THE CONTINUITY DILEMMA AND HARTREE–FOCK INSTABILITIES*

N. MOISEYEV and J. KATRIEL
Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel

Received 3 May 1974
Revised manuscript received 4 July 1974

The stability criteria of the Hartree–Fock wavefunctions are implemented in the context of the Roothaan–Hartree–Fock procedure. Use is made of modified SCF equations, in which the total energy, rather than orbital energies, appears. The procedure is applied to the $2\,^3S$ state of helium.

1. Introduction

The complications associated with the Hartree–Fock equations are essentially due to the possible existence of more than one set of orbitals by which they are satisfied [1]. Furthermore, the Hartree–Fock equations constitute an extremum condition, and only a further investigation of the solutions enables the identification of those that correspond to a local minimum [2, 3]. An even more acute problem is associated with the search of the absolute minimum. This has been very well known in particular in the context of the symmetry dilemma [4]. The instability associated with the removal of the equivalence restriction [5] is essentially related to the symmetry dilemma situation.

The above mentioned complications give rise to a set of irregular phenomena associated with the dependence of the lowest lying Hartree–Fock solution on parameters appearing in the hamiltonian (such as the nuclear charge). Discontinuities in the solution as a function of such physical parameters have been studied in the context of the symmetry dilemma [6, 7]. They may appear also without an associated symmetry breakdown [8], in which case the characterizing feature is the discontinuity itself. The physical and intuitive requirement of having a smooth dependence of the solution on the physical parameters can only be satisfied if one does not insist on following the lowest energy solution. The dilemma here is between the continuity requirement and the absolute minimum requirement. This situation will be referred to as the continuity dilemma.

The possible conversion of a stable solution of the Hartree–Fock equations to an unstable one, and the associated emergence of a different stable solution is presently investigated. The stability criteria, implemented in the context of the Roothaan–Hartree–Fock procedure, are straightforwardly applied. The relevance to some aspects of correlation is briefly discussed.

2. Self-consistent field equations and the stability criterion

For a two electron system with a hamiltonian

$$H = h_1 + h_2 + 1/r_{12} ,$$

the open-shell Roothaan–Hartree–Fock problem can be formulated as follows [9]. Let

$$\Psi = \Phi_c(1)\,\Phi_d(2) \pm \Phi_d(1)\,\Phi_c(2) ,$$

the plus and minus signs referring to the singlet and triplet respectively. Here

* Based on a part of a thesis to be submitted by N.M. to the senate of the Technion - Israel Institute of Technology, in partial fulfilment of the requirements for the D.Sc. degree.

$$\Phi_c = \sum_{i=1}^{n_c} C_i \chi_i \quad \text{and} \quad \Phi_d = \sum_{j=1}^{n_d} D_j \eta_j .$$

From the energy expression

$$E = \sum_{ij} \sum_{kl} C_i C_j H_{ijkl} D_k D_l \times \left[\sum_{ij} \sum_{kl} C_i C_j S_{ijkl} D_k D_l \right]^{-1} ,$$

where

$$H_{ijkl} = \langle \chi_i(1)\, \eta_k(2) | H | [\chi_j(1)\, \eta_l(2) \pm \eta_l(1)\, \chi_j(2)] \rangle$$

and

$$S_{ijkl} = \langle \chi_i(1)\, \eta_k(2) | [\chi_j(1)\, \eta_l(2) \pm \eta_l(1)\, \chi_j(2)] \rangle ,$$

the two sets of pseudo secular equations

$$(\mathbf{H}^c - E\mathbf{S}^c)\, \boldsymbol{C} = 0 , \qquad (\mathbf{H}^d - E\mathbf{S}^d)\, \boldsymbol{D} = 0$$

are obtained via the variation principle.

Here

$$H^c_{ij} = \sum_{kl} H_{ijkl} D_k D_l , \qquad S^c_{ij} = \sum_{kl} S_{ijkl} D_k D_l .$$

Analogous relations hold for $\mathbf{H}^d$ and $\mathbf{S}^d$. The two sets of pseudo secular equations are solved iteratively for the *total* energy E and the coefficients $\boldsymbol{C}$ and $\boldsymbol{D}$. A somewhat similar derivation of the Hartree–Fock equations has recently been discussed by Mayer [10].

