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Comparison of Minimization Procedures for UHF Wave Functions

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The Roothaan, McWeeny and Fletcher methods of minimizing the electronic energy in the SCF method are compared. The CN radical is used as an example using the *ab initio* UHF method. It is concluded that a combination of the Fletcher and Roothaan methods should be generally applicable and also highly efficient.

Introduction

The unrestricted Hartree-Fock method [1] has proved useful [2] in the calculation of isotropic hyperfine coupling constants if the quartet spin state is annihilated after minimization. It has been noted already, using the *ab initio* UHF method [3], using Roothaan's repeated diagonalisation method [4], that convergence is not always achieved and it was necessary to combine the minimization process with McWeeny's [5, 6] steepest descent method where a finite circle of convergence is assured. These observations were generally in accord with those of Sleeman [7], who has demonstrated the need of a good starting approximation when using McWeeny's method. However even after providing an improved density matrix, for example by the initial use of the Roothaan method, convergence can still be slow.

Sleeman also showed that the divergence or oscillatory behaviour observed during minimization by the Roothaan method is not removed by various extrapolation procedures which speed up convergence in well-behaved cases. Berthier and Millie [8] showed that the convergence problem in Roothaan's method, at least in the open shell case, is associated with the sequence of occupied and virtual orbitals, and, provided that the right occupied orbitals are selected in each iteration cycle, no difficulty arises. Since it is not clear, and this remark is particularly applicable to large molecular systems, how to select the right occupied orbitals this latter method appears to have limited applicability.

The Method of Conjugate Gradients

The modifications of the equations given by Fletcher [9] for the closed shell case are small when applied to UHF wavefunctions. The MO's for the $p\alpha$ and $q\beta$ spin electrons can be written as

$$\boldsymbol{\psi} = \boldsymbol{\omega a}\,; \quad \boldsymbol{\phi} = \boldsymbol{\omega b}\,, \tag{1}$$

where $\boldsymbol{\omega}$ is a row matrix of the n basis orbitals, and $\boldsymbol{a}$ and $\boldsymbol{b}$ are $n \times p$ and $n \times q$ matrices respectively. The corresponding representations of the first order density matrices are

$$\boldsymbol{P}=\boldsymbol{a}\boldsymbol{a}^{\dagger}; \quad \boldsymbol{Q}=\boldsymbol{b}\boldsymbol{b}^{\dagger}. \tag{2}$$

The essence of the Fletcher method is to set, for example,

$$\boldsymbol{a}=\boldsymbol{Y}^{\alpha}(\boldsymbol{Y}^{\alpha\dagger}\boldsymbol{S}\boldsymbol{Y}^{\alpha})^{-1/2}, \tag{3}$$

where $\boldsymbol{S}$ is the overlap matrix of the basis orbitals, such that $\boldsymbol{P}$ can be written in terms of $\boldsymbol{Y}^{\alpha}$

$$\boldsymbol{P}=\boldsymbol{Y}^{\alpha}(\boldsymbol{Y}^{\alpha\dagger}\boldsymbol{S}\boldsymbol{Y}^{\alpha})^{-1}\boldsymbol{Y}^{\alpha\dagger}. \tag{4}$$

Following Fletcher it can be shown that the gradient of the energy for the α spin electron wavefunctions $\boldsymbol{\nabla E}^{\alpha}$ is given by

$$\boldsymbol{\nabla E}^{\alpha}=2[(\boldsymbol{I}-\boldsymbol{S}\boldsymbol{P})\boldsymbol{F}^{\alpha}\boldsymbol{Y}^{\alpha}(\boldsymbol{Y}^{\alpha\dagger}\boldsymbol{S}\boldsymbol{Y}^{\alpha})^{-1}] \tag{5}$$

and similarly

$$\boldsymbol{\nabla E}^{\beta}=2[(\boldsymbol{I}-\boldsymbol{S}\boldsymbol{Q})\boldsymbol{F}^{\beta}\boldsymbol{Y}^{\beta}(\boldsymbol{Y}^{\beta\dagger}\boldsymbol{S}\boldsymbol{Y}^{\beta})^{-1}], \tag{6}$$

where $\boldsymbol{F}^{\alpha}$ and $\boldsymbol{F}^{\beta}$ are the representations of the Fock Hamiltonian. The total gradient $\boldsymbol{\nabla E}$ is the partitioned matrix

$$\boldsymbol{\nabla E}=(\boldsymbol{\nabla E}^{\alpha}:\boldsymbol{\nabla E}^{\beta}) \tag{7}$$

i. e. an $n \times (p+q)$ matrix. The resulting equations have been programmed in the manner suggested by Fletcher [9, 10].

Results and Discussion

In our experience the Roothaan method, with or without incorporating extrapolation procedures, near the energy minimum is incomparably faster than any other technique. We therefore wish to reserve this method exclusively for that situation. Since difficulties may exist in the minimization procedure using molecular orbitals obtained initially by diagonalising the one-electron Hamiltonian matrix we require an efficient method to approach the minimum energy region.

