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A multiconfigurational SCF computational method for the resolution of the vibrational Schrödinger equation in polyatomic molecules

F. Culot, J. Liévin

Laboratoire de Chimie Physique Moléculaire, CP. 160/09, Université Libre de Bruxelles,
ave. F.D. Roosevelt, B-1050 Bruxelles, Belgium
Fax: 32-2-6504232; e-mail: jlievin @ulb.ac.be

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Summary. A new variational method for solving the molecular vibration problem is proposed. The so-called VMCSCF method (vibrational multiconfigurational self-consistent field) is based on the super-CI algorithm, previously developed in the framework of electronic *ab initio* calculations. This approach makes direct use of the generalised Brillouin theorem to ensure self-consistency. The method is dedicated to the study of strongly interacting states (vibrational resonances), which are one of the main sources of perturbation in vibrational spectra. The interest of the method to tackle resonance interactions is illustrated by means of test calculations performed on the water and formaldehyde molecules.

Key words: Vibrational structure calculations – Anharmonic couplings – Vibrational resonances – Brillouin theorem

1 Introduction

Extensive work has been done in the last decade to develop methods of resolution of the pure vibrational or rovibrational Schrödinger equation, beyond the harmonic and rigid rotor approximations. Such vibrational structure studies were made possible by the constant improvements in computational Quantum Chemistry methods which now allow the determination of accurate potential energy surfaces (PES). The recent development of analytical derivation techniques (see for instance [1–5]) is a very important contribution to this state of affairs, along with some numerical approaches [6, 7] that can be used in principle at any level of theory, including the most precise multireference CI.

The resolution of the vibrational Schrödinger equation makes the connection between Quantum Chemistry and experimental spectroscopy. It allows the theorist to predict spectroscopic properties, starting from *ab initio* PES, and enables the spectroscopist to derive empirical PES from infrared spectra. Numerous experimental techniques have recently appeared such as stimulated emission pumping (SEP), laser induced fluorescence (LIF) and Fourier transform spectroscopy (FTIR) allowing the study of highly excited vibrational states and even chaotic regions [8–10]. To exploit and interpret these data one needs refined theoretical tools to make predictions of properties like energy or transition moment and to analyse the content of the wave function. The long-term goal of these studies, both experimental and theoretical, is the understanding of the dynamical behaviour of highly excited polyatomic molecules.

Among the theoretical methods, those arising from the application of the variational principle are of greatest interest. They are not limited, as the perturbative approaches, to the representation of small amplitude motions from the equilibrium position and can moreover take the interactions between quasi-degenerate levels (resonances) straightforwardly into account.

Different implementations of the variational method are reported in the literature. They differ by the form of the nuclear kinetic energy operator $\hat{T}_N$, by the analytical form of an approximated nuclear potential function $\hat{V}_N$, by the method used to determine the parameters of this potential and by the choice of vibrational coordinates and basis functions in which the hamiltonian matrix is set up. The respective advantages and disadvantages of these methodological alternatives are discussed in the literature [11, 12] and we will only summarise hereafter the more important trends.

Internal coordinates are often preferred to normal ones [11–19] because they allow for better separability and factorisability of the hamiltonian, as well as a more sensible representation of the PES for large amplitude motions. However, the analytical form of the kinetic operator is different for each type of molecule in those kinds of coordinates, and its determination is quite a tedious task. Furthermore, a different computer program has to be written for different kinds of molecule or coordinate systems.

In the normal coordinate system, also used by some authors [20–31], the form of the hamiltonian (Watson hamiltonian) is simpler and is only specific to linear [32] or non-linear [33] molecules. It is however important to take care, as reported in [34], of the pathological singularities that occur when a non-linear molecule significantly samples linear geometries. Moreover, in order to factorise the Watson hamiltonian as a sum of products of one-mode terms, the inertia matrix has to be expanded in a Taylor series [33] or fixed to its equilibrium value. This latter approximation further simplifies the hamiltonian matrix and interferes only slightly with the Coriolis coupling terms.

The potential function, $\hat{V}_N$, can either be deduced from experiments, by means of a least-squares fit to spectroscopic data [19, 35–37], or, more often, it can be constructed from ab initio calculations of the electronic energy as a function of the nuclear coordinates.

Once $\hat{T}_N$ and $\hat{V}_N$ have been determined, the next step is the set-up of the hamiltonian matrix in a carefully chosen basis set. This choice will determine the accuracy of the results and attention must be paid [11] to the completeness of the basis set, and to its ability to properly manage the singular terms of $\hat{T}_N$.

The choice of an appropriate one-dimensional basis set for each vibrational motion is decisive, as it defines the building blocks of the n-dimensional wave function and will therefore determine its quality (flexibility and compactness). Among the different kinds of basis functions that have been presented in the literature, the most standard *delocalised* primitives are Morse, associated Legendre and Fourier functions, respectively, used for stretching, bending and torsional internal coordinate motions and simple harmonic oscillators for normal modes. The introduction of *localised* one-dimensional basis sets, through the so-called discrete variable representation method (DVR) [17, 18], is certainly one of the major recent advances in this field.

The building up of the multi-dimensional basis sets by simple products of one-dimensional primitives often leads to the resolution of huge secular matrices, even for small systems. To give an order of magnitude, the number of such products (given by $p^{(3N-6)}$, for an N-atomic system and basis sets of p primitives for each vibrational motion) is 8×10^3 and 64×10^6, respectively, for $N = 3$ to 4 (with $p = 20$). Although these numbers correspond to upper limits of the actual sizes of the multi-dimensional expansions (such estimations do not take the symmetry of the system into account), they clearly show that new alternatives for diminishing the basis set sizes will be welcomed for tackling larger systems.

One solution adopted by different authors [38–43] is to consider some kind of effective decoupling between the modes, on the basis of physical criteria such as the symmetry of the modes, their frequency, or the value of potential coupling terms. An attractive way of reducing the size of the hamiltonian matrix is to optimise the wave function by successive steps [15, 17, 18, 44, 45]. The philosophy of this approach is to solve the one-dimensional problems formed by each separate mode and use the eigenfunctions as a basis set for some two- or three-dimensional calculations, and so on, until the full $(3N - 6)$-dimensional problem is solved. Another interesting approach consists of optimising variationally the basis set in a compact form and using it in a further variational calculation. This idea is developed in a family of methods [20, 24, 43, 48–50] based on the self-consistent field (SCF) and configuration interaction (CI) models, directly derived from standard electronic *ab initio* methodology. In the so-called VSCF method [20] (vibrational SCF), the variational method is applied to a trial function expressed as a single vibrational configuration, i.e. a single product of an anharmonic oscillator's functions $\{\phi\}$:

$$\Psi_{\mathrm{VSCF}} = \prod_{v=1}^{N_{\mathrm{V}}} \phi_k^v(\xi_v), \tag{1}$$

where N_{V} is the total number of vibrational degrees of freedom ($N_{\mathrm{V}} = 3N - 5$ or $3N - 6$, respectively, for a linear or non-linear N-atomic molecule), ξ_v is the vibrational coordinate associated with the vth oscillator and k is the corresponding quantum number. This leads to a set of coupled equations, one for each of the N_{V} oscillators, in which an effective potential describes the interaction of this oscillator with the mean field created by the other ones. The system of coupled equations can be solved iteratively either by numerical [48, 49] or analytical [20, 46] techniques. In this latter solution, each anharmonic oscillator (AO) function is linearly expanded over a basis set of analytical functions $\{\Omega\}$:

$$\phi_k^v(\xi_v) = \sum_{a=0}^{p} d_{ak}\,\Omega_a(\xi_v). \tag{2}$$

As in any mean field approach, the VSCF method introduces a correlation error due to the effective nature of the interactions between the oscillators. This error can be large when the interactions are strong [26], and a further variational treatment is required to explicitly introduce the correlation effects. The latter treatment consists of a configuration interaction calculation, i.e. the diagonalisation of the nuclear hamiltonian matrix in a basis set of vibrational configurations (simple products of AOs), built from the AO's basis set resulting from the previous VSCF optimisation. The CI wave function can then be written as

$$\Psi_{\mathrm{CI}} = c_0\Psi_0 + \sum_{i=1}^{M} c_i\Psi_i, \tag{3}$$

where Ψ_0 represents the reference configuration (Eq. (1)), i.e. the configuration on which the VSCF optimisation has been performed and the $\{\Psi_i\}$ are virtual vibrational configurations resulting from the replacement in Ψ_0 of one or more AOs by virtual VSCF AOs. The so called VSCF/CI two-step procedure is quite flexible. It can be performed on any VSCF configuration and the virtual configuration space, of dimension M, can be limited using different criteria [50] (energy threshold, vibrational quantum number range for each mode or maximum total number of vibrational excitations).

