THE COMPLETE ACTIVE SPACE SELF-CONSISTENT FIELD METHOD AND ITS APPLICATIONS IN ELECTRONIC STRUCTURE CALCULATIONS

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I. INTRODUCTION

Modern applications of the electronic structure theory for molecular systems based are almost entirely upon the molecular-orbital (MO) concept, introduced in molecular spectroscopy by Mulliken[1]. This is not surprising. The success of the Hartree–Fock method[2,3], in describing the electronic structure of most closed-shell molecules has made it natural to analyse the

wavefunction in terms of the molecular orbitals. The concept is simple and has a close relation to experiment through Koopmans' theorem[4]. The two fundamental building blocks of Hartree–Fock (HF) theory are the molecular orbital and its occupation number. In closed-shell systems each occupied molecular orbital carries two electrons, each with opposite spin. The orbitals themselves are only defined as an occupied one-electron subspace of the space spanned by the eigenfunctions of the Fock operator. Transformations between them leave the total HF wavefunction invariant. Normally the orbitals are obtained in a delocalized form as solutions to the Hartree–Fock equations. This formulation is the most relevant one in studies of spectroscopic properties of the molecule, that is, excitation and ionization. The invariance property, however, makes a transformation to localized orbitals possible. Such localized orbitals can be of value for an analysis of the chemical bonds in the system.

The Hartree–Fock method can be extended to open-shell systems in two ways. In the restricted Hartree–Fock (RHF) method[5], the open-shell orbitals are added to the closed-shell orbitals and the resulting wavefunction is then projected to have the correct spin and space symmetry. In some cases this leads to a wavefunction comprising more than one Slater determinant. An alternative formulation is the unrestricted Hartree–Fock (UHF) method[6], where the spin orbitals for a closed-shell electron pair are no longer assumed to be equal. As a result the method is capable of describing the spin polarization of paired electrons in the presence of unpaired spins. The method has for this reason been used extensively in studies of the spin polarization of radicals. In contrast to the closed-shell Hartree–Fock method the UHF method also gives a qualitatively correct description of bond dissociation[7]. The serious drawback of the UHF method is, however, that it cannot easily be projected to give a wavefunction which is an eigenfunction of the total spin. If such a projection is attempted *a priori* to a variational treatment, very complex equations for the molecular orbitals are obtained. The simplicity of the Hartree–Fock method is lost and the gain in accuracy is not large enough to make such an approach useful in practical applications.

All variants of the Hartree–Fock method lead to a wavefunction in which all the information about the electron structure is contained in the occupied molecular orbitals (or spin orbitals) and their occupation numbers, the latter being equal to 1 or 2.

The concept of the molecular orbital is, however, not restricted to the Hartree–Fock model. A set of orbitals can also be constructed for more complex wavefunctions, which include correlation effects. They can be used to obtain insight into the detailed features of the electronic structure. These are the natural orbitals, which are obtained by diagonalizing the spinless first-order reduced density matrix[8]. The occupation numbers (η) of the natural orbitals are not restricted to 2, 1 or 0. Instead they fulfil the condition

$$0 < \eta < 2 \qquad (1)$$

If the Hartree–Fock determinant dominates the wavefunction, some of the occupation numbers will be close to 2. The corresponding MOs are closely related to the canonical Hartree–Fock orbitals. The remaining natural orbitals have small occupation numbers. They can be analysed in terms of different types of correlation effects in the molecule[9,10]. A relation between the first-order density matrix and correlation effects is not immediately justified, however. Correlation effects are determined from the properties of the second-order reduced density matrix. The most important terms in the second-order matrix can, however, be approximately defined from the occupation numbers of the natural orbitals. Electron correlation can be qualitatively understood using an independent electron-pair model[11]. In such a model the correlation effects are treated for one pair of electrons at a time, and the problem is reduced to a set of two-electron systems. As has been shown by Löwdin and Shull[9,10] the two-electron wavefunction is determined from the occupation numbers of the natural orbitals. Also the second-order density matrix can then be specified by means of the natural orbitals and their occupation numbers. Consider as an example the following simple two-configurational wavefunction for a two-electron system:

$$\Phi = C_1(\varphi_1)^2 - C_2(\varphi_2)^2 \qquad (C_2 > 0) \qquad (2)$$

where $(\varphi_1)^2$ is the HF wavefunction. The MOs φ_1 and φ_2 are the natural orbitals and have occupation numbers $\eta_1 = 2C_1^2$ and $\eta_2 = 2C_2^2$. The diagonal of the second-order density matrix, $\rho_2(1,2)$, is with real orbitals obtained as

$$\rho_2(1,2) = \tfrac{1}{2}\eta_1 \varphi_1(1)^2 \varphi_1(2)^2 + \tfrac{1}{2}\eta_2 \varphi_2(1)^2 \varphi_2(2)^2$$
$$- (\eta_1\eta_2)^{1/2} \varphi_1(1)\varphi_2(1)\varphi_1(2)\varphi_2(2) \qquad (3)$$

The last term is the one which describes the correlation of the electron pair by the orbital φ_2. If φ_1 is a bonding MO and φ_2 the corresponding antibonding orbital, the last term in (3) ensures that there is one electron on each atom when the bond dissociates. If, as another example, $\varphi_1 = 2s$ and $\varphi_2 = 2p$ in the Be atom, the last term in (3) decreases the probability of finding both electrons on the same side of the nucleus and increases the probability of finding the electrons on opposite sides (angular correlation). This effect is very large in beryllium and accounts for 95% of the correlation energy in the valence shell.

For systems with more than two electrons, the simple picture illustrated above obviously breaks down. The approximate validity of the independent electron-pair model, however, also makes it possible to estimate different correlation effects in many-electron systems from an inspection of the natural-orbital occupation numbers.

The correlation error is normally defined as the difference between the exact eigenvalue of the non-relativistic Hamiltonian for the molecule and the HF energy. While this definition works well for closed-shell systems, it becomes less meaningful when degeneracies, or near-degeneracies, occur

between different electronic configurations. For example, the HF energy for the H_2 molecule at large internuclear distances is in error by more than 7 eV. Obviously, the electrons of two non-interacting hydrogen atoms are not correlated. The reason behind this is, of course, that the Hartree–Fock model breaks down in cases where several configurations become degenerate or near-degenerate. This is the case in most bond dissociation processes, and also along the reaction path for a symmetry-forbidden chemical reaction, to mention just two examples. Thus while the Hartree–Fock model is a valid approximation for most (but not all) molecules around their equilibrium geometry, it cannot in general be used as a qualitatively correct model for energy surfaces.

The complete active space self-consistent field (CASSCF) model[12-14] is an attempt to generalize the HF model to such situations, while trying to keep as much of the conceptual simplicity of the HF approach as possible. Technically, the CASSCF is by necessity a more complex model, since it is based on a multiconfigurational wavefunction. The building blocks are, as in the Hartree–Fock method, the occupied molecular orbitals (the inactive and active orbitals). The number of orbitals is, however, in general larger than $(N + 1)/2$ (N being the number of electrons). The number of electron configurations generated by the orbital space is therefore larger than unity. The total electronic wavefunction is formed as a linear combination of all the configurations, in the N-electron space, that fulfil the given spin and space symmetry requirements. It is 'complete' in the configurational space spanned by the active orbitals. The inactive orbitals are kept doubly occupied in all these configurations; they represent an 'SCF sea' in which the active electrons move. These orbitals then have occupation numbers exactly equal to 2, while the active orbitals have occupation numbers varying between 0 and 2. The choice of the inactive and active orbital subspaces will be discussed in detail later, but it is obvious that the inactive orbitals should be chosen as orbitals which are not expected to contribute to near-degeneracy correlation effects (e.g. core orbitals).

The conceptual simplicity of the CASSCF model lies in the fact that once the inactive and active orbitals are chosen, the wavefunction is completely specified. Such a model also leads to certain simplifications in the computational procedures used to obtain optimal orbitals and configuration-interaction (CI) coefficients, but that is of less importance in the present context. The major technical difficulty inherent to the CASSCF model is the size of the complete CI expansion, N_{CAS}. It is given by the so-called Weyl formula, that is, the dimension of the irreducible representation of the unitary group $U(n)$ associated with n active orbitals, N active electrons and a total spin S[15]:

$$N_{CAS} = \frac{2S + 1}{n + 1}\binom{n + 1}{N/2 - S}\binom{n + 1}{N/2 + S + 1} \tag{4}$$

Obviously N_{CAS} increases strongly as a function of the size n of the active orbital space. In practice this means that there is a rather strict limit on the size of this space. Experience shows that this limit is normally reached for n around 10–12 orbitals, except for case with few active electrons or holes. As shown by the large number of CASSCF calculations performed during the last six years, this limitation does not create any serious problem in most applications. It should be remembered that the CASSCF is an extension of the Hartree–Fock model. As such it is supposed to produce a good zeroth-order approximation to the wavefunction, when near-degeneracies are present. This goal can in most cases be achieved with a few active orbitals. The CASSCF model has not been developed for treating dynamical correlation effects, but to provide a good starting point for such studies. There are, however, cases where more active orbitals are needed than it is possible to handle with the computational methods available. Cr_2 is such a case, where a full valence (3d and 4s active) calculation fails to describe the nature of the bond[16]. Only a weak 4s–4s bond is formed with a bond distance around 2.5 Å. The true bond length is 1.68 Å[17], indicating considerable 3d–3d bonding. In order to account for this bonding, dynamical correlation in the 3d shell must be included in the wavefunction. The 4s,4p near-degeneracy also has to be included. This results in an active orbital space including 3d, 4s, 4p and 4d on both atoms: 12 electrons distributed in 28 orbitals. Such a calculation is impossible. There does not seem to exist today an *ab initio* quantum-chemical method which is capable of a consistent treatment of the Cr–Cr bond, and this molecule therefore represents a major challenge in the development of new computational methods.

It should be pointed out, however, that the size of the CI expansion used in a CASSCF calculation is almost always much larger than those normally used in earlier applications of the multiconfigurational SCF (MCSCF) method[18]. It was only when the graphical unitary group approach (GUGA) for full CI calculations was invented in the years 1975–78[15,19] that an efficient computational procedure for CASSCF calculations could be developed[12-14].

The idea behind the CASSCF model is, of course, not at all new. It was realized very early that full CI calculations in a valence orbital basis would be a valid model for studies of potential curves, e.g. for the diatomic molecules. Such calculations were already being used 20 years ago for qualitative studies of excited-state potential curves[20,21].

The generalized valence bond (GVB) method developed by Gaddard and coworkers[22] does not employ a full CI in the valence shell, but includes only the configurations needed to describe proper dissociation of a chemical bond. As will be demonstrated later, such a wavefunction represents a restricted form of the CASSCF wavefunction, where the active subspace is partitioned into subsets with a fixed number of electrons occupying the orbitals in each subset (acutally the GVB function is further restricted by allowing only specific spin couplings within each subset).

The fully optimized reaction space (FORS) model suggested by Ruedenberg and coworkers[23,24] is equivalent to the CASSCF model in its basis concepts, while differing in the technical implementation. The final wavefunction is expanded in the full list of configurations generated by a set of 'reaction orbitals' (in CASSCF language: active orbitals). Normally the MCSCF orbital optimization is performed in a smaller configuration space, presumably due to limitations inherent to the computational procedure used. It is pointed out that in the cases studied only 5% of the full set of configurations were necessary in determining molecular orbitals which, when used in a full CI calculation, yields an energy less than a millihartree from the fully optimized value[24]. On the other hand it is emphasized that the final full CI calculation is necessary in order to obtain reliable energies for an energy surface for chemical reactions: 'Experience has shown that there exists no justifiable selection of a small number of configurations, such as 5% of the FRS, to represent a system without energy bias' (Ref. 24, p. 74).

It is not clear, however, how valid the notion of optimizing the MOs in a smaller CI basis is in the general case. It involves a selection of the most important configurations in a first step and a subsequent enlargement of the basis in a stepwise procedure, until all important configurations have been included. Even though this might be a straightforward procedure in simple cases (like those illustrated in Ref. 24), it may lead to difficulties in more complex and unknown situations where the primary selection of configurations is not so easy. Examples of such cases will be given later. The possibility for general reductions of the configuration space has not been implemented into the CASSCF programs, since they destroy the simple structure of the model. They are also not necessary. The limitation of the CASSCF method is set by one's ability to do large complete CI calculations. The orbital optimization can always be performed without any serious extra effort (apart from the fact that MCSCF is an interative procedure; thus the CI secular problem has to be solved several times). Recently CASSCF calculations including as many as 178 916 configurations have been performed with full optimization of the orbitals[25].

The CASSCF model and its implementation into efficient computer programs will be discussed in more detail in the following sections. The main emphasis will, however, not be put on the technical problems concerning the search for efficient MCSCF optimization schemes. A comprehensive discussion of these problems has recently been published in this series[26]. The present contribution will instead concentrate around problems concerning the application of the CASSCF method to different chemical problems, ranging from accurate calculations of properties of small molecules to studies of the chemical bond in transition-metal compounds. Nevertheless a discussion on the computational strategies developed to obtain a CASSCF wavefunction is necessary and will be given below. However, the main emphasis will be on the

problems encountered when the CASSCF method is used to solve chemical problems. One section includes a discussion of the choice of active orbitals. In most applications this is not a trivial problem. A number of examples from recent applications will be included in a later section.

II. OPTIMIZATION OF A COMPLETE ACTIVE SPACE SELF-CONSISTENT FIELD WAVEFUNCTION

A CASSCF study starts with the selection of the inactive and active orbital subspaces. This must be done with great care, as will be discussed in detail later. The major problem is to construct a wavefunction which gives a balanced description of near-degeneracy and dynamical correlation effects for the section of the energy surface studied.

