

CHAPTER 5

MULTICONFIGURATIONAL QUANTUM CHEMISTRY FOR GROUND AND EXCITED STATES

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Abstract: One frequently used quantum chemical approach for studies of spectroscopy and photochemistry is the Complete Active Space (CAS) SCF method in combination with multiconfigurational second order perturbation theory (CASPT2). In this chapter we shall describe these two approaches. The basic idea behind them is the request that the wave function should give a proper description of the electronic structure already at the lowest level of theory. This should be possible for all possible arrangements of the electrons: in chemical bonds, in excited states, in dissociated states, at transition states for chemical reactions, etc. It should also be possible for all atoms of the periodic systems. The CASSCF wave function fulfills, in principle, this requirement because it is full CI, albeit in a limited space of active orbitals. CASSCF can therefore be regarded as an extension of the Hartree-Fock (HF) method to any arrangement of the electrons. The addition of dynamic electron correlation is as crucial here as it is in the HF method. The suggested solution is to compute this energy using second order perturbation theory (CASPT2) because it is relatively simple and allows applications to a wide variety of systems and many electrons. The review will focus on the methods themselves. Applications will be described in other chapters of the book

Keywords: Multiconfigurational methods, CASSCF, CASPT2

5.1. INTRODUCTION

This chapter will discuss that Complete Active Space (CAS) SCF method [1, 2] and multiconfigurational second order perturbation theory, CASPT2 [3, 4]. The CASSCF method was introduced almost thirty years ago. The aim was to be able to deal with electronic structures that could not be described even qualitatively using a single electronic configuration.

Actually, the method itself is much older. It was formulated by P.-O. Löwdin in his famous 1955 paper, where he notes that in a limited spin-orbital basis, the

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best wave function will be a full CI with both the CI coefficients and the MOs optimized using the variational principle [5]. He called this the *Extended Hartree-Fock* scheme. He derived the condition for optimum orbitals, which was later to be known as the extended Brillouin's theorem (The Levy-Berthier- Brillouin (BLB) theorem) [6, 7]. The key ingredients of the CASSCF method are already formulated here. Löwdin moreover refers to unpublished work by J. C. Slater and the book by Frenkel from 1934. Nothing is new under the sun. An important forerunner to the CASSCF method was the *Fully Optimized Reaction Space-FORS* introduced by K. Ruedenberg in 1976 [8]. He defined an *orbital reaction space* in which a complete CI expansion was used (in principle) and all orbitals were optimized. In practice, it was necessary to use only a selected set of configurations in this step because of the difficulty to perform the large CI calculations that were needed.

The development that finally lead to a code that could be used for production was based on two main ingredients: the possibility to perform full CI calculations effectively for large expansions comprising up to at least a million configuration state functions (CFs), and the possibility to optimize the orbitals and CI coefficients in an effective way. The first problem was solved by the development of the Graphical Unitary Group Approach (GUGA) by I. Shavitt in the late 70 s. He gave a detailed recipe for direct full CI calculations for a general spin-state [9, 10]. The second problem had been a nightmare for those who tried to perform MCSCF calculations in the 60 s and early 70 s. The methods used were based on an extension of the HF theory formulated for open shells by Roothaan in 1960 [11]. An important paradigm shift came with the *Super-CI* method, which was directly based on the BLB theorem [12]. One of the first modern formulations of the MCSCF optimization problem was given by J. Hinze in 1973 [13]. He also introduced what may be called an approximate second order (Newton-Raphson) procedure based on the partitioning: $U = 1 + T$, where U is the unitary transformation matrix for the orbitals and T is an anti-Hermitian matrix. This was later to become $U = \exp(T)$. The full exponential formulation of the orbital and CI optimization problem was given by Dalgaard and Jørgensen in 1978 [14]. Variations in orbitals and CI coefficients were described through unitary rotations expressed as the exponent of anti-hermitian matrices. They formulated a full second order optimization procedure (Newton-Raphson, NR), which has since then become the standard. Other methods (e.g. the Super-CI method) can be considered as approximations to the NR approach.

The GUGA method was in Shavitt's formulation limited to rather small CI expansions due to the problem of storing a large number of two-electron coupling coefficients. This problem was solved by P.-Å. Malmqvist with the introduction of the Split GUGA approach, where only one-electron coupling coefficients were used [15]. It now became possible to use CI expansions of the order of 10^6 CFs. Technically, it was, however, even more efficient to solve the CI problem in a basis of pure Slater determinants instead of spin-projected CFs and some modern programs (for example the MOLCAS software) use this approach in the inner loops of the CI code, while keeping the GUGA formalism.

An important addition to this development of the CASSCF formalism was the method introduced by Malmqvist to compute transition density matrices between

CASSCF wave functions with their own sets of optimized orbitals, which were then not orthogonal to each other. The *CAS State interaction CASSI*, method made it possible to compute efficiently first and second order transition density matrices for any type of CASSCF wave functions [16, 17]. The method is used to compute transition dipole moments in spectroscopy and also in applications where it is advantageous to use localized orbitals, for example in studies of charge transfer reactions [18]. Today, the same approach is used to construct and solve a spin-orbit Hamiltonian in a basis of CASSCF wave functions [19].

The CASSCF method itself is not very useful for anything else than systems with few electrons unless an effective method to treat dynamical correlation effects could be developed. The Multi-Reference CI (MRCI) method was available but was limited due to the steep increase of the size of the CI expansion as a function of the number of correlated electrons, the basis set, and the number of active orbitals in the reference function. The direct MRCI formulation by P. Siegbahn helped but the limits still prevented applications to larger systems with many valence electrons [20]. The method is still used with some success due to recent technological developments [21]. Another drawback with the MRCI approach is the lack of size-extensivity, even if methods are available that can approximately correct the energies. Multi-reference coupled-cluster methods are studied but have not yet reached a state where real applications are possible.

So, is there an alternative? In single configurational quantum chemistry the Møller-Plesset second order perturbation theory (MP2) has been used for a long time to treat electron correlation [22]. Today we have a long experience of this approach and know that it is surprisingly accurate in predicting structures and properties of closed shell molecules. It is therefore rather obvious to ask the question whether such an approach could also work with a CASSCF reference function. Actually, one should expect it to be even more accurate because the CASSCF wave function already includes the most important CFs, those which cannot be treated with low order perturbation theory. On the other hand, the applications would now be more demanding covering not only ground states, but also excited states, transition states for chemical reactions, and systems where MP2 is known not to work, for example, transition metal complexes. A preliminary program was written immediately after the introduction of the CASSCF method [23] but this first attempt failed because the entire interacting space could not be included in the first order wave function due to technical difficulties in computing the necessary third and fourth order CASSCF density matrices. It was not until the late 80s until this problem was solved and a full first order wave function could be constructed with a general CASSCF reference function of arbitrary complexity [3, 4]. Today, the CASPT2 method is probably the most widely used method to compute dynamic correlation effects for multiconfigurational (CASSCF) wave functions.

In this review we shall briefly describe the CASSCF and CASPT2 methods and how they can be used in practical applications. Other chapters in the book will describe applications, focusing on excited states and photochemistry.

5.2. MULTICONFIGURATIONAL WAVE FUNCTIONS AND ACTIVE SPACES

Assume that you have selected an AO basis set for a given molecular system with N electrons. It has the size m (m molecular orbitals corresponding to $2m$ spin-orbitals). Transform this basis set in some way to a set of orthonormal one-electron functions. From these new spin-orbitals you can construct $\binom{2m}{N}$ Slater determinants. You can then expand your wave function, Ψ in these determinants:

$$\Psi = \sum_{\mu} C_{\mu} \Phi_{\mu}. \quad (5-1)$$

Applying the variational principle leads to the well known secular equation that determines the expansion coefficients:

$$\sum_{\nu} (H_{\mu\nu} - ES_{\mu\nu}) C_{\nu} = 0, \quad (5-2)$$

where $H_{\mu\nu}$ are the Hamiltonian matrix elements over the determinant basis and $S_{\mu\nu}$ are the corresponding overlap integrals. This approach is called *Full Configuration Interaction, FCI*, and constitutes the best solution to the Schrödinger equation that can be obtained with the given basis set. It becomes the exact solution when the basis set becomes infinite and complete. It is the trade mark of ab initio quantum chemistry that it can, in principle, be driven towards the exact solution by increasing the basis set and improving the wave function.