The exact variational solution corresponding to the chosen basis set (2) is obtained when no restrictions are introduced in the sum appearing in Eq. (3). The corresponding variational calculation will be referred to hereafter as VFCI (vibrational full-CI). In this case, the wave function being invariant to any unitary transformation of the basis set, the optimisation of the AOs basis set is no longer required.

The VSCF/CI procedure can be efficient, even with a small number of configurations, when these are carefully selected using the appropriate criteria, and when the vibrational states of interest are essentially represented by a single vibrational configuration. In that case, the CI-coefficient c_0 in Eq. (3) is close to 1.0. In contrast, when two or more configurations interact strongly, the VSCF/CI method fails. The eigensolutions dramatically depend on the choice of the Ψ_0 configuration and a basis set dependency problem occur. This comes from the fact that the VSCF procedure provides an AO's basis set optimised for a given single configuration but not for a set of strongly coupled configurations. The problems discussed above will of course disappear if the CI expansion tends to the full-CI limit.

VFCI-like calculations (vibrational full-CI) are possible from a computational point of view, for small molecules only, essentially for 3-atom [35, 36, 51–55] and 4-atom [19, 53, 55] molecules. The latter case is however close to the computational limit, with large basis sets (up to 500 000 functions in [53]) requiring special techniques to cope with such large matrices.

Alternatives to the VFCI method therefore are welcomed for treating larger molecules at a similar level of accuracy. One solution consists of reducing the size of the multi-dimensional wave function by a more efficient optimisation of the one-dimensional basis sets. Even for small molecules, it can be helpful to find more compact wave functions than those obtained for VFCI. Indeed, the compactness of the wave functions can greatly clarify the physical interpretation of spectroscopic observations (bands assignments, analysis of intensity features, understanding of anharmonic couplings, etc.).

The problem of the optimisation of a multi-dimensional basis set in terms of a previously optimised one-dimensional one is of course not specific to the vibrational SCF theory but has also been encountered in electronic SCF theory for a few decades. The solution universally adopted in atomic [56] and molecular [57–61] electronic calculations is to replace the single-configurational SCF approach by a multiconfigurational one (MCSCF), involving at least the most important configurations and implying the simultaneous optimisation of both orbitals and configuration mixing coefficients.

MCSCF methods in a rovibrational context have not been exploited till now, except in a formal attempt by Tobin and Bowman [62] and in test calculations performed with a second-order algorithm by Schwenke [63]. This kind of method would however be particularly well adapted to study the strong vibrational configuration mixings that frequently occur in polyatomic molecules. They correspond to resonance phenomena [64] (Fermi, Darling–Dennisson and Coriolis resonances) generated by the rapid increase of the density of states with the vibrational excitation energy.

The importance of configuration mixing in the study of the vibrational structure of molecules has motivated us to develop a vibrational MCSCF method (VMCSCF) and write the corresponding computer program. The algorithm has been elaborated in taking benefit of the large experience of MCSCF techniques acquired up to now in Quantum Chemistry. The algorithm developed in this work is based on the super-CI method proposed by Grein and Chang [65] in the molecular electronic context, implemented in Quantum Chemistry packages [66, 67] and applied to many molecular problems. The super-CI algorithm is an interesting alternative to the methods based on Lagrangian multiplicators [57] or on second-order density matrices [59, 60]. It uses the generalised Brillouin theorem to enforce the variational self-consistency.

The present paper is devoted to the description of an MCSCF algorithm for the vibrational problem (VMCSCF) and to some test calculations. In Sect. 2, we recall the general expression of the Brillouin theorem and describe the philosophy of the super-CI algorithm; Sect. 3 is devoted to a detailed analysis of the different steps of the algorithm, the implementation of a "state average" optimisation option is discussed in Sect. 4 and we present some test calculations on water and formaldehyde in Sect. 5.

A detailed formulation of the Brillouin theorem for vibrational self-consistent wave functions and an analysis of the symmetry and orthogonality properties of the Brillouin singly excited functions, for both the non-degenerate and degenerate cases, will be presented in a forthcoming paper.

2 The Brillouin theorem and its relation to the VMCSCF optimisation algorithm

The generalised Brillouin theorem (GBT) [68–70] is a direct consequence of the stability of a self-consistent wave function to a small perturbation applied on the anharmonic mode-oscillators or, in the electronic context, the molecular orbitals. It states that the hamiltonian matrix element between a self-consistent wave function (the solution of our problem) and a single excitation is zero.

Let us write a general multiconfigurational function as

$$\Psi_{\mathrm{VMC}} = \sum_i c_i \Psi_i, \tag{4}$$

where Ψ_i is a vibrational configuration, i.e. a simple product of anharmonic mode-oscillator functions.

The single excitation is generated by the replacement of one occupied oscillator (an oscillator present in Ψ_{VMC}) by another, either occupied or unoccupied. If we consider the replacement of the oscillator k by the oscillator 1 on the mode v, we can write the associated Brillouin condition:

$$\langle \Psi_{\mathrm{VMC}} | H | \Psi^v_{kl} \rangle = 0, \tag{5}$$

where Ψ^v_{kl} is a multiconfigurational function defined as

$$\Psi^v_{kl} = \sum_i c_i (\Psi_i(v; k \to l) - \Psi_i(v; l \to k)). \tag{6}$$

$\Psi_i(v; k \to l)$ corresponds to the replacement of ϕ^v_k by ϕ^v_l in the configuration ψ_i.

The second term of Eq. (6) corresponds to the reverse excitation and has to be taken into account in order to keep the oscillator's basis set orthogonal.

Equation (6) can be rearranged to

$$\Psi_{kl}^{v} = \sum_{n} b_n \Psi_n, \tag{7}$$

where the $\{\Psi_n\}$ are the configurations involved in the single excitations.

A direct consequence of this theorem is that the reference function cannot mix with any single excitation in a CI calculation involving only the reference and the single excitations. The main idea behind the super-CI algorithm is to force a trial reference function to respect that condition. The algorithm is then built on two successive CI steps leading, respectively, to the optimisation of the MC coefficients ($\{c\}$ in Eq. (4)) and of the AO coefficients ($\{d\}$ in Eq. (2)). The first CI solves the MC problem (4), with frozen $\{d\}$ coefficients. The second one diagonalises the hamiltonian matrix in the so-called SX space, corresponding to the superposition of the reference function and its single excitations, with frozen $\{c\}$ coefficients. The effect of the single excitations is then incorporated into the reference by a transformation of the oscillator's basis set.

3 Optimisation algorithm

Let us mention briefly the successive steps of the algorithm before describing them extensively; some further extensions to the algorithm, needed for the determination of excited states, will be discussed afterwards.

1. Determination of an initial guess for the oscillators $\{\phi\}$.
2. Resolution of the CI problem associated to the configurations of Ψ_{VMC} (MC space); build-up and diagonalisation of the hamiltonian matrix in this basis set.
3. Creation of the single excitations according to expression (6).
4. Canonical orthonormalisation of the single excitations.
5. Build-up of the hamiltonian matrix in the basis set formed by the reference and the single excitations (SX space).
6. Diagonalisation of the matrix defined at step 5.
7. Back-transformation to the original single-excitations set.
8. Transformation of the oscillator's set, using the expression of the eigenfunction obtained at step 6.
9. Resolution of the CI (MC) problem associated with the configurations of Ψ_{VMC} in this new basis set.
10. Back to step 4 and iteration until convergence.

3.1 Initial guess

As the Brillouin theorem is only valid at the first order of perturbation, it is important to start with a good initial guess, which will reasonably allow one to ignore the higher-order terms. This can be achieved by a VSCF calculation on one of the configurations involved in the MC expansion. The initial oscillators can also be taken from a previous MCSCF calculation.