Once the orbital space has been given, the total wavefunction is completely specified. What remains is to find the optimal molecular orbitals and CI coefficients, by application of the variation principle. In the last five years we have seen an outstanding development of efficient methods for optimizing the variables of an MCSCF wavefunction. Before 1980 almost all MCSCF optimization schemes in use were of the first-order type based on extensions of the Hartree–Fock iterative method[18,27], or on the so-called 'super-CI' method developed originally by Grein and coworkers[28] and also used by Ruedenberg et al. in applications of the FORS method[23,29]. A second-order optimization procedure was actually proposed and used (in an approximated form) by Levy[30] before 1970, but its large-scale implementation into general MCSCF programs had to wait until the late 1970s. An efficient second-order optimization scheme was reported by Yaffe and Goddard[31] in 1976. The development of similar and also higher-order procedures in the general MCSCF case includes contributions from a number of different research groups and the reader is referred to the review by Olsen et al.[26] for a comprehensive list of references. Two other recent contributions should be added to this list, since they give important improvements of the second-order algorithms in the non-local regions[32,33]. The work of Werner and Knowles deserves special attention. The CASSCF program developed by them has outstanding convergence properties; in fact no calculation reported has needed more than three iterations in order to converge to less than 10^{-7} a.u. in the energy. The CI scheme used can handle expansions comprising more than 10^5 terms.

A. The Orbital Space and the Complete Active Space Self-consistent Field Wavefunction

In order to proceed, a few preliminaries are needed. They will be given in this section. The basic quantity of interest is the molecular orbital. Therefore, the

calculation normally starts by defining an orthonormal orbital space

$$\{\varphi_i(\mathbf{r}); i = 1, \ldots, m\} \tag{5}$$

Normally these molecular orbitals are obtained as expansions in a set of atom-centred basis functions (the linear combination of atomic orbitals (LCAO) method), m being the number of such functions. Recently, two-dimensional numerical integration methods have been developed to solve the MCSCF equations for linear molecules[34]. The dimension m is then, in principle, infinite (practice, it is determined by the size of the grid used in the numerical integration). The molecular-orbital space is further divided into three subspaces: the *inactive*, the *active* and the *external* orbitals. The inactive and active subspaces constitute the *internal* (occupied) orbital subspace, while the external orbitals are unoccupied. The CASSCF wavefunction is formed as a linear combination of configuration state functions (CSFs) generated from these orbitals in the following way.

1. The inactive orbitals are doubly occupied in all CSFs.
2. The remaining (active) electrons occupy the active orbitals. Using these electrons and orbitals, a *full* list of CSFs which have the required spin and space symmetry is constructed. The CASSCF wavefunction is written as a linear combination of all these CSFs, comprising a complete expansion in the active orbital subspace.

The optimization step then consists of finding those expansion coefficients and molecular orbitals that make the energy stationary with respect to all parameters. It has been suggested[33] that the deep-lying inactive orbitals (the 'core' orbitals) should be determined in a preceding SCF calculation and kept frozen during the optimization step. In second-order optimization procedures, this will reduce the computational efforts. If a first-order procedure is used, this problem does not arise, since the work done in the orbital optimization is practically independent of the number of inactive orbitals. Sometimes, however, there are other reasons to keep the core orbitals frozen in a calculation. For instance, large parts of the 'basis-set superposition error (BSSE)' can be avoided in this way. The core orbitals are then free-atom orbitals, orthogonalized against each other and kept frozen. This technique is, for example, used to avoid the BSSE in CASSCF calculations on transition-metal compounds[35]. It is especially important when moderately small atomic basis sets are used. CASSCF calculations have also been performed with the core electrons replaced by an effective core potential (ECP)[35,36]. Using this technique the CASSCF model can be extended to systems containing several heavy atoms, a current example being transition-metal[35] clusters.

As pointed out in the introduction, the CASSCF configuration space quickly becomes unmanageably large when the number of active orbitals is increased. While this does not create any serious problems in most applic-

ations, there are cases when a larger number of active orbitals is needed. In such cases a restricted form of the CASSCF wavefunction may be used. The active orbitals are divided into subgroups and the number of electrons is kept fixed within each subgroup. An example[16] of a calculation where such a partitioning of the active space was found necessary is Cr_2. A full valence calculation of the chromium dimer corresponds to distributing 12 electrons among 12 active orbitals (formed from the atomic 3d and 4s orbitals). With no symmetry restrictions, 226 512 singlet ($S = 0$) CSFs can be formed in this orbital space. For the $^1\Sigma_g^+$ ground state of Cr_2 the number of CSFs is reduced to 28 784. Even if possible with the programs available today, such a calculation would be time-consuming. A simple way to reduce the size of the CSF space is to divide the valence orbitals into the following three blocks:

$$\{3d\sigma_g, 3d\sigma_u, 4s\sigma_g, 4s\sigma_u\} \qquad \{3d\pi_u, 3d\pi_g\} \qquad \{3d\delta_g, 3d\delta_u\} \qquad (6)$$

The $^1\Sigma_g^+$ ground state of Cr_2 has the following orbital occupation (excluding all core orbitals):

$$(4s\sigma_g)^2(3d\sigma_g)^2(3d\pi_u)^4(3d\delta_g)^4 \qquad (7)$$

Thus four electrons occupy σ orbitals, four occupy π orbitals and four occupy δ orbitals. The above configuration represents the wavefunction in an SCF picture. It is worth noting that this configuration has a weight of less than 50% of the total CASSCF configuration for Cr_2 at the experimental bond distance[16]. Correct dissociation can be obtained by allowing only excitations which keep the number of electrons in the orbital groups (6) fixed at the values given by (7). With four electrons in each of the groups (6), the number of CSFs is reduced from 28 784 to 3088, a number which is much easier to handle in the calculation. It is actually possible to divide the first group into two (one for $3d\sigma$ and one for 4s), which would reduce the number further. A wavefunction of this restricted type resembles a GVB treatment of the system. The GVB method[22] is, however, further restricted by allowing only specific spin couplings of the active orbitals.

It can be assumed that the configurations left out in a constrained wavefunction of the type given above will be less important for the dissociation process. This may, however, not be the case close to equilibrium. Obviously a calculation on Li_2, which does not include excitations from the bonding σ orbitals to the π orbitals, would not be very meaningful[37]. A test was performed on the less obvious case of the nitrogen molecule at the experimental geometry. An extended contracted Gaussian AO basis was used (13s, 8p, 3d and 2f contracted to 8s, 5p, 2d and 1f). First a CASSCF calculation was performed with the active orbitals (see Section III for a motivation of this choice)

$$(2\sigma_g, 2\sigma_u, 3\sigma_g, 3\sigma_u, 4\sigma_g, 4\sigma_u, 1\pi_g, 1\pi_u) \qquad (8)$$

TABLE I

Some properties of N_2 computed with CASSCF wavefunctions (for details see text).

Method	r_e (Å)	D_e (eV)	Θ_e (a.u.)[a]
CASSCF $(2\sigma_g, 2\sigma_u, 3\sigma_g, 3\sigma_u, 4\sigma_g, 4\sigma_u, 1\pi_u, 1\pi_g)$	1.102	9.58	-1.288
Constrained CASSCF	1.105	9.30	-1.337
MR-CI[b]	1.101	9.46	–
MBPT(4)[c]	–	–	-1.149
SCF	1.069	–	-0.903[d]
Expt	1.098[e]	9.91[e]	-1.09 ± 0.06[f]

[a]Quadrupole moment.
[b]Ref. 38.
[c]Full fourth-order MBPT result from Ref. 39.
[d]Ref. 39.
[e]Ref. 40.
[f]Ref. 41.

Constraints were then applied, such that the number of electrons in σ orbitals was fixed at six and the number of electrons in π orbitals at four. The results of the two calculations are presented in Table I, where the effects on some of the properties of the nitrogen molecule are given. For comparison the corresponding SCF values are also presented. As can be seen from these results, the effects of the constraints on the CASSCF wavefunction are not negligible. They are, however, considerably smaller than the difference between the CASSCF and the SCF values. Better agreement with experiment can only be obtained by including dynamical correlation effects, for example, by means of a large multireference CI calculation[38] or a many-body perturbation theory (MBPT) calculation[39].

Thus, in many cases it is possible to reduce the computational effort by adding constraints to the CASSCF wavefunction in the ways discussed above. The simple structure of the model is then lost to some extent. The selection of an active orbital space is extended to include several active subspaces with a fixed number of electrons attributed to each of them. It is not difficult to proceed one step further and allow limited excitations between the different subspaces. The number of electrons is then not fixed, but is allowed to vary between given limits.

The wavefunctions generated using the model discussed above will in the following be called constrained complete active space (CCAS) wavefunctions. In the examples given above the different active subspaces were of different symmetry. Rotations between active orbitals are redundant variables in the CASSCF orbital optimization process. This is no longer the case when the active CSF space is reduced. In principle, it is necessary to introduce rotations

between the active orbitals. With the blocking illustrated above, these extra rotations are zero by symmetry, and in this respect there is no difference between a CAS and a CCAS orbital optimization process. As illustrated for Cr_2 it might, however, also be of interest to block active orbitals within a given symmetry species. Obviously this will always be the case when the molecule does not possess any symmetry. In such cases, orbital rotations between active subspaces has to be introduced into the optimization process (see below for details).

B. Optimization of the Wavefunction

The CAS (or CCAS) wavefunction, $|0\rangle$, is obtained as a superposition of the CSFs, $|\mu\rangle$, generated by the active orbital subspace(s)

$$|0\rangle = \sum_{\mu=1}^{M} C_{\mu}^{(0)}|\mu\rangle \tag{9}$$

The configuration state functions are in the CAS case most easily generated using the graphical unitary group approach (GUGA)[19]. All necessary information about the CSFs and their relative ordering (the 'lexical ordering') is contained in a compressed table, the distinct row table (DRT). Reduction of the CSF space from CAS to CCAS can be performed relatively easily, by deleting certain vertices and paths in the DRT (see Ref. 19 for details on the DRT).

The Hamiltonian is assumed to be spin-independent. It can then be written, in second quantized form, in terms of the spin-averaged excitation operators (the generators of the unitary group[42])

$$\hat{E}_{pq} = \sum_{\sigma} \hat{a}_{p\sigma}^{\dagger} \hat{a}_{q\sigma} \tag{10}$$

where $\hat{a}_{p\sigma} (\hat{a}_{p\sigma}^{\dagger})$ are the normal annihilation (creation) operators for an electron in the molecular orbital φ_p with spin σ. The generators (10) fulfil the following commutation relations:

$$[\hat{E}_{pq}, \hat{E}_{rs}] = \delta_{qr}\hat{E}_{ps} - \delta_{sp}\hat{E}_{rq} \tag{11}$$

The Hamiltonian is, in the algebraic approximation defined by the finite MO basis, given as

$$\hat{H} = \sum_{p,q} h_{pq}\hat{E}_{pq} + \tfrac{1}{2}\sum_{p,q,r,s}(pq|rs)(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}) \tag{12}$$

where h_{pq} and $(pq|rs)$ are the normal one- and two-electron integrals. The total energy of the system

$$E_0 = \langle 0|\hat{H}|0\rangle/\langle 0|0\rangle \tag{13}$$

is, with $|0\rangle$ normalized to unity, obtained as

$$E_0 = \sum_{p,q} h_{pq} D_{pq}^{(00)} + \sum_{p,q,r,s} (pq|rs) P_{pqrs}^{(00)} \tag{14}$$

where $D_{pq}^{(00)}$ and $P_{pqrs}^{(00)}$ are the first- and second-order reduced density matrices, which according to (12) are obtained as

$$D_{pq}^{(00)} = \langle 0|\hat{E}_{pq}|0\rangle \tag{15a}$$

$$P_{pqrs}^{(00)} = \tfrac{1}{2}\langle 0|\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}|0\rangle \tag{15b}$$

In the energy expression (14), the orbitals occur in the integrals h_{pq} and $(pq|rs)$. The density matrix elements (15) contain the CI expansion coefficients. Using (9) we obtain

$$D_{pq}^{(00)} = \sum_{\mu,\nu} C_{\mu}^{(0)} C_{\nu}^{(0)} A_{pq}^{\mu\nu} \tag{16a}$$

$$P_{pqrs}^{(00)} = \sum_{\mu,\nu} C_{\mu}^{(0)} C_{\nu}^{(0)} A_{pqrs}^{\mu\nu} \tag{16b}$$

where $A_{pq}^{\mu\nu}$ and $A_{pqrs}^{\mu\nu}$ are the one- and two-electron coupling coefficients which are used in forming the Hamiltonian matrix in the CSF basis:

$$A_{pq}^{\mu\nu} = \langle \mu|\hat{E}_{pq}|\nu\rangle \tag{17a}$$

$$A_{pqrs}^{\mu\nu} = \tfrac{1}{2}\langle \mu|\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}|\nu\rangle \tag{17b}$$

with the Hamiltonian matrix element given as

$$H_{\mu\nu} = \langle \mu|\hat{H}|\nu\rangle = \sum_{p,q} h_{pq} A_{pq}^{\mu\nu} + \sum_{p,q,r,s} (pq|rs) A_{pqrs}^{\mu\nu} \tag{18}$$

The formulation presented above is based on the assumption that molecular orbitals and CI expansion coefficients are real.