The connection with the conventional Roothaan HF equations follows by observing that

$$\mathbf{H}^c = \mathbf{F}^c + \langle \Phi_d | h | \Phi_d \rangle \mathbf{S}^c ,$$

where $\mathbf{F}^c$ is the Fock matrix for the orbital Φ_c. Thus

$$(\mathbf{H}^c - E\mathbf{S}^c)\, \boldsymbol{C} = 0 = (\mathbf{F}^c - \epsilon_c \mathbf{S}^c)\, \boldsymbol{C} ,$$

where

$$\epsilon_c = E - \langle \Phi_d | h | \Phi_d \rangle$$

is the conventional orbital energy for the orbital Φ_c.

Similarly

$$\epsilon_d = E - \langle \Phi_c | h | \Phi_c \rangle ,$$

so that

$$\epsilon_c + \epsilon_d = 2E - (\langle \Phi_c | h | \Phi_c \rangle + \langle \Phi_d | h | \Phi_d \rangle) = E + C ,$$

where C is the interelectronic repulsion term.

The solution of the Roothaan–Hartree–Fock equations corresponds to a *local minimum* of the energy provided that the matrix of the second derivatives of the energy with respect to the variational parameters $\boldsymbol{C}$ and $\boldsymbol{D}$ is positive definite.

This matrix can be constructed out of the three submatrices

$$\left. \frac{\partial^2 E}{\partial C_p\, \partial C_q} \right|_{\text{extremum}} = \frac{2}{N} [H^c_{pq} - E S^c_{pq}] ,$$

$$\left. \frac{\partial^2 E}{\partial D_p\, \partial D_q} \right|_{\text{extremum}} = \frac{2}{N} [H^d_{pq} - E S^d_{pq}] ,$$

$$\left. \frac{\partial^2 E}{\partial C_p\, \partial D_q} \right|_{\text{extremum}} = \frac{4}{N} \sum_{i=1}^{n_c} \sum_{j=1}^{n_d} C_i D_j (H_{piqj} - E S_{piqj}) ,$$

with

$$N = \sum_{ij} \sum_{kl} C_i C_j S_{ijkl} D_k D_l .$$

The second derivatives matrix is thus readily available, using terms which have already been constructed in the Roothaan–Hartree–Fock procedure.

3. The continuity dilemma

Some unusual correlation effects were recently observed in the lowest ^3S states of He [11, 12]. Their essential feature is that correlation appears to pull the electrons closer together rather than push them apart. This is exhibited by the behaviour of the correlation contribution to $\langle r_{12}^2 \rangle$, i.e., $\langle r_{12}^2 \rangle_{\text{exact}} - \langle r_{12}^2 \rangle_{\text{HF}}$, plotted in fig. 1. This behaviour is in agreement with the results of Boyd and Katriel [12] concerning the shape of the Coulomb hole. However, a direct observation of the Hartree–Fock values of $\langle r_{12}^2 \rangle$ versus Z, also plotted in fig. 1, as well as of the Hartree–Fock pair distribution functions, is unable to detect any unusual features whatsoever. A similar observation was made with respect to the indetectability of a second order transition from a plot of the energy versus the physical parameter [7]. The availability of the correlated values of the pair distribution functions and of $\langle r_{12}^2 \rangle$ made the magnification of the Hartree–Fock irre-

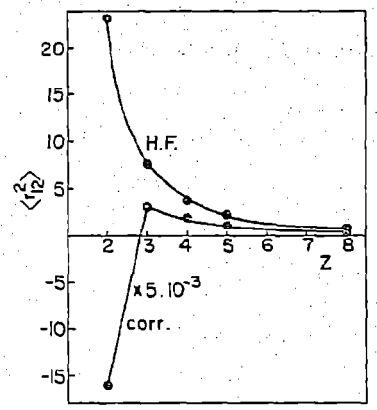

Fig. 1. The Hartree–Fock and correlation contributions to $\langle r_{12}^2 \rangle$ for the $2\,^3S$ state of the He sequence.

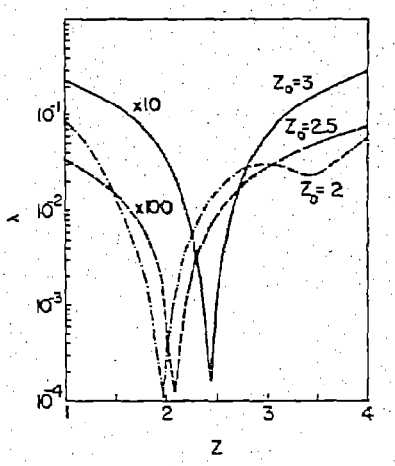

Fig. 2. The discontinuous eigenvalue ("soft mode") for $N_{1S} = N_{2S} = 2$. Z_0 is the value of the nuclear charge for which the non-linear parameters were optimized.

