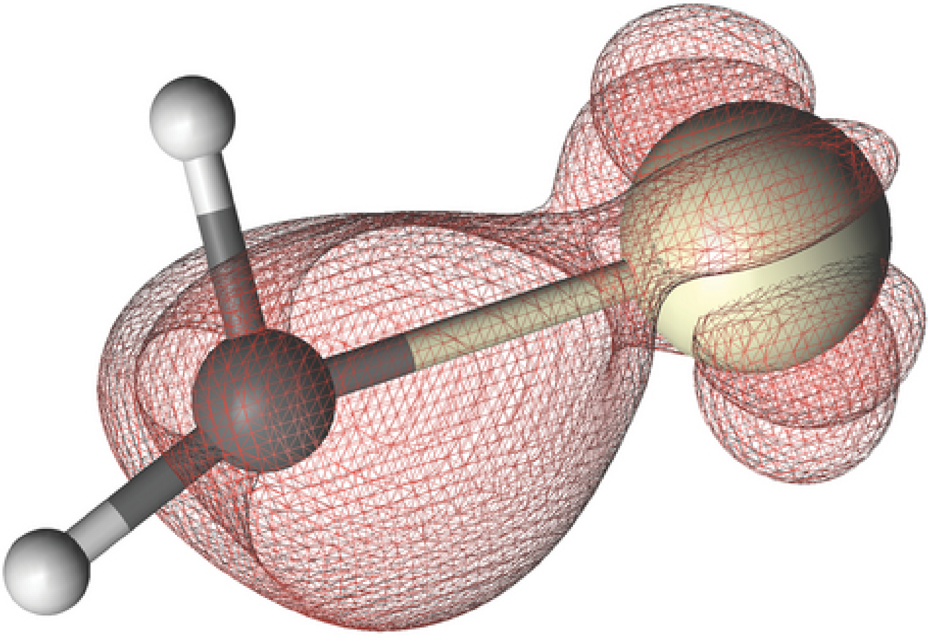
Multiconfigurational Quantum Chemistry



Björn Roos | Roland Lindh | Per Åke Malmqvist
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By

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PREFACE

The intention of this book is to introduce the reader into the multiconfigurational approaches in quantum chemistry. These methods are more difficult to learn to use and there does not exist any textbook in the field that takes the students from the simple Hartree–Fock method to the advanced multireference methods such as multireference configuration interaction (MRCI), or the complete active space self-consistent field (CASSCF) method. The intention is to describe these and other wave function-based methods such that the treatment can be followed by any student with basic knowledge in quantum mechanics and quantum chemistry. Using many illustrative examples, we shall show how these methods can be applied in various areas of chemistry, such as chemical reactions in ground and excited states, transition metal, and other heavy element systems. These methods are based on a well-defined wave function with exact spin and symmetry and are therefore well suited for detailed analysis of various bonding situations. A simple example is the oxygen molecule, which has a $^3\Sigma_g^-$ ground state. Already this label tells us much about the wave function and the electronic structure. It is a triplet state ($S = 1$), it is symmetric around the molecular axis (Σ), it is a *gerade* function, and it is antisymmetric with respect to a mirror plane through the molecular axis. None of these properties are well defined in some methods widely used today. It becomes even worse for the first excited state, $^1\Delta_g$, which cannot be properly described with single configurational methods due to its multiconfigurational character. This failure can have severe consequences in studies of oxygen-containing biological systems. It is true that these wave function-based methods cannot yet be applied to as large systems as can, for example, density functional theory (DFT), but the method development is fast and increases the possibilities for every year.

Computational quantum chemistry is today dominated by the density functional theory and to some extent coupled-cluster-based method. These methods are simple to use and DFT can be applied to larger molecules. They have, however, several drawbacks and failures for crucial areas of applications, such as complex electronic structures, excited states and photochemistry, and heavy element chemistry. Many students learn about the method and how to use it but have often little knowledge about the more advanced wave function-based methods that should preferably be used in such applications.

The intention with this contribution is to demystify the multiconfigurational methods such that students and researchers will understand when and how to use them. Moreover, the multiconfigurational electron structure theory, in association with the molecular orbital picture, has a significant educational and pedagogic value in explaining most chemical processes—the Woodward–Hoffmann rules can only be explained with molecular orbital theory; strict electron density theory will fail.