The energy expression (14) is a function of the molecular orbitals, appearing in the one- and two-electron integrals, and of the CI expansion coefficients through the first- and second-order reduced density matrices (15). In an MCSCF optimization procedure the CI coefficients and the parameters determining the MOs (normally the LCAO expansion coefficients) are varied until the energy reaches a stationary value. A number of procedures for performing the optimization have been described in the literature (see Ref. 26 for an extensive review). Here only the basic features of these procedures will be outlined, and the reader is referred to the literature for further details[26,43].

In order to describe the variations of the CI coefficients, the orthogonal complement to (9), $|K\rangle$, is also introduced:

$$|K\rangle = \sum_{\mu=1} C_{\mu}^{(K)}|\mu\rangle \qquad (K = 1,\ldots,M-1) \tag{19}$$

The variation of the MC function is described by a unitary operator, $\exp(\hat{S})$, where $\hat{S}$ is an anti-Hermitian operator

$$\hat{S} = \sum_{K \neq 0} S_{K0}(|K\rangle\langle 0| - |0\rangle\langle K|) \tag{20}$$

Similarly orbital rotations can be described by the unitary operator, $\exp(\hat{T})$, with $\hat{T}$ defined as

$$\hat{T} = \sum_{p > q} T_{pq}(\hat{E}_{pq} - \hat{E}_{qp}) \tag{21}$$

The anti-Hermiticity of $\hat{T}$ follows from the fact that $\hat{E}_{qp} = \hat{E}_{pq}^{\dagger}$ (see Eq. (10)). A general variation of the wavefunction can now be written as the combined operation of $\hat{S}$ and $\hat{T}$:

$$|0'\rangle = \exp(\hat{T})\exp(\hat{S})|0\rangle \tag{22}$$

Since the operators $\hat{T}$ and $\hat{S}$ do not commute, the order of the two operations is not irrelevant. The order used above is the one commonly used in the formulation of the problem. The reverse order can be shown to lead to much more complex algebra, needed to determine the transformed state $|0'\rangle$[44]. Owing to the definitions of $\hat{S}$ and $\hat{T}$, the varied wavefunction (27) will remain normalized and the new molecular orbitals defined as

$$\varphi' = \exp(\hat{T})\varphi \tag{23}$$

will remain orthonormal. The parameters in $\hat{S}$ and $\hat{T}$ thus constitute a set of variables that can be used to determine the stationary point for the energy. These parameters are, however, not in general linearly independent and care has to be taken to delete redundant variables from the parameter space. This is a trivial problem for CAS (and CCAS) wavefunctions, as will be illustrated below.

The transformed energy expression can, with the aid of (22), be written as

$$E' = \langle 0|\exp(-\hat{S})\exp(-\hat{T})\hat{H}\exp(\hat{T})\exp(\hat{S})|0\rangle \tag{24}$$

The conditions for a stationary value of the energy as a function of S and T are now easily obtained following a power expansion of the exponential factors in (24). The first-order terms should vanish at the stationary point, which immediately gives the relations

$$\langle 0|[\hat{H}, \hat{S}]|0\rangle = 0 \tag{25a}$$

$$\langle 0|[\hat{H}, \hat{T}]|0\rangle = 0 \tag{25b}$$

or with the use of Eqs (20) and (21),

$$\langle 0|\hat{H}|K\rangle = 0 \qquad K \neq 0 \tag{26a}$$

$$\langle 0|\hat{H}(\hat{E}_{pq} - \hat{E}_{qp})|0\rangle = 0 \tag{26b}$$

The first condition simply states that the reference state $|0\rangle$ should not interact with the orthogonal complement, that is, it is a solution to the secular problem

$$(\mathbf{H} - E\mathbf{1})\mathbf{C} = 0 \tag{27}$$

The second condition is the generalized Brillouin theorem, first derived by Levy and Berthier[45].

Condition (26b) is, for CASSCF wavefunctions, automatically fulfilled if both p and q belong to the same orbital space (inactive, active or external). From now on the following index labelling will be used:

$$
\begin{array}{ll}
i, j, k, l & \text{inactive orbitals} \\
t, u, v, x & \text{active orbitals} \\
a, b, c, d & \text{external orbitals} \\
p, q, r, s & \text{all orbitals}
\end{array}
$$

For rotations in the inactive and external subspaces we trivially obtain:

$$\hat{E}_{ij}|0\rangle = 2\delta_{ij}|0\rangle \tag{28a}$$

$$\hat{E}_{ab}|0\rangle = 0 \tag{28b}$$

since the inactive orbitals are doubly occupied in all CSFs, while the external orbitals are empty. For the active subspace on the other hand,

$$\hat{E}_{tu}|0\rangle = \sum_K \langle K|\hat{E}_{tu}|0\rangle|K\rangle \tag{29}$$

since the CSF space is complete in the active orbital space. Also for real orbitals,

$$\hat{E}_{ut}|0\rangle = \sum_K \langle 0|\hat{E}_{tu}|K\rangle|K\rangle \tag{30}$$

Using (29) and (30) in (26b), it follows immediately by using also (26a) that

$$\langle 0|\hat{H}(\hat{E}_{tu} - \hat{E}_{ut})|0\rangle = 0 \tag{31}$$

Since the energy is invariant to rotations within a given orbital subspace, they can be excluded from the orbital rotations. The only rotations which have to be included are those which occur between the three orbital subspaces, described by the generators $\hat{E}_{ai}, \hat{E}_{at}$ and $\hat{E}_{ti}$. No redundant variables will remain in the calculation. Such variables are sometimes a problem in general MCSCF calculations, where the MC expansion is not complete[26,44]. They have to be deleted from the calculation, in order to avoid singularities. The problem becomes even worse if some rotation parameters are near-redundant. Such situations can lead to difficult convergence problems, which, however, sometimes can be overcome by introducing higher-order terms in the expansion of the energy (see for example Werner and Knowles' treatment of

internal–internal rotations[33]). This problem is less severe in CASSCF cal-
culations since only rotations between the orbital subspaces are applied. There
are, however, two cases which can also lead to convergence problems here. If
an active orbital has an occupation number that is very close to 2, the energy
will depend only weakly upon rotations between this orbital and the inactive
orbitals. The same situation occurs when an orbital has a very small
occupation number. Rotations between this orbital and the external subspace
then become near-redundant. The easiest way to avoid this problem is to move
the corresponding orbital into the inactive (or external) subspace. This is,
however, not always possible. The situation may, for example, arise on one
part of an energy surface, but not on others. Optimization methods like those
recommended by Werner and Knowles[33] may then have to be used. It should
be emphasized, however, that situations of this kind are rather unusual.
Calculations with active orbital occupation numbers as high as 1.995 and as
low as 0.001 have been found to converge without problems without using any
special techniques.

In constrained CASSCF calculations, rotations between the different sub-
blocks of the active orbital space have to be included as variational
parameters. This is, however, only necessary when orbitals in different sub-
blocks have the same symmetry.

The most commonly adopted procedure for optimizing the variational
parameters in (24) is the non-linear Newton–Raphson procedure[26,30,46]. The
energy expression is expanded to second order in the parameters S and T. By
assuming the first-order derivatives of this expression to be zero, a linear
equation system is obtained in S and T[26,43]:

$$\begin{bmatrix} \mathbf{g}^{(c)} \\ \mathbf{g}^{(o)} \end{bmatrix} + \begin{bmatrix} \mathbf{H}^{(cc)} & \mathbf{H}^{(co)} \\ (\mathbf{H}^{(co)\dagger})^{+} & \mathbf{H}^{(oo)} \end{bmatrix} \begin{bmatrix} \mathbf{S} \\ \mathbf{T} \end{bmatrix} = 0 \qquad (32)$$

where $\mathbf{g}^{(c)}$ and $\mathbf{g}^{(o)}$ are the gradients (26) (c for the configuration and o for the
orbital part). The Hessian matrix $\mathbf{H}$ consists of three parts: the congfiguration–
configuration, the orbital–configuration and the orbital–orbital parts. Ex-
plicit expressions for these matrices will not be presented here. They are
available in the literature[26,43]. Special formulae for the orbital–orbital part
corresponding to the different types of rotations occurring in a CASSCF
calculation have been given by Siegbahn et al.[47].

In a straightforward application of the Newton–Raphson approach,
Eq. (32) is solved iteratively for S and T until the convergence criteria (26) are
fulfilled to the desired accuracy. This process converges nicely if the initial
choice of the orbitals and the CI coefficients are close to the final result. The
energy is then in the 'local region' where the second-order approximation is
valid. Obviously such situations will not be very common in actual applic-
ations. In practice the starting orbitals are often obtained from a preceding
SCF calculation, or even estimated from atomic densities[48], while the CI

coefficients are obtained by solving Eq. (27) using the starting orbitals. It then often happens that the Hessian matrix has many negative eigenvalues. In order to force convergence in such situations, level-shifting and mode-damping procedures must be used[26]. The most efficient of these procedures is probably the augmented Hessian method with step restriction, which was originally introduced by Lengsfield[49]. The linear equations (31) are in this method replaced by an eigenvalue equation, which automatically introduces a level shift into the Hessian. A damping factor can also easily be introduced which sets an upper limit to the norm of the rotation vector[50]. Even using such methods it is not certain that convergence can be obtained in an acceptable number of iterations, if the starting values of the parameters place the energy far from the local region. Werner and Meyer[51] recognized that the small radius of convergence inherent to the Newton–Raphson approach stems from the fact that the energy is a periodic, rather than quadratic, function of the orbital rotations T. They instead proposed the use of an expansion of the energy to second order in $V = U - 1$, where U is the unitary transformation matrix for the orbitals, $U = \exp(T)$. The orthonormality conditions are then exactly accounted for, and the energy is now a periodic function of the orbital parameters T. This method has been successfully applied in very extensive CASSCF calculations and shows, at least for the cases treated so far, beautiful convergence properties[25,33]. Three to four iterations are normally sufficient for a convergence to seven decimal places in the total energy.

The solution of the system of equations (31) (or the corresponding augmented Hessian secular problem) is not trivial when the dimension of the CI expansion becomes large. If the coupling terms are neglected the problem splits into two parts, a secular problem for the CI coefficient (Eq. (27)) and a separate problem for the orbital rotations. The CI problem can be efficiently treated for large CI expansions using direct CI methods[13,25,52], as will be discussed in more detail below. Such direct iteration schemes can, however, also be used when the coupled problem (31) is solved. Direct MCSCF was first introduced in an MCSCF program written by Lengsfield[53]. It was later introduced into CASSCF programs[25,26,33,54]. A possible extension of such methods that avoids the two-electron transformation step has been discussed by Almlöf and Taylor[55]. In all these approaches the linear (or, in the case of the method of Werner and Meyer, the non-linear) equation system (or secular problem) is solved using an iterative process, where the essential step consists of performing the matrix multiplication Hc where c is the solution vector and H is the Hessian matrix (e.g. as in Eq. (31)). In the direct methods, the Hessian is never explicitly constructed. Instead the matrix multiplication above is obtained using the explicit expressions for the matrix elements of H in terms of the basic quantities involved, that is, the one- and two-electron integrals and the first- and second-order reduced density matrices (16).

C. The Configuration-interaction Secular Problem

The CAS-CI expansion can be very long. It is therefore essential to have an efficient procedure for solving the corresponding secular problem. Such procedures must necessarily be based on the direct CI concept[52], since the storage and handling of a Hamiltonian matrix would severely limit the possibility of using long CI expansions. The special features of the CAS-CI allow certain simplifications, which are not possible in normal MR-CI calculations. Thus, the number of two-electron integrals appearing in the Hamiltonian matrix elements (18) is limited by the small size of the active orbital space. It is therefore no problem to store these integrals in the primary memory of the computer. As a result they can be randomly accessed. The problematic parts are the one- and two-electron coupling coefficients $A_{pq}^{\mu\nu}$ and $A_{pqrs}^{\mu\nu}$. An automatic procedure for computing these coefficients efficiently is necessary. The number of coupling coefficients can become large and is actually the limiting factor for the size of the CI expansion. The first of these problems was solved by the graphical unitary group approach (GUGA) by Paldus and Shavitt[15,19]. The GUGA is especially efficient in the CAS case, since it was originally based on the graphical representation of the complete configurational space. The one-electron coupling coefficients are obtained as a product of attached segments of a loop generated by the two interacting configurations:

$$A_{pq} = \prod_{k=p}^{q} \omega(T_k, b_k) \tag{33}$$

with one factor for each orbital in the range $\{p, q\}$. T_k and b_k specify the shape and orientation of the segment in the graph. For more details see the papers by Shavitt[19]. The two-electron coupling coefficients can be obtained in a similar way, as shown by Paldus and Boyle[56]:

$$A_{pqrs} = \tfrac{1}{2} \prod_{k \in s_1} \omega(T_k, b_k) \sum_x \prod_{l \in s_2} \omega_x(T_l, b_l) \tag{34}$$

where s_1 and s_2 are sets of orbital levels which are within one or both of the ranges $\{p, q\}$ and $\{r, s\}$. The summation x is over intermediate spin coupling.

The above approach represents an efficient way of computing the coupling coefficients. It does not, however, solve the problem of storage and handling of the large number of two-electron coupling coefficients generated for large CAS-CI expansions. A direct implementation of the above procedure sets the practical limit to around 10^4 CSFs[13].