As already mentioned [3] the CN radical, using a minimal basis set of SCF atomic orbitals expressed as LCGO's [11], has proved difficult to minimize and therefore suggests itself as a good test case. In Figs. 1 and 2 the electronic energy of CN (at 2.2 and 2.0 a.u. respectively) has been plotted as a function of time. All minimization procedures commence with those orbitals obtained by diagonalising the one-electron Hamiltonian. In Fig. 1 the superiority of the Fletcher method is apparent (curve (ii)). The poor convergence of the McWeeny method (curve (i)) has been attributed by Hillier and Saunders to [12] "the presence of inner shell molecular orbitals which give rise to large variations in the excitation energies". It is claimed [12] that the energy weighted steepest descent (EWSD) method corrects this deficiency.

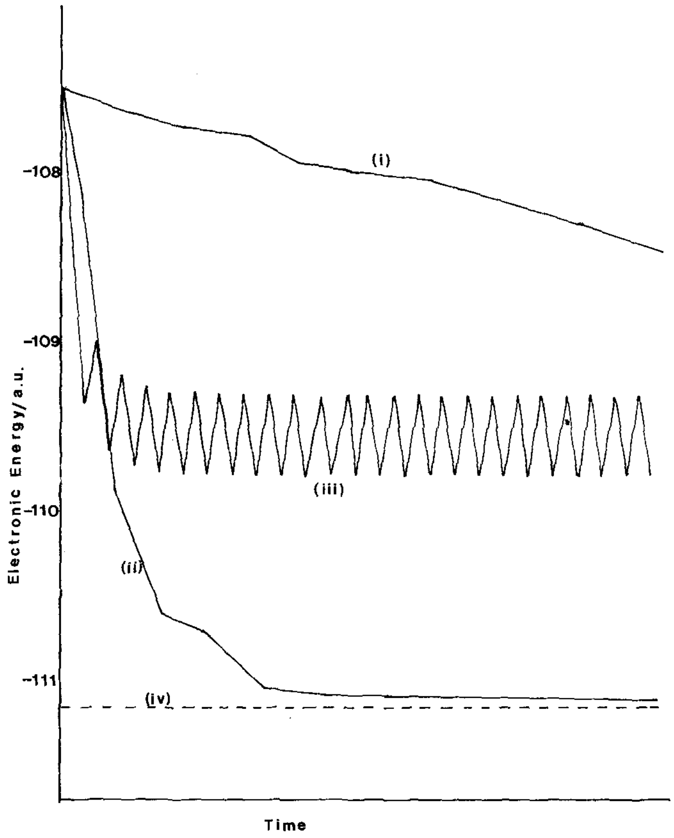

Fig. 1. Minimization of the CN radical (bond distance 2.2 a.u.). i) McWeeny, ii) Fletcher, iii) Roothaan, iv) minimum energy obtained by using Roothaan's method after McWeeny's or Fletcher's method

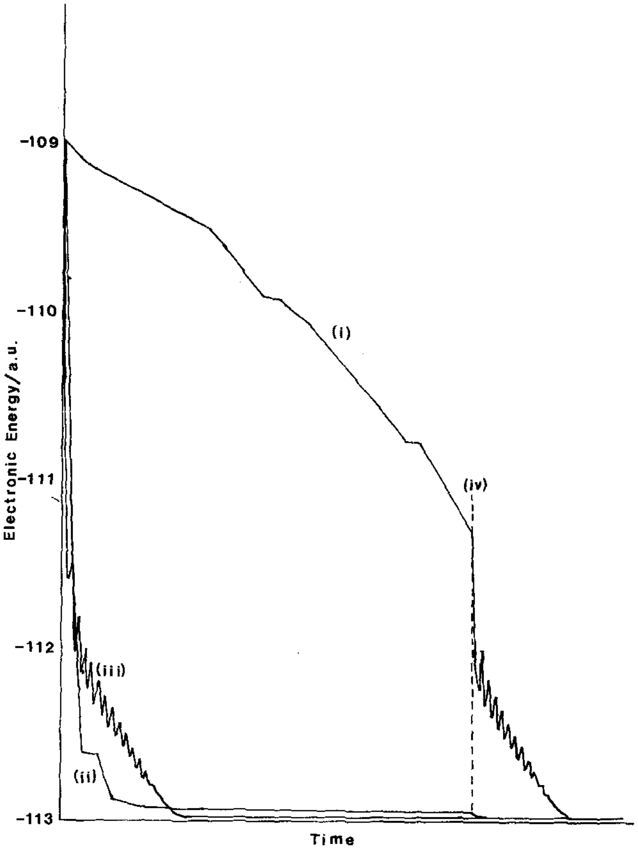

Fig. 2. Minimization of the CN radical (bond distance 2.0 a.u.). i) McWeeny, ii) Fletcher, iii) Roothaan, iv) at this time all minimization methods were changed to Roothaan's method

In a situation where the Roothaan method is convergent (Fig. 2) the Fletcher method is initially superior. However the Roothaan method is much more efficient near the minimum. Although one example has no bearing on the general behaviour it is concluded that the efficiency of minimization will be satisfactory within, say, 0.1% of the energy minimum and outside this range the Fletcher method will always minimize the energy with, hopefully, a satisfactory convergence rate.

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