3.2 Resolution of the CI secular problem associated with the MC space

This step is equivalent to a standard CI calculation performed in the MC space. There is no systematic way of choosing the configurations in an ordinary MCSCF calculation; they are taken one by one according to their alleged importance. One must at least include those necessary to represent all the states having a lower energy than the optimised states; otherwise the variational procedure could converge on one of these non-included lower states. This manual choice is coherent with the general philosophy of the method which tends to concentrate as much information as possible in a small number of configurations carefully chosen and fully optimised. One can however test the validity of the choice by using the VMCSCF optimised oscillators in a larger CI calculation and, if some important contributions occur, extend the set of MC configurations to these new terms. The definition of a set of active oscillators in which all possible excitations are performed (which is the vibrational equivalent to the electronic CASSCF [61] or FORS [71] approach) will be detailed in a forthcoming paper.

3.3 Generation of the Brillouin single excitations

Generating the single excitations means determining their number and their relevant features for the evaluation of hamiltonian matrix elements, i.e.: the number of configurations involved in each single excitation, the quantum numbers which characterise those configurations and the CI coefficients that multiply them. This is complicated by a series of factors:

1. The number of configurations in each single excitation is variable.
2. The sign of the CI coefficient changes if one considers a direct or a reverse excitation.
3. The same configuration can appear in a vast number of single excitations.

Computationally, this implies that one has to link a series of information (number of configurations, CI coefficients, signs, reference numbers of the configurations) in several vectors.

3.4 Canonical orthonormalisation of the SX space

As already observed in the electronic framework [58], the single excitations are not mutually orthogonal; only the reference function is rigorously and systematically orthogonal to the whole set of single excitations which, moreover, are generally not linearly independent. In order to simplify the CI (SX) calculation, one must eliminate the linear dependencies and orthogonalise the set. The canonical orthonormalisation scheme proposed by Löwdin [72] allows one to perform those two operations simultaneously and proceeds by diagonalising the overlap matrix. One defines the overlap matrix element S_{ij} by the following relation:

$$S_{ij} = \langle \psi_i^{\mathrm{SX}} | \psi_j^{\mathrm{SX}} \rangle, \tag{8}$$

where Ψ_i^{SX} refers to the ith function of the SX space, i.e. the reference function or one of its single excitations.

The redundant eigenvectors of this matrix are associated with a zero, or in practice very small, eigenvalue. These are eliminated from the set and the remaining ones are weighted by the reverse of the square root of their eigenvalue in order to normalise them to unity. One writes the normalised eigenvectors, the so-called canonical vectors (CSX), as

$$\psi_k^{\mathrm{CSX}} = (s_k)^{-1/2} \sum_i p_i^k \psi_i^{\mathrm{SX}}, \tag{9}$$

where s_k represents the kth eigenvalue of the overlap matrix (8). If we set $q_i^k = (s_k)^{-1/2} p_i^k$, Eq. (9) can be rearranged to

$$\psi_k^{\mathrm{CSX}} = \sum_i q_i^k \psi_i^{\mathrm{SX}}. \tag{10}$$

The reference is orthogonal to the whole set of single excitations and is therefore left unchanged by this transformation.

3.5 Build-up of the hamiltonian matrix in the SX space

Since the canonical functions have a very complex expression, they are indeed combinations of single excitations which in turn are linear combinations of configurations; the build-up of hamiltonian matrix elements between canonical functions is therefore done in several steps:

1. Calculation of the hamiltonian matrix elements between all the configurations included in the single excitations and the reference function

$$H_{lm} = \langle \psi_l | H | \psi_m \rangle. \tag{11}$$

2. Calculation of the hamiltonian matrix elements in the space formed by the reference and the original (non-orthogonalised) single excitations

$$H_{ij}^{\mathrm{SX}} = \langle \psi_i^{\mathrm{SX}} | H | \psi_j^{\mathrm{SX}} \rangle. \tag{12}$$

These matrix elements can be developed to (cf. Eq. (7))

$$H_{ij}^{\mathrm{SX}} = \sum_l \sum_m b_l b_m H_{lm}. \tag{13}$$

3. Transformation of the matrix to the canonical set.

The hamiltonian matrix elements between canonical vectors can be written as

$$H_{kl}^{\mathrm{CSX}} = \langle \psi_k^{\mathrm{CSX}} | H | \psi_l^{\mathrm{CSX}} \rangle. \tag{14}$$

Replacing (10) into (14), one obtains

$$H_{kl}^{\mathrm{CSX}} = \sum_i \sum_j q_i q_j H_{ij}^{\mathrm{SX}}. \tag{15}$$

3.6 Diagonalisation of H_{kl}^{CSX} and identification of the reference function

This operation can now be done by an ordinary diagonalisation procedure since the basis set is orthonormal. We are indeed only interested in a single eigenvector, the one corresponding to the reference function, but there is generally no one-to-one correspondence between any eigenfunction of the SX problem and the reference. Such a relation exists only when the optimised state is the fundamental one.

In such a case the *good* SX eigenfunction is the lowest. One has then to test every eigenvector and keep the one in which the reference has the largest coefficient.

However, the procedure can be adapted to give in all cases a dominant coefficient to the reference function in the lowest-lying eigenvector. By shifting the reference's diagonal hamiltonian matrix element to an arbitrary energy under the fundamental state, one can assign the lowest eigenvalue to the reference function. This trick, known as the level-shift technique in Quantum Chemistry [73, 74], allows a much better convergence on excited states since it removes the strong mixing that appears between accidentally degenerate SX eigenfunctions. The use of such an artefact is justified because, by virtue of the Brillouin theorem, H^{SX} is block-diagonal at convergence. One can then change arbitrarily the reference's energy and leave all the eigenvectors unchanged. In that context one could use a Davidson algorithm to calculate only the lowest eigenfunction. Nevertheless, this diagonalisation takes only a small fraction of the computer time needed to run the whole procedure.

3.7 Back-transformation to the original single excitations

To transform the oscillator's basis one has to use the expression of the SX function in the $\{\Psi^{\mathrm{SX}}\}$ single-excitations set. Indeed, the canonical functions are meaningless in the sense of the Brillouin theorem.

Let us write the SX eigenfunction, in terms of the canonical vectors,

$$\psi_{\mathrm{ESX}} = \sum_k r_k \Psi_k^{\mathrm{CSX}}. \tag{16}$$

Replacing the canonical vectors by their expression (10) leads to

$$\psi_{\mathrm{ESX}} = \sum_k r_k \sum_i q_i^k \Psi^{\mathrm{SX}}. \tag{17}$$

By inverting the summations and rearranging, one obtains

$$\psi_{\mathrm{ESX}} = \sum_i \Psi_i^{\mathrm{SX}} \sum_k r_k q_i^k. \tag{18}$$

If we set $a_i = \sum\limits_k r_k q_i^k$, we can rewrite Eq. (18) to

$$\psi_{\mathrm{ESX}} = \sum_i a_i \psi_i^{\mathrm{SX}} \tag{19}$$

or, returning to the original notation for the single excitations,

$$\psi_{\mathrm{ESX}} = a_{00}\psi_0 + \sum_{v=1}^{N_v} \sum_k \sum_{l \neq k} a_{kl}^v \psi_{kl}^v, \tag{20}$$

where a_{kl}^v represents the weight of the single excitation associated with the replacement of the oscillator k by the oscillator l on the mode v. Those coefficients will be used in the next step to transform the AO basis set. For a perfectly converged MCSCF wave function, they should all be equal to zero, except a_{00}. This latter property can also be used as an indirect test of the Brillouin theorem.

3.8 Transformation of the oscillator's basis set

In a basis set of $p + 1$ primitive oscillators, an arbitrary anharmonic oscillator of quantum number k on the mode v is transformed according to

$$\phi_k^v[n+1] = a_{kk}^v \phi_k^v[n] + \sum_{l=0, l \neq k}^{p} a_{kl}^v \phi_l^v[n], \tag{21}$$

where n is the number of iterations.

This latter transformation applies to all the basis functions, occupied or virtual. To perform it we need to determine all the $(p + 1)^*(p + 1)$ a_{kl}^v coefficients. These are taken from Eq. (20) completed by two orthonormality relations

$$(a_{kk}^v)^2 = 1 - \sum_{l=0, l \neq k}^{p} (a_{kl}^v)^2, \tag{22}$$

$$a_{lk}^v = -a_{kl}^v. \tag{23}$$

Expression (22) implies, as a phase condition on ψ_{ESX}, that the coefficient of the reference function must be positive. The orthogonality constraint (23) is satisfied to the first order.

