11th International Workshop on Computational Electronics
TU Wien, 25-27 May 2006

Convergence of Density Functional Iterative Procedures with a Newton-Raphson Algorithm

J.W. Jerome*, L.-H. Ye, P.R. Sievert, I.G. Kim, and A.J. Freeman
* Department of Mathematics, Northwestern University, 2033 Sheridan Road, Evanston, IL 60208 USA
e-mail: jwj@math.northwestern.edu
Department of Physics, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208 USA

INTRODUCTION

State of the art first-principles calculations of electronic structures aim at finding the ground state electronic density distribution. The performance of such methodologies is determined by the effectiveness of the iterative solution of the nonlinear density functional equation. We present a novel approach based on the appropriate density mapping. We start with the simplest density functional model, i.e., the atomic Thomas-Fermi model.

Traditional mixing methods may not be appropriate for the larger complex systems of current technological interest. Mixing employs successive approximation iterates of a fixed point mapping. Such iterates are often found to converge very slowly or not at all. Attempting to resolve this, we have designed a quadratically convergent operator version of the Newton-Raphson method. From the minimization of the Thomas-Fermi functional, one obtains by variational methods a nonlinear integral mapping for which the ground state density function is a fixed point.

THOMAS-FERMI MODEL

After the functional minimization, we obtain, for the atomic number Z, the following mapping for the nonnegative density ρ in SI units:

$$\frac{5\kappa}{3}\rho^{2/3}(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{|\mathbf{r}|} + \frac{e^2}{4\pi\epsilon_0}\int \mathrm{d}^3r' \, \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = 0, \tag{1}$$

where $\kappa = 3^{5/3}\pi^{4/3}\hbar^2/(10m)$. Here, the usual Lagrange multiplier μ, which fixes the number of electrons, has been set to zero, as appropriate for the neutral atom [1]. After assuming spherical symmetry, we introduce a new variable $Q(r) = r^{3/2}\rho(r)$ which regularizes the density at the origin. We then obtain the mapping in the form

$$Q^{\mathrm{out}} = R \circ P\left[Q^{\mathrm{in}}\right], \tag{2}$$

where

$$P[\bullet] \equiv \left[\int_r^\infty \mathrm{d}r' \; \bullet \left(\frac{r'-r}{\sqrt{r'}}\right)\right]^{3/2} \tag{3}$$

and

$$R[\bullet] = \frac{N}{4\pi\int_0^\infty \mathrm{d}r' \; \bullet \; \sqrt{r'}} \bullet, \tag{4}$$

where N is the number of electrons.

OPERATOR NEWTON-RAPHSON METHOD

To apply the Newton-Raphson method, we introduce the mapping $Y = I - R \circ P$. In terms of this mapping, the iterates are given by $Q^{\mathrm{new}} = Q^{\mathrm{old}} + \delta Q$, where δQ is determined by the implicit relation

$$Y'\left[Q^{\mathrm{old}}\right]\delta Q = -Y\left[Q^{\mathrm{old}}\right]. \tag{5}$$

DISCUSSION

We observed that $\int_0^\infty \mathrm{d}r \delta Q(r)\sqrt{r} = 0$, which ensures the charge conservation for the Newton-Raphson algorithm. The figures are based upon simulations involving a damped Newton-Raphson implementation of Eq. (5) with simple integration rules. An iteration history is included. A discussion of the Thomas-Fermi model using the variable $\chi = Q^{2/3}$ may be found in Ref. [2].

ACKNOWLEDGMENT

This work was supported by the ONR (Grant No. N00014-05-C-0241) and NSF through its MRSEC program.

REFERENCES

[1] E. H. Lieb, Reviews of Modern Physics **54**, 603 (1981).
[2] B. H. Bransden and C. J. Joachain, *Physics of Atoms and Molecules* (Prentice Hall, Harlow, 2003) Chap. 8.

ISBN 3-901578-16-1

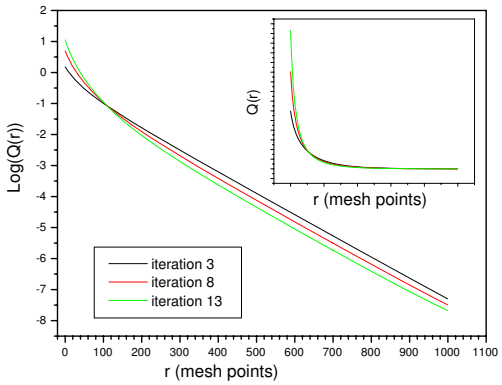

Fig. 1. $Q(r)$ for the 3rd, 8th and 13th iterations in logarithmic scale. Inset represents the same data in linear scale.

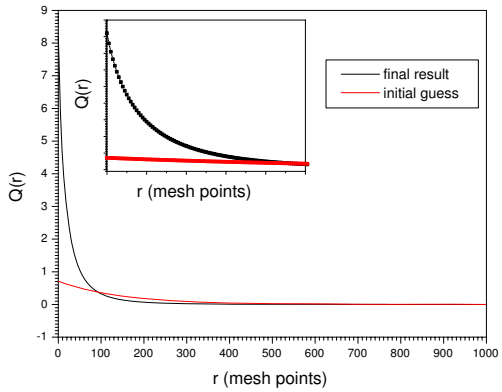

Fig. 2. Initial exponentially decreasing guess and the converged result. Inset magnifies the data around the origin.

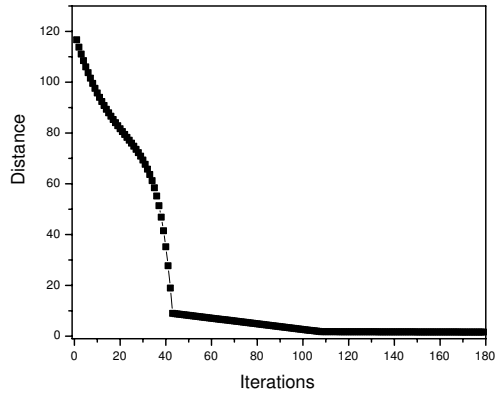

Fig. 3. Variation of successive iteration distances which is determined by $\sum_m \left|Q^{(i)}(r_m) - Q^{(i-1)}(r_m)\right|$.