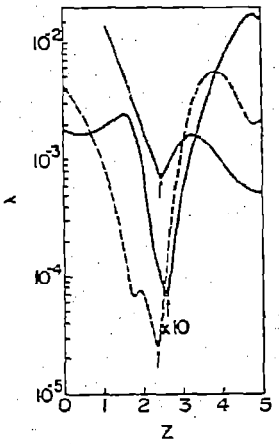

Fig. 3. The discontinuous eigenvalues for $N_{1S} = N_{2S} = 3$ (dashed line) and $N_{1S} = N_{2S} = 4$ (full lines). The non-linear parameters were optimized at $Z_0 = 3$.

gularity possible. In general, however, such a smooth background is not readily available.

A direct way of detecting the irregular features within the Hartree–Fock computation would, no doubt, be highly desirable. This is just the kind of result furnished by the behaviour of the second derivatives matrix. The approach of a second or higher order transition in the HF solution is indicated by one of the eigenvalues of this matrix diminishing very rapidly. One does not obtain negative eigenvalues for the simple reason that beyond the critical value of the physical parameter for which the instability occurs, a different solution is obtained. In a first order transition one jumps from one local minimum to another. This results in a discontinuous change of curvature at the energy minimum, which is reflected by a discontinuity in at least one of the eigenvalues of the second derivatives matrix.

4. Computations and results

The Roothaan–Hartree–Fock computations for the ^3S state of the helium isoelectronic sequence were carried out with basis sets of primitive STO's. The exponential parameters were determined by optimization for a certain nuclear charge and then kept constant while the linear coefficients were iterated to self consistency for varying nuclear charges. This was necessary in order to avoid the need of considering possible instabilities induced by the variations of the exponential parameters. A series of such computations with various basis sizes was carried out, and the second derivatives matrix of the energy with respect to the linear parameters was constructed and diagonalized. The existence of a critical point is very clearly indicated by the Z dependence of at least one of the eigenvalues of the second derivatives matrix. The discontinuous eigenvalue is plotted in figs. 2 and 3 as a function of the nuclear charge. The dependence of the location of the discontinuity upon the choice of the nuclear charge for which the optimization of the

exponential parameters was carried out, is studied in fig. 2. Although this dependence is not entirely negligible, it does appear to be of secondary significance even for the very restricted basis set used ($N_{1s} = N_{2s} = 2$; N_{1s} and N_{2s} being the number of primitive STO's per orbital). The dependence on the basis size is studied in fig. 3, again showing a consistent and essentially convergent picture. These sets of results clearly show that a discontinuity of second or perhaps higher order occurs somewhere between $Z = 2$ and $Z = 3$, probably at about $Z \approx 2.4$.

The analogies between the presently discussed discontinuities and physical phase transitions have already been pointed out [7]. They are further enhanced by the similarity of the behaviour of the discontinuous eigenvalue to that of the "soft mode" characterizing second order phase transitions [13].

Acknowledgement

This work is part of a research project supported by the U.S. – Israel Binational Science Foundation. Special thanks are due to R.E.X. Domany for his many useful suggestions during the course of this work. A most stimulating discussion with Professor Hans Primas is gratefully acknowledged.

References

[1] R.E. Stanton, J. Chem. Phys. 48 (1968) 257.
[2] D.J. Thouless, Nucl. Phys. 21 (1960) 225.
[3] W.H. Adams, Phys. Rev. 127 (1962) 1650.
[4] P.-O. Löwdin, Rev. Mod. Phys. 35 (1963) 496.
[5] S. Huzinaga and A. Hart-Davis, Phys. Rev. A8 (1973) 1734, and references therein.
[6] J. Katriel, Intern. J. Quantum Chem. 6 (1972) 541.
[7] J. Katriel and E. Domany, Intern. J. Quantum Chem., to be published.
[8] N. Moiseyev and J. Katriel, to be published.
[9] J. Katriel, D.Sc. Thesis, Technion (1972).
[10] I. Mayer, Acta Phys. Hung. 34 (1973) 83.
[11] R.J. Boyd and C.A. Coulson, J. Phys. B6 (1973) 782.
[12] R.J. Boyd and J. Katriel, Intern. J. Quantum Chem., to be published.
[13] B. Donovan and J.F. Angress, Lattice vibrations (Chapman and Hall, London, 1971) pp. 107–112.