

The Multiconfigurational Self-Consistent-Field Method

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1 Introduction

These notes describe the multiconfigurational self-consistent-field (MCSCF) method, which is a general approach for describing chemical systems in which a single electron configuration is no longer an adequate description of the electronic structure. This commonly happens in reactions that break or form chemical bonds, diradicals, and metals of the first transition row. A single-determinant, restricted Hartree-Fock (RHF) wavefunction does not dissociate properly for homolytically breaking a covalent bond of a closed-shell molecule, as it includes unphysical ionic terms at large distances. Unrestricted Hartree-Fock (UHF) provides a qualitatively correct potential energy curve, but the results are often quantitatively poor, and the wavefunction is no longer an eigenfunction of the spin operator \hat{S}^2 . To keep a spin eigenfunction, we need to include at least *two* determinants in our zeroth-order wavefunction to homolytically break a single covalent bond for a closed-shell molecule, because at dissociation, there should be two degenerate electron configurations, $\cdots(\sigma)^2$ and $\cdots(\sigma^*)^2$.

In the MCSCF method, one writes the wavefunction in CI form as a linear combination of Slater determinants (or configuration state functions, CSF's), and the CI coefficients are determined variationally, as usual for CI wavefunctions. However, the orbitals are obtained not as those that minimize the energy of a single Slater determinant, as in Hartree-Fock theory, but as those which minimize the CI energy of the MCSCF wavefunction.

2 Types of MCSCF Wavefunctions

The MCSCF wavefunction is written in CI form as:

$$\Psi_{MCSCF} = \sum_I^{CI} c_I \Phi_I, \quad (1)$$

where Φ_I are individual Slater determinants (or CSF's) which have been selected by the user for inclusion in the wavefunction. For the purposes of these notes, we will assume these are simply Slater determinants, with no real loss of generality. If these determinants are selected by hand, we have

a general MCSCF wavefunction. If these determinants are selected as all possible ones that can be formed within a given set of “active” orbitals, we have a complete-active-space self-consistent-field (CASSCF) wavefunction, which has been popularized [1] by Roos et al. This approach has also been called full-optimized reaction space (FORS) [2, 3] by Ruedenberg and co-workers. CASSCF or FORS has the advantage that the method is somewhat more “black box,” the user having only to select an active space and not a list of individual configurations. Additionally, the wavefunction tends to be easier to converge for CASSCF than for general MCSCF. An intermediate solution is the restricted-active-space self-consistent-field (RASSCF) approach of Malmqvist et al. [4], which is an SCF version of the restricted-active-space configuration interaction (RASCI) method [5] of Olsen et al. In the RASCI, the orbitals are split into at least three groups, labelled RAS I, RAS II, and RAS III. The determinants are chosen as all those which have no more than n holes in RAS I, and no more than m particles in RAS III, where n and m are provided by the user.

3 The Basic MCSCF Equations

From the CI expression 1, we can write the energy as

$$E = \sum_{IJ}^{CI} c_I^* c_J H_{IJ}, \quad (2)$$

where H_{IJ} denotes the matrix element of the electronic Hamiltonian between determinants Φ_I and Φ_J . These matrix elements can all be written in terms of one- and two-electron integrals (Slater’s rules). Here we will write our results in terms of the unitary group generators (or shift operators) [6]:

$$\hat{E}_{pq} = a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}, \quad (3)$$

where $a_{p\alpha}^\dagger$ is a creation operator for an electron in orbital p with α spin, $a_{q\alpha}$ is an annihilation operator for an electron in orbital q with α spin, etc. The Hamiltonian in terms of these operators is:

$$\hat{H} = \sum_{pq}^K (p|h|q) \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs}^K (pq|rs) (\hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps}), \quad (4)$$

and the matrix element $H_{IJ} = \langle \Phi_I | \hat{H} | \Phi_J \rangle$ becomes

$$H_{IJ} = \sum_{pq} \gamma_{pq}^{IJ} h_{pq} + \frac{1}{2} \sum_{pqrs} \Gamma_{pqrs}^{IJ} (pq|rs), \quad (5)$$

where γ_{pq}^{IJ} and Γ_{pqrs}^{IJ} are simply the coefficients in front of the one- and two-electron integrals for this matrix element, and are called the *coupling coefficients*. Specifically, they are

$$\gamma_{pq}^{IJ} = \langle \Phi_I | \hat{E}_{pq} | \Phi_J \rangle, \quad (6)$$

$$\Gamma_{pqrs}^{IJ} = \langle \Phi_I | \hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} | \Phi_J \rangle. \quad (7)$$