DEDICATION

In memory of and dedicated to Björn O. Roos, 1937–2010.

The work on this book was started in 2009 by Professor Björn O. Roos. He was in charge of the planning and wrote significant parts before passing away on February 22, 2010. Despite being marked by the deteriorating impact of his condition, Björn spent most of his limited awake time working on this project. Inspired by Björn's enthusiasm and dedication to multiconfigurational wave function theory, we decided to complete the work, as outlined by him, as a testament and a tribute for his contributions in this field.

Thanks Björn!

CONVENTIONS AND UNITS

In this book, we use the conventional systems of units of quantum chemistry, which are the Hartree-based atomic units (au), a set of rational units derived from setting the reduced Planck constant $\hbar = 1$, the electron mass $m_e = 1$, the elementary charge $e = 1$, and the Coulomb constant (4π times the vacuum permittivity) $4\pi\epsilon_0 = 1$, see Tables 1 and 2. The resulting formulae then appear to be dimensionless, and to avoid confusion they are sometimes written in full, that is,

$$-\frac{\hbar^2}{2m_e}\nabla^2 = -\frac{1}{2}\nabla^2 \tag{1}$$

for the kinetic energy term for an electron. Similarly, the electrostatic interaction energy between two electrons can be written with or without the explicit constants:

$$\frac{e^2}{4\pi\epsilon_0 r} = \frac{1}{r}. \tag{2}$$

The first form can be used with any (rational) units. The Bohr, or Bohr radius, and the Hartree, are then used as derived units for length and energy, with symbols a_0 and E_h, respectively. The speed of light is numerically equal to $1/\alpha$, the reciprocal Sommerfeld fine-structure constant, in atomic units.

Throughout the book, we follow the conventions in Table 3 except where otherwise stated. For example, Ψ will be used as the symbol for a wave function, whereas Φ will be used for configuration state functions. The Hartree–Fock determinant might then in one circumstance be denoted by Ψ if it is the wave function at hand or perhaps as Φ_0 if it is part of an MCSCF expansion.

TABLE 1 One Atomic Unit in Terms of SI Units

Quantity	Symbol	Value
Action	$\hbar$	$1.054\ 571\ 628 \times 10^{-34}$ J s
Mass	m_e	$9.109\ 382\ 15 \times 10^{-31}$ kg
Charge	e	$1.602\ 176\ 487 \times 10^{-19}$ C
Coulomb constant	$4\pi\epsilon_0$	$4\pi \times 10^7/c^2$ F/m (exact)
Length	a_0	$0.529\ 177\ 208\ 59 \times 10^{-10}$ m
Energy	E_h	$4.359\ 743\ 94 \times 10^{-18}$ J
Electric dipole moment	ea_0	$8.478\ 352\ 81 \times 10^{-30}$ C m
Time	$\hbar/E_h$	$2.418\ 884\ 326\ 505 \times 10^{-17}$ s
Temperature	E_h/k_B	315 774.648 K

Note: Most of the values above have been taken from web pages of the National Institute of Standards and Technology: `http://physics.nist.gov/cuu/`.

TABLE 2 Constants and Conversion Factors

Quantity	Symbol	Value
The fine structure constant	α	0.007 297 352 537 6
Vacuum speed of light	$c = \frac{1}{\alpha}$	137.035 999 679 au
Avogadro's number	N_a	$6.022\ 141\ 79 \times 10^{23}$
Energy	$1E_h =$	$4.359\ 743\ 94 \times 10^{-18}$ J
	$1E_h =$	627.509 469 kcal/mol
	$1E_h =$	27.211 383 86 eV
	$1E_h =$	219 474.631 3705 cm^{-1}
Electric dipole moment	$1ea_0 =$	$8.478\ 352\ 81 \times 10^{-30}$ C m
	$1ea_0 =$	0.393 430 Debye

Note: Most of the values above have been taken from web pages of the National Institute of Standards and Technology: `http://physics.nist.gov/cuu/`.