In order to keep a basis set perfectly orthogonal (to all order of perturbation), it is nevertheless advised to orthogonalise the new basis set. Otherwise, the orthogonality could be progressively deteriorated by the higher-order terms along the successive iterations. In our implementation, a Schmidt orthogonalisation procedure is used for this purpose.

Two different options can be chosen to transform the oscillators: one can transform the actual oscillators and re-evaluate the mode integrals in the new basis set or one can transform directly the mode integrals. The expression of the oscillators is not needed to run the calculation, the evaluation of the hamiltonian matrix only requires the mode integrals, it is then faster to transform them directly. However, it is highly desirable to know the AO coefficients in order to monitor the convergence of the procedure. It is also crucial to produce the converged oscillators in order to determine the wave function completely so that it could be used to run a further VMCSCF or VCI calculation or to evaluate any vibrational property such as a dipole moment matrix element. We chose to transform separately the oscillators and the integrals at each iteration to avoid a costly re-evaluation of the integrals and keep all the information on the wave function.

3.8.1 Transformation of the LCHO basis set. Applying transformation (21) to an anharmonic oscillator (2), one obtains the expression

$$\phi_k^v[n+1] = \sum_{a=0}^{m} d_{ak}[n+1]\, \Omega_a(\xi_v) = \sum_{l=0}^{m} a_{kl}^v \sum_{b=0}^{m} d_{bk}[n]\, \Omega_b(\xi_v). \tag{24}$$

The expression of the new $\{d\}$ coefficients is derived by multiplying (24) to the left by $\Omega_a^*(\xi_v)$ and integrating over ξ_v:

$$d_{ak}[n+1] = \sum_{l=0}^{m} a_{kl}^v d_{al}[n]. \tag{25}$$

3.8.2 Integrals transformation. Let us write the matrix element of a one-mode operator $f(\xi_v)$ taken between two transformed functions $\phi_k^v[n+1]$ and

$\phi_m^\nu[n+1]$:

$$\left\langle a_{kk}^\nu \phi_k^\nu[n] + \sum_{l=0,\, l\neq k}^{p} a_{kl}^\nu \phi_l^\nu[n] \,|f(\xi_\nu)|\, a_{mm}^\nu \phi_m^\nu[n] + \sum_{n=0,\, l\neq m}^{p} a_{nm}^\nu \phi_n^\nu[n] \right\rangle, \quad (26)$$

which can be rearranged to

$$\left\langle \phi_k^\nu[n+1] \,|f(\xi_\nu)|\, \phi_m^\nu[n+1] \right\rangle = \sum_{l=0}^{p} \sum_{n=0}^{p} a_{kl}^\nu a_{mm}^\nu \left\langle \phi_l^\nu[n] \,|f(\xi_\nu)|\, \phi_n^\nu[n] \right\rangle. \quad (27)$$

This expresses the relation between the mode integrals at iterations n and $n+1$.

3.9 Resolution of the MC problem in the new basis set

This step is identical to the second step but is performed in the new AO basis set. It produces a new guess for the CI (MC) coefficients that can be used along with the new oscillator's coefficients to run a further iteration of the procedure.

3.10 Convergence criteria

The procedure from steps 4 to 9 is applied iteratively until convergence obeys the following criteria:

1. The energy of the SX eigenfunction must converge to the MC energy, since the two functions must be identical at convergence:

$$|E_{\mathrm{MC}}[n] - E_{\mathrm{ESX}}[n]| = \delta_1 \leqslant \delta. \quad (28)$$

2. The difference between the SX energies at iterations n and $n-1$ must converge beyond a user-fixed threshold:

$$|E_{\mathrm{ESX}}[n] - E_{\mathrm{ESX}}[n-1]| = \delta_2 \leqslant \delta'. \quad (29)$$

3. The difference between the MC energies at iterations n and $n-1$ must converge beyond a user-fixed threshold:

$$|E_{\mathrm{MC}}[n] - E_{\mathrm{MC}}[n-1]| = \delta_3 \leqslant \delta''. \quad (30)$$

4. The Brillouin theorem must be verified; i.e. all the single excitations must have a zero, or arbitrary small, coefficient on the SX eigenfunction.

All these conditions must be satisfied simultaneously. The first three can be merged in a single condition

$$\delta_1 + \delta_2 + \delta_3 \leqslant \delta_t \quad (31)$$

where δ_t is a user-fixed threshold.

In our implementation of the algorithm, condition (31) is tested at every iteration. If the criterion is satisfied, the Brillouin conditions are tested (a threshold of 10^{-5} has been fixed for the largest SX coefficient). The program continues running until all the conditions are satisfied or until the maximum allowed number of iterations is reached.

4 State average MCSCF optimisation

The procedure described above is perfectly adapted to converge on isolated states, usually of low energy. When several states in a close energy range are interacting, the convergence can be spoiled by the so-called "root-flipping" phenomenon. This occurs when one optimises an excited state which interacts with another one of slightly lower energy. The MCSCF procedure tends usually to stabilise the optimised state and destabilise the others so that two states of close energy can be inverted. In such circumstances the procedure can converge on an unwanted state, if it converges at all. This problem is not characteristic of our algorithm but is also encountered by all the MCSCF procedures developed for the electronic problem. In that context, several solutions have been suggested in the literature [75]:

1. Constrain the wave function to be orthogonal to all the lower-energy state wave functions.
2. Freeze some oscillators (or molecular orbitals) that ensure a good representation of the lower-energy states.
3. Increase the number of MC configurations.
4. Optimise the basis set (oscillators or MO) for the average of several states, usually a group of closely interacting states.

The first two proposals imply a severe constraint on the variational procedure and lead only to a partially optimised wave function. Furthermore, it would be very difficult to implement the orthonormality constraint in our algorithm.

The third proposal works fairly well and is straightforward to apply, but it is opposite to the MCSCF philosophy which aims to optimise a compact wave function.

The state-average optimisation of the oscillator's basis set seems to be the best compromise since it leads to a balanced representation of the interacting states. Indeed, the procedure does not favour any of the states included and would not deteriorate any of them. Furthermore, a redistribution of the state's energy-ordering will not generate a dramatic change in the oscillator's basis set, since it is optimised for the average of those states. This ensures a much smoother and safer convergence of the MCSCF procedure.

Another advantage of this technique is to represent all the optimised states in the same basis set so that they are mutually orthogonal. This can be very helpful in eliminating some zeroth-order overlap terms, which are meaningless in the computation of transition dipole moments [26]. For that purpose one must include in the average the two states involved in the transition.

This approach has been widely used in the electronic context. Its transcription to the Grein and Chang algorithm has been described by Ruedenberg [58]. We will detail, in the following subsection, its implementation in our algorithm and its impact on the resolution of the SX problem.

4.1 The state-averaging formalism

Let us consider, for the sake of simplicity, a two-state system, the generalisation to an *n*-state system being straightforward. We want to minimise the weighted average energy of the states 0 and 1 which can take the form

$$W_0 E_0 + W_1 E_1 = W_0 \langle \Psi_0 | H | \Psi_0 \rangle + W_1 \langle \Psi_1 | H | \Psi_1 \rangle , \tag{32}$$

where W_0 and W_1 are the weights given to the states.

The only steps modified by the state average option are those involved in the build-up of the SX hamiltonian matrix, namely steps 4 and 5. The MC problem is left unchanged and the single excitations keep the same expression. The single excitations coming out of Ψ_0 and Ψ_1 are built on the same configuration set, but with different values of the MC coefficients. The first set of single excitations is built with the MC coefficients of Ψ_0 and the second uses the MC coefficients of Ψ_1. One writes the hamiltonian matrix $\tilde{\boldsymbol{H}}^{\mathrm{SX}}$ as the average of the original $\boldsymbol{H}^{\mathrm{SX}}$ matrices corresponding to the individual states involved (cf. Eq. (12)):

$$\tilde{\boldsymbol{H}}^{\mathrm{SX}} = W_0 \boldsymbol{H}^{\mathrm{SX}}(0) + W_1 \boldsymbol{H}^{\mathrm{SX}}(1). \tag{33}$$

In order to keep the SX basis set orthonormal one has to build the overlap matrix in the same way:

$$\tilde{\boldsymbol{S}} = W_0 \boldsymbol{S}(0) + W_1 \boldsymbol{S}(1). \tag{34}$$

A canonical orthonormalisation, similar to the one described earlier, is then performed and the rest of the procedure follows on, as if we had optimised a single state.