In practice, it is not possible to solve the FCI equation except for small systems with few electrons and very limited basis sets. Wave function quantum chemistry therefore seeks as good approximations to the FCI equations as possible. Many such approaches are available today, each of them having their own advantages and disadvantages. The simplest approximation is to use only one Slater determinant and then use the variation principle to find the best orbitals for this approximation. This is the Hartree-Fock, HF, method. It is a surprisingly good approach in many cases and often yields a total energy that is in error with less than one percent. It would be an exact solution if the electrons did not interact with each other. The HF method uses a mean-field approximation for the electron–electron interaction. The remaining error describes the part of the electron repulsion that is not covered by this approximation and is commonly called *electron correlation*. It can be recovered by adding more determinants to the CI expansion. A variety of methods have been developed to do this, the most accurate being the coupled cluster expansion of the CI wave function. We shall not discuss these methods further but instead concentrate on the case where one determinant is not sufficient to describe the electronic structure even qualitatively. Let us start with an example, the nitrogen molecule, N_2 . First, we perform a full CI calculation using a small double-zeta (DZ) basis set: $3s2p$. This gives a total of 18 basis functions. Freezing the $1s$ electrons reduces the number to 16 with 10 electrons (10in16 FCI). The FCI in this basis set is

only about 10^6 determinants. By combining the determinants to linear combinations that are eigenfunctions of the spin-operator and only keeping the combinations that have $S=0$ (singlets) we can further reduce the variational space to half a million, which is a routine calculation. Having done the calculations, we can analyze the results in terms of the natural orbitals (NOs), the eigenfunctions of the first order reduced density matrix. The occupation numbers (the eigenvalues of the matrix) are a good measure of the importance of the corresponding orbitals in the FCI wave function. Orbitals with small occupation numbers will only appear in configurations that have a small weight in the FCI expansion, and vice versa. Figure 5-1 shows how these occupation numbers varies as a function of the internuclear distance in the molecule. Some representative numbers are also given in Table 5-1.

Let us take a close look at these natural orbitals. The two first ($2\sigma_g$ and $2\sigma_u$) are derived from the nitrogen $2s$ orbitals and remain almost doubly occupied for all distances. The occupation numbers varies between 1.97 and 1.99. The next three orbitals (notice that the π orbitals are doubly degenerate) have strongly varying occupation numbers. Close to equilibrium they are almost doubly occupied and are the orbitals that constitute the triple bond in the nitrogen molecule. At large distances the occupation drops to one. The electrons are moved to the corresponding antibonding orbitals $1\pi_g$ and $3\sigma_u$. This wave function with six singly occupied orbitals describes the dissociated system, two nitrogen atoms in a 4S_u state. The

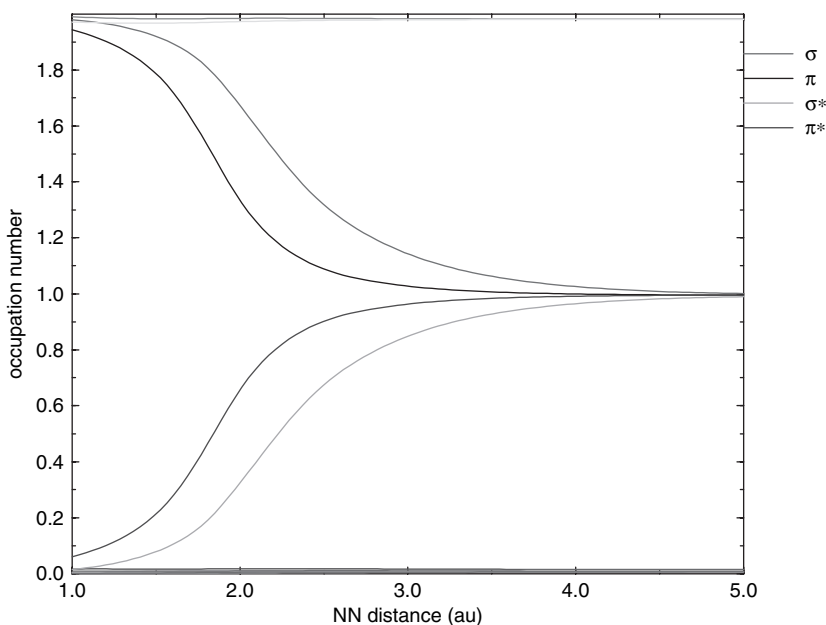


Figure 5-1. The natural orbital occupation numbers for the N_2 molecule as a function of bond distance for the DZ FCI calculation

Table 5-1. Natural orbital occupation numbers for some representative internuclear distances for the DZ FCI calculation

R(au)	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$1\pi_u$	$1\pi_g$	$3\sigma_u$	$4\sigma_g$	$4\sigma_u$	$5\sigma_g$	$2\pi_u$	$2\pi_g$	$5\sigma_u$
1.00	1.971	1.990	1.979	1.943	0.060	0.015	0.017	0.009	0.002	0.004	0.001	0.000
1.10	1.969	1.987	1.973	1.925	0.078	0.022	0.017	0.009	0.003	0.005	0.001	0.000
1.20	1.968	1.986	1.965	1.902	0.100	0.031	0.017	0.009	0.003	0.006	0.001	0.001
1.40	1.967	1.983	1.939	1.836	0.165	0.059	0.016	0.009	0.004	0.008	0.002	0.001
1.60	1.968	1.983	1.894	1.721	0.277	0.105	0.016	0.009	0.005	0.009	0.003	0.001
1.80	1.970	1.983	1.812	1.536	0.457	0.187	0.017	0.009	0.006	0.010	0.004	0.001
2.00	1.973	1.984	1.672	1.334	0.657	0.325	0.017	0.010	0.007	0.010	0.005	0.002
3.20	1.980	1.983	1.103	1.017	0.974	0.888	0.016	0.013	0.007	0.007	0.006	0.005
100.	1.981	1.981	0.995	0.995	0.995	0.995	0.014	0.014	0.006	0.006	0.006	0.006

remaining eight orbitals have small occupation numbers. Another thing to note is the typical pairing of the natural orbitals. For each bonding orbital there is a corresponding antibonding orbital such that the sum of the two occupation numbers is close to two.

Let us now use this information to reduce the computational effort. We can limit the orbital space used to performed the FCI calculation to the orbitals that have occupation numbers that are in a given range, say between 0.02 and 1.98 and then assume that we can treat the rest of the CI space using a simpler method, like singles and doubles CI or perturbation theory. In our case it means that we need only eight orbitals: the $2s$ derived orbitals $2\sigma_g$ and $2\sigma_u$, and the bonding and antibonding σ and π orbitals, corresponding to eight orbitals and ten electrons (10in8 FCI). The FCI expansion is now reduced from 566896 spin projected configurations functions (CFs) to only 176.

We shall compare the potential curves obtained with the two different methods. Second order perturbation theory (CASPT2) has been used to estimate the remaining correlation effects in the FCI calculation with the smaller number of orbitals. This approach will be described in detail below. The spectroscopic constants are presented in Table 5-2. As can be seen, the two results are almost identical. The results are obviously far from experiment because of the small basis set used but that is not relevant to the present discussion. With the smaller number of orbitals we can now perform much more advanced calculations using larger basis sets and approach the experimental values. As an illustration, such a result is also given in the table.

Let us finally also compare the NO occupation numbers for the 10in16 and the 10in8 calculations. They are also presented in Table 5-2. As we can see they have not changed much. The largest changes are found the the $2\sigma_g$ and $2\sigma_u$ orbitals. The reason is that we have not included the correlating orbitals $4\sigma_g$ and $4\sigma_u$ orbitals in the FCI orbital space. It is a general result that the occupation orbitals of strongly occupied orbitals very stable quantities that do not change much when we extend

Table 5-2. Spectroscopic constants for the N_2 molecule obtained with different methods and the DZ basis set

Method	$R_e(\text{\AA})$	D_0 (eV)	ω_e (cm^{-1})	ωx_e (cm^{-1})		
10in16 FCI	1.150	6.82	2002	1.41		
CASPT2 10in8	1.150	6.81	2001	1.45		
CASPT2 10in8 ^a	1.102	9.56	2340	19.0		
Expt.	1.098	9.76	2358	14.3		
NO occupation numbers at $R(\text{NN})=1.10 \text{\AA}$.						
	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$1\pi_u$	$1\pi_g$	$3\sigma_u$
10in16 FCI	1.969	1.987	1.973	1.925	0.078	0.022
10in8 FCI	1.988	1.995	1.981	1.933	0.073	0.021

^aObtained with the basis set: ANO-RCC 8s7p4d3f2g, Ref [71].

the orbital space. We finally notice that it is not possible to reduce the FCI wave function to a single determinant. Only in the region around equilibrium is the wave function dominated by a single configuration as can be seen from the NO occupation numbers in Table 5-1.

5.2.1. Complete Active Spaces and the CASSCF Method

The above simple example is an illustration of the idea underlying the concept of active orbital spaces and the Complete Active Space (CAS) wave function (the word complete was used instead of the word full to describe this type of wave functions). The method is based on the partitioning of the orbital space into three subspaces; inactive, active and virtual orbitals. The FCI space is reduced such that only CFs with the inactive orbitals doubly occupied are included in the CI expansion and no terms where the virtual orbitals are occupied. This corresponds to an FCI expansion within the active orbitals space. In the above example, the inactive orbitals are the nitrogen $1s$ generated orbitals $1\sigma_g$ and $1\sigma_u$, while the active orbitals are those derived from the nitrogen valence orbitals $2s$ and $2p$. Other choices might have been possible, for example to leave $2\sigma_g$ and $2\sigma_u$ inactive (6in6 active space) because their occupation number is close to two independent of the internuclear distance, or to include also the correlation orbitals $4\sigma_g$ and $4\sigma_u$ (10in10). The choice of the active space is thus governed by an a priori knowledge of which orbitals are going to have occupation numbers that differ from two or zero for a given chemical problem. In the above example, it was the dissociation of the nitrogen molecule. Other typical examples are: energy surfaces for chemical reactions, excitation processes, etc. Each problem is unique and one has to carefully investigate, which orbitals may become active during the process under study. If this cannot be decided from chemical knowledge of the system, one might have to perform exploratory calculations using methods that can handle large active spaces, for example, the RASSCF method (see below for details about this approach). The CASSCF method was introduced more than 25 years ago and today we have gained considerable experience about the choice of the active space in different types of applications [1, 2].

