INTERNALLY CONTRACTED MCSCF-SCEP CALCULATIONS

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Abstract

The internally contracted MCSCF-SCEP method is reviewed. Some technical details concerning the optimal organization and vectorization of the program are discussed, and timings for calculations on a CRAY-1 with up to 637524 configurations and up to 172908 variational parameters are analyzed. Some examples of internally contracted and uncontracted calculations are compared. The stability of calculated electric dipole moments and electronic transition moments with respect to the number of reference configurations and internal orbitals is investigated. Finally, a brief survey of recent applications of this method for calculating potential energy functions and radiative lifetimes of electronically excited states is presented.

I. INTRODUCTION

In recent years considerable progress has been made in the calculation of accurate multireference configuration expansions (MR-CI). Conventional MR-CI procedures have been applied for quite a long time, (1-4,6) but these methods could handle only a limited number of configurations ($\approx 2 \times 10^4$), and therefore configuration selections (2) or transformations to pseudo natural

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orbitals (5,6) were mostly required. The goal of including in the wavefunction all singly and doubly excited configurations relative to an arbitrary set of reference configurations, and thus avoiding the configuration selection and the related uncertainties of the results, has been achieved by the development of direct multireference CI procedures (7-12). In these methods the required eigenvectors are calculated iteratively without storing the Hamiltonian matrix, which makes possible the optimization of much longer configuration expansions than with conventional CI methods.

A severe disadvantage of most direct MR-CI methods is the fact that the number of configurations and the computational effort strongly depends on the number of reference configurations (13). Already for simple diatomic molecules which contain two first row atoms, sometimes 20-30 reference configurations are necessary in order to describe dissociation properly. When using large basis sets as required for calculating accurate molecular properties, one can then generate typically $10^7$-$10^8$ singly and doubly substituted configuration state functions. Although configuration expansions of this size can now be handled even on minicomputers (11), such calculations are still quite expensive.

The number of configurations can be reduced without losing much accuracy if only the "first-order interacting configuration space" (14-16) is considered, i.e. by omitting all configurations which do not interact directly with the reference wave function. This concept can only partly be exploited with schemes which depend on particular spin couplings, as is the case for methods based on the graphical unitary group approach (GUGA) (7,8,11), for example. Meyer has shown that a set of configurations which exactly span the first order interacting space can easily be generated by successively applying spin-coupled pair annihilation and creation operators to the reference configurations (16). This method is applied in the MCSCF-SCEP method (9) which is reviewed in the present paper.

The number of variational parameters and hence the computational effort can be further reduced by contracting certain classes of configurations with fixed coefficients. So far, two contraction schemes have been proposed, both of which make use of the fact that the configuration state functions can be factorized into an internal and an external part. The first scheme, which has been proposed and applied by Siegbahn (17), is called the "external contraction". In this case all configurations $\psi_P^a$ and $\psi_S^a$ which belong to the same internal hole states $P$ or $S$ but have different external orbitals $a,b$ are contracted with coefficients $(C_P)^{ab}$ and $(C_S)^a$, respectively, which are obtained by first order perturbation theory. Then, for each internal state only one