The state average option is, in fact, workable only if one uses the energy shift technique [74]. The presence of several identical single excitations generate a degeneracy or quasi-degeneracy in the canonical function rather than a redundancy. This can be easily shown for the trivial case formed by the combination of two single excitations, in a two-mode system

$$c_1 \phi_0^1 \phi_0^2 + c_2 \phi_0^1 \phi_1^2. \tag{35}$$

We wish to optimise the two first roots of this system:

$$\begin{aligned} \Psi_0 &= c_1 \phi_0^1 \phi_0^2 + c_2 \phi_0^1 \phi_1^2, \\ \Psi_1 &= -c_2 \phi_0^1 \phi_0^2 + c_1 \phi_0^1 \phi_1^2. \end{aligned} \tag{36}$$

Let us write the single excitation from 0 to 2 on the second mode:

$$\begin{aligned} \Psi_i^{\mathrm{SX}}(0) &= c_1 \phi_0^1 \phi_2^2, \\ \Psi_i^{\mathrm{SX}}(1) &= -c_2 \phi_0^1 \phi_2^2, \end{aligned} \tag{37}$$

and from 1 to 2 on the same mode:

$$\begin{aligned} \Psi_j^{\mathrm{SX}}(0) &= c_2 \phi_0^1 \phi_2^2, \\ \Psi_j^{\mathrm{SX}}(1) &= c_1 \phi_0^1 \phi_2^2. \end{aligned} \tag{38}$$

We can then compute the overlap matrix elements according to (34) as

$$\begin{aligned} \tilde{S}_{ij} &= W_0 c_1 c_2 - W_1 c_1 c_2, \\ \tilde{S}_{ii} &= \tilde{S}_{jj} = W_0 c_1^2 - W_1 c_2^2. \end{aligned} \tag{39}$$

If $W_0 = W_1 = 0.5$, the overlap matrix takes the form

$$\tilde{\boldsymbol{S}} = \begin{pmatrix} \dfrac{c_1^2 + c_2^2}{2} & 0 \\ 0 & \dfrac{c_1^2 + c_2^2}{2} \end{pmatrix}. \tag{40}$$

This matrix has two degenerate, but distinct, eigenvalues. In the case of an ordinary one-state optimisation, these two single excitations would have led to a redundancy and one of them would have been eliminated by the canonical orthonormalisation procedure. The degeneracy obtained here cannot be eliminated easily, especially if, as in more general cases, quasi-degeneracies occur more often than exact degeneracy. The use of the level-shift trick is then the only way to prevent the reference function from mixing strongly with accidentally degenerate SX functions.

5 Test calculations

5.1 General framework

The algorithm presented in the previous sections aims at optimising, by means of the variational method, the one-dimensional oscillator basis sets corresponding to a multiconfigurational reference wave function. As is usually done in electronic structure calculations, the MCSCF optimisation is often preliminary to a further configuration interaction calculation based on a larger multi-dimensional expansion. The major advantage of such a two-step procedure is to considerably reduce the number of configurations to be included in the CI wave function. This gain is expected to be more important when strong couplings occur. The goal of the test calculations presented in this section is to bring out the efficiency of our MCSCF algorithm for providing compact and well-balanced wave functions.

In a first attempt to apply the present algorithm, we have implemented it into a general VSCF/CI computer program (program POLYMODE [50]) that was quite compatible with the super-CI method. The new program is consequently based on the same methodological choices as the original one, i.e. the use of:

(i) normal coordinates;
(ii) the Watson hamiltonian, factorised as a sum of one-mode terms by fixing the inertia matrix to its equilibrium value;
(iii) a quartic expansion of the PES;
(iv) basis sets of harmonic oscillators (HOs).

In addition to the availability of an existing CI code, another reason for this choice was to allow test calculations on 3- and 4-atom molecules to be performed using the same program. However, as mentioned in Sect. 1, this level of theory suffers from different approximations. We will thus not try here to compete with published larger-scale calculations performed with more adapted coordinate system and basis sets. Our purpose in the present work is to show what gain an MCSCF procedure can bring, using a given quartic ab initio PES. We will thus not refer to the corresponding experimental values or to other converged variational results, but rather to the FCI results obtained within the same methodological framework and the same PES.

It must be stressed that the VMCSCF optimisation algorithm developed in this work is not limited to this particular context and can be adapted to any kind of hamiltonian or primitive basis functions.

5.2 Application to the water molecule

The first series of test calculations were done on the ground electronic state of the water molecule, using an *ab initio* potential energy surface calculated [26] at the SD-CI level with a triple zeta doubly polarised gaussian basis set. Although this potential is far from the best available today, it was chosen in order to be consistent with previous VSCF/CI calculations [26] and to show how the MCSCF optimisation can overcome the drawbacks of the one-configurational VSCF approximation. Let us cite nevertheless, as the best reference PES for water, the one fitted by Jensen [36]. This PES was fit, within the MORBID model, to a large collection of spectroscopical data on several isotopomers. A modified version of this PES has recently been used in large-scale DVR calculations by Choi and Light [51], demonstrating its accuracy up to high vibrational energies (30 000 cm^{-1}).

We will focus here on two vibrational states (referred to as 200 and 002[1]) involved in a so-called "Darling–Dennisson" resonance. This system represents a classical example of such a phenomenon and has been analysed in the context of perturbation theory by Nielsen in 1951 [64]. However, the high degree of diagonal and non-diagonal anharmonicity showed by these states is not ideally represented by perturbation theory. It is also a good test for an MCSCF method since it requires the optimisation of the ninth and tenth states of the same (a_1) symmetry which are close in energy and interact strongly. In a previous study on H_2O [26], we showed that the vibrational transition dipole moments are very sensitive to the optimisation of the oscillator's basis set. In the particular case of the 000 → 002 transition, the single configuration VSCF optimisation distorted so much the wave function of the 002 state that the calculated transition moment was 510 times bigger than the converged FCI value. This system is therefore an ideal test case for our method which has been designed to correct the shortcomings of the VSCF procedure.

5.2.1 Vibrational energies. The calculations were done in an LCHO basis set of 10 HOs and with an MC expansion chosen including the lowest-lying 11 configurations plus the 102 one, which appeared to be important in preliminary calculations. In order to make the VMCSCF calculation converge on the two states of interest, we proceeded in two stages, using the state averaging formalism. In the first step, we made the procedure converge on a state average solution including the 11 lowest-lying vibrational states, with an identical weight of 1/11 given to each of them. The converged oscillators from this calculation were then used to start the second step of the procedure, where only the 200 and 002 states were considered in the average with an identical weight of 0.5. The convergence of this latter calculation has been quite difficult to achieve; we had to modify the weight of the two desired states stepwise, increasing them slightly, making the calculation converge, then using the new oscillators for a further run with a slightly greater weight and so on.

We also tried, in a third step, to reach convergence on each of the separate states, but this attempt failed due to dramatic problems of root-flipping induced by the strong mixing existing between both states.

The LCHO basis set optimised at the two-state average VMCSCF level was then used in a larger CI calculation. The CI configuration list was generated by applying the excitation criteria described below. We selected every possible excitation of 4, 6 and 4 quanta on ν_1, ν_2 and ν_3, respectively, with respect to the ground vibrational state, with a limit of 10 on the sum over all vibrational quantum numbers. This leads to a configuration space of 92 functions. Let us introduce the

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[1] This notation lists the quantum numbers associated to the symmetric stretching (ν_1), the bending (ν_2) and the antisymmetric stretching modes (ν_3), respectively

Table 1. Effect of the one-dimensional basis set optimisation on the absolute vibrational energies (in cm^{-1}) of the $|200\rangle$ and $|002\rangle$ resonant states of water

Method	Optimised on state[a]	$\|200\rangle$ state	$\|002\rangle$ state
VSCF	200	12471	12865
	002	12690	12524
VSCF/CI(12)	200	12404	12645
	002	13015	12593
VMCSCF(12;2)	Average	12382	12588
VSCF/CI(92)	200	12360	12522
	002	12413	12517
VMCSCF(12;2)/CI(92)	Average	12360	12524
FCI(500)		12360	12517

[a] Refers to the state for which the oscillator's basis set has been optimised

following notation for the two-step variational calculation:

$$\text{VMCSCF}(m;\, n)/\text{CI}(k),$$

where m is the number of configurations in the reference MCSCF wave function, n is the number of averaged states and k is the number of configurations in the second step CI calculation.

