JOURNAL OF COMPUTATIONAL PHYSICS 41, 200–202 (1981)

Note

On "Theory and Method for Accelerating the Convergence of Self-Consistent Electronic Structure Calculations"

In a recent article in this *Journal* Ferreira [1] presented a method for accelerating convergence in self-consistent field calculations. In this note we point out that this convergence procedure is basically Newton's method for finding the roots of an equation. We also correct the convergence criteria for the one parameter case and suggest alternate approaches for the case of N-parameters.

1. *The Single Parameter Case*

We wish to solve for

$$\begin{aligned} V_{i+1}^i &= (1-\alpha)\, V_i^i + \alpha V_i^f \\ &= V_i^i + \alpha(V_i^f - V_i^i) \end{aligned} \tag{1}$$

such that

$$\Delta(V^i)_{i+1} \equiv V_{i+1}^f - V_{i+1}^i = 0$$

(we use Ferreira's notation throughout).

Newton's method can be described by first expanding $\Delta(V)_{k+1}$ about some V_k,

$$\Delta(V)_{k+1} \simeq \Delta(V_k) + (V_{k+1} - V_k)\,\Delta'(V_K) + \cdots,$$

and then setting $\Delta(V)_{k+1} = 0$. If we neglect terms of $(V_{k+1} - V_k)^2$ and higher we find

$$V_{k+1} = V_k - \Delta(V_k)/\Delta'(V_k), \tag{2}$$

which gives the best linear approximation to V. Assuming that an analytic expression for $\Delta'(V)$ is unavailable we can take

$$\begin{aligned} \Delta'(V_i^i) &= \frac{(V_i^f - V_i^i) - (V_{i-1}^f - V_{i-1}^i)}{V_i^i - V_{i-1}^i} \\ &= T(V_i^i) - 1. \end{aligned} \tag{3}$$

Equations (2) and (3) combine to give

$$V_{k+1} = V_k + \frac{\Delta(V_k)}{1 - T(V_k)} = V_k + \alpha_p \Delta(V_k), \tag{4}$$

0021-9991/81/050200-03$02.00/0

which is Ferreira's result for one parameter (in the strictest sense this is no longer Newton's method and is known as the secant method [2]).

2. *Convergence*

The convergence of Newton's method relies on the fact that Δ' and Δ'' do not change signs in the region of our root search [3]. In particular if V^* is the root of $\Delta(V^*) = 0$ the method will

a. converge monotonically if $\Delta(V_0)\,\Delta''(V_0) > 0$ and Δ', Δ'' do not change signs in the interval (V_0, V_1),

b. exhibit oscillatory convergence if $\Delta(V_0)\Delta''(V_0) < 0$ and Δ', Δ'' do not change signs in the interval (V_0, V_1), or

c. fail to converge.

Assuming convergence, Newton's method converges quadratically—the secant method is of order[2] ~ 1.62. Note that the sign of $\alpha_p = 1/\Delta'(V)$ alone does not determine stability.

3. *The N-Parameter Case*

The N-dimensional generalization of Newton's method was given by Kantorovich and Akilov [3] and has been used to solve ordinary and generalized Hartree–Fock problems [4]. In the Newton–Kantorovich (NK) method

$$\mathbf{V}_{k+1}^i = \mathbf{V}_k^i - [\boldsymbol{\Delta}'(\mathbf{V}_k^i)]^{-1}\,\boldsymbol{\Delta}(\mathbf{V}_k^i) \tag{5}$$

where $\boldsymbol{\Delta}'(\mathbf{V})$ is the Fréchet derivative of $\boldsymbol{\Delta}$ at $\mathbf{V}$.

$$[\boldsymbol{\Delta}'(\mathbf{V})]_{i,j} = \partial \Delta_i(\mathbf{V})/\partial V_j. \tag{6}$$

The NK method has not found its way into more general SCF work because of the difficulty in obtaining an analytic expression for $\boldsymbol{\Delta}'(\mathbf{V})$.

Two methods of approximating $\boldsymbol{\Delta}' = \mathbf{T} - \mathbf{1}$ come to mind immediately. The first is numerically, as in Eq. (18) in Ref. [1]. There are two difficulties with this: (1) for large N, many iterations will be necessary before the NK method can be started and (2) as $\mathbf{V}_k$ approaches the solution, the difference between $\mathbf{V}_k$ and $\mathbf{V}_{k+1}$ may be small enough to make Eq. (18) of Ref. [1] ill conditioned.

The second approach to approximating $\boldsymbol{\Delta}'$ would consider a model of the system simple enough to allow an analytic evaluation of $[\boldsymbol{\Delta}']^{-1}$. As long as this approximation is sufficiently close [3] to the exact expression, this approximate Newton–Kantorovich sequence [Eq. (5)] will converge to the same solution as the exact NK sequence. This author hopes to have the results of such calculations available shortly.

ACKNOWLEDGMENT

I wish to thank G. Rosensteel for many helpful talks.

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RECEIVED: September 24, 1980

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