem Phys 2010, 12, 5058.

55. Siegbahn, P. E. M. Int J Quantum Chem 1983, 23, 1869.

56. Ruttink, P. J. A.; van Lenthe, J. H.; Zwaans, R.; Groenenboom, C. J Chem Phys 1991, 94, 7212.

57. Szalay, P. G.; Füsti-Molnár, L. J Phys Chem 1996, 100, 6288.

58. Ben Amor, N.; Maynau, D.; Malrieu, J.-P.; Monari, A. J Chem Phys 2008, 129, 064112.

59. Brandow, B. H. Rev Mod Phys 1967, 39, 771.

60. Brandow, B. H. Adv Quantum Chem 1977, 10, 187.

61. Kirtman, B. J Chem Phys 1968, 49, 3890.

62. Certain, P. R.; Hirschfelder, J. O. J Chem Phys 1970, 52, 5977.

63. Lindgren, I. J Phys B 1974, 7, 2441.

64. Klein, D. J. J Chem Phys 1974, 61, 786.

65. Hose, G.; Kaldor, U. J Phys B 1979, 12, 3827.

66. Shavitt, I.; Redmon, T. L. J Chem Phys 1980, 73, 5711.