The CAS CI procedure is thus a method which can be used to partition the full CI space into one part that comprises the most important CFs and another much larger part, which it is believed that one can treat using other quantum chemical approaches, like for example perturbation theory. One problem with the approach is the size of the CI expansion. The number of CFs of a given spin symmetry S for N electrons and m orbitals is given by Weyl's formula:

$$\frac{2S+1}{m+1} \binom{m+1}{N/2-S} \binom{m+1}{N/2+S+1} \quad (5-3)$$

This number increases quickly with the number of active orbitals and with today's computational technology the practical limit lies around 15 orbitals unless the number of electrons (or the number of holes) is much smaller than 15. If we want to

be able to treat larger active spaces we have to reduce the CI expansion. One way to do this that have been found quite useful in some applications is the *Restricted Active Space (RAS)* method [24]. We saw in the above example that the $2\sigma_g$ and $2\sigma_u$ orbitals had occupation numbers rather close to two. Let us restrict the excitation level from these orbitals to be between zero and two, that is, only CFs with at least two electrons in these orbitals will be included in the wave function. Likewise, we can add the $4\sigma_g$ and $4\sigma_u$ orbitals to the active space but restrict the number of electrons in these orbitals to be two or less. This is the RAS method, which will be described in more detail below.

5.2.1.1. Optimization of orbitals and CI coefficients

There are two types of parameters that determine the RAS wave function: the CI coefficients and the molecular orbitals. When both of them are optimized the result will be a RASSCF (CASSCF) wave function, which is an extension of the SCF method to the multiconfigurational case. Below we shall briefly show how the optimization is done in practice in most modern programs (more details can, for example, be found in Ref. [25]).

The energy expression for a general CI wave function can be written in the form:

$$E = \sum_{p,q} D_{pq} h_{pq} + \sum_{p,q,r,s} P_{pqrs} (pq|rs), \quad (5-4)$$

where h_{pq} and $(pq|rs)$ are the one- and two-electron integrals, respectively. They contain information about the MOs. D_{pq} and P_{pqrs} are the reduced one- and two-body matrices, which are built from the CI wave function:

$$\begin{aligned} D_{pq} &= \sum_{\mu,\nu} C_{\mu} C_{\nu} A_{pq}^{\mu\nu} \\ P_{pqrs} &= \sum_{\mu,\nu} C_{\mu} C_{\nu} A_{pqrs}^{\mu\nu}, \end{aligned} \quad (5-5)$$

where $A_{pq}^{\mu\nu}$ and $A_{pqrs}^{\mu\nu}$ are structure constants that are independent of the parameters determining the wave function. They depend only on the way in which we construct the CF basis set Φ_{μ} (Eq. 5-1). There are two alternatives, either we use Slater determinants or we use spin-projected linear combinations of determinants. The latter choice has the advantage of giving a more compact wave function that is also an eigenfunction of the spin operators S_z and S^2 . The former choice has the advantage of making it easier to solve the secular Equation (5-2) because of the simpler form of the structure constants in a basis of determinants. In order to solve the secular Equation (5-2) for large CI expansions one has to find an effective way of computing the structure constants. This was done by I. Shavitt 30 years ago based on spin projected CFs [9, 10]. He developed a graphical representation of the unitary group approach for spin projection that made it possible to compute the matrix elements in an effective way and also to construct a lexical ordering of the CFs. With this method it became possible to do calculations with up to

about 10^5 CFs. The bottleneck was the large number of two-electron constants that were generated. P.-Å. Malmqvist later developed a method that avoided the construction of these constants and made it possible to increase the size of the CI expansion one order of magnitude [15]. However, it also became clear that the use of determinants instead of spin-projected CFs was more effective. The MOLCAS code today uses spin-projected CFs in the construction and analysis of the wave function but transforms to determinants in the CI section of the program [24].

In order to optimize the MCSCF wave function we have to determine the CI coefficients and the orbital parameters, that is, the AO expansion coefficients for the MOs. The condition for optimal parameters is that the gradient of the energy is zero with respect to variations of the parameters:

$$\frac{\delta E}{\delta p_i} = 0, \quad (5-6)$$

Where p_i are the variational parameters. An iterative procedure is used to arrive at this point, which is based on an expansion of the energy to second order in the parameters:

$$E(\mathbf{p}) = E(0) + \mathbf{p}^\dagger \mathbf{g} + \mathbf{p}^\dagger \mathbf{H} \mathbf{p} + \dots, \quad (5-7)$$

where \mathbf{p} is the vector of the parameters, \mathbf{g} is the gradient of the energy and \mathbf{H} the Hessian matrix, the second derivatives. Setting the derivative of this equation to zero one obtains an estimate of the optimal values of the parameters. These are the Newton-Raphson equations:

$$0 = \mathbf{g} + \mathbf{H} \mathbf{p}. \quad (5-8)$$

Most MCSCF programs use one or another variant of this iterative method. It is often approximated. One problem is that the Hessian matrix contains terms that couple variations in the MO coefficients with those of the CI vector. They are difficult to evaluate for large CI expansions and are often neglected. It is usually no problem for CASSCF wave functions, but can slow down or even prevent convergence in the RASSCF case. More approximations are possible. The super-CI method that is used in the MOLCAS program approximates the Hessian with an effective one-electron Fock-type operator [26]. Update procedures based on previous calculations of the gradients are used to update the Hessian, thereby also reintroducing the coupling between then two sets of parameters. We shall not go through the optimization procedure in detail here but refer the interested reader to the text books, for example [25].

5.2.1.2. *The CASSCF wave function and the choice of active orbitals*

The CASSCF energy (but not RASSCF) is invariant to rotations among the inactive orbitals (compare SCF) and also to rotations among the active orbitals. This can be used, for example, to transform to localized orbitals, or to *pseudo-natural orbitals*,

which diagonalize the first order density matrix in the sub-space of active orbitals. True natural orbitals are obtained by diagonalizing the full density matrix and will not preserve the CASSCF wave function because of the mixing of inactive and active orbitals that occurs.

The key problem is the choice of the active space. Today the CASSCF method has been used for 25 years and a considerable experience has been gained. We shall go through some of this below, but one should remember that every problem is unique and there is no real standard solution except in rather trivial cases. We shall, however, go through some typical cases, which may be helpful for similar studies.

5.2.1.2.1. Main group elements If a molecule contains only main group atoms there are some general rules that can be used. For small molecules, less or equal to four atoms (hydrogens not included), the best choice is to use all valence orbitals: for Li, B and C (and similar for the higher rows in the periodic table) this means four orbitals, $2s$ and $2p$. For the heavier elements N, O, and F one can leave the $2s$ orbital inactive. This choice makes it possible to compute all dissociation paths and other transformations of the system. As an example of how this can be applied we refer to a recent study of the S_3O molecule. An earlier study had used a very small active space and obtained erroneous results [27]. The use of an active space 16in12 (all p-type orbitals) gives results in full agreement with experiment and other types of calculations [28]. This is a quite general result. The method also gives accurate geometries, when optimized at the CASPT2 level. The active space may have to be extended for excited state calculations, in particular if Rydberg states are involved.

What about larger molecules? Here there are no general rules. It depends on the problem under consideration. It is often possible to leave the CH bonds inactive (unless they are involved in a chemical transformation). A molecule like butadiene (C_4H_6) then needs 12 active orbitals (12in12). One can now break all CC bonds. Usually, the active site is only part of a larger molecule and we then need only active orbitals that are localized to that part. For example, a long alkyl chain with an active end group only needs orbitals there to be active. The choice of the active space does not in itself limit the size of molecules that can be studied.

5.2.1.2.2. Excited states of planar unsaturated molecules A large number of applications have been performed in this area. We thus have a lot of experience of how to choose the active space. The general rule is to include all π -orbitals. This will allow studies of the valence excited states. However, they are often mixed with Rydberg states and it is therefore necessary to include also such orbitals in the active space, This should not be done by adding diffuse functions to the AO basis set on all atoms. Instead proceed as follows: Perform a calculation on the positive ion. Find the charge center and place a set of pre-selected Rydberg functions there. Rules of how to choose these basis functions are available [29–31]. Rydberg orbitals are

usually not needed when the calculations are performed in a solvent, for example, using the PCM model.

Now, this active space will easily become too large for most unsaturated molecules. It is then necessary to reduce the active space. How this is done depends on the problem. Rydberg orbitals are only needed for excitation energies above about 5 eV, so if one is only interested in lower excited states, they can be left out. Still this may not be enough. Again, if only the lower excited states are to be studied, one can usually leave the lowest π -orbitals inactive and move the highest to the virtual space. One should do this with care and use as many active orbitals as possible.