The original idea of Paldus[57] was to generate the two-electron coefficients as a matrix product of the one-electron coefficients

$$A_{pqrs}^{\mu\nu} = \tfrac{1}{2} \sum_\kappa A_{pq}^{\mu\kappa} A_{rs}^{\kappa\nu} - \tfrac{1}{2} \delta_{qr} A_{ps}^{\mu\nu} \tag{35}$$

where the sum runs over the complete set of CSFs. Eq. (35) follows directly from the definiton (17b) by using the resolution of identity. This method was used by Robb and Hegarty[58] to construct a formula tape for the CI calculation.

In direct CI calculation the update vector for the CI coefficients, σ, is given by

$$\sigma_\mu = \sum_\nu H_{\mu\nu} C_\nu \qquad (36)$$

Siegbahn[59] realized that (35) could be used efficiently in (36) by ordering the coupling coefficients A_{pq} after the intermediate index. In his notation the first term in (35) gives rise to the following contribution to σ:

$$\Delta\sigma_\mu = \tfrac{1}{2} \mathrm{Tr}(\mathbf{A}^\mu \mathbf{ID}) \qquad (37)$$

where $\mathbf{A}^\mu$ is a matrix of coupling coefficients $(A^\mu_{\kappa,pq} = A^{\mu\kappa}_{pq})$, $\mathbf{I}$ is a matrix of two-electron integrals $(I_{pq,rs} = (pq|rs))$ and $\mathbf{D}$ is the product of $\mathbf{A}$ with the coefficient vector $\mathbf{C}$ $(D_{rs,\kappa} = \sum_\nu A^{\kappa\nu}_{rs} C_\nu)$. Eq. (37) can efficiently be adapted to a vector processor, thereby making complete CI calculations very effective on computers like the CRAY. Prior to this work the CI problem was the main bottleneck in vectorizing CASSCF program systems.

A radically different use of the factorization (35) was made by Knowles and Handy[60]. They realized that, if the CI expansion was based on determinants instead of spin-adapted CSFs, it was possible to perform the CI calculations without a precomputed list of coupling coefficients. The reason for this is simply that for determinants the one-electron coupling coefficients take the trivial values ± 1 or 0. Using a 'canonical' addressing scheme for the CI vectors, it was possible to construct an effectively vectorized code for CAS-CI calculations. The power of the program was demonstrated in a recent CASSCF calculation on the $^5\Delta$ ground state of FeO[25]. The number of Slater determinants used in the largest calculation was 230 045 corresponding to 178 910 CSFs. The calculation of the residual vector (36) took 36 seconds of CPU time on a CRAY-1S.

D. Simplified Optimization Procedures

The discussion above has centred around full second-order optimization methods where no further approximations have been made. Computationally such procedures involve two major steps which consume more than 90% of the computer time: the transformation of two-electron integrals and the update of the CI vector. The latter problem was discussed, to some extent, in the previous section. In order to make the former problem apparent, let us write down the explicit formula for one of the elements of the orbital–orbital parts of the Hessian matrix (31), corresponding to the interaction between two

inactive–external rotations T_{ia} and T_{jb}:

$$\tfrac{1}{2}H^{(00)}_{ia,jb} = 2[4(ai|bj) - (ab|ij) - (aj|bi)] + 2\delta_{ij}F'_{ab} - 2\delta_{ab}F'_{ij} \qquad (38)$$

where F'_{ab} and F'_{ij} are elements of a Fock matrix

$$F'_{pq} = h_{pq} + \sum_{r,s}D_{rs}[(pq|rs) - \tfrac{1}{2}(pr|qs)] \qquad (39)$$

with r and s being restricted to the internal (inactive plus active) orbital space. D_{rs} are the elements of the first-order density matrix. In order to compute the matrix element (38) the Fock matrix (39) must be known and also the two-electron integrals $(ai|bj)$, etc. The Fock matrix is easily obtained using the well established procedures of the closed-shell Hartree–Fock method. The molecular two-electron integrals are obtained by a four-index transformation from the integrals over the AO basis functions. The transformation is called 'second order' since molecular integrals with two indices in the usually large external space have to be formed. In a direct procedure the Hessian matrix is not formed explicitly but is directly multiplied with the vector **T**, leading to expressions of the form

$$\sum_{j,b}[4(ai|bj) - (ab|ij) - (aj|bi)]T_{jb} \qquad (40)$$

This expression can be expressed as a sum over AO integrals, multiplied by a 'density matrix', thus avoiding two-electron transformations[55]. Similar transformations can be made for other parts of the Hessian. The price to be paid is that the AO integral list has to be read once for every update (4), which is a very I/O intensive process. It is therefore doubtful whether such a procedure is advantageous in a conventional scheme, where the AO integrals are precomputed. The situation would be different if the integrals were computed when needed, as suggested in Ref. 55.

For large AO basis sets, (most CASSCF calculations are today performed with basis sets in the range of 80–150 Gaussian-type orbitals (GTOs) and for a moderately small CI expansion (less than 1000 CSFs)) the transformation step will dominate the calculation in a second-order procedure. It might therefore be worth while to look for methods in which this transformation is avoided as much as possible. Such procedures were actually first used in MCSCF calculations. They are based on the generalized Brillouin theorem (26b). One, the so-called first-order method, which has proven to have near-quadratic convergence in practical applications, is the super-CI method, first development by Grein and coworkers[28] and later used by Ruedenberg et al.[29]. The orbital rotations and CI coefficients are here found by an iterative solution of a secular problem in the variational space spanned by the CI states $|0\rangle$, $|K\rangle$ (or alternatively the CSF space), and the configurations generated in the generalized Brillouin theorem (the Brillouin states)

$$(\hat{E}_{pq} - \hat{E}_{qp})|0\rangle \qquad (41)$$

The coefficients of the Brillouin states are used as the rotation parameters for the orbitals[28]. Alternatively the first-order density matrix is generated and diagonalized. The corresponding natural orbitals (selected via an overlap criterion) are used as input for the next iteration[12,29].

The super-CI method can be regarded as an approximation in the augmented Hessian variant of the Newton–Raphson (NR) procedure (see for example Ref. 43). However, in its original formulation, it does not constitute any simplification when compared with the NR method. The matrix elements between the Brillouin states (41) are actually more difficult to compute than the corresponding Hessian matrix elements, since they involve third-order density matrix elements[47].

The orbital optimization was, in the first implementation of the CASSCF method, performed using an approximate version of the super-CI method, which avoided the calculation of the third-order density matrix[12]. This was later[14] developed as a procedure entirely based on the average MCSCF Fock operator[61]:

$$F_{mn} = \sum_p D_{mp}^{(00)} h_{pn} + \sum_{p,q,r} P_{mpqr}^{(00)}(np|qr) \tag{42}$$

Contributions from the inactive orbitals are easily obtained in (42) from atomic two-electron integrals (or super-matrix elements) as was the case for the matrix F' defined in Eq. (39). The second-order density matrix can be expressed using the first-order density matrix, if any of the indices m, p, q, or r refer to inactive orbitals. The remaining part has all four indices in the active subspace. Thus the only molecular two-electron integrals explicitly occurring in (42) have three indices in the active orbital space. The fourth index, n, runs over all orbitals. To transform these integrals from AO to MO basis requires around $n_a n_b^4/2$ operations, where n_a is the number of active orbitals and n_b is the number of AO basis functions. The second-order transformation needed to form the Hessian matrix elements requires on the other hand around $n_o n_b^4$ operations, where n_o is the number of occupied orbitals (inactive and active)[29]; n_o can be much larger than n_a in calculations on systems with many electrons. A first-order transformation can further be made entirely in core memory (except for the read of a sorted and symmetry-blocked list of AO integrals). This is generally not possible for a second-order transformation, where the half-transformed integrals have to be written to mass storage. Thus a first-order transformation runs much more effectively on vector processors like CRAY-1 and even more so on a single-user computer like the FPS-164.

In Ref. 14 an approximate super-CI approach was developed, where the Hamiltonian was replaced by the one-electron Hamiltonian

$$\hat{H}_0 = \sum_{p,q} \hat{E}_{pq} F_{pq} \tag{43}$$

This Hamiltonian was used to compute the matrix elements between the

Brillouin states

$$\hat{E}_{ai}|0\rangle \tag{44a}$$

$$\hat{E}_{at}|0\rangle \tag{44b}$$

$$\hat{E}_{ti}|0\rangle \tag{44c}$$

which corresponds to the only non-redundant rotations appearing in a CASSCF calculation. The matrix elements could be expressed entirely in first- and second-order density matrices together with the Fock matrix (42). The interaction between the Brillouin states and the reference state $|0\rangle$ is given exactly in terms of the Fock matrix (42)

$$\langle 0|\hat{H}(\hat{E}_{pq} - \hat{E}_{qp})|0\rangle = F_{pq} - F_{qp} \tag{45}$$

The solution of the super-CI secular problem takes very little time compared to the remaining parts of the calculation. It can be implemented with or without CI coupling.

As already pointed out, the super-CI procedure can be regarded as an approximate version of the augmented Hessian approach. This is of course also true for the method described above, the only difference being that the approximations made are more severe.

This is, however, of little importance as long as the MCSCF process converges within a satisfactory number of iterations. It can be estimated that the first-order transformation is 3–5 times as fast as the second-order transformation. Thus a first-order procedure could compete with second-order procedures if the number of iterations needed are not more than three times as many, provided of course that the calculation is not dominated by the CI step. The most efficient second-order procedure seems to be that of Werner and Knowles[25,33]. They use three macro-iterations and about 30–50 micro-iterations to converge to less than 10^{-7} a.u. in the energy. A first-order transformation is performed in each micro-iteration and a second-order one in each macro-iteration. It seems that first-order procedures can compete with this performance in many cases. With reasonable starting vectors, convergence to 10^{-6} a.u. is often reached in less than 10 iterations.

First-order methods often show good convergence in calculations on ground-state energy surfaces (that is, the lowest state in each symmetry), and compete well with the Newton–Raphson procedure in the non-local regions. It is often a useful compromise, therefore, to start a calculation with a first-order scheme, and switch to second order when the local region has been reached. The situation is different for excited states where CI coupling often becomes necessary for a calculation to converge at all. Here second-order schemes with full CI coupling are liable to be the more efficient procedures. CI coupling can also be introduced into super-CI methods. Such calculations

have, however, not been performed so far, so experience about their convergence behaviour is still lacking.

Experience in a variety of applications of the CASSCF method has shown it to be a valuable tool for obtaining good zeroth-order approximations to the wavefunctions. Attempts have been made to extend the treatment to include also the most important dynamical correlation effects. While this can be quite successful in some specific cases (see below for some examples), it is in general an impossible route. Dynamical correlation effects should preferably be included via multireference CI calculations. It is then rarely necessary to perform very large CASSCF calculations. Degeneracy effects are most often described by a rather small set of active orbitals. On the other hand experience has also shown that it is important to use large basis sets including polarization functions in order to obtain reliable results. The CASSCF calculations will in such studies be dominated by the transformation step rather than by the CI calculation. A mixture of first- and second-order procedures, as advocated above, is then probably the most economic alternative.

III. APPLICATIONS

In this section, some illustrative examples of the CASSCF method will be given. The emphasis will not be on the technical problem of solving the MCSCF equations but rather on the chemical problems encountered when using the CASSCF method as a tool for electronic structure calculations. Most of the examples have been selected from recently published results.

CASSCF, like most other MCSCF procedures, is a method which makes it possible to study systems where degeneracies or near-degeneracies occur between different configurations. In such cases the Hartree–Fock model is not a valid zeroth-order approximation. The CASSCF model studies these effects with as little bias as possible, since the only decision made by the user is the selection of the inactive and active orbitals, and of course the AO basis set. The method is not primarily aiming at studies of dynamical correlation effects.

However, a sharp limit does not exist between near-degeneracy and dynamical correlation effects. A simple example is H_2 where the $1\sigma_u$ orbital describes near-degeneracy effects for large bond distances, while it is conventionally considered as contributing to the dynamical correlation for bond distances around equilibrium. A simple solution to this dilemma is formally to define near-degeneracy correlation as the effect due to all configurations generated within the valence orbital space. A formal definition of the dynamical correlation energy E_{DC} can then be obtained as

$$E_{DC} = E_{exact} - E_{VCAS} \tag{46}$$

where E_{exact} is the exact eigenvalue of the Hamiltonian and E_{VCAS} is the CASSCF energy of a calculation with all valence orbitals active. The choice of

the valence orbitals would for H and He be 1s, for Li–Ne 2s and 2p, for Na–Ar, 3s and 3p, and for K–Zn 3d, 4s and 4p, etc. It is obviously not possible to compute E_{VCAS} for most molecules. The definition above is therefore rather formal. However, there is another reason for writing it down. Dynamical correlation effects are intuitively considered as creating a Coulomb hole around each electron, making the average distance between a pair of electrons slightly larger. The magnitude of these correlations are probably measured well by the diagonal of the second-order density function $\rho_2(\mathbf{r}, \mathbf{r})$. Near-degeneracy effects are, on the other hand, often of a different nature. They separate the electrons in a pair much more effectively. An obvious example is again H_2 at large internuclear separation. The effect of the $1\sigma_u$ orbital here leads to a total separation of the two electrons, such that one electron is localized at each of the two atoms. The beryllium atom constitutes a similar example. An SCF calculation gives the total energy $- 14.572$ a.u.[62]. A corresponding valence CASSCF calculation (including 2s and 2p in the active space) gives an energy lowering of $- 0.0455$ a.u., accounting for almost all of the correlation energy for the $(2s)^2$ electron pair in Be. The remaining dynamical valence correlation energy was estimated to be only $- 0.0022$ a.u., which is only 5% of the total value. This estimate was also done by a CASSCF calculation with the active orbitals 2s, 2p, 3s, 3p, 3d, 4s and 4p. The reason for the small dynamical correlation energy is the effective separation of the two electrons effected by the 2p orbital, leading to a sharp decrease in $\rho_2(\mathbf{r}, \mathbf{r})$. The separation was illustrated by Eq. (3) in the introduction. In beryllium, the coefficient in front of the last term in (3) is as large as 0.3. (Total separation is obtained with the value 1.0.)