The VMCSCF(12; 2) and VMCSCF(12; 2)/CI(92) energy results are compared in Table 1 with the corresponding VSCF and VSCF/CI(k) (with $k = 12$ and 92[2]) and FCI results, obtained in [26] within the same methodological scheme. FCI calculations involve 500 configurations. The VSCF and VSCF-CI values were obtained by optimising separately the LCHO basis set either on the 200 or on the 002 states.

Figure 1 illustrates the evolution of the individual energies of the 200 and 002 states together with their energy separation ΔE, as a function of the level of calculation. The FCI results correspond to the converged variational solutions within our methodological choices (potential, coordinates, basis sets) and can therefore serve as reference values. In order to give an order of magnitude of the error induced by these choices on the energy splitting ΔE between the resonant states, let us compare the FCI value of 157 cm^{-1} with the corresponding experimental value of 243.5 cm^{-1} [76, 77] and the best variational calculation [51] of 242.3 cm^{-1}.

Coming back to internally consistent comparisons, we see that the VMCSCF and VMCSCF/CI results are close to the corresponding reference FCI values. On the other hand, the shortcomings of the VSCF and VSCF/CI methods also clearly come out. If at the VSCF level the optimisation of the 200 state gives qualitatively reasonable results, the same is not true when the 002 state serves to optimise the oscillator's basis set. An energy inversion of the two states occurs, with an even

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[2] These numbers refer to the same configuration lists as those of the VMCSCF calculations

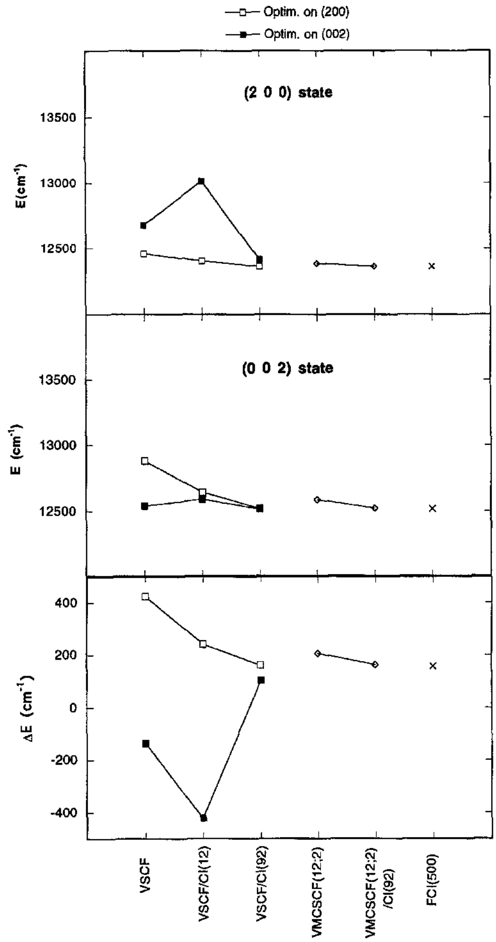

Fig. 1. Absolute and relative energies of the (200) and (002) states of water as a function of the level of calculation (notations are defined in the text). Convergence to the reference FCI values is observed

more pronounced effect at the VSCF/CI(12) level of calculation. Larger CI calculations are needed to correct this optimisation artefact and it still remains a basis set effect of 58 cm^{-1} on ΔE at the VSCF/CI(92) level, this effect being mostly due (53 cm^{-1}) to the 200 state.

5.2.2 Vibrational wave functions. The values of the CI coefficients corresponding to the main configurations (larger than 0.10) in the same calculations as above are shown in Tables 2 and 3 for the 200 and 002 states, respectively.

The comparison between the 12 and 92 configurations basis sets shows the very stable and consistent behaviour of the VMCSCF approximation. No new major contribution appears in the larger CI set and the main coefficients are not significantly altered, for both states. The situation is different at the VSCF-CI level, especially for the 002 state, some contributions surge and the weights of the principal configurations change between the two configurations set. It is clear that those new contributions help to compensate for the distorted VSCF optimisation.

A comparison of the one-mode functions, optimized at both VSCF and VMCSCF levels, clearly demonstrates the basis set effect. This is illustrated by

Table 2. Configuration interaction coefficients obtained for the |200⟩ state of water by various variational optimisation procedures

Configurations	VSCF/CI(12)		VMCSCF	VSCF/CI(92)		VMCSCF
	200[a]	002[a]	(12;2)	200[a]	002[a]	(12;2)/CI(92)
200	0.983	0.946	0.959	0.974	0.833	0.968
002	0.049	0.018	0.179	0.1187	0.181	0.179
102	0.132	0.123	0.131	0.160	0.114	0.126
100					0.341	
300					0.323	
400					0.144	
120	0.111	0.269				

[a] Refers to the state for which the oscillator's basis set has been optimised

Table 3. Configuration interaction coefficients obtained for the |002⟩ state of water by various variational optimisation procedures

Configurations	VSCF/CI(12)		VMCSCF	VSCF/CI(92)		VMCSCF
	200[a]	002[a]	(12;2)	200[a]	002[a]	(12;2)/CI(92)
200	0.076	0.033	0.177	0.156	0.124	0.177
002	0.961	0.948	0.979	0.940	0.974	0.975
102	0.240	0.003	0.016	0.242	0.021	0.026
100					0.152	
300						
400						
120		0.269				

[a] Refers to the state for which the oscillator's basis set has been optimised

the plots of LCHO coefficients (expansion coefficients of Eq. (2)), given in Fig. 2 for the $v = 2$ functions on modes 1 and 3. One observes a perfect matching of the VMCSCF mode functions with the corresponding VSCF ones only when these functions are occupied in the VSCF reference configuration. Large discrepancies are observed in the opposite case.

The role played by configuration 102, added to the MCSCF configuration list, clearly appears. It contributes significantly to the wave function of the 200 state, at all levels of calculations (see Table 2). It however contributes quite differently to the 002 state (see Table 3) depending on the way the basis set has been optimised. It has a consistent small weight at the VMCSCF and VMCSCF/CI levels, but at the VSCF/CI level, the same is observed only when the VSCF optimisation has been performed on the 002 state. This can be explained by the fact that the 102 configuration is a single excitation with respect to 002. According to the Brillouin theorem, the off-diagonal CI hamiltonian matrix element between 102 and 002 is zero when the basis set has been optimised on the 002 state. The important weight (0.24) arising from an optimisation on the 200 state does not have any physical meaning, but is only an expression of the distortion of the wave function expanded in a non-adapted basis set.

These results clearly show the compactness of the VMCSCF wave function, giving a consistent description of the system with a small number of configurations and is a much better starting point for a further CI calculation.

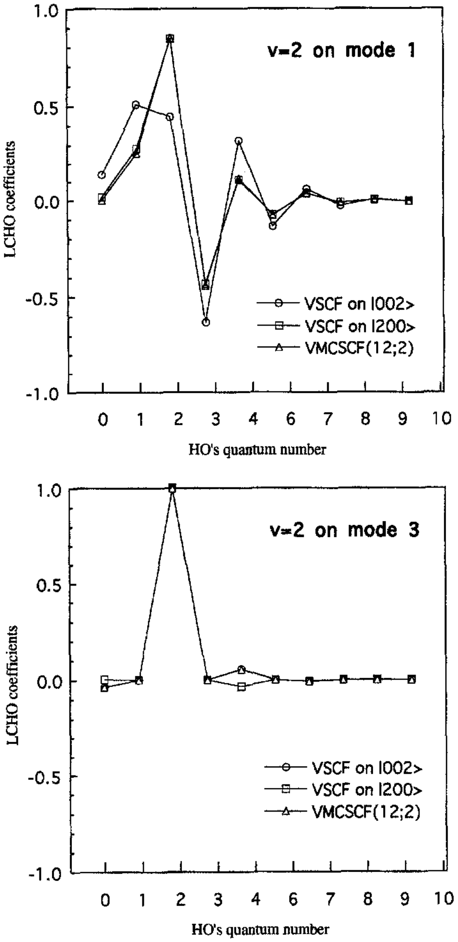

Fig. 2. Comparison of one-mode functions corresponding to $v = 2$ on modes 1 and 3, optimised at the VSCF and VMCSCF levels of calculation. Abscissa refers to the quantum number of the harmonic oscillator basis functions

5.3 Application to the formaldehyde molecule

An interesting case of vibrational resonances involving a three-state mixing is encountered in the formaldehyde molecule. Those states, referred[3] to as $3_1 6_1$, $2_1 6_1$ and 5_1, lie around[4] $8600\,\mathrm{cm}^{-1}$ and are, respectively, the second, third and fourth states of b_2 symmetry belonging to the electronic ground state. The normal modes are numbered in the following way: ν_2, ν_3, ν_5 and ν_6, respectively, refer to the C–O stretching, the in-plane bending, the asymmetric C–H stretching and the rocking.