When the molecule contains hetero atoms such as nitrogen or oxygen one may want to include also lone-pair orbitals of σ -type in the active space. Note, however, that $\sigma \rightarrow \pi^*$ excitations are of another symmetry than $\pi \rightarrow \pi^*$ excitations for planar systems. One can therefore often use a different active space for these two types of excitations. The CASSCF method is frequently used to study photochemical processes that involve conical intersections, intersystem crossings, etc. where simpler approaches, as for example, time-dependent (TD) DFT do not work well. Here, one is only interested in the lower excited states of different spin-multiplicities and the demands on the active space are not so high.

5.2.1.2.3. Transition metal compounds The CASSCF method has been used extensively to study compounds containing transition metals. The choice of the active space is almost never trivial for such systems and must be closely related to the chemical process under study. The CASSCF method is usually used together with the CASPT2 method (which will be described in detail below) to add dynamic correlation effects. That combination often makes it necessary to use a larger active spaces than one would need, for example, if one was combining CASSCF with MRCI calculations even if that is also non-trivial in many cases.

The complexity of choosing the active space was clear already in the first application of the CASSCF/CASPT2 method to a transition metal [4]. The problem was to describe the electronic spectrum of the Ni atom. We present in Table 5-3 the results obtained with different active spaces (from Ref. [4]). Calculations were performed for each state separately. We note first the large errors obtained with the SCF method (open shell restricted SCF). The results are improved with the

Table 5-3. Excitation energies for the Ni atom with different active spaces. The ground state is chosen as $d^9s^1, ^3D$

State	SCF	3d,4s	3d,4s,4p	3d,3d',4s,4p	with 3p corr	Expt.
$d^8s^2, ^3F$	-1.62	0.47	0.22	-0.18	-0.08	0.03
$d^{10}, ^1S$	4.35	0.40	0.42	1.87	1.77	1.74
$d^9s^1, ^1D$	0.33	0.33	0.32	0.25	0.32	0.33

Data from Ref. [4].

minimal active space $3d, 4s$ (10in6) but are still in error with more than 1 eV. The reason is the crowded $3d$ space, which will affect the shape of the $3d$ orbitals in a way that depends on the number of electrons. The crowdedness of the $3d$ space results in a situation where the electronic structure is better described with a double set of $3d$ orbitals which allows one or more of the electrons to reside in a more diffuse orbital. To describe this *double shell* effect one needs one more set of $3d$ orbitals, $3d'$, to be added to the active space. In addition one needs to add a set of $4p$ orbitals to describe the strong correlation effects in the $4s$. In all this gives an active space of 14 orbitals (10in14). The results of such a calculation is also shown in Table 5-3. The computed excitation energies are greatly improved with errors not exceeding 0.21 eV. If one then also includes the dynamic correlation effects of the $3p$ electrons one arrives at the final results where the errors in computed excitation energies are all smaller than 0.11 eV. Note that scalar relativistic effects are included in these results (for details we refer to Ref. [4]). There we can also find references to earlier MCSCF and MRCI results that have also noted the importance of the second $3d'$ shell.

How do we transfer this experience to transition metal complexes. First of all: the second $3d$ shell is only needed when we study processes where the occupation of the $3d$ shell changes. In a study of the bonding in a molecule like Cr_2 we do not need them. But we still need to include the $4p$ shell (as it turns out only the $4p\pi$ orbitals are needed), which leads to an active space of 12in16 ($3d, 4s, 4p\pi$). Such a calculation yields an accurate description of the elusive ground state potential for Cr_2 [32]. The situation becomes more complex for transition metal complexes. Here, we do not need to include the $4s$ orbital, which is pushed up in energy but instead we have to consider the ligand orbitals. As an example, let us consider the complex $\text{Cr}(\text{CO})_6$. In addition to the $3d$ orbitals we need to include the six σ lone-pairs of the CO ligands, but not all of them, only those that interact with the $3d$ orbitals. The $3d$ orbitals transform according to the $t_{2g}(3d_\pi)$ and $e_g(3d_\sigma)$ irreducible representations (irreps). The corresponding ligand orbitals should therefore also be included in the active space. For a CO ligand they are two e_g σ orbitals with four electrons and three t_{2g} unoccupied π^* orbitals. Together with the five $3d$ orbitals with six electrons, this an active space of 10 orbitals with 10 electrons (10in10). There is no need to add more orbitals to account for a double shell effect since this is taken care of by the empty ligand orbital, which will acquire some $4d$ character. For a more detailed discussion of the 10in10 rule see Ref. [31].

In the tetrahedral $\text{Ni}(\text{CO})_4$ complex we have a formal d^{10} system and there is no CO to Ni σ donation. We therefore need no CO σ orbitals in the active space. Instead we add empty orbitals of the same symmetry as the $3d$ orbitals, e and t_2 . These orbitals will turn out to be a mixture of CO π^* orbitals and Cr $3d'$ and thus include the double shell effect. The 10in10 active space turns out to be quite general and can be used for many transition metal complexes. This active space will allow studies of the ground state and ligand field excited states. If charge transfer states are considered, one has to extend the active space with the appropriate ligand orbitals.

The situation is, however, not always so simple. Metals in high oxidation states tend to form covalent bonds with the ligands and this may require more ligand orbitals to be active. An extreme case is the permanganate ion MnO_4^- where Mn is formally in the oxidation state VII with no $3d$ orbitals occupied. Such a situation is of course very unbalanced and a large charge transfer takes place from *all* ligand $2p$ orbitals to the metal. A calculation on this molecule therefore requires an active space of 17 orbitals (5 $3d$ plus 4×3 $\text{O}2p$) with 24 electrons, a calculation that is on the limit of what today's technology can handle. For more details, see Ref. [33]. K. Pierloot has analyzed a number of these difficult cases and it is recommended to read her reviews on the subject [34, 35]. Let us finally add that the importance of the double shell effect will decrease for the heavier second and third row transition metals because the d orbitals are now more diffuse, an effect that is further increased by relativity.

5.2.1.2.4. Lanthanide and actinide chemistry CASSCF/CASPT2 calculations on actinide compounds have been quite successful in several recent applications. Examples are the early actinide diatoms Ac_2 to U_2 [36, 37], the electronic spectrum of the UO_2 molecule [38], the uranyl ion in water, a combined quantum chemical and molecular dynamics study [39], and several other actinide compounds. The choice of the active space for these compounds is never trivial. For uranium, for example, one would preferably use the $5f$, $6d$, and $7s$ one each atom, that is 13 orbitals with 6 electrons. This was obviously impossible for the uranium dimer. A compromise had to be made. Experimental calculations showed that a strong triple bond $\sigma_g^2 \pi_u^4$ was formed with little occupation of the antibonding orbitals. These orbitals were therefore made inactive, resulting in an active space of six electrons in 20 orbitals, which could be handled [37]. Another example is the UO_2 molecule. Here we were interested in computing the electronic spectrum. The ground state of the molecule is ${}^3\Phi_u$ with the open shell $5f\phi 7s$. Other $5f$ and $7p$ orbitals become occupied in the excited states. It was known from the calculations on the uranyl ion UO_2^{2+} that one needed an active space of 12 in 12 to describe the UO bonds properly [40]. It was, however, impossible to add all these orbitals to those needed to describe the electronic spectrum for UO_2 . A sequence of active orbitals was therefore used to see if the excitation energies converged before the maximum possible active space was reached. This did not happen and we refer to the original paper for details [38]. Other examples of applications of the CASSCF/CASPT2 method in actinide chemistry can be found in the literature. Wahlgren and co-workers have, for example, studied electron transfer reactions for uranyl(V)-uranyl(VI) complexes in solution [41]. K. Pierloot has studied the electronic spectrum of the uranyl ion and the complex with chlorine, $\text{UO}_2\text{Cl}_4^{2-}$ with excellent agreement with experiment. It is difficult to give any general rules for how one should choose the active space for these compounds. The two early elements Ac and Th are actually transition metals with the electronic structure dominated by $6d$ and $7s$ and no $5f$. The latter orbitals start to become populated for Pa and become increasingly dominant for the heavier elements. High oxidation

states, which is common in actinide compounds, favor $5f$, which makes the choice of the active space easier. But higher oxidation states also often gives strong covalent bonding, thus requiring several ligand orbitals to be active, as in the uranyl ion.

Very few calculations have so far been performed for lanthanides and not much is known about the choice of the active space. However, most lanthanide complexes have the metal in oxidation state $3+$. Furthermore, are the $4f$ orbitals inert and do not interact strongly with the ligands. It is therefore likely that in such complexes only the $4f$ orbitals have to be active unless the process studied includes charge transfer from the ligands to the metal. In systems with the metal in a lower oxidation state, the choice of the active space would show similar problems as in the actinides, in particular because the $5d$ orbitals may also take part in the bonding. As an example we might mention a recent study of the SmO molecule and positive ion where 13 active orbitals were shown to produce results of good accuracy [42].