The important conclusion to be drawn from the discussion above is that there exists a strong interplay between near-degeneracy effects and dynamical correlation. Strong near-degeneracy effects lead to effective separation of the electron pair, and thus to a reduction in the dynamical correlation effects. A method which only takes into account near-degeneracy effects will in general not give a balanced description of the total correlation effects over an energy surface, for example along a dissociation channel. This is, of course, well known and is the reason why full valence MCSCF calculations in general give binding energies which are too low. It is sometimes possible to counter-balance this effect by adding a few more active orbitals. The principle behind this is that the active space should contain one correlating orbital for each strongly occupied orbital. The N_2 molecule is an example. The SCF configuration in N_2 is

$$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4 \tag{47}$$

where the 1s orbitals have not been given. The $3\sigma_g$ and $1\pi_u$ orbitals are correlated to the corresponding antibonding orbitals $3\sigma_u$ and $1\pi_g$ in a full valence calculation. No correlation is, however, introduced into $2\sigma_g$ and $2\sigma_u$. A FORS calculation by Ruedenberg *et al.* gave for this type of wavefunction a

binding energy of $9.06\,eV^{24}$. The most important dynamical structure-dependent correlation effects can be accounted for by adding two more orbitals to the active subspace, $4\sigma_g$ and $4\sigma_u$. At small internuclear distances these orbitals introduce left–right correlation into the pairs $(2\sigma_g)^2$ and $(2\sigma_u)^2$, while at large distances they introduce the corresponding angular correlation in $(2s)^2$ on each of the two atoms. The calculated binding energy with this active space is $9.57\,eV^{63}$, a value much closer to the experimental value, $9.90\,eV^{40}$. Obviously, there is no chance to obtain an exact balance between atomic and molecular correlation energies in this way. Unfortunately it does not seem to be much easier to reach this goal with the multireference CI method, as shown for example by Siegbahn's work[38] on N_2. Convergence in dissociation energies can only be achieved simultaneously with convergence in the total correlation energy.

A similar situation as for N_2 occurs for the water molecule. Here the SCF configuration is in C_{2v} symmetry

$$(2a_1)^2(3a_1)^2(1b_2)^2(1b_1)^2 \tag{48}$$

The orbitals $3a_1$ and $1b_2$ are correlated by the corresponding antibonding orbitals $4a_1$ and $2b_2$ in a full valence description of the molecule. This is, however, an unbalanced situation, since only one of the OH bonds is correlated (together with the oxygen lone pair $3a_1$). A bond angle of only $103°$ is for example obtained[14]. Balance is approximately restored by adding two more orbitals, $5a_1$ and $2b_1$, which includes the corresponding correlation effects into $2a_1$ and $1b_1$. The computed angle is now $104.8°$ (expt $104.5°$), and also other properties of the molecule are improved (see Ref. 14 for more details). It should be noted that these 'extra valence' orbitals have rather large occupation numbers, 0.013 for $5a_1$ and 0.021 for $2b_1$. A more intricate example of the same problem of balance in the dynamical and near-degeneracy correlations will be given below for the C_2 molecule.

In calculations on larger systems it will, of course, not be possible to include all valence orbitals into the active subspace. It is also not necessary. Studies of an energy surface, i.e. for an chemical reaction, will normally be concentrated in regions where only one or two of the chemical bonds are broken. The calculation can then be performed by choosing as active orbitals only those taking part in the bond-breaking process. However, only semi-quantitative results can be expected from such calculations. Additional dynamical correlation effects have to be include via configuration-interaction calculations.

A. The C_2 Molecule

The C_2 molecule offers an example where near-degeneracy effects have large amplitudes even near the equilibrium internuclear separation. The ground

state is $^1\Sigma_g^+$ with the electronic configuration (excluding the 1s orbitals)

$$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4 \tag{49}$$

The electrons in $2\sigma_u$ are essentially non-bonding, giving a biradical character to the molecule. Strong interaction with the configuration

$$(2\sigma_g)^2(3\sigma_g)^2(1\pi_u)^4 \tag{50}$$

can be expected, leading to a separation of the two electrons on different atoms. This effect is well known[64,65]. The relative weight of the two configurations $(C_I/C_{II})^2$ is in the present calculation 0.19 at $R(\text{C--C}) = 2.35$ a.u. (the experimental value is 2.348 a.u.[66]). This is a large value, even if it is still far from the value 1.0 which corresponds to two completely separated electrons. One would therefore assume that an SCF treatment of the C_2 molecule would not give very accurate results for spectroscopic constants. Such a calculation was performed by Dupuis and Liu[67]. Surprisingly enough they obtained much better results with the single-configuration wavefunction (49) than with an MCSCF wavefunction including both configurations (49) and (50) (MC-2). The R_e and ω_e values were in the former case 2.341 a.u. and 1905 cm^{-1} (expt 2.348 and 1855)[67], while the two-configurational treatment gave the results 2.261 a.u. and 2188 cm^{-1}, respectively. The surprising results is not so much the poor values obtained with MC-2 but the good values obtained in the SCF treatment. Obviously, configuration (50) is balanced by other configurations with an opposite effect on the potential curve, finally making the SCF wavefunction a reasonable approximation around $R = R_e$. That this is the case will be illustrated below.

The $^1\Sigma_g^+$ is nearly degenerate with the $^3\Pi_u$ state with the electronic configuration

$$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)(1\pi_u)^4 \tag{51}$$

The experimental T_e value is only 0.08 eV[67]. The wavefunction for this state can be expected to be more dominated by the SCF configuration (51) than was the case for the $^1\Sigma_g^+$ state, since the excitation $(2\sigma_u)^2 \rightarrow (3\sigma_g)^2$ is not possible here. In an attempt to compute the T_e value by the CASSCF method one is then faced with an imbalance in the near-degeneracy correlation effects which must be accounted for either by extending the active subspace outside the valence shell or by including dynamical correlation effects via a CI calculation. It is clear from the preceding discussion that a more balanced description, on the CAS level, can be achieved by adding a $4\sigma_g$ orbital to the active space, thus accounting for the larger dynamical correlation in the $2\sigma_u$ electron pair in the $^3\Pi_u$ state. For a correct description of dissociation it is then also necessary to add a $4\sigma_u$ orbital.

Using the criteria for selecting the active subspace which were discussed above, it should not be necessary to include this orbital, since $2\sigma_g$ is correlated

CASSCF results for the $X^1\Sigma_g^+$ and a $^3\Pi_u$ states of C_2.

State		DZ basis[a]		Large basis[b]	Expt[c]
		$n_a = 8^d$	$n_a = 10^e$	$n_a = 10$	
$^1\Sigma_g^+$	$R_e(\text{Å})$	1.284	1.284	1.253	1.243
	$D_e(\text{eV})$	5.56	5.57	6.06	6.32
	$\omega_e(\text{cm}^{-1})$				
$^3\Pi_u$	$R_e(\text{Å})$	1.357	1.362	1.325	1.312
	$D_e(\text{eV})$	5.01	5.28	5.89	6.24
	$\omega_e(\text{cm}^{-1})$				
	$T_e(\text{eV})$	0.55	0.29	0.17	0.08

[a] 9s, 5p contracted to 4s, 2p (Ref. 68).
[b] 13s, 8p contracted to 7s, 5p (Ref. 68) adding one diffuse s-type (exponent 0.04) and one p-type (exponent 0.025) function. Polarization functions: 4 d-type functions (exponents 2.179, 0.865, 0.362, 0.155) contracted (2, 1, 1) (Ref. 69).
[c] Ref. 67.
[d] Active orbital space: $2\sigma_g, 2\sigma_u, 3\sigma_g, 3\sigma_u, 1\pi_u$ and $1\pi_g$.
[e] Active space as in d with $4\sigma_g$ and $4\sigma_u$ added.

by $3\sigma_u$. However, at dissociation, $4\sigma_g$ and $4\sigma_u$ become degenerate. Both have to be included in order to make the calculation size-consistent, that is, the energies at $R = \infty$ should be equal to twice the energy obtained in a corresponding CASSCF calculation on the free atom. This criterion has not always been met in earlier calculations, probably resulting in dissociation energies[14,70] somewhat too large.

Two sets of preliminary CASSCF calculations were preformed in order to test the above assumption. A double-zeta (DZ) AO basis was used. One calculation was made with a full valence active space, while the two orbitals $4\sigma_g$ and $4\sigma_u$ were added in the second calculation. Some of the results of these calculations are reported in Table II. The addition of the two extra valence orbitals had a very small effect on the potential curve for the $^1\Sigma_g^+$ state, but the T_e value of the $^3\Pi_u$ state dropped from 0.55 to 0.29 eV with the addition of these active orbitals. The rather poor overall agreement with experiment obtained in these calculations is, of course, due to the limited basis set used, but they illustrate the importance of the $4\sigma_g$ orbital for a balanced description of the two potential curves.

The larger active space was then used in a new set of calculations which used a considerably larger AO basis. The 13s, 8p basis of van Duijneveldt[68] was contracted $(7, 1, 1, 1, 1, 1, 1/4, 1, 1, 1, 1)$. Additional diffuse functions were added, one of s-type (exponent 0.04) and of one p-type (exponent 0.025). Three 3d polarization functions were also included, contracted from four primitive GTOs with exponents 2.179, 0.865, 0.362 and 0.155. The exponents and the contraction coefficients were chosen according to the polarized basis-set

TABLE III
Occupation numbers for the active orbitals in C_2 around equilibrium and at large internuclear separation (large basis, $n_a = 10$).

State	R (a.u.)^a	$2\sigma_g$	$3\sigma_g$	$4\sigma_g$	$2\sigma_u$	$3\sigma_u$	$4\sigma_u$	$1\pi_u$	$1\pi_g$
$^1\Sigma_g^+$	2.30	1.980	0.406	0.005	1.589	0.013	0.002	3.792	0.212
	2.35	1.979	0.392	0.005	1.603	0.014	0.002	3.779	0.225
	2.40	1.979	0.398	0.005	1.616	0.015	0.002	3.765	0.238
	∞	1.950	1.000	0.007	1.950	1.000	0.007	1.044	1.044
$^3\Pi_u$	2.45	1.981	1.038	0.010	1.905	0.019	0.007	2.887	0.152
	2.50	1.980	1.039	0.010	1.904	0.020	0.007	2.882	0.158
	2.55	1.979	1.039	0.010	1.903	0.021	0.007	2.875	0.165
	∞	1.950	0.522	0.007	1.950	0.522	0.007	1.521	1.521

^{a}In atomic units (1 Å $= 1.88976$ a.u.).

concept[69]. No f-type functions were used in these calculations. While f-type functions certainly are important in calculations of dynamical correlation effects (i.e. by MR-CI methods), they seem to have only small effects on results obtained in calculations which mainly include-degeneracy correlations[70]. The final basis set consists of 130 primitive GTOs contracted to 88 basis functions. The first-order approximate super-CI method was used to optimize the orbitals. Between five and 10 iterations were necessary to obtain an energy which converged to 10^{-7} a.u. when using starting vectors from a nearby point on the potential curve. The first point was obtained with starting vectors from an SCF calculation on the closed-shell configuration (49). Here 16 iterations were needed to meet the same convergence threshold.

The results of these calculations are presented in the last column of Table II and in Tables III and IV. The computed values for the dissociation energies are consistent with the results obtained for N_2 in a similar calculation[63]. The C_2 molecule has a triple bond ($\cdot C\equiv C\cdot$) like N_2. The dissociation energy for the ground state is in error by 0.26 eV, while the corresponding error for N_2 is 0.33 eV, in both cases amounting to about 0.1 eV per bond. In view of the well known difficulty in calculating dissociation energies with higher accuracy, even using large-scale multireference CI methods (see for example Ref. 38), these results must be considered as very satisfactory. Table III gives the occupation numbers for the natural orbitals of the active subspace. The two extra valence orbitals, $4\sigma_g$ and $4\sigma_u$, have as expected only small occupation numbers in the $^1\Sigma_g^+$ state. They were also found to have very little effect on the computed potential curve, as the smaller (DZ basis) calculation showed. The situation is, as expected, different in the $^3\Pi_u$ state, where the occupation numbers for these orbitals are more than doubled.