Our VMCSCF method is particularly well suited for this particular system of relatively low-energy and strongly mixed states, it represents then a good test case, complementary to the higher-energy but lower-dimensionality case of the water molecule. To perform our vibrational calculation, we have used the adjusted

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[3] This notation shows the conventional label of the vibrational modes, with the corresponding quantum number in subscript, if it is different from zero

[4] Energy given relative to the PES equilibrium energy

ab initio potential energy surface computed by Romanowski et al. [20]. We also followed their vibrational study of those states, at the VSCF-CI level, to compare it with our VMCSCF approach, both in its ordinary and state-averaged forms.

We again aim in this section at demonstrating the ability of a small dimension VMCSCF calculation to provide a well-balanced wave function describing a set of interacting states. This latter set represents the smallest possible to get a variational eigenfunction of these states. The multiconfigurational development has been limited to the first four configurations allowing the representation of the lower four states of b_2 symmetry, both in the VSCF-CI and VMCSCF calculations. We of course do not intend with this minimal configurations expansion to compete with absolute energies obtained recently by Bramley and Carrington [53] from large-scale CI calculations involving between 130000 and 500000 functions. Our aim here, as for water, is to show the adequacy of the MCSCF optimisation for providing compact and well-balanced reference wave functions.

As for water, the wave function has been optimised in several steps, although no serious problems of convergence were encountered. We first performed a VSCF calculation on the three states of interest, the anharmonic oscillators obtained by this procedure for the $3_1 6_1$ were used subsequently as initial guess for a VMCSCF optimisation on the average of the three interacting states. Using the oscillators coming out of this latter calculation as a new initial guess, we were able to produce the VMCSCF wave functions for each state separately (i.e. without any state-averaging), which was impossible for the two states studied in the water molecule.

5.3.1 Vibrational energies. The vibrational energies obtained at those various levels of approximation are compared to the corresponding experimental results [78] in Table 4. One can notice, as before, the ambiguity generated by the VSCF-CI procedure which leads to an inversion of the $3_1 6_1$ and 5_1 states when the oscillator's basis set is optimised at the VSCF level. The VMCSCF optimisation on the average of the three states gives a balanced representation of them; the energies are closer to the experimental values (55 cm^{-1} of deviation, on average), as well as the spacing between the three states (28 cm^{-1} of deviation, on average).

The VMCSCF optimisation on each state lowers the vibrational energies from 6 to 21 cm^{-1}, since it operates a more complete variational optimisation, without any average constraint. However, although the ordering is respected, the spacing is deteriorated. The optimised states are stabilised but the others are destabilised. For instance, when the oscillators are optimised for the 5_1 state, the 5_1 and $3_1 6_1$ states

Table 4. Absolute energies (in cm^{-1}) of the first four b_2 vibrational states of formaldehyde, obtained by different variational optimisation procedures

State	VSCF/CI(4) optimised on state[a]			VMCSCF(4;3)	VMCSCF(4;1) optimised on state[a]			Exp[b]
	$3_1 6_1$	5_1	$2_1 6_1$		$3_1 6_1$	5_1	$2_1 6_1$	
6_1	7048.2	7152.0	7048.1	7059.1	7094.5	7100.1	7055.5	7026.6
$3_1 6_1$	8547.4	8705.1	8551.0	8555.9	8539.2	8590.1	8630.0	8496.7
5_1	8746.8	8619.2	8744.8	8703.7	8847.3	8682.0	8739.7	8620.8
$2_1 6_1$	8840.7	8917.1	8837.5	8827.2	8997.7	8868.5	8821.1	8777.5

[a] Refers to the state for which the oscillator's basis set has been optimised

[b] See ref. [78]

Table 5. Configuration interaction coefficients obtained by different variational methods for the $3_1 6_1$, 5_1 and $2_1 6_1$ states of formaldehyde

State	Configuration		
	$3_1 6_1$	5_1	$2_1 6_1$
Separate VSCF/CI optimisation for each state			
$3_1 6_1$	0.965	0.259	0.0496
5_1	0.553	0.827	0.102
$2_1 6_1$	0.108	0.511	0.853
VMCSCF optimisation for the average of the three states			
$3_1 6_1$	0.927	0.367	0.070
5_1	0.366	0.855	0.367
$2_1 6_1$	0.075	0.366	0.927
Separate VMCSCF optimisation for each state			
$3_1 6_1$	0.960	0.271	0.065
5_1	0.576	0.795	0.190
$2_1 6_1$	0.088	0.447	0.890

is get closer. Such behaviour could increase artificially the mixing of the two states and in some way distort the wave function. The same problem occurs between the $2_1 6_1$ and 5_1 states when the basis set is optimised on the $2_1 6_1$. Inversely, the optimisation on the $3_1 6_1$ state tends to isolate it from the others since it is the lowest lying.

5.3.2 Vibrational wave function. The configuration interaction coefficients calculated by the three techniques described above are given in Table 5. As suspected, the distortions in the energy spacing are expressed in the wave function by the relative importance of the coupling CI coefficients. When the basis set is optimised for each state separately, both at the VSCF-CI and VMCSCF levels, the $3_1 6_1$ configuration has a large coefficient in the 5_1 wave function as well as the 5_1 configuration in the $3_1 6_1$ state. In contrast, the wave function associated with the $3_1 6_1$ state is quite pure, having a weight of 0.96 on the main configuration.

The averaged optimisation gives a much better balanced representation of the three states, the $2_1 6_1$ and $3_1 6_1$ interacting perfectly symmetrically with the 5_1 and very weakly with each other.

These results tend to demonstrate, in a vibrational framework, that the state-average MCSCF method, universally used today in Quantum Chemistry, is a powerful tool for tackling clusters of interacting states in a balanced way.

6 Conclusion

The method described above is a vibrational adaptation of the MCSCF method, widely used in Quantum Chemistry, allowing a complete variational optimisation of the wave function. The computational bottleneck of vibrational spectroscopy is the anharmonic mode coupling phenomenon, which plays the same role as electronic correlation in Quantum Chemistry. The MCSCF methods address part of this problem by treating very completely the most important interaction terms. As a consequence, they will return a compact and well-balanced wave function, which can be useful for a subsequent physical interpretation. By contrast, the traditional SCF-CI methods, which are efficient in many circumstances, lead to an incomplete and ambiguous basis set optimisation, that can only be compensated by a large CI expansion, if strong interactions appear. Our tests on strongly interacting vibrational states in water and formaldehyde show that such situations occur as well in vibrational spectroscopy as in Quantum Chemistry. The huge methodological literature available in this latter field is a great reservoir of ideas for the present and future development of our optimisation algorithm. The use of a CI calculation in a VMCSCF-optimised oscillator's basis set, the state-averaging option and the very essence of the algorithm, based on the generalised Brillouin theorem are some examples of Quantum Chemistry techniques transported to the vibrational context.

As the VMCSCF wave function concentrates a maximum of information in a minimal configurations set, it is very important to select carefully the configurations included in the MC expansion. For that purpose, a CI calculation in a larger set can be a good guide, it can also be used after a properly converged VMCSCF to improve the precision of the results by including higher-order contributions.

The state averaging allows a better balanced representation of the interacting states with a coherent set of mixing coefficients and good energy spacing of the considered states, even with a minimal number of configurations. It also makes the procedure converge faster when *root-flipping* problems occur and can represent several *optimal* states in a single orthogonal basis set.

Another interesting development would consist of extending the procedure towards the CASSCF approach. As in the electronic problem, this would allow incorporation of a greater number of configurations in the MC expansion and change the arbitrary selection of configurations in a choice of active oscillators. This in turn could give a deeper physical insight into the nature of the coupling between the different kinds of vibrational motions in the molecule. The VMCSCF method could also be an interesting tool in the calculation of infrared intensities on which the coupling anharmonicities have a great effect. The latter two aspects will be studied jointly in a forthcoming paper.