5.2.2. The Restricted Active Space Method

The major problem with the CASSCF method is the limited number of active orbitals that can be used. However, one notes in many applications that some of these orbitals will have occupation numbers rather close to two for the whole process one is studying, while others keep low occupation numbers. The restricted Active Space (RAS) SCF method was developed to handle such cases [15, 24]. Here, the active space is partitioned into three subspaces: RAS1, RAS2, and RAS3 with the following properties:

- RAS1 is in principle doubly occupied, but one or more electrons may be excited into any of the other orbital subspaces. It thus has a maximum number of holes.
- RAS2 has the same properties as the active space in CASSCF, thus all possible occupations are allowed.
- RAS3 is in principle empty but one or more electrons may be excited into these orbitals. It is thus defined by a maximum number of electrons.

With this recipe we can construct a number of different types of MCSCF wave functions. With an empty RAS2 space we obtain SDT...-CI wave functions depending how many holes we allow in RAS1 and how many electrons we allow in RAS3. If we add a RAS2 space and allow up to two holes in RAS1 and max two electron sin RAS3 we obtain what has traditionally been called the second order CI wave function. Many other choices are possible. Since we have reduced the CI space, we can use more active orbitals distributed over the three subspaces. Recent application have used more than 30 active orbitals. The RASSCF method has so far not be extensively used because there is no obvious way to treat dynamic correlation effects unless one can use the MRCI method. However, ongoing work attempts to extend the CASPT2 method (see below) to RASPT2, which may make the RASSCF method more useful in future applications (P.-Å. Malmqvist, unpublished work).

5.2.3. The RASSCF State Interaction Method (RASSI)

Assume that we have computed CASSCF wave function for two different electronic states. Now we want to compute transition properties, for example, the transition dipole moment. How can we do that. The two states will in general be described by two non-orthonormal sets of MOs, so the normal Slater rules cannot be applied. Let us start by considering the case where two electronic states μ and ν are described by the same set of MOs. The transition matrix element for a one-electron operator \hat{A} is then given by the simple expression:

$$\langle \mu | \hat{A} | \nu \rangle = \sum_{p,q} D_{pq}^{\mu\nu} A_{pq}, \quad (5-9)$$

where A_{pq} are the matrix elements of the one-electron operator and $D_{pq}^{\mu\nu}$ the transition density matrix elements, which we can easily compute from the two sets of CI-coefficients and the one-electron coupling coefficients. But what happens if the two states are represented by two different MO bases, which are then in general not orthonormal? 25 years ago this was considered to be a difficult problem. One could use the Slater-Löwdin rules to compute the matrix element 5-9 [5] but such a calculation involved the cumbersome calculation of determinants of overlap integrals between the two sets of MOs. A surprisingly simple solution to the problem was presented by P.-Å. Malmqvist in 1986 [16, 17]. He showed that if one makes a non-unitary transformation of the two sets of MOs such that they become bi-orthonormal, the simple formula 5-9 becomes again valid. He also showed how one can simultaneously transform the two RASSCF wave functions to the new MO basis by a series of one-electron transformations. The method cannot be applied to general MCSCF wave functions but to all functions that are closed under de-excitation (meaning that no states outside the original CI space are generated). The CASSCF and RASSCF wave functions belong to this category.

The RASSI method can be used to compute first and second order transition densities and can thus also be used to set up an Hamiltonian in a basis of RASSCF wave function with separately optimized MOs. Such calculations have, for example, been found to be useful in studies of electron-transfer reactions where solutions in a localized basis are preferred [43]. The approach has recently been extended to also include matrix elements of a spin-orbit Hamiltonian. A number of RASSCF wave functions are used as a basis set to construct the spin-orbit Hamiltonian, which is then diagonalized [19, 44].

5.2.4. RASSCF and the Excited State

The CAS(RAS)SCF method is one of the best methods to study excited states and photochemical processes because it can in a balanced way treat closed and open shell electronic states of varying complexity and also of different spin, which is necessary in studies of intersystem crossing. However, calculations on excited states is often more complicated than those for a well defined ground state. Preferably,

one would like to treat each excited separately, producing its own set of optimized orbitals but this is most often not possible. The energy spectrum may be dense and states of the same energy might be close in energy, which often leads to convergence problems in the CASSCF calculations. Even more serious is that the wave functions for the different electronic states are not orthogonal to each other. This may not be serious if the overlap integral is small but that cannot be assured and may also vary for different points on an energy surface.

Most applications in spectroscopy and photochemistry has therefore used a simplified approach. A *state average* calculation is performed where the same set of MOs is used for a number of electronic states of the same spin and symmetry. Thus, the CI problem is solved for a number of roots (say M) and the orbitals are optimized for the average energy, E_{aver} of these states:

$$E_{aver} = \sum_{I=1}^M \omega_I E_I, \quad (5-10)$$

where w_I are weight factors, which can be chosen. Normally, they are set to be equal, but other choices are possible if one is interested specifically in a given electronic state. The average energy can be written as

$$E_{aver} = \sum_{p,q} D_{pq}^{aver} h_{pq} + \sum_{p,q,r,s} P_{pqrs}^{aver}(pq|rs), \quad (5-11)$$

where the density matrices in Equation 5-4 have been replaced by average values. The modifications of the code that are needed for such calculations are thus trivial.

State average orbitals are not optimized for a specific electronic state. Normally, this is not a problem and a subsequent CASPT2 calculation will correct for most of it because the first order wave function contains CFs that are singly excited with respect to the CASSCF reference function. However, if the MOs in the different excited states are very different it may be needed to extend the active space such that it can describe the differences. A typical example is the double shell effect that appears for the late first row transition metals as described above.

5.3. MULTICONFIGURATIONAL SECOND ORDER PERTURBATION THEORY — CASPT2

We have above discussed the CASSCF method and how we can choose the active space. We noted that this choice was closely connected to the method we use to compute the effects of dynamic correlation, in this case the CASPT2 method. The development of this approach was inspired by the success of the Møller-Plesset second order perturbation theory (MP2), which has been used for a long time to treat electron correlation for ground states, where the reference function is a single determinant. It was assumed that such an approach would be even more effective with the more accurate CASSCF reference function. A first attempt was made soon

after the introduction of the CASSCF method [23], but it was not until all technical problems were solved in the late 80s that an effective code could be written [3, 4].

It is in principle simple to define a CASPT2 procedure. We first have to define the interacting space of electronic configurations. They turn out to be formally the same excited states as in MP2:

$$\hat{E}_{pq}\hat{E}_{rs}|CASSCF\rangle, \quad (5-12)$$

where \hat{E}_{pq} , etc. are single excitation operators. This space contains all singly and doubly excited states with respect to the CASSCF wave function. Notice that they are not single configurations but linear combinations with coefficients determined by the CASSCF multiconfigurational wave function. The orbital indices must contain at least one in the inactive or in the virtual space. Configurations with all indices active belong to the CAS-CI space and do not interact with the CASSCF reference function.

The next step is to determine the zeroth order Hamiltonian. In MP2 it is simply obtained from the eigenvalues, ε_p of the HF operator:

$$\hat{H}_0 = \sum_p \varepsilon_p \hat{E}_{pp} \quad (5-13)$$

The success of the MP2 method for closed shell HF reference functions makes it interesting to try to develop a Hamiltonian that has the MP2 case as the limit when there are no active orbitals. For this purpose a *generalized Fock operator* was defined:

$$\hat{F} = \sum_{p,q} f_{pq} \hat{E}_{pq}, \quad (5-14)$$

with

$$f_{pq} = h_{pq} + \sum_{r,s} D_{rs} [(pq|rs) - \frac{1}{2}(pr|qs)]. \quad (5-15)$$

It has the property that $f_{pp} = -IP_p$ when the orbital p is doubly occupied and $f_{pp} = -EA_p$ when the orbital is empty (IP = Ionization potential and EA = electron affinity). The value will be somewhere between these two extremes for active orbitals. Thus, we have for orbitals with occupation number one: $f_{pp} = -\frac{1}{2}(IP_p + EA_p)$. This formulation is somewhat unbalanced and will favor systems with open shells, leading for example to somewhat low binding energies [45]. The energy of an orbital excited out of, should be close to the IP of that orbital. With this formulation it is too high. In the same spirit we want the energy of an orbital that is excited into to be EA like, so it is too low. This results in too low energies for open shell states resulting in too low excitation energies and dissociation energies or other relative energies where the process goes from a closed shell like state to an open shell. There is, however, a possibility to correct for this misbehavior of the zeroth order Hamiltonian:

5.3.1. A Modified Zeroth Order Hamiltonian

The systematic error caused by the definition of the zeroth order Hamiltonian, as described above, leads to too low relative energies for systems with open shells. A consequence is that dissociation and excitation energies will be too low because the dissociated or excited state has usually more open shell character than the reference state. Is there a way we can remedy this systematic error? The diagonal elements of the generalized Fock operator can for an active orbitals be estimated as:

$$F_{pp} = -\frac{1}{2} (D_{pp}IP_p + (2 - D_{pp})EA_p). \quad (5-16)$$

This formula is correct for $D_{pp} = 0$ and 2 and also for a singly occupied open shell. Thus, for an open shell ($D_{pp} = 1$) we obtain:

$$F_{pp} = -\frac{1}{2} (IP_p + EA_p). \quad (5-17)$$

If we excite out of this orbital or into it, does not matter. The energy is in either case given by Eq. (5-17). We would like the energy to be $-IP_p$ when we excite out of it and $-EA_p$ when we excite into it. Thus, we would like to introduce a shift σ_p^{EA} that replaces 5-17 with $-EA_p$ when we excite into this orbital. That shift is given by;

$$\sigma_p^{EA} = \frac{1}{2} D_{pp} (IP_p - EA_p). \quad (5-18)$$

Similarly when we excite out of the orbital we want the shift to be:

$$\sigma_p^{IP} = -\frac{1}{2} (2 - D_{pp}) (IP_p - EA_p). \quad (5-19)$$

The problem is that we cannot easily compute the ionization energy and the electron affinity. In a recent work we therefore suggested to use a simple parametrized version of the shift where $IP_p - EA_p$ is replaced with an average shift parameter ϵ [46]:

$$\begin{aligned} \sigma_p^{EA} &= \frac{1}{2} D_{pp} \epsilon \\ \sigma_p^{IP} &= -\frac{1}{2} (2 - D_{pp}) \epsilon, \end{aligned} \quad (5-20)$$

where ϵ will be determined by comparison to accurate experimental results. The parameter ϵ is an average value for $(IP_p - EA_p)$. To obtain a feeling for how this quantity varies we show it in Figure 5-2 for all atoms in the periodic table.