The general structure of the correlation effects can be easily deduced from Table III. Consider first the $^1\Sigma_g^+$ state. Adding together the occupation

numbers for $2\sigma_g$ and $3\sigma_u$ gives a number very close to 2. Similarly $2\sigma_u$ and $3\sigma_g$ contain two electrons, while $1\pi_u$ and $1\pi_g$ have a total occupation number of 4. An overall description of the wavefunction can be formalized as

$$(2\sigma_g, 3\sigma_u)^2 (2\sigma_u, 3\sigma_g)^2 (1\pi_u, 1\pi_g)^4 \tag{52}$$

The above occupations correspond to a constrained CASSCF wavefunction with the active subspace divided accordingly. This description is, however, not valid for the entire potential curve. At internuclear distances larger than 3 a.u. (around 1.6 Å), the bonding changes completely and the dominant configuration is now

$$(2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^2 \, {}^1\Sigma_g^+ \tag{53}$$

Configuration (53) has a weight of 74.4% at the internuclear separation 3.2 a.u., where the weight of configuration (49) has dropped to only 9.3%. This behaviour is not difficult to understand. The (weak) bonding at the larger distances is more effective with σ orbitals. The orbitals are, at these distances, only weakly hybridized. Thus $2\sigma_g$ and $2\sigma_u$ are well represented as carbon 2s orbitals, while $3\sigma_g$ and $1\pi_u$ are composed of 2p atomic orbitals. The change of the dominant configuration takes place around 3 eV above the minimum, which is halfway towards dissociation. It is thus clear that a constrained CASSCF (or a generalized valence bond) wavefunction according to (52) cannot be used in a complete description of the potential curve. At large internuclear distances the occupation of the carbon 2p shell is 2.044 on each atom. The active space here describes the well known 2s–2p near-degeneracy effect in the carbon atom, corresponding to the double excitation

$$(2s)^2 (2p)^2 \, {}^3P \rightarrow (2p)^4 \, {}^3P \tag{54}$$

Turning now to the ${}^3\Pi_u$ state, a more complex structure is found. Here the sum of all σ occupation numbers is 4.96 instead of 5.00 as configuration (51) would indicate. Thus there exists in the wavefunction for this state non-negligible contributions from configurations with more than four π electrons. The most important of these configurations corresponds to the double excitation $(2\sigma_u)^2 \rightarrow (1\pi_g)^2$, which gives angular correlation to the electron pair in the $2\sigma_u$ orbital. Why are these configurations not equally important in the wavefunction for the ${}^1\Sigma_g^+$ state? The answer to this question has already been given. The $2\sigma_u$ electrons are, in the ground state, effectively correlated by the $3\sigma_g$ orbital. Further dynamical correlation effects then become less important. Thus we see here another example of the intricate balance between different types of correlation effects. As a result it is not possible to use the same simple spin-pairing picture for the ${}^3\Pi_u$ wavefunction around equilibrium as could be done for the ${}^1\Sigma_g^+$ wavefunction.

Table IV presents the weights of the most important configurations for the two spectroscopic states of C_2. The success of the SCF calculation done by

TABLE IV

Weights (%) of the most important configurations for the $X^1\Sigma_g^+$ and a $^3\Pi_u$ states of C_2 (large basis, $n_a = 10^a$).

		R (a.u.)		
		2.30	2.35	2.40
$^1\Sigma_g^+$	$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$	70.7	70.9	71.1
	$(2\sigma_g)^2(3\sigma_g)^2(1\pi_u)^4$	14.4	13.5	12.6
	$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(1\pi_g)^2$	2.6	2.8	3.0
	$(2\sigma_g)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_g)^2$	1.4	1.4	1.5
	$(2\sigma_g)^2(2\sigma_u)(3\sigma_g)^2(1\pi_u)^3(1\pi_g)$	6.5	6.8	7.0
	Total	95.6	95.4	95.2

		R (a.u.)		
		2.45	2.50	2.55
$^3\Pi_u$	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)(1\pi_u)^3$	88.0	87.6	87.2
	$(2\sigma_g)^2(2\sigma_u)(3\sigma_g)^2(1\pi_u)^2(1\pi_g)$	3.5	4.0	4.1
	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)(1\pi_u)(1\pi_g)^2$	2.7	2.8	3.0
	Total	94.2	94.4	94.3

^{a}The weight is given as $\sum C_i^2$ where the sum is over all CSFs corresponding to the same orbital occupation.

Dupuis and Liu[67] and the corresponding failure of the two-configurational MCSCF treatment for the $^1\Sigma_g^+$ state is clearly explained by the occupation numbers presented in the upper part of the table. The SCF configuration (49) has a weight which varies rather slowly with the distance R. The configuration (50) added by Dupuis and Liu in their MC treatment has a weight that decreases with R. Three other configurations appear in the table with a total weight close to that of configuration (50). They all describe bond breaking, and their summed weight will increase with R. The effect of the strongly bonding configuration (50) is thus almost completely balanced, and the SCF configuration will therefore give reasonable values for the spectroscopic constants, as obtained by Dupuis and Liu. Of course, such a behaviour is completely fortuitous, and does not mean that the SCF wavefunction gives a valid description of the $^1\Sigma_g^+$ state of the C_2 molecule.

Finally, the results obtained above on the CASSCF level of approximation were checked by a set of multireference CI calculations using the externally contracted CI (CCI) method of Siegbahn[38]. Two sets of calculations were performed, which differed in the choice of the reference configurations. In the first set the reference space was chosen as the CASSCF CSFs with coefficients larger than 0.1 around equilibrium. For the $^1\Sigma_g^+$ state this gave seven reference configurations and for $^3\Pi$ eight. The calculation at large internuclear distance

TABLE V
MR-CCI results for the $X^1\Sigma_g^+$ and $a^3\Pi_u$ states of C_2 (large basis)[a].

State		$n_{ref} = 7$[b]		$n_{ref} = 10$[c]	Expt
$^1\Sigma_g^+$	R_e(Å)	1.244	(1.255)	1.249 (1.260)	1.243
	D_e(eV)	5.79	(5.76)	5.94 (5.83)	6.32
	ω_e(cm^{-1})				

		$n_{ref} = 8$[b]			Expt
$^3\Pi_u$	R_e(Å)	1.319	(1.319)		1.312
	D_e(eV)	5.85	(5.86)		6.24
	ω_e(cm^{-1})				
	T_e(eV)	-0.06	(-0.10)		$+0.08$

[a]Values within parentheses have been obtained by adding Davidson's correction[71] to the CCI results.
[b]The reference states are selected from the CASSCF configurations with a weight greater than 1%.
[c]As a but with the threshold 0.25%.

used the C(^{3}P) HF configuration as the reference state. The results of these calculations are presented in the second column of Table V. Comparing with the CASSCF result (Table II, large basis) we note an improvement in the equilibrium properties but not in the D_e and T_e values (the CCI calculation places $^3\Pi_u$ slightly below $^1\Sigma_g^+$). The calculations for the $^1\Sigma_g^+$ state were repeated with the threshold for the reference configurations lowered to 0.05. This resulted in an increase in D_e, but it still does not represent an improvement over the CASSCF results. Adding a Davidson correction[71] to the CCI results deteriorates the results even further for the $^1\Sigma_g^+$ state, while the $^3\Pi_u$ state is not affected. Obviously the Davidson correction, which was originally derived for a closed-shell reference CI, does not work for the highly degenerate $^1\Sigma_g^+$ state. The results obtained from these CI calculations seem to indicate that it is equally difficult to obtain a balanced description of the dynamical correlation effects as it is to achieve this goal for the near-degeneracy correlation in the CASSCF method. It should, however, be pointed out that the CI calculations were rather small (193 944 single and double excitations were included in the $^3\Pi_u$ wavefunction). Further studies of the convergence of the results with a lowering of the threshold could therefore have been carried out, probably leading to better agreement with experiment than was obtained in the present study. However, the purpose of this study of the C_2 molecule has been to illustrate the usefulness of the CASSCF method, rather than pressing the calculations towards the basis-set limit. A comprehensive account of the calculations on the C_2 and also the C_2^+ systems will be presented elsewhere[72].

B. The BH Molecule

The BH molecule represents a challenge for the CASSCF model quite different from that of C_2. In an eight-electron system like C_2 (with the four 1s electrons inactive), the number of active orbitals cannot exceed 10–12. The problem is then to find an active orbital space that represents the correlation effects, both near-degenerate and dynamical, in a balanced way. This situation is rather general since systems with 6–10 active electrons are common in CASSCF calculations. The BH molecule on the other hand can, to a very good approximation, be treated with four active electrons, leaving the two 1s electrons in an inactive orbital. A much larger active orbital space can then be used, and it becomes possible to include a large fraction of the dynamical correlation effects in to the CASSCF wavefunction. One might argue that for a four-electron system a full CI approach could just as well be used, the only remaining problem being the choice of an appropriate basis set. Such calculations have also been performed on BH, but with a smaller AO basis than was employed in the study to be discussed below[73]. A full CI with the present basis would comprise around 200 000 CSFs, which is not a very large number. Full CI calculations with 944 348 CSFs have been performed by Harrison and Handy for the FH molecule[73]. Obviously, a CASSCF calculation can in this case only be an approximation to the full CI result, albeit a very accurate one. The CASSCF method offers, however, several advantages compared to the brute-force CI method. It presents a wavefunction which is much more compact (645 CSFs was used for the $^1\Sigma^+$ states of BH). CASSCF calculations do not depend on the basis set in the same way as a full CI calculation does. Maybe the difference in approach is best summarized by noting that the CASSCF method will concentrate the information from a full CI treatment into a smaller, but optimized, set of molecular orbitals. This is of course only true if the active subspace can be sufficiently extended so that the results will converge towards the full CI limit. This does not seem to be a problem in a four-electron case. CASSCF calculations yielding results close to the full CI limit will of course very quickly become impossible when the number of electrons increases. The calculations on FH by Harrison and Hand, mentioned above, were done with eight electrons distributed in 18 orbitals[73]. With this CI calculation inserted into an MCSCF program, one probably has a good estimate of the upper limit of the CASSCF method in any of its present implementations.

A detailed account of the CASSCF results for the $X^1\Sigma^+$, $B^1\Sigma^+$ and $A^1\Pi$ potential curves of the BH molecule was given in 1981[74]. The main features of these results will be repeated here, together with some additional data concerning the structure of the CASSCF wavefunction. The calculations were performed using an AO basis set of 56 contracted Gaussian functions: B, 8s, 6p, 3d; H, 6s, 3p. The first calculations were made with 10 active orbitals:

6σ and 2π. Remaining correlation effects were estimated using second-order perturbation theory[75]. As a result of this study the final active subspace included 14 orbitals ($6\sigma, 3\pi$ and 1δ), resulting in a wavefunction comprising 645 CSFs of $^1\Sigma^+$ symmetry.

The total correlation energy of the BH molecule in the $X^1\Sigma^+$ ground state at equilibrium internuclear distance has been estimated by Meyer and Rosmus to be 0.152 a.u.[76]. Of this 0.048 a.u. correspond to 1s–1s and 1s–valence correlation. The valence correlation energy in BH is thus 0.104 a.u. The CASSCF calculation, utilizing the basis set and active space given above, recovers 89% (0.093 a.u.) of the total valence correlation energy, the remaining error being 0.30 eV. These values can be compared to the pair natural-orbital CI (PNO-CI) valence correlation energy (0.091 a.u.) obtained by Meyer and Rosmus, using a similar basis set[76]. The coupled electron-pair approximation (CEPA) corrected value was 0.100 a.u., but this is of course not an upper bound. The natural-orbital occupation numbers are presented in Table VI. The values reported show that the active space used includes in the wavefunction natural orbitals with occupation numbers down to around 10^{-3}. The most important correlation effect in the $^1\Sigma^+$ states is the angular correlation of the σ electrons affected by the 1π natural orbital. To a smaller extent, the 2π orbital plays the same role in the $^1\Pi$ state. Horizontal correlation is concentrated into one antibonding σ orbital, 4σ in the $X^1\Sigma^+$ and $A^1\Pi$ states and 5σ in the $B^1\Sigma^+$ state. The 4σ orbital is, in the B state, a Rydberg orbital with mainly B(3s) character. The remaining σ and π orbitals have small occupation numbers. They describe higher-order radial and angular correlation effects. The δ orbitals have very low occupation numbers in the $^1\Sigma^+$ states (the value is

TABLE VI

Natural-orbital occupation numbers of the CAS
wavefunction for BH (at $R = 2.40$ a.u.).

Orbital	State		
	$X^1\Sigma^+$	$B^1\Sigma^+$	$A^1\Pi$
2σ	1.956	1.929	1.926
3σ	1.864	0.996	0.984
4σ	0.025	0.955	0.037
5σ	0.009	0.021	0.008
6σ	0.007	0.004	0.007
7σ	0.002	0.001	0.002
$1\pi^a$	0.123	0.081	0.016
$2\pi^a$	0.014	0.008	0.014
$3\pi^a$	0.002	0.005	0.003
$1\delta^a$	0.000	0.000	0.005

[a]Summed over the two components.

TABLE VII
Some properties of the BH molecule computed with the CASSCF
method. Experimental values within parentheses[a].

Property	$X^1\Sigma^+$	$B^1\Sigma^+$	$A^1\Pi$
R_e (Å)	1.233	1.216	1.230
	(1.232)	(1.216)	(1.219)
D_e (eV)	3.52	1.88	0.50
	(3.57)	(2.05)	$(0.70)^b$
T_e (cm^{-1})	–	52512	24017
		(52336)	(23135)
Dipole	1.310	-4.677	0.591
moment (D)	(1.270)	$(-)$	(0.58)
$\Delta G_{v+\frac{1}{2}}^c$			
$v=0$	2265.9	2237.2	1993.2
	(2269.3)	(2248.2)	(2086.2)
1	2171.0	2052.0	1642.2
	(2173.8)	(2073.7)	(1830.4)
2	2077.3	1855.0	–
	(2080.5)	(1875.8)	(1479.6)

[a]Refs 66 and 77.
[b]Experimental value estimated in Ref. 78.
[c]Intervals between the first vibrational levels.

0.0002), but are, as expected, of considerably greater importance in the $A^1\Pi$ state, where one π orbital is occupied.

