

number. All three of these predictions are in agreement with what has been seen experimentally.

The more general conclusions of this analysis include the following: (1) highly non-Franck-Condon vibrational propensities due to the appearance of d/dR and R^{-2} factors in the radial and angular nonadiabatic coupling matrix elements (see 11a and 11b); (2) strong J dependence for one component of each λ -doublet and weak J dependence for the other; (3) propensity for small changes in the rotational quantum number, with the minimum change determined by the \bar{l} value of the ejected electron; (4) weak J dependence for the vibration-induced rates and strong J dependence for rotation-induced rates.

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An Automatic Grid Generation Scheme for Pseudospectral Self-Consistent Field Calculations on Polyatomic Molecules

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We describe a stable and efficient approach to generating a reliable polyatomic grid for self-consistent electronic structure calculations using the pseudospectral method. Systematic convergence of spectroscopic constants to the Roothaan Hartree-Fock values as the grid size is increased is demonstrated. The approach offers an estimated 1-2 order of magnitude reduction over alternative numerical self-consistent field algorithms in the number of grid points per atom required to produce accurate results.

I. Introduction

In a series of previous papers,¹⁻³ a new algorithm for solution of self-consistent electronic structure equations has been proposed and implemented. The algorithm involves a synthesis of conventional quantum chemical techniques with the pseudospectral method,⁴ an efficient numerical method originally applied to large-scale hydrodynamic simulations⁵ and recently employed in various contexts in chemical physics problems.⁶ The essential feature of the approach is use of both a basis set and a numerical grid representation of the solution, allowing accurate evaluation of derivatives and integrals but also permitting multiplications to be carried out efficiently on the physical space grid. The net results for the Hartree-Fock equations are elimination of two-electron integrals and an N^3 scaling of both integral evaluation and Fock matrix assembly, thus potentially yielding 2-3 orders of magnitude reduction in computation time for large molecules.

In ref 3, quantitatively accurate results (as compared to equivalent calculations done via the Roothaan procedure⁷) for the

water molecule were obtained for the dissociation energy, force constants, and equilibrium geometry. This demonstrated that the pseudospectral method was capable of achieving the high accuracy required for quantum chemical calculations on polyatomic molecules. However, a cumbersome nonlinear optimization procedure was required to achieve these results. Furthermore, this procedure is not easily generalized to large polyatomics. Consequently, a more automated and universal implementation is required if the pseudospectral method is to become a useful quantum chemical approach which is easily applied to a user-specified molecular system.

In this paper, the most difficult step in that direction is taken. The key problem identified in ref 3 is that of automatic grid generation for a polyatomic system. A practical solution to that problem is described below. There are still details of the scheme which can be improved; we expect that such improvement will allow reduction of the number of grid points required. However, the method as depicted should be directly applicable to an arbitrary polyatomic system. The explicit demonstration of this (along with any improvements developed along the way) will appear in subsequent publications. Here, we report results for the water molecule which are analogous in quality to those in ref 3. In contrast to the work reported in that paper, the grid design implemented here is a systematic procedure which should not require reoptimization for each molecular species.

No new timing results are presented here; the principal concern is description of the grid generation algorithm and establishment of accuracy for that algorithm. However, the conclusions regarding the number of grid points per atom, which is a critical parameter in determining the efficiency of any numerical self-consistent field (SCF) method, are in accord with those in ref 3. The requisite number of points is 1 or more orders of magnitude less than that used in previously described numerical schemes, whether for the Hartree-Fock (HF) equations or in the less demanding context of local density theory. The reason such large

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