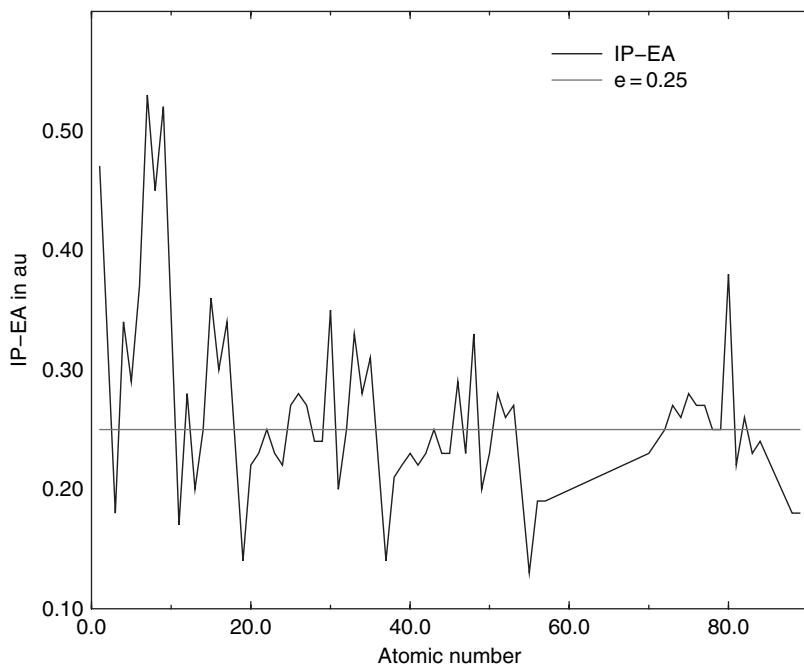


Figure 5-2. The quantity $(IP_p - EA_p)$ for all atoms of the periodic table. The horizontal line corresponds to $\epsilon = 0.25$

Inspection of Figure 5-2 shows that if we insist on a constant value for ϵ it should lie somewhere between 0.2 and 0.3. The precise value is actually not terribly important because the results vary only slowly for moderate changes of it. A large number of test calculations were performed where the dissociation energies for diatomic molecules were computed, IPs for transition metal atoms and the electronic spectrum of benzene [46]. Improvements of the results were obtained in almost all cases. For example, the RMS error in the dissociation energies for 49 diatomic molecules were reduced from 0.224 eV ($\epsilon = 0$) to 0.096, 0.090, and 0.098 eV for $\epsilon = 0.20, 0.25,$ and 0.30 , respectively. The effect on other molecular properties were negligible within this parameter range. Based on this experience it was decided to use $\epsilon = 0.25$. This value also gave improved results for the ionization energies of first row transition metal atoms and for the electronic spectrum of benzene. We refer to Ref.[46] for details. Later experience has shown that this modified zeroth order Hamiltonian works well in a wide variety of applications and it is today the default choice in the MOLCAS program. ϵ should not be used as an empirical parameters to improve the results of a specific applications. If large errors are found, they most likely have other sources, the most common one being an inadequate choice of the active orbital space.

5.3.2. Intruder States in CASPT2

The second order energy in Møller-Plesset perturbation theory (MP2) can be written as:

$$E_2 = \sum_{i,j,a,b} \frac{\langle \Psi_0 | \hat{H} | \Psi_{ijab} \rangle^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}, \quad (5-21)$$

where Ψ_0 is the Hartree-Fock reference function, Ψ_{ijab} a doubly excited states and the ϵ are orbital energies for the occupied orbitals i, j and the virtual orbitals a, b , respectively. The method works well when there is an appreciable HOMO-LUMO energy gap such that the denominators in Eq. (5-21) are always positive and large. This is not always the case in CASPT2 calculations. Active orbitals with large occupation numbers can have energies close to the inactive orbitals, while those with small occupation numbers can have energies close to the virtual orbitals. As a result, it may happen that the denominator in the energy expression becomes small, or even negative. We call this an intruder state. One can see three different cases:

1. The interaction between this state and the CASSCF reference function is zero or very small. The effect on the second order energy will then be negligible, unless the denominator is very close to zero.
2. The interaction is large, say larger than 0.01 au. This is the most serious type of intruder states and the only sound way to remove it is to add the orbital that causes the intruder state to the active space.
3. In the case of an intruder state of intermediate strength, one can in many cases remove them by a level shift technique that will be described below. But also in this case is it better if one can extend the active space such that the intruder states disappear.

One way to remove the intruder state is to use a level shift technique [47]. A level shift, ϵ , is added to the zeroth order Hamiltonian, such that the first order equation becomes:

$$\begin{aligned} (\hat{H}_0 - E_0 + \epsilon) \tilde{\Psi}_1 &= -(\hat{H}_1 - E_1) \Psi_0 \\ \hat{H}_0 \Phi_\mu &= \epsilon \Phi_0 \\ \tilde{\Psi}_1 &= \sum_{\mu} \tilde{C}_\mu \Phi_\mu, \end{aligned} \quad (5-22)$$

where the tilde denotes quantities obtained with the level shift. For simplicity, we have in the above equations assumed the the first order interacting space, Φ_μ to be diagonal in \hat{H}_0 . Solving these equations, we obtain:

$$\begin{aligned} \tilde{C}_\mu &= - \frac{\langle \Phi_\mu | \hat{H}_1 | \Psi_0 \rangle}{\epsilon_\mu - E_0 + \epsilon} \\ \tilde{E}_2 &= - \sum_{\mu} \frac{|\langle \Phi_\mu | \hat{H}_1 | \Psi_0 \rangle|^2}{\epsilon_\mu - E_0 + \epsilon} \end{aligned} \quad (5-23)$$

The level shift will remove the intruder states, but the problem is that the result will depend on the level shift and that is not acceptable. However, it is possible to remove this ambiguity by a back transformation of the second order energy to the unshifted value with the intruder states removed. We can write the second order energy as:

$$\tilde{E}_2 = E_2 + \varepsilon \sum_{\mu} |\tilde{C}_{\mu}|^2 \left(1 + \frac{\varepsilon}{\epsilon_{\mu} - E_0} \right), \quad (5-24)$$

where E_2 is the second order energy without a level shift. If we now assume that the denominators in the above expression are large, we can approximately obtain E_2 as:

$$E_2 \approx \tilde{E}_2 - \varepsilon \left(\frac{1}{\tilde{\omega}} - 1 \right) = E_2^{LS}, \quad (5-25)$$

where $\tilde{\omega}$ is the weight of the CASSCF reference function in the level shifted CASPT2 calculation. E_2^{LS} is thus to first order in ε the same as the unshifted energy. It will differ from E_2 only if there are intruder states, which makes $\epsilon_{\mu} - E_0$ small. A number of test calculations have been performed, which shows that the results are very little affected by the level shift if there are no intruder states. For example, the dissociation energy for the N_2 molecule varies only with 0.07 eV for level shifts in the range 0.0–0.5. For more details, we refer to the original article [47] and an article, where the approach was tested in a number of different applications [48]. Finally, it should be noted that level shifts should only be used when needed to remove weak intruder states. Strong intruders should be removed by extending the active space. The level shift value should preferably not be larger than about 0.3 and one should carefully check the weight of the CASSCF reference function to see that it remains constant as a function of the parameters of the calculation, for example, the geometry.

An alternative is to use an imaginary level shift as suggested by Forsberg and Malmqvist [49]. It removes effectively the intruder states with very little effect on the properties of the system. Level shifts of the order 0.0–0.2 are recommended. We refer to the paper for further details [49].