TABLE 3 Notation Convention Used in This Book

Symbol	Meaning
Ψ	Wave function
Φ	Configuration state function
φ	Orbital (spatial part)
ψ	Spin orbital
σ	Spin wave function
χ	Basis function
ρ	Electronic density
η	Occupation number of (spin)orbital

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INTRODUCTION

How do we define multiconfigurational (MC) methods? It is simple. In Hartree–Fock (HF) theory and density functional theory (DFT), we describe the wave function with a single Slater determinant. Multiconfigurational wave functions, on the other hand, are constructed as a linear combination of several determinants, or configuration state functions (CSFs)—each CSF is a spin-adapted linear combination of determinants. The MC wave functions also go by the name Configuration Interaction (CI) wave function. A simple example illustrates the situation. The H_2 molecule (centers denoted A and B) equilibrium is well described by a single determinant with a doubly occupied σ orbital:

$$\Psi = (\sigma_g)^2, \tag{1.1}$$

where σ_g is the symmetric combination of the $1s$ atomic hydrogen orbitals ($\sigma_g = \frac{1}{\sqrt{2}}(1\mathrm{s}_\mathrm{A} + 1\mathrm{s}_\mathrm{B})$; the antisymmetric combination is denoted as σ_u). However, if we let the distance between the two atoms increase, the situation becomes more complex. The true wave function for two separated atoms is

$$\Psi \propto (\sigma_g)^2 - (\sigma_u)^2, \tag{1.2}$$

which translates to the electronic structure of the homolytic dissociation products of two radical hydrogens. Two configurations, σ_g and σ_u, are now needed to describe the electronic structure. It is not difficult to understand that at intermediate distances

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the wave function will vary from Eq. 1.1 to Eq. 1.2, a situation that we can describe with the following wave function:

$$\Psi = C_1(\sigma_g)^2 + C_2(\sigma_u)^2, \tag{1.3}$$

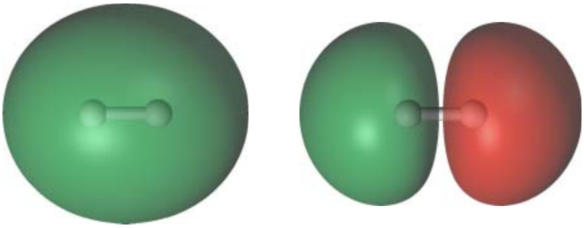
where C_1 and C_2, the so-called CI-coefficients or expansion coefficients, are determined variationally. The two orbitals, σ_g and σ_u, are shown in Figure 1.1, which also gives the occupation numbers (computed as $2(C_1)^2$ and $2(C_2)^2$) at a geometry close to equilibrium. In general, Eq. 1.3 facilitates the description of the electronic structure during any σ bond dissociation, be it homolytic, ionic, or a combination of the two, by adjusting the variational parameters C_1 and C_2 accordingly.

This little example describes the essence of multiconfigurational quantum chemistry. By introducing several CSFs in the expansion of the wave function, we can describe the electronic structure for a more general situation than those where the wave function is dominated by a single determinant. Optimizing the orbitals and the expansion coefficients, simultaneously, defines the approach and results in a wave function that is qualitatively correct for the problem we are studying (e.g., the dissociation of a chemical bond as the example above illustrates). It remains to describe the effect of dynamic electron correlation, which is not more included in this approach than it is in the HF method.

The MC approach is almost as old as quantum chemistry itself. Maybe one could consider the Heitler–London wave function [1] as the first multiconfigurational wave function because it can be written in the form given by Eq. 1.2. However, the first multiconfigurational (MC) SCF calculation was probably performed by Hartree and coworkers [2]. They realized that for the ^1S state of the oxygen atom, there where two possible configurations, $2s^22p^4$ and $2p^6$, and constructed the two configurational wave function:

$$\Psi = C_1\Phi(2s^22p^4) + C_2\Phi(2p^6). \tag{1.4}$$

The atomic orbitals were determined (numerically) together with the two expansion coefficients. Similar MCSCF calculations on atoms and negative ions were simultaneously performed in Kaunas, Lithuania, by Jucys [3]. The possibility was actually



σ-Bonding (1.98) σ-Antibonding (0.02)

Figure 1.1 The σ and σ^* orbitals and associated occupation numbers in the H_2 molecule at the equilibrium geometry.

suggested already in 1934 in the book by Frenkel [4]. Further progress was only possible with the advent of the computer. Wahl and Das developed the *Optimized Valence Configuration (OVC) Approach*, which was applied to diatomic and some triatomic molecules [5, 6].