Some selected properties of the three potential curves for BH are presented in Table VII. A more complete account can be found in Ref. 74. The agreement with experiment is excellent for the $X^1\Sigma^+$ ground state, and it is difficult to see how it could be improved by a more extensive calculation. The $B^1\Sigma^+$ state is characterized by a double minimum potential resulting from the crossing between an ionic, B^+H^-, state with the Rydberg state dissociating into boron $(2s)^2(3s)$ and hydrogen. The inner minimum, which is dominantly a Rydberg state, is the only one observed experimentally and the results presented in Table VII correspond to properties of this part of the potential curve only. The agreement with experiment is satisfactory. The remaining errors are most probably due to a less accurate description of the ionic configuration. The diffuse character of the hydrogen negative ion is pathologically difficult to describe with Gaussian basis sets.

Also the $A^1\Pi$ state involves two dominant configurations. The interaction between the boron $(2s)^2$ $(2p)$ ground state and hydrogen is repulsive in this symmetry. A attractive potential between the excited boron $(2s)$ $(2p)^2$ configuration and hydrogen crosses over the repulsive curve, resulting in an

adiabatic potential with a maximum and a shallow minimum. The repulsive part of the potential is probably better described by the present basis set, which was optimized for the boron $(2s)^2$ $(2p)$ ground state. The result is too large a T_e value and too small a dissociation energy. Even if the errors are small they have a large effect on the calculated vibrational levels. Four bands have been found experimentally (cf. Table VII) but for the theoretical curve only three levels were found below the maximum. These results illustrate some of the difficulties encountered in calculations on potential curves involving electronic configurations of very different character. For BH this is mainly a basis-set problem, but for larger systems the problem of a balanced treatment of the different correlation effects also becomes crucial. The C_2 molecule was an illustration of such a situation.

C. The N–N Bond in N_2O_4

It has already been stated several times that the primary purpose of the CASSCF method lies in producing a qualitatively correct zeroth-order wavefunction for a molecular system, rather than yielding accurate numerical results. The C_2 and BH molecules represent cases where it was possible to go beyond this more limited goal, for C_2 by a careful balance of atomic and molecular correlation effects, and for BH by including a large fraction of the dynamical correlation effects. The present example, the N–N bond in dinitrogen tetroxide, is of a different nature. The aim here is not to obtain results of high accuracy, but to explain why the N–N bond in this molecule is so long, a problem which has remained unsolved in spite of numerous experimental and theoretical investigations over the past 30 years.

The experimental value for the N–N bond length in N_2O_4 varies between 1.76 and 1.78 Å[79,80], which is much longer than the bond length found, for example, in hydrazine, N_2H_4, 1.47 Å[81]. Several theoretical investigations have been performed in order to explain the long N–N bond in N_2O_4. The SCF optimized values have been obtained with AO sp basis sets and also with basis sets including d-type polarization functions. The former basis set gives the value 1.67 Å, while the inclusion of polarization functions shortens the bond length to 1.59 Å, almost 0.2 Å smaller than experiment[82]. Obviously, this molecule cannot be described on the SCF level of approximation. The bond is weak and it might be expected that inclusion of the N–N antibonding σ^* orbital, to correlate the bonding σ electron pair, could have a large effect on the bond distance. Such a calculation has also been performed using a one-pair GVB wavefunction and a split valence 4-31G basis set[80]. The resulting N–N distance was 1.80 Å, in apparent agreement with experiment. The problem is, however, that inclusion of polarization functions in the basis set decreases this value to 1.67 Å[82], which is again 0.1 Å shorter than the experimental value. The GVB treatment is equivalent to a CASSCF calculation with two active

Ni $d^9s\ ^3D$ forms only a weak bond of the van der Waals type with C_2H_4. The reason is the repulsion between the 4s electron of Ni and the closed shells of the ligand, which cannot be counterbalanced by a charge transfer (CT) from the 3d orbitals, which are much more contracted than the diffuse 4s orbital. The situation is quite different for the singlet state, $^1A_1$ with C_{2v} symmetry, which dissociates into Ni $d^9s\ ^1D$ plus ethene. Here it becomes possible to unshield the Ni 3d orbitals by a hybridization of the 4s and one 3d orbital, thus reducing the repulsion and making bonding via back-donation possible. The elucidation of this bonding mechanism in the low-spin transition-metal ligand bond is another illustration of the strength of the CASSCF method in predicting the basic features of complex electronic structures.

The bonding between a transition metal and an olefin is usually discussed in terms of the Dewar–Chatt–Duncanson (DCD) model[104]. In this model, bonding occurs via a simultaneous donation of electrons from the olefin π orbital to the metal and a back-donation from the metal $3d_{xz}$ orbital to the empty π^* orbital. The complex is assumed to have C_{2v} symmetry with Ni on the positive z axis, the C–C bond on the x axis and the plane of the ethene molecule perpendicular to the Ni–C–C plane. Such a model involves four orbitals: the π and π^* orbitals of C_2H_4 and the 4s and $3d_{xz}$ orbitals of nickel. This would also be the natural starting point in a GVB treatment. The corresponding SCF electron configuration would be $(a_1)^2(b_2)^2$, where a_1 is a linear combination of 4s, and π, and b_2 a linear combination of $3d_{xz}$ and π^*. The inactive subspace includes the remaining four 3d orbitals. The formal valence state for nickel is, in this model, d^{10} with the 4s acceptor orbital empty and the $3d_{xz}$ donating orbital doubly occupied.

CASSCF calculations were performed on $Ni(C_2H_4)(^1A_1)$, but without the (as we shall see) biased selection of active orbitals, which the above discussion would suggest[94]. All 3d orbitals were included in the active subspace, together with the 4s orbital and the π and π^* orbitals of C_2H_2 (actually the C–C σ and σ^* orbitals were also included, but this is of less importance for the following discussion). The results of the calculations revealed that the simple CT picture of the bonding is incomplete. It turns out that the atomic character of the Ni(^1D) atom is to some extent preserved also in the complex. The electronic configuration for the ^1D state of nickel can be written as (excluding the core electrons 1s–3p):

$$(3d\pi)^4(3d\delta)^4(3d\sigma, 4s)_S \qquad (57)$$

where the $M = 0$ component has been chosen. The other four components can be obtained by switching the 3d hole to one of the other four orbitals. The singlet coupled pair $(3d, 4s)_S$ can alternatively be obtained as a linear combination of two closed shells

$$(3d, 4s)_S = (sd_+)^2 - (sd_-)^2 \qquad (58)$$

losing any of the described characteristics, to constrain the subspace into a σ and π block, with six σ orbitals (and 10 electrons) and six π orbitals (and eight electrons). The CI expansion then contains 976 symmetry-adapted CSFs. CASSCF calculations using such an active subspace and a DZP basis set yield an N–N bond distance of 1.80 Å, and a dissociation energy into two NO_2 fragments of 7 kcal mol^{-1}. These results are very satisfactory. The bond distance is slightly too long, which is expected from the level of approximation used. The experimental dissociation energy has been estimated[83] to be around 13 kcal mol^{-1}. Better agreement with this value can only be expected with a substantially larger AO basis set, and a more extensive level of correlation.

An analysis of the natural orbitals shows that the repulsive resonance structures will indeed contribute to the wavefunction also in N_2O_4. The occupation fo the σ, σ^* orbital pair was, in the 10-electron calculation, almost exactly 2. In the 18-electron calculation the occupation is 2.06, showing the presence of configurations of the type $(On, \pi) \rightarrow (\sigma^*, \pi^*)$. The weight of these configurations is smaller in N_2O_4 than in two non-interacting NO_2 fragments. Since they stabilize the NO_2 radicals and are repulsive towards dimer formation, their effect will be to weaken and lengthen the N–N bond.

The NO_2 dimer is a beautiful example of the power of the CASSCF method in elucidating complex electronic structures. A detailed account of the calculations has been presented elsewhere[84].

D. Transition-metal Chemistry

Chemical bonds involving transition-metal atoms are often of a complex nature. Several factors contribute to this complexity. Many atoms contain several unpaired electrons, resulting in many close-lying spectroscopic states. The spin and space symmetry of the lowest molecular state is then difficult to postulate in advance. Most transition-metal atoms have a $(3d)^n(4s)^2$ ground-state electronic configuration. In molecules the bonding state is often $(3d)^{n+1}(4s)$. The energy difference between these two configurations is then a crucial parameter. It is often very difficult to compute and large errors are sometimes encountered on the SCF or MCSCF level of approximation. Taking Ni as an example, one finds at the HF level a splitting of 1.25 eV[85] between the $(3d)^8(4s)^2\,^3F$ ground state and $(3d)^9(4s)\,^3D$, while the experimental value is -0.03 eV. Including the dynamical correlation effects of the 3d shell, using standard basis sets, reduces the splitting to 0.4 eV[86]. Also, the difference in shape between the atomic orbitals in the two configurations causes problems.

The most severe problem is most probably the large dynamic correlation effects inherent in a 3d shell with many electrons. Omission of these effects sometimes even leads to an incorrect qualitative description of the chemical bond. A drastic example is the Cr_2 molecule, mentioned in the introduction,

where a full valence CCAS calculation predicts a bond length which is 0.8 Å too long[16], and a bond energy which is only a small fraction of the true value. Large structure-dependent correlation effects in the 3d shell are responsible for the failure of the simpler model to give a proper description of the multiple bond in Cr_2.

As a consequence it is mandatory to use a higher level of theory in studies of 3d systems, for example, by combining CASSCF and multireference CI calculations. A number of studies of transition-metal systems published during the last three years have followed this strategy. They range from calculations on diatomic molecules to large transition-metal complexes like ferrocene[87] and (Mo_2Cl^{4-})[88]. Some examples of such calculations can be found in Refs 86–96. It would be outside the scope of this review to include a comprehensive discussion of all these studies. Therefore only two illustrative examples have been selected: the NiH molecule and the complex between a nickel atom and an ethene molecule.

1. The NiH Molecule

This molecule was the first system containing a transition-metal atom to be studied with the CASSCF method[86]. It is the simplest molecule containing a nickel atom, and is therefore a suitable prelude to studies of more complex nickel-containing systems. Some molecular parameters are also known experimentally, and can be used to judge the quality of the calculations.

The lowest states of NiH are formed from $Ni(d^9s\ ^3D)$ interacting with a hydrogen atom. Three doublet states, $^2\Delta$, $^2\Sigma^+$ and $^2\Pi$, can be formed, of which $^2\Delta$ is known to be the ground state. This state is characterized as having an NiH σ bond and a $3d\delta$ open shell, the remaining eight electrons being in closed shells. The simplest CAS wavefunction giving a proper description of the dissociation process would consider only two electrons in two orbitals, the NiH bonding and antibonding pair. For technical reasons the open-shell orbital $3d\delta_{xy}$ also has to be include into the active subspace, which then includes three electrons in three orbitals. It is, however, unclear as to what extent the $3d\sigma$ orbital is involved in the bonding, and the preliminary calculations, therefore, also included this orbital, together with two electrons. In the σ symmetry there are then four electrons distributed among three orbitals. Only one of them consequently is weakly occupied. Such an active subspace is ambiguous, since the weakly occupied orbital can be used to correlate only one of the strongly occupied orbitals. At large internuclear separations the choice will obviously be the NiH bonding orbital, but at smaller bond distances this choice is not immediately clear. The correlation energy gained by correlating the $3d\sigma$ orbital is now of the same order. Thus there exist two close-lying local minima on the energy surface. This is a typical situation where convergence problems can be expected in a CASSCF

calculation. The remedy is, of course, to introduce a second weakly occupied orbital into the active subspace. The ambiguity is then removed, and a consistent treatment of the bond-breaking mechanism is obtained. This is not a unique case. Convergence problems in CASSCF calculations are often due to an unbalanced choice of the active subspace leading to ambiguities in the character of the weakly occupied orbitals.

The final active subspace chosen for NiH ($^2\Delta$) thus consists of five electrons distributed among five orbitals. The corresponding CASSCF calculations give the molecular parameters: $r_e = 1.525\,\text{Å}, D_e = 1.45\,\text{eV}$ and $\omega_e = 1642\,\text{cm}^{-1}$. These results are not very accurate. The experimental values are[66]: $r_e = 1.475\,\text{Å}$ and $\omega_e = 1927\,\text{cm}^{-1}$. The dissociation energy is not known, except for an upper limit of $3.07\,\text{eV}$[66]. A subsequent MR-CI calculation, including correlation of all the valence electrons, improves the results to: $r_e = 1.470\,\text{Å}$, $D_e = 2.28\,\text{eV}$ and $\omega_e = 1911\,\text{cm}^{-1}$, in very good agreement with experiment.

The study of NiH also included calculations of a number of excited states of both d^9s and d^8s^2 origin. It was not possible to base the CI calculations of all these states on independent CASSCF determinations of the orbitals, owing to convergence problems in the Newton–Raphson procedure. These problems occurred for some states which were not the lowest of its symmetry, and were most probably due to an incomplete inclusion of CI–orbital coupling. The CI calculations were therefore performed with orbitals obtained from CASSCF calculations using average density matrices for the states of interest. It was not possible, however, to use this procedure for full potential curve calculations, since some of the states change character adiabatically due to avoided crossings. Also, averaging the densities for d^8s^2 and d^9s in the nickel atom does not give a good orbital basis for the different spectroscopic states of the atom. The spectrum of NiH around the equilibrium internuclear separation is on the other hand quite insensitive to the choice of the molecular-orbital basis. Using average orbitals in CI calculations of molecular spectra is therefore a procedure which should be used with much care.

