The General MCSCF Method with Full Symmetry Reduction*

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Abstract

A general multi-configuration self-consistent field (MCSCF) model is presented. The model permits the determination of wavefunctions for a collection of different physical states, achieves all possible group-theoretical reductions, and exhibits quadratic convergence.

A general algebraic formalism which implements the MCSCF model for a wide variety of electronic systems was published some years ago by Roothaan and Detrich (1983). Rather than presenting here a review of that algebra, we confine ourselves in this paper to a discussion of the special merits of that approach, which can be considered the culmination of a development in MCSCF theory over a fifteen-year period (Hinze and Roothaan 1967; Docken and Hinze 1972; Ruedenberg et al. 1979; Levy 1969, 1970, 1973; Polezzo 1975; Kuprievich and Schramko 1975; Kendrick and Hillier 1976; Dalgaard and Jørgensen 1978; Dalgaard 1979; Roothaan et al. 1979; Yeager and Jørgensen 1979; Lengsfield 1980; Werner and Meyer 1980). The present method uses a variational energy expression in terms of non-redundant variables. Starting with reference vectors of orbital and configuration expansions, the variational process is concerned with rotations in the orbital and configuration spaces so as to obtain a better energy. When properly defined, the angles of rotation constitute a non-redundant set of variational variables; they are collected in a single vector of rotations, which is not to be confused with either the orbital or the configuration expansion vectors.

Using a Taylor expansion of the energy in terms of these angles, and dropping all terms of third and higher order, the variational optimum is obtained from a set of linear equations of the form

$$\sum_{j} H_{ij} x_j = -g_i, \tag{1}$$

or

$$\boldsymbol{H}\boldsymbol{x} = -\boldsymbol{g}, \qquad (1')$$

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where x is the vector of rotations, while g and H are the gradient vector and the (symmetrical) Hessian matrix, respectively, of the first and second derivatives of the energy with respect to these rotations.

Since the process just described is based on a second order truncation of the energy expression, the angles which solve equation (1) yield only an approximation to the solution of the variational problem. Consequently a rotation over the computed angles yields new reference vectors which yield a better approximation to the variational optimum. Successive iterations exhibit quadratic convergence; thus if the initial reference vectors are accurate within $10^{**}(-1)$, subsequent iterations will yield an accuracy of $10^{**}(-2)$, $10^{**}(-4)$, $10^{**}(-8)$, etc.

This iterative procedure, which we call the new method, replaces the more traditional nested procedures of solving the pseudo-eigenvalue equations for the orbital vectors, the self-consistency of the latter, and the secular equation solution for the configuration vector(s). While the traditional method requires the computation and storage of the first derivatives only, the new method requires the second derivatives as well; hence the new method became feasible only in the mid-1970s when sufficiently large and cheap computer memories became available. The new method is also inherently much simpler, and it has much better convergence behaviour, than the traditional method.

The variational energy expression we use is the weighted average of the energies of several physical states. Each state in turn may be represented by a superposition of several configurations; however, all configurations must be constructed from a common set of orbitals. The model permits a great variety of calculations: the participating states, the numerical values of the weights, and the configurations used for each state, can all be freely chosen. It is also possible to omit any orbital rotations without compromising the calculation. These choices can be tailored to the physical situation at hand, as well as to the level of approximation desired for the calculation. It is important to note that the wavefunctions for all the states which participate in the calculation always form an orthonormal set which is properly diagonal with respect to the Hamiltonian.

For a closed shell ground state, a traditional SCF calculation uses of course one state with a weight of $1 \cdot 0$, and one configuration; a better wavefuction can of course be obtained by using an appropriate MCSCF configuration expansion for that one state, again with a weight of $1 \cdot 0$.

To calculate a radiative process between a ground state and a first excited state, the recommended procedure is a calculation using two states with equal weights of 0.5, each state being constructed from an appropriate configuration expansion. Note that this calculation does not suffer from the often-encountered difficulties caused by a lack of orthogonality of the two states, or by an inconsistency between two sets of orbitals used for those two states.

A more complicated physical situation is provided by an inelastic electron-atom or electron-molecule scattering process. Each target state which participates in the process should be present in the variational energy expression. The weights could be chosen equal, but more often one would choose the weights proportional to the expected cross sections for those states in the scattering process. It should be clear by now that virtually all MCSCF models which have been proposed to date are special cases of the general model presented here; the complete active space self-consistent field (CASSCF) model is an important example (Ruedenberg and Sundberg 1976; Roos *et al.* 1980). If we permit no rotations at all for the orbital vectors, we obtain a conventional configuration interaction (CI) calculation as another special case; equation (1) thus provides an iterative method, which is quadratically convergent, to solve the secular equation for the required root(s). Omitting some, but not all, of the orbital rotations yields a partially frozen orbital model which may be useful under certain circumstances.

An all-important feature of the present MCSCF model is that a full symmetry reduction has been achieved. Thus matrix elements which vanish because of symmetry are absent altogether, and matrix elements which are equal because of symmetry occur only once. To achieve this for a large class of systems in a general formal algebra, we adopted the restriction that the symmetry group must be simply reducible. As defined by Wigner (1965), such a group is characterised by: (a) inverse elements are in the same class; (b) when decomposing the product of two irreducible representations into a sum of such representations, no representation in that sum occurs more than once. These two properties guarantee the existence of Clebsch–Gordan coefficients, which considerably simplifies the calculation of all required matrix elements. The assumption that the symmetry group is simply reducible covers atoms and the vast majority of molecules.

The primitive many-electron wavefunctions we use are the so-called configuration state functions, or CSFs; they are of course the appropriate linear combinations of Slater determinants which belong to irreducible representations of the symmetry group. The basic operators we use in conjunction with the CSFs are various replacement operators; we distinguish one-electron, two-electron, and entire CSF replacement operators. With the help of these operators we can express the transformations of the wavefunctions in the variational process, and compute all required matrix elements, in completely reduced form.

Most other MCSCF treatments use second quantisation as the basic description of many-electron systems. In that framework, Slater determinants rather than CSFs are the primitive wavefunctions, and creation and annihilation operators rather than replacement operators are used to express variational transformations and to calculate matrix elements. One drawback of this approach is that the close analogy between orbital and configuration rotations is not apparent. Another drawback is that a complete symmetry reduction is not natural in this framework, and has to date not been formulated.

The second quantisation formulation of the MCSCF model is closely related to the graphical unitary group approach, or GUGA, in large CI calculations; essentially, the unitary group is the collection of all orbital transformations. The matrix elements which need to be calculated are between Slater determinants; this calculation is greatly simplified by exploiting the properties of the unitary group. As mentioned before, these matrix elements are in general not in reduced form.

Our MCSCF model uses a subgroup of the full unitary group, namely the subgroup of orbital transformations which preserve the symmetry of the

Hamiltonian. The matrix elements which need to be calculated are between CSFs; this leads to expressions in terms of 3n-j symbols and coefficients of fractional parentage, or CFPs, for the symmetry group of the system. Hence if the technology to calculate 3n-j symbols and CFPs is in place, our MCSCF model will rival GUGA in simplicity and straightforwardness, while permitting a full symmetry reduction.

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