An important methodological step forward was the formulation of the *Extended Brillouin's (Brillouin, Levy, Berthier) theorem* by Levy and Berthier [7]. This theorem states that for any CI wave function, which is stationary with respect to orbital rotations, we have

$$\langle \Psi | \hat{H} \hat{E}^{-}_{ai} | \Psi \rangle = 0, \tag{1.5}$$

where $\hat{E}^{-}_{ai}$ is an operator (see Eq. 9.32) that gives a wave function $\hat{E}^{-}_{ai}|\Psi\rangle$ where the orbitals φ_i and φ_a have been interchanged by a rotation. The theorem is an extension to the multiconfigurational regime of the Brillouin theorem, which gives the corresponding condition for an optimized HF wave function. A forerunner to the BLB theorem can actually be found already in Löwdin's 1955 article [8, 9].

The early MCSCF calculations were tedious and often difficult to converge. The methods used were based on an extension of the HF theory formulated for open shells by Roothaan [10]. An important paradigm change came with the *Super-CI* method, which was directly based on the BLB theorem [11]. One of the first modern formulations of the MCSCF optimization problem was given by Hinze [12]. He also introduced what may be called an approximate second-order (Newton–Raphson) procedure based on the partitioning: $U = 1 + T$, where U is the unitary transformation matrix for the orbitals and T is an anti-Hermitian matrix. This was later to become $U = exp(T)$. The full exponential formulation of the orbital and CI optimization problem was given by Dalgaard and Jørgensen [13]. Variations in orbitals and CI coefficients were described through unitary rotations expressed as the exponential of anti-Hermitian matrices. They formulated a full second-order optimization procedure (Newton–Raphson, NR), which has since then become the standard. Other methods (e.g., the Super-CI method) can be considered as approximations to the NR approach.

One of the problems that the early applications of the MCSCF method faced was the construction of the wave function. It was necessary to keep it short in order to make the calculations feasible. Thus, one had to decide beforehand which where the most important CSFs to include in the CI expansion. Even if this is quite simple in a molecule like H_2, it quickly becomes ambiguous for larger systems. However, the development of more efficient techniques to solve large CI problems made another approach possible. Instead of having to choose individual CSFs, one could choose only the orbitals that were involved and then make a full CI expansion in this (small) orbital space. In 1976, Ruedenberg introduced the *orbital reaction space* in which a complete CI expansion was used (in principle). All orbitals were optimized—the *Fully Optimized Reaction Space—FORS* [14].

An important prerequisite for such an approach was the possibility to solve large CI expansions. A first step was taken with the introduction of the *Direct CI* method in 1972 [15]. This method solved the problem of performing large-scale SDCI calculations with a closed-shell reference wave function. It was not useful for MCSCF, where a more general approach is needed that allows an arbitrary number of open shells and all possible spin-couplings. The generalization of the direct CI method to such cases was made by Paldus and Shavitt through the *Graphical Unitary Group Approach (GUGA)*. Two papers by Shavitt explained how to compute CI coupling coefficients using GUGA [16, 17]. Shavitt's approach was directly applicable to full CI calculations. It formed the basis for the development of the *Complete Active Space (CAS) SCF* method, which has become the standard for performing MCSCF calculations [18, 19].

However, an MCSCF calculation only solves part of the problem—it can formulate a qualitatively correct wave function by the inclusion of the so-called static electron correlation. This determines the larger part of the wave function. For a quantitative correct picture, we need also to include dynamic electron correlation and its contribution to the total electronic energy. We devote a substantial part of the book to describe different methods that can be used. In particular, we concentrate on second-order perturbation theory with a CASSCF reference function (CASPT2). This method has proven to be accurate in many applications also for large molecules where other methods, such as MRCI or coupled cluster, cannot be used. The combination CASSCF/CASPT2 is the main computational tool to be discussed and illustrated in several applications.

This book mainly discusses the multiconfigurational approach in quantum chemistry; it includes discussions about the modern computational methods such as Hartree–Fock theory, perturbation theory, and various configuration interaction methods. Here, the main emphasis is not on technical details but the aim is to describe the methods, such that critical comparisons between the various approaches can be made. It also includes sections about the mathematical tools that are used and many different types of applications. For the applications presented in the last chapter of this book, the emphasis is on the practical problems associated with using the CASSCF/CASPT2 methods. It is hoped that the reader after finishing the book will have arrived at a deeper understanding of the CASSCF/CASPT2 approaches and will be able to use them with a critical mind.