The coupling coefficients have the following properties due to the anticommutation relations of creation and annihilation operators:

$$\gamma_{pq}^{IJ} = (\gamma_{qp}^{IJ})^*, \quad (8)$$

$$\Gamma_{pqrs}^{IJ} = \Gamma_{rspq}^{IJ} = (\Gamma_{srqp}^{JI})^* = (\Gamma_{qpsr}^{JI})^*. \quad (9)$$

Using equation (5), we obtain for the energy

$$E = \sum_{IJ}^{CI} c_I^* c_J \left[\sum_{pq} \gamma_{pq}^{IJ} h_{pq} + \frac{1}{2} \sum_{pqrs} \Gamma_{pqrs}^{IJ} (pq|rs) \right]. \quad (10)$$

We can rewrite this in a simpler form by summing over the CI coefficients in the inner loops as:

$$E = \sum_{pq} h_{pq} \gamma_{pq} + \frac{1}{2} \sum_{pqrs} \Gamma_{pqrs} (pq|rs), \quad (11)$$

with

$$\gamma_{pq} = \sum_{IJ}^{CI} c_I^* c_J \gamma_{pq}^{IJ}, \quad (12)$$

$$\Gamma_{pqrs} = \sum_{IJ}^{CI} c_I^* c_J \Gamma_{pqrs}^{IJ}, \quad (13)$$

which are called the one- and two-particle density matrices, respectively. Note that some researchers write the two-particle density matrix Γ with the factor of 1/2 absorbed into it.

Having a convenient form for the MCSCF energy, we need to be able to differentiate this energy with respect to orbital rotations so that we may minimize the energy with respect to the orbitals. The final, optimized orbitals \mathbf{C} may be written as some unitary transformation \mathbf{U} of the original orbitals \mathbf{C}^0 :

$$\mathbf{C} = \mathbf{C}^0 \mathbf{U}, \quad (14)$$

with \mathbf{C} and \mathbf{C}^0 being matrices of the MO coefficients with a number of rows equal to the number of AO's and the number of columns being the number of MO's. The matrix \mathbf{U} , as long as it is a strictly unitary matrix, does not spoil the orthogonality of the original orbitals.

3.1 Exponential Parameterization

The most common way of parameterizing \mathbf{U} is to write it as the exponential of an anti-Hermitian matrix,

$$\mathbf{U} = e^{\mathbf{R}}, \quad (15)$$

where

$$\mathbf{R}^\dagger = -\mathbf{R}. \quad (16)$$

An “independent pair,” is one whose rotation *does* change the total energy. For example, rotating the $1a_1$ with the $3a_1$ orbital for our methylene TCSCF does change the total energy, because these orbitals are not treated equivalently in the TCSCF: $1a_1$ is doubly occupied in both configurations, but $3a_1$ is only doubly occupied in one of the configurations. When performing an MCSCF, we only need to perform orbital rotations for the independent pairs. For the dependent pairs, we do not need their orbital gradients, their Lagrangian elements, or corresponding elements of the (actual or approximate) MO Hessian. In fact, attempting to optimize the dependent pairs could actually lead to numerical problems.

A restricted active space self-consistent-field (RASSCF) procedure [4] is the MCSCF generalization of a restricted active space configuration interaction (RASCI) [5] treatment. In this approach, the CI divides the orbitals into different sets (RAS I, RAS II, RAS III, etc.), and places restrictions on the maximum number of holes and particles for each set. Because the orbitals within a given RAS set are treated equivalently in the CI, pairs of orbitals from the same RAS space are dependent pairs. However, rotations that mix the different RAS spaces will typically change the energy, so these are independent pairs.

References

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