5.3.3. The Multi-state CASPT2 Method

The first order CASPT2 wave function is internally contracted, meaning that it consists of a CASSCF wave function plus a linear combination of the states comprising the first order interacting space. The reference CASSCF wave function is thus fixed and the coefficients building it cannot vary. This is normally a good approximation as long as the different solutions to the CASSCF Hamiltonian are well separated in energy. However, situations occur where this is no longer true. Different CASSCF wave function of the same symmetry can sometimes be close in energy. This happens, for example, in the neighborhood of conical intersections

and in cases of valence-Rydberg mixing of excited states. For more elusive systems it may even happen for ground states as a recent study of the CrH molecule has illustrated [50]. In such cases a single state CASSCF/CASPT2 calculation will not be meaningful. A multistate variant of the CASPT2 method, MS-CASPT2, has been developed to deal with these situations [51].

The idea is quite simple: Assume that N CASPT2 calculations have been performed starting from a set of CASSCF reference functions, $\Phi_i, i = 1, N$, obtained with a set of state averaged orbitals. The first order (CASPT2) wave functions are denoted: $\chi_i, i = 1, N$. Let the N function $\Psi_i = \Phi_i + \chi_i$ form the basis for a pseudo-variational calculation, where all third order terms appearing in the Hamiltonian matrix will be neglected.

The overlap integrals between the basis functions are:

$$\langle \Phi_i | \Phi_j \rangle = \delta_{ij} \tag{5-26}$$

$$\langle \Phi_i | \chi_j \rangle = 0 \tag{5-27}$$

$$\langle \chi_i | \chi_j \rangle = s_{ij}, \tag{5-28}$$

which gives:

$$S_{ij} = \langle \Psi_i | \Psi_j \rangle = \delta_{ij} + s_{ij}. \tag{5-29}$$

The following Hamiltonian matrix elements are also known:

$$\langle \Phi_i | \hat{H} | \Phi_j \rangle = \delta_{ij} E_i \tag{5-30}$$

$$\langle \Phi_i | \hat{H} | \chi_j \rangle = \epsilon_{ij}, \tag{5-31}$$

where E_i is the CASSCF energy for state i and the diagonal elements ϵ_{ii} are the CASPT2 correlation energies.

It remains to compute the matrix elements: $\langle \chi_i | \hat{H} | \chi_j \rangle$. To do that we partition the Hamiltonian into the zeroth order plus the first order contribution. This partitioning is state dependent:

$$\hat{H} = \hat{H}_{0i} + V_i. \tag{5-32}$$

The second term will be neglected in the matrix element, since it corresponds to a third order contribution to the energy. We thus have:

$$\langle \chi_i | \hat{H} | \chi_j \rangle \approx \langle \chi_i | \hat{H}_{0i} | \chi_j \rangle \approx \langle \chi_i | \hat{H}_{0j} | \chi_j \rangle. \tag{5-33}$$

We can now use the first order equations for states i and j to express the matrix elements in already known quantities:

$$\begin{aligned} \langle \chi_i | \hat{H}_{0i} | \chi_j \rangle &= E_{0i} s_{ij} - \epsilon_{ij} \\ \langle \chi_i | \hat{H}_{0j} | \chi_j \rangle &= E_{0j} s_{ij} - \epsilon_{ji}, \end{aligned} \tag{5-34}$$

where E_{0i} is the zeroth order energy for state i : $E_{0i} = \langle \Phi_i | \hat{H}_{0i} | \Phi_i \rangle$. The consistency of the approximation can be checked by comparing the two expressions. In practice the average value is used:

$$\langle \chi_i | \hat{H} | \chi_j \rangle = \frac{1}{2} (\langle \chi_i | \hat{H}_{0i} | \chi_j \rangle + \langle \chi_i | \hat{H}_{0j} | \chi_j \rangle). \quad (5-35)$$

Adding the contributions together we obtain the Hamiltonian matrix in the basis Ψ_i :

$$H_{ij} = \langle \Psi_i | \hat{H} | \Psi_j \rangle = \delta_{ij} E_i + \frac{1}{2} (E_{0i} + E_{0j}) s_{ij} + \frac{1}{2} (\epsilon_{ij} + \epsilon_{ji}). \quad (5-36)$$

The matrix element contains terms of zeroth, first and second order only. The corresponding secular equation is:

$$(\mathbf{H} - E\mathbf{S})\mathbf{C} = 0. \quad (5-37)$$

Introduce a new vector $\mathbf{C}' = \mathbf{S}^{1/2}\mathbf{C}$. The transformed secular equation takes the form:

$$(\mathbf{H}' - E\mathbf{1})\mathbf{C}' = 0, \quad (5-38)$$

where $\mathbf{H}' = \mathbf{S}^{-1/2}\mathbf{HS}^{-1/2}$. Truncation of this Hamiltonian to second order gives:

$$H'_{ij} = \delta_{ij} E_i + \frac{1}{2} (\epsilon_{ij} + \epsilon_{ji}). \quad (5-39)$$

The crucial approximation made above is the use of an average matrix element as in 5-35. If the two matrix elements 5-31 are not equal to a good approximation, the method will not work well. This is often a matter of choosing the active space. When the same set of orbitals is used for a number of electronic states it is vital that the active space is large enough to cover the differences that may occur between the electronic structures of the different states. Merchán and Serrano-Andrés have analyzed this situation for the case of a conical intersection and shown that more extended active spaces are needed [52].

The MS-CASPT2 method should be used when it is suspected that several CASSCF states are close in energy, a situation that often obtains in photochemistry where close avoided crossings are common and even conical intersections. It may also be crucial in order to separate valence and Rydberg excited states as illustrated in the original publication for the case of ethylene. Another example was given by Merchán and Serrano-Andrés in a study of the excited states of n-tetrasilane [52].

5.4. APPLICATIONS OF THE CASSCF/CASPT2 METHOD

With the development of the CASPT2 method in 1990 it became possible to apply the combined CASSCF/CASPT2 approach to a variety of quantum chemical problems. The early studies of the Ni atom pointed to the difficulties in the choice of the active space for transition metal systems but also to the potential accuracy that could be obtained for such systems if the active space could be properly chosen. The 10in10 active space was used in an early study of the $M(\text{CO})_x$ compounds ($M=\text{Cr}$, Fe , Ni) [53] and Ferrocene [54]. The latter study showed that the CASPT2 method was able to describe the structure properly in contrast to earlier studies using MP2. Another important early application was the study of the electronic structure and the spectroscopy of the blue copper proteins, in particular plastocyanin [55–58]. These studies illustrated how the present theoretical approach could be used for studies of transition metal complexes of biological significance. However, applications in transition metal chemistry are sometimes difficult or even impossible. One such case is systems with the metal in a very high oxidation state as illustrated for example by the permanganate ion where the metal ion is formally in oxidation state VII. In such cases the metal ligand bonds become very covalent and involve all ligand orbitals putting very heavy demands on the active space. K. Pierloot has analyzed several such cases [33, 34]. If the system contains more than one transition metal, the calculations can become virtually impossible if the process studied involves a change of the occupation of the $3d$ shells such that the double shell effect has to be taken into account. A recent example is a study of model complexes of the enzyme tyrosinase, which contains a bridged Cu_2O_2 complex as the central unit [59]. The CASPT2 method is unable to predict a reasonable value of the energy of a side on peroxide structure relative to that of a bis(μ -oxo) structure. The change is accompanied by a change of the oxidation state of the copper ions and to describe that by the CASPT2 method one has to include the double shell effect, which leads to an excessively large active space. If on the other hand there is no change of the oxidation state of the metal, the CASSCF/CASPT2 method is able to produce accurate results as has been shown in a number of applications to complexes involving a transition metal dimer as a central unit. Examples are diatoms like Cr_2 , Mo_2 and W_2 [60] and larger complexes like PhCrCrPh [61]. More examples from transition metal chemistry can be found in Ref. [31].

More recently, the CASSCF/CASPT2 method with spin-orbit coupling has been applied to a number of problems in actinide chemistry. Some recent examples are: the electronic spectrum of UO_2 [38], the electronic structure of PhUUPh [62], the diactinides Ac_2 , Th_2 , Pa_2 , and U_2 [36, 37], etc. Some of this work has recently been reviewed [63].

Another early application of the CASSCF/CASPT2 method was to the electronic spectrum of the benzene molecule [64]. The spectrum of this molecule was very well described by the semi-empirical methods of the 50s and 60s. Actually a first semi-quantitative analysis was performed as early as 1938 by Goepfert-Mayer and Sklar [65]. It turned out to be very difficult to reproduce these results with the *ab initio* methods that were developed in the 60s and 70s. The CASPT2 calculations

were made with the first version of the code with the original definition of the zeroth order Hamiltonian, no level-shift and no multi-state possibilities. Still the results were quite promising and it might be interesting to take a look at them in retrospect. They are presented in Table 5-4.

Two sets of calculations were performed. One used the natural selection of the active space: the six π orbitals. The results are presented in the first column of Table 5-4. As we can see, all values are smaller than experiment. This is particularly true for the ${}^1E_{1u}$ state, which also had a small CASSCF reference weight. The reason was an interaction with a nearby Rydberg state of the same symmetry. Today we know that the too low excitation energies are due to the systematic error of the zeroth order Hamiltonian and we know how to correct for it. In 1992 another more crude solution was attempted: to double the active space, thus moving important correlation effects to the variational space and diminishing the systematic error. This was partly successful and the results are now fortuitously good. These are vertical excitation energies and we expect them to be about 0.1 eV higher than the experimental values for the band maxima. The real error of, for example, the ${}^1B_{2u}$ state is thus about 0.3 eV. Using the IPEA shifted Hamiltonian one obtains instead 5.02 eV, which is very close to the real vertical excitation energy [46]. A detailed discussion of the vibrational progressions in the two first bands of the benzene spectrum can be found in Ref. [66] which also shows the location of the vertical energies with respect to the band maxima.