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2

MATHEMATICAL BACKGROUND

2.1 INTRODUCTION

From a basic point of view, orbitals are not *the* orbitals of some electron system, but they are *a* convenient set of one-electron basis functions. They may, or may not, solve some differential equations.

The ones that are most used in contemporary Quantum Chemistry are described in more technical detail further on. Here we just mention a few basic properties, and some mathematical facts and notations that come in handy. Later in the book it also describes the methods whereby the wave functions, which are detailed descriptions of the quantum states, can be approximated.

This chapter is also concerned with the practical methods to represent the many-electron wave functions and operators that enter the equations of quantum chemistry, specifically for bound molecular states.

It ends with some of the tools used to get properties and statistics out from multiconfigurational wave functions. They all turn out to be, essentially, "matrix elements," computed from linear combinations of a basic kind of such matrix elements: the density matrices.

2.2 CONVENIENT MATRIX ALGEBRA

There are numerous cases where linear or multilinear relations are used. Formulas may be written and handled in a very compact form, as in the case of orbitals being

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built from simpler basis functions (or other orbitals). The one-particle basis functions $\chi_k, k = 1, \dots, n$ are arranged in a row vector, formally a $1 \times n$ matrix, and the coefficients for their linear combinations, often called MO coefficients, in an $n \times m$ matrix $\mathbf{C}$, so that the orbitals $\{\phi_k\}_{k=1}^m$, can be written very concisely as a matrix product:

$$(\phi_1, \phi_2, \dots, \phi_m) = (\chi_1, \chi_2, \dots, \chi_n) \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1m} \\ C_{21} & C_{22} & \cdots & C_{2m} \\ \cdots & \cdots & \cdots & \cdots \\ C_{n1} & C_{n2} & \cdots & C_{nm} \end{pmatrix} \tag{2.1}$$

that is, $\phi = \chi\mathbf{C}$.

As an example, the orbital optimization procedure in a Quantum Chemistry program is frequently carried out by matrix operations such as, for example, the matrix exponential function, as shown in Chapter 9. The same approach can be extended also to handle many-particle wave functions.

Mathematically, the Schrödinger equation is usually studied as a partial differential equation, while computational work is done using basis function expansions in one form or another. The model assumption is that the wave functions lie in a Hilbert space, which contains the square-integrable functions, and also the limits of any convergent sequence of such functions: molecular orbitals, for example, would have to be normalizable, with a norm that is related to the usual scalar product:

$$\langle \phi_k | \phi_l \rangle \stackrel{\text{def}}{=} \int_{\mathcal{R}^3} \phi_k^*(\mathbf{r}) \phi_l(\mathbf{r}) \, d\mathbf{r}^3 \quad \text{and} \quad \|\phi_k\| \stackrel{\text{def}}{=} \sqrt{\langle \phi_k | \phi_k \rangle}.$$

This space of orbitals, together with the norm and scalar product, is called $L^2(\mathcal{R}^3)$, a separable Hilbert space, which means that it can be represented by an infinite orthonormal basis set. Such a basis should be ordered, and calculations carried out using the first N basis functions would be arbitrarily good approximations to the exact result if N is large enough. There are some extra considerations, dependent on the purpose: for solving differential equations, not only the wave functions but also their derivatives must be representable in the basis, and so a smaller Hilbert space can be used. For quantum chemistry, this can be regarded as requiring that the expectation value of the kinetic energy operator should be finite, and the wave function should then lie in a subspace of $L^2(\mathcal{R}^3)$, where also $\|\nabla\phi\|$ is finite (a so-called Sobolev space). While this is naturally fulfilled for most kinds of bases, it is not always so, for example, for finite element functions, wavelets, and in complete generality, issues such as completeness, convergence rate, and accuracy can be complicated.

Operators tend to be positions, partial derivatives, or functions of these. State vectors are usually wave functions with position variables, with spin represented by additional indices such as α or β. Examples are as follows:

$$\hat{\nabla} = \mathbf{e}_x \frac{\partial}{\partial x} + \mathbf{e}_y \frac{\partial}{\partial y} + \mathbf{e}_z \frac{\partial}{\partial z},$$