Is it possible to improve the results for NiH on the CASSCF level of accuracy by extending the active subspace? The answer to this question is most probably 'no'. The next important feature to include would be the radial correlation effects in the 3d shell of the nickel atom. The active subspace then has to include two sets of 3d orbitals together with the NiH σ and σ^* orbitals: 11 electrons distributed among 12 orbitals. Such a calculation is well within the limits of the present capabilities, but it is not at all certain that it would give a balanced description of the correlation effects of the entire potential curve:

A simpler molecule which exhibits the same features as NiH, of large intra-atomic correlation effects, is FH. The SCF configuration for this molecule is

$$(2\sigma)^2(3\sigma)^2(1\pi)^4 \tag{55}$$

where 2σ is the fluorine 2s orbital, 3σ the FH bond and 1π the fluorine $2p\pi$ orbitals. It is well known that inter-pair correlations are important for the description of the bonding in this molecule. A CASSCF description of the most important dynamical correlation effects in the molecule is obtained with an active space where the orbitals $4\sigma, 5\sigma$ and 2π are added to the SCF orbitals (55). At large separations 4σ will become the hydrogen 1s orbital, 5σ the fluorine 3s orbital and 2π the 3p orbital pair. A CASSCF calculation using such an active subspace gives a D_e value of 6.00 eV and $r_e = 0.921 Å$[97], to be compared with the experimental values 6.12 eV and $0.917 Å$[66]. Although these values are quite satisfactory, they are clearly the result of an unbalanced treatment of the 2p–2p correlations in fluorine. The $3p_z$ orbital is not included in the active subspace at large separations. The double excitation

$$(3\sigma)(1\pi) \rightarrow (4\sigma)(2\pi) \tag{56}$$

describes the corresponding inter-pair correlation effect at small internuclear separations, but vanishes at dissociation where 4σ becomes the singly occupied hydrogen 1s orbital[98]. This type of imbalance is very difficult to correct for in an MCSCF calculation with a small number of active orbitals. It is tempting to attempt to remedy the imbalance by adding one more σ orbital to the active space. Such a calculation gives a dissociation energy of 5.56 eV and $r_e = 0.922$. The inter-pair correlations at dissociation are now much better described, but the effect of the new orbital is much smaller at equilibrium. The occupation number varies from 0.0055 at large separations to only 0.0017 at equilibrium. Actually, the smaller calculation does give a more balanced treatment of the inter-pair correlation effects, in the negative sense of neglecting about the same amount in the molecule and the separate atoms.

It is clear that an enlargement of the active subspace in NiH, which tries to account for the 3d pair correlation effects, will run into balance problems similar to those experienced in FH. The conclusion seems rather clear: structure-dependent dynamical correlation effects in systems with high electron density cannot be accounted for in an MCSCF treatment in a balanced way. Large CI or MBPT treatments then become necessary and the calculations have to include a large fraction of the total correlation energy, in order to give reliable results for relative energies.

2. The Nickel–Ethene Complex

The weak chemical bond formed between a nickel atom (in the d^9s electronic configuration) and an ethene (C_2H_4) molecule will be considered as a final example. The results to be discussed below are not unique to this system. The main features have been found in a number of transition-metal compounds of the type TM–X where X is a ligand molecule[93-95,99-103].

Ni d^9s ^3D forms only a weak bond of the van der Waals type with C_2H_4. The reason is the repulsion between the 4s electron of Ni and the closed shells of the ligand, which cannot be counterbalanced by a charge transfer (CT) from the 3d orbitals, which are much more contracted than the diffuse 4s orbital. The situation is quite different for the singlet state, $^1A_1$ with C_{2v} symmetry, which dissociates into Ni d^9s ^1D plus ethene. Here it becomes possible to unshield the Ni 3d orbitals by a hybridization of the 4s and one 3d orbital, thus reducing the repulsion and making bonding via back-donation possible. The elucidation of this bonding mechanism in the low-spin transition-metal ligand bond is another illustration of the strength of the CASSCF method in predicting the basic features of complex electronic structures.

The bonding between a transition metal and an olefin is usually discussed in terms of the Dewar–Chatt–Duncanson (DCD) model[104]. In this model, bonding occurs via a simultaneous donation of electrons from the olefin π orbital to the metal and a back-donation from the metal $3d_{xz}$ orbital to the empty π^* orbital. The complex is assumed to have C_{2v} symmetry with Ni on the positive z axis, the C–C bond on the x axis and the plane of the ethene molecule perpendicular to the Ni–C–C plane. Such a model involves four orbitals: the π and π^* orbitals of C_2H_4 and the 4s and $3d_{xz}$ orbitals of nickel. This would also be the natural starting point in a GVB treatment. The corresponding SCF electron configuration would be $(a_1)^2(b_2)^2$, where a_1 is a linear combination of 4s, and π, and b_2 a linear combination of $3d_{xz}$ and π^*. The inactive subspace includes the remaining four 3d orbitals. The formal valence state for nickel is, in this model, d^{10} with the 4s acceptor orbital empty and the $3d_{xz}$ donating orbital doubly occupied.

CASSCF calculations were performed on Ni(C_2H_4)($^1A_1$), but without the (as we shall see) biased selection of active orbitals, which the above discussion would suggest[94]. All 3d orbitals were included in the active subspace, together with the 4s orbital and the π and π^* orbitals of C_2H_2 (actually the C–C σ and σ^* orbitals were also included, but this is of less importance for the following discussion). The results of the calculations revealed that the simple CT picture of the bonding is incomplete. It turns out that the atomic character of the Ni(^1D) atom is to some extent preserved also in the complex. The electronic configuration for the ^1D state of nickel can be written as (excluding the core electrons 1s–3p):

$$(3d\pi)^4(3d\delta)^4(3d\sigma, 4s)_S \tag{57}$$

where the $M = 0$ component has been chosen. The other four components can be obtained by switching the 3d hole to one of the other four orbitals. The singlet coupled pair $(3d, 4s)_S$ can alternatively be obtained as a linear combination of two closed shells

$$(3d, 4s)_S = (sd_+)^2 - (sd_-)^2 \tag{58}$$

where

$$(sd_+) = (1/\sqrt{2})(3d + 4s) \tag{59a}$$

$$(sd_-) = (1/\sqrt{2})(3d - 4s) \tag{59b}$$

The results of the CASSCF calculation shows that (58) is a natural starting point for a discussion of the bonding mechanism. When the molecule is formed, a continuous shift of the occupations of (sd_+) and (sd_-) takes place and (58) changes to

$$C_1(sd_+)^2 - C_2(sd_-)^2 \tag{60}$$

where C_1 is now larger than C_2. The s character of sd_+ also decreases somewhat. The 3d orbital that combines with 4s to form these hybrids is $3d_{y^2-z^2}$. Thus the (sd_+) orbital concentrates the charge along a line perpendicular to the Ni–C–C plane, with a diminished density in the bonding region. On the other hand (sd_-) is pointing along the line through Ni and bisecting the C–C bond. This orbital acquires some 4p character, which moves the charge to the back side of the Ni atom. The occupation numbers for (sd_+) and (sd_-) in $Ni(C_2H_4)$, at equilibrium, are 1.81 and 0.20 respectively. Occupation numbers for corresponding hybrid orbitals in some other NiX compounds are given in Table VIII.

The bonding mechanism is now clear. It involves five orbitals: $(sd_+), (sd_-), 3d_{xz}, \pi$ and π^*. When $Ni(^1D)$ approaches the ligand the electrons move from (sd_-) to (sd_+), which reduces the repulsion between nickel and the ligand π orbital. A much more effective interaction between the π system of C_2H_4 and the nickel 3d orbitals becomes possible, leading to the formation of a weak bond between $3d_{xz}$ and π^* and some delocalization of the π orbital onto the nickel atom. The total donation of charge to nickel is 0.42 electrons while 0.61 electrons are transferred in the opposite direction.

The sd hybridization of d^9s nickel is not possible in the triplet states, which explains the weak bonding. The singlet state is, on the other hand, bound with almost 20 kcal mol^{-1} with respect to $Ni(^1D)$ plus ethene[94]. A similar bond

TABLE VIII
Occupation numbers for the sd_+ and sd_- hybrids in some NiX complexes (singlet states).

X	sd_+	sd_-	Ref.
C_2H_4	1.81	0.20	94
C_2H_2	1.80	0.21	95
CO	1.94	0.06	101
H_2O	1.27	0.73	101
PH_3	1.72	0.29	101
N_2 (end on)	1.8	0.2	100

energy is found for $Ni(C_2H_2)$[95]. The same bonding mechanism is also present in NiCO, which for a long time was believed to have a triplet ground state ($^3\Delta$). CASSCF and CI studies have shown that the ground state in NiCO is $^1\Sigma^+$ with a binding energy[101] of 29 kcal mol^{-1}. The constrained space orbital variation (CSOV) method[105] has been used to give a detailed analysis of the bonding in XCO for X = Fe, Ni and Cu[103]. Also, low-spin complexes of other transition metals experience the same type of hybridization. Examples which have been studied with the CASSCF methods are $FeCO$[103] and FeN_2^1[100].

IV. SUMMARY AND CONCLUSIONS

The complete active space (CAS) SCF method has been reviewed. Current methods for optimization of an MCSCF wavefunction have been discussed with special reference to the CASSCF method. The strength of the method in solving complex electronic structure problems has been illustrated with examples from the current literature. The strength of the method lies in its simplicity. It is a pure orbital method in the sense that the user only has to worry about selecting an appropriate inactive and active orbital space in order to define the wavefunction. That this selection is far from trivial has been illustrated in some of the examples. FH, N_2O_4 and $Ni(C_2H_4)$ give different aspects to this problem.

The present review has presented some illustrations of the CASSCF method. The method has been applied to a number of problems not considered here. Core ionization and shake-up spectra have been successfully analysed in terms of near-degeneracy effects in the ionized states. The shake-up spectra of p-nitroaniline[106] and p-aminobenzonitrile[107] highlight this type of application. Studies of valence ionization spectra have been done for N_2[108], ozone[109] and acetylene[110].

One obvious use of the CASSCF method is in studies of energy surfaces for chemical reactions. A number of such calculations have been reported in the literature. Some of the studies in transition-metal chemistry have already been mentioned. In this context, a study of the elimination and addition reactions of methane and ethane with nickel is also worth mentioning[110].

A number of reactions including only first- and second-row atoms have also been studied. Some illustrative examples are: the intramolecular transformation of methylene peroxide to dioxirane[111]; the photolytic decomposition of oxathiirane[112]; the reaction of singlet molecular oxygen with ethene[113]; and the dissociation of diimide[114].

The CASSCF method has also been applied in studies of molecular properties. Thus a careful analysis of the electrical properties of LiH has been undertaken, with respect to both correlation and basis-set effects. For larger systems the CASSCF can recover a considerable portion of the correlation contribution to molecular properties, but cannot provide very high accuracy

because of the limitation in the number of active orbitals. A comparison of CASSCF, CI(SD) and MBPT methods for the calculation of some molecular properties can be found in Ref. 115.

The CASSCF method is able to give a correct zeroth-order description of a wavefunction in situations where the simple independent-particle model breaks down. It is, however, not possible to use the method for accurate quantitative determinations of molecular parameters, except in special cases. The BH and C_2 molecules here serve as good illustrations. In general, however, a specific treatment of the dynamical correlation effects is necessary, in order to obtain results of chemical accuracy. Such calculations are today usually based on some form of the configuration-interaction technique. The most commonly used method is the externally contracted CI scheme[38]. The computational effort for such calculations is strongly dependent on the number of reference configurations used as a basis for the singles and doubles CI expansion. In most cases it is not possible to include all CASSCF CSFs into the reference space, but a rather restricted selection has to be made, based on the relative weights. In most cases such a selection is straightforward, but cases exist where it becomes difficult or even impossible to select a small reference space for the CI step. Cr_2 is a drastic example of such a case.

An alternative method, named internally contracted CI, was suggested by Meyer[116] and was applied by Werner and Reinsch[117] in the MCSCF self-consistent electron-pair (SCEP) approach. Here only one reference state is used, the entire MCSCF wavefunction. The CI expansion is then in principle independent of the number of configurations used to build the MCSCF wavefunction. In practice, however, the complexity of the calculation also strongly depends on the size of the MCSCF expansion. A general configuration-interaction scheme which uses, for example, a CASSCF reference state, therefore still awaits development. Such a CI wavefunction could preferably be used on the first-order interacting space, which for a CASSCF wavefunction can be obtained from single and double substitutions of the form[118]:

$$|pq\rangle = \hat{E}_{pq}|0\rangle \qquad (61a)$$

$$|pqrs\rangle = \hat{E}_{pq}\hat{E}_{rs}|0\rangle \qquad (61b)$$

where $|0\rangle$ is the CASSCF wavefunction. The single substitutions (61a) do not interact directly with $|0\rangle$, but they are important for the correlation corrections to the first-order density matrix. The calculation of the matrix elements between the CSFs (61) leads to expressions in terms of density matrices up to order 6, which is still an unsolved complication. The CI expansion based on the configuration space (61) is, however, independent of the size of the CASSCF wavefunction. It also constitutes a consistent basis for a cluster theory based on CASSCF.

In conclusion CASSCF has during its six years of existence proved to be a very general and valuable tool for electronic structure calculations. Like all other methods, it has its limitations and drawbacks. There are, however, only a few cases where CASSCF could not be used as an appropriate starting approximation. This does not mean that its present state is without problems. There is still room for improvement in the CI step, which for large expansions is the most time-consuming part of a CASSCF calculation. A method to constrain the CAS expansion in consistent ways will also be of great value, making it possible to increase the active space further. However, the most important problem for future developments is, in my opinion, the search for unbiased methods to treat dynamical correlation effects either using CI methods, as suggested above, or preferably a cluster expansion based on the CASSCF as the reference state.

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