The results obtained for the electronic spectrum of benzene triggered a large number of applications to unsaturated organic molecules. Several hundreds of systems were studied. A number of reviews have been written on the subject, which the reader is referred to [29–31, 67]. The accuracy of these calculations are usually about 0.2 eV for vertical excitation energies. Also transition intensities, which are computed at the CASSCF level of theory, are in general in good agreement with experiment, which is quite helpful for the assignment of the experimental spectra.

Today, the emphasis has shifted from pure electronic spectroscopy to photochemistry, for which the CASSCF/CASPT2 method is ideally suited. When one moves on an excited state surface through a photochemical reaction, the nature of the wave function changes drastically. In the Franck-Condon region it may represent an excited valence or even Rydberg state while in the transition state region it is typically characterized by an avoided crossing, an intersystem crossing, or a conical intersection where its nature is strongly multiconfigurational. Several

Table 5-4. The electronic spectrum of benzene computed in 1992

Active space	6in6	6in12	Expt.
${}^1B_{2u}$	4.58	4.70	4.90
${}^1B_{1u}$	5.89	6.10	6.20
${}^1E_{1u}(V)$	6.52	7.06	6.94
${}^1E_{1u}(R)$	–	7.67	7.59
${}^1E_{2g}$	7.68	7.77	7.80

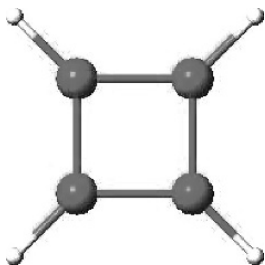


Figure 5-3. The planar quadratic transition state of cyclobutadiene

energy surfaces may be close in energy and affect the outcome of the reaction (see for example Ref. [68]). That work that concerned the photodissociation of 1,2-dioxoethane, a model compound for the bio-luminescent molecule luciferine, showed that energy surfaces have to be computed at the CASPT2 level of theory. It is not enough, as is often seen, to compute them at the CASSCF level and then just compute CASPT2 energies at the crucial points on the surface (intersystem crossings, conical intersections, etc.). It is clear that single configurational quantum chemical methods cannot in general handle problems in photochemistry. The area has recently been reviewed [69] and a number of further examples will be given in other chapters of this volume.

We shall finish with a small example that illustrates the difference between the multiconfigurational wave function approach described in this chapter and the commonly used density functional (DFT) theory. It concerns the quadratic cyclobutadiene system, which is a transition state between the two equivalent rectangular forms of the molecule (cf. Fig. 5-3).

The system is anti-aromatic with 4 π electrons in 4 orbitals. The symmetry is D_{4h} and the orbitals belong to the following irreps (in energy order): a_{1u} , e_g , and b_{2u} . The first orbital is doubly occupied and the remaining two electrons are distributed among the two components of the e_g orbital. This gives rise to the four electronic states presented in Table 5-5, where we have given the symmetry labels also for the D_{2h} subgroup in which all calculations are performed.

The question is: what is the ground state of this system. Intuitively one would guess ${}^3A_{2g}$ according to Hund's rule. If we perform a CASSCF/CASPT2 calculation

Table 5-5. The electronic states with the configuration $(a_{1u})^2(e_g)^2$ in quadratic cyclobutadiene

$D_{4h}(D_{2h})$	electronic configuration
${}^3A_{2g}({}^3B_{1g})$	$(e_{gx}e_{gy})T$
${}^1B_{2g}({}^1B_{1g})$	$(e_{gx}e_{gy})S$
${}^1B_{1g}({}^1A_g)$	$(e_{gx})^2 - (e_{gy})^2$
${}^1A_{1g}({}^1A_g)$	$(e_{gx})^2 + (e_{gy})^2$

with the four π orbitals active and a TZP quality basis set, we obtain, however, a different result as presented in Table 5-6.*

The ground state is $^1B_{1g}$. The reason is a strong interaction with the configuration $(a_{1u})(b_{2u})$, which forms a singlet state of the same symmetry. This state will actually contribute 7% to the CASSCF wave function.

Corresponding DFT(B3LYP) results obtained with the same basis set are also presented in the table. They are completely different. The triplet state is the ground state with the first singlet state 0.86 eV higher in energy. The reason for this failure is the multideterminantal nature of the wave functions. The wave function associated with a DFT calculation is assumed to be a single determinant. This works well only for the triplet state. Let us assume that the energy for this state is written as $E_0 - K$, where K is the exchange integral $(e_{gx}e_{gy}|e_{gx}e_{gy})$. The corresponding singlet state, $^1B_{2g}$, is in DFT described by the determinant $|e_{gx}\alpha, e_{gy}\beta|$, which is only half of the singlet wave function and gives the energy E_0 , if we assume that the orbitals in the two states are the same. The computed energy difference between the two determinants is then K and from the results in Table 5-6 we obtain the value 0.65 eV for this parameter. The true energy of the singlet state is $E_0 + K$ and we can compute it from the knowledge of K . It is given in the last column of the table. The same exercise can be performed for the $^1B_{1g}$ and $^1A_{1g}$ states. They have the energies $E_1 - K$ and $E_1 + K$, respectively, while DFT computes the energy E_1 for both of them. If we use the same value of the exchange integral, we obtain the other two energies in the last column of the table. We can see some improvement in the results but the difference from the CASPT2 result is still as large as 0.69 eV for the $^1B_{2g}$ state and DFT still predicts a triplet ground state.

One notices that the multideterminantal nature of the wave functions occurs in three different ways in this little example: The open shell singlet state needs two determinants to be properly described, the $^1B_{1g}$ and $^1A_{1g}$ contains two determinants that differ by two spin-orbitals, and finally there is a strong mixing of a second $^1B_{1g}$ state in the ground state wave function. One might argue that this is a very special case, but it is not. It is actually a situation that commonly occurs in photochemical reactions. Near a transition state or a conical intersection there will be strong

Table 5-6. Energies of the lower excited states in quadratic cyclobutadiene

$D_{4h}(D_{2h})$	CASPT2	DFT	Corrected DFT
$^1B_{1g}(^1A_g)$	0.00	0.00	0.00
$^3A_{2g}(^3B_{1g})$	0.18	-0.86	-0.21
$^1A_{1g}(^1A_g)$	1.38	0.00	1.30
$^1B_{2g}(^1B_{1g})$	1.78	-0.21	1.09

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interaction between two or more configurations with wave functions that differ in two spin-orbitals, like the ${}^1B_{1g}$ and ${}^1A_{1g}$ states here. Mixing in of other configurations with a sizable weight also frequently happens. Time dependent DFT is sometimes used to study photochemical processes but will run into problems when important configurations differ from the ground state (closed shell) determinant with two or more spin-orbitals. A semi-empirical method that corrects for these deficiencies to some extent is the DFT-MRCI approach of S. Grimme and co-workers [70].

5.5. SUMMARY AND CONCLUSIONS

We have in this chapter given a brief review of the multiconfigurational CASSCF and CASPT2 methods. The emphasis has been on the methods, its advantages and limitations in different areas of applications, more than the applications themselves. They are described in other chapters of the book.

The CASSCF/CASPT2 method has been designed to deal with quantum chemical situations, where the electronic structure is complex and not well described, even qualitatively, by single configurational methods. The method relies on the possibility to choose an active space of orbitals that can be used to construct a full CI wave function that describes the system qualitatively correct. When this is possible, the method is capable of describing complex electronic structures quite accurately. Examples of such situations are found in excited states, in particular photochemical reactions that is the subject of this book, but also in transition metal, and actinide chemistry.

The most severe limitation of the approach is the active space. A number of applications would need an active space that goes beyond what is today possible. This is maybe most evident in transition metal and actinide chemistry as was exemplified earlier in this chapter. Such extensions of the active almost always involves orbitals with occupation numbers either close to two or zero. As described above, the RASSCF method is quite useful in handling such situations because it can deal with much larger active spaces than CASSCF. It is therefore interesting to notice the ongoing development of a RASPT2 method that will deal with the dynamic correlation effects for a RASSCF reference function (P.-Å. Malmqvist, unpublished work). Another development, which is important for the possibility to apply the approach to larger molecules is the Cholesky decomposition technique that has recently been implemented in the MOLCAS software (F. Aquilante et al., unpublished work). The method concentrates the list of two-electron integrals by performing a Cholesky decomposition and storing only the non-redundant Cholesky vectors. This leads to a considerable saving of space and time thus extending the size of the systems that can be studied. The method has been implemented with a variety of wave function based (and DFT) methods, among them RASSCF and CASPT2. In the near future it will therefore be possible to perform such calculations with several thousand basis functions. With these perspectives it is hoped that the CASSCF/CASPT2 (RASSCF/RASPT2) method will continue to be a viable tool for quantum chemical studies of systems with a non-trivial electronic structure.

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