Finally we shall insist on the fact that the computer program based on convenient but quite crude methodological choices (normal coordinates, HOs basis sets) was not designed to challenge other large-scale variational methods. It was however judged sufficient for illustrating the interest of an MCSCF-like method to give compact wave functions. A plan for the future is to implement the present algorithm into a state-of-the-art variational program and show how it can be helpful for reducing the size of the subsequent CI calculations.

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References

1. Jørgensen P, Simons J (eds) (1986) Geometrical derivatives of energy surfaces and molecular properties, NATO ASI Series C: Mathematical and Physical Sciences, Vol 166

2. Koch H, Jensen HJ, Helgaker TU, Jørgensen P, Scuseria GE, Schaefer III HF (1990) J Chem Phys 92:4924
3. Stanton JF, Watts JD, Bartlett RJ (1990) J Chem Phys 94:404
4. Colwell SM, Jayatilaka D, Maslen PE, Amos RD, Handy NC (1991) Int J Quantum Chem 40:179
5. Scuseria GE (1991) J Chem Phys 94:442
6. Harding LB, Ermler WC (1985) J Comput Chem 6:13
7. Sana M (1981) Int J Quantum Chem 19:139; Sana M (1982) Theoret Chim Acta 60:543
8. Delon A, Jost R (1991) J Chem Phys 95:5686; Delon A, Jost R, Lombardi M (1991) J Chem Phys 95:5701
9. Holland JK, Newham DA, Mills IM, Herman M (1992) J Mol Spectrosc 151:346
10. Pique JP, Manners J, Sitja G, Joyeux M (1992) J Chem Phys 96:6495
11. Bramley MJ, Green WH, Handy NC (1991) Mol Phys 73:1183
12. Jensen P (1992) in: Wilson S, Dierksen GHF (eds) Methods in computational molecular physics, NATO ASI Series C: Physics, Vol 293, p 423
13. Hoy AR, Mills IM, Strey G (1972) Mol Phys 24:1265
14. Carter S, Handy NC (1986) Comp Phys Rep 5:117
15. Tennyson J (1986) Comp Phys Rep 4:1
16. Carter S, Handy NC (1987) J Chem Phys 87:4294
17. Bačič Z, Light JC (1989) Annu Rev Phys Chem 40:469
18. Tennyson J, Miller S, Henderson JR (1992) in: Wilson (ed) Methods in computational chemistry, Vol 4, Plenum Press, New York
19. Bramley MJ, Carter S, Handy NC, Mills IM (1993) J Mol Spectrosc 157:301
20. Romanowski H, Bowman JM, Harding LB (1985) J Chem Phys 82:4155
21. Ermler WC, Rosenberg BJ, Shavitt I (1985) in: Bartlett RJ (ed) Comparison of ab initio quantum chemistry with experiment for small molecules. Reidel, Dordrecht, 171
22. Maslen PE, Handy NC, Amos RD, Jayatilaka D (1992) J Chem Phys 97:4233
23. Gaw JF, Willets A, Green WH, Handy NC (1991) in: Bowman JM (ed) Advances in molecular vibrations and collision dynamics, Vol 1B. JAI Press, Greenwich, Connecticut
24. Hidalgo A, Zuñiga J, Bastida A, Requena A (1989) Int J Quantum Chem 36:49
25. Cantarella E, Culot F, Liévin J (1992) Physica Scripta 46:489
26. Culot F, Liévin J (1992) Physica Scripta 46:502
27. Carney GD, Kern CW (1975) Int J Quantum Chem Symp 9:317
28. Whitehead RJ, Handy NC (1975) 55:356
29. Foord A, Smith JG, Whiffen DH (1975) Mol Phys 29:1685
30. Suzuki I (1975) Bull Chem Soc Japan 48:1685
31. Handy NC, Carter S (1981) Chem Phys Lett 79:118; ibidem 83:216
32. Watson JKG (1970) Mol Phys 19:465
33. Watson JKG (1968) Mol Phys 15:479
34. Carter S, Handy NC (1982) J Mol Spectrosc 95:9
35. Carter S, Handy NC, Mills IM (1990) Phil Trans R Soc Lond A332:309
36. Jensen P (1989) J Mol Spectrosc 133:438
37. Dinelli BM, Miller S, Tennyson J (1994) J Mol Spectrosc 163:71
38. Romanowski H, Bowman JM (1984) Chem Phys Lett 110:235
39. Halonen L, Child MS, Carter S (1982) Mol Phys 47:1097
40. Benjamin I, Roosmalen OS, Levine RD (1984) J Chem Phys 81:3352
41. Epa VC (1990) J Chem Phys 93:3773
42. Bowman JM, Gazdy B (1991) J Chem Phys 94:454
43. Hidalgo A, Zuñiga J, Francés JM, Bastida A, Requena A (1991) Int J Quantum Chem 40:685
44. Carter S, Handy NC (1986) Mol Phys 57:175
45. Bramley MJ, Handy NC (1993) J Chem Phys 98:1378
46. Carney GD, Sprandel LL, Kern W (1978) 32:305
47. Bowman JM (1978) J Chem Phys 68:608
48. Makarewicz J (1987) Mol Phys 61:547
49. Wierzbicki A, Bowman JM (1988) Computer Phys Comms 51:225
50. Romanowski H, Bowman JM (1985) QCPE Bull 5:64
51. Choi SE, Light JC (1992) J Chem Phys 97:7031

52. Henderson JR, Tennyson J, Sutcliffe BT (1993) J Chem Phys 98:7191
53. Bramley MJ, Carrington T (1993) J Chem Phys 99:8519
54. Bramley MJ, Tromp JW, Carrington T, Corey GC (1994) J Chem Phys 100:6175
55. McNichols A, Carrington T (1993) Chem Phys Lett 202:464
56. Froese Fischer C (1977) The Hartree–Fock method for atoms. A numerical approach. Wiley, New York
57. Wahl AC, Das G (1977) in: Schaefer III HF (ed) Modern theoretical chemistry, Vol 3. Plenum Press, New York, p 51
58. Ruedenberg K, Cheung LM, Elbert ST (1979) Int J Quantum Chem 16:1069
59. Werner HJ (1987) in: Lawley KP (ed) Advances in Chem Phys, Ab initio methods in quantum chemistry, Part 2, Vol LXVII. Wiley, New York, p 1
60. Jensen HJAa, Ågren H, Olsen J (1991) in: Clementi E (ed) Modern techniques in computational chemistry: MOTECC-91. ESCOM, Leiden, p 599
61. Roos BO (1987) in: Lawley KP (ed) Advances in Chem Phys, Ab initio methods in quantum chemistry, Part 2, Vol LXVII. Wiley, New York, p 399
62. Tobin L, Bowman JM (1980) Chem Phys 47:151
63. Schwenke DW (1992) J Chem Phys 96:3426
64. Nielsen HH (1951) Rev Mod Phys 32:90
65. Grein F, Chang TC (1971) Chem Phys Lett 91:149
66. Ruedenberg K, Cheung LM, Elbert ST (1980) Nat Resour Comput Chem Software Cat 1, Program QM01 (ALIS)
67. Roos BO, Karström G, Malmqvist P-Å, Sadlej AJ, Widmark PO (1991) in: Clementi E (ed) Modern techniques in computational chemistry: MOTECC-91. ESCOM, Leiden, p 435
68. Brillouin L (1934) in: Hermann (ed) Les Champs Self-consistents de Hartee et de Fock, Act Sci et Ind 159
69. Levy B, Berthier G (1968) Int J Quantum Chem 2:307
70. Godefroid M, Liévin J, Metz JY (1991) Int J Quantum Chem 40:243
71. Ruedenberg K, Schmidt MW, Dombek MM, Elbert ST (1982) Chem Phys 71:41; ibidem 71:51; ibidem 71:65
72. Löwdin PO (1970) in: Löwdin PO (ed) Advances in quantum chemistry, Vol 5. Academic Press, New York, p 185
73. Saunders VR, Hillier IH (1973) Int J Quantum Chem 7:699
74. Grein F, Banerjee A (1975) Int J Quantum Chem Symp 9:147
75. Werner HJ (1981) J Chem Phys 74:5794
76. Hoy AR, Mills IM, Strey G (1972) Mol Phys 24:1265
77. Hoy AR, Bunker PR (1979) J Mol Spectrosc 74:1
78. Reisner DE, Field RW, Kinsey JL, Dai HL (1984) J Chem Phys 80:5968