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Study of bifurcations in a model Hartree-Fock calculation

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Abstract. The Hartree-Fock procedure is used to study the behaviour of the ground state of a system of M spinless electrons distributed over N equivalent and equidistant sites ($M \leqslant N$) as a function of the strength of the mutual repulsion between the electrons. Below a critical strength, all initial configurations are seen, after repeated iterations, to converge to a unique solution. Above this critical strength, in addition to the initial configurations which lead to a unique solution, there exist configurations which on repeated iterations give rise to stable two-period solutions. Although the number of independent stable two-period solutions depends on the coupling strength, for no value of the coupling are stable solutions of periodicity higher than two seen.

Keywords. Bifurcations; Hartree-Fock calculation; periodic solutions.

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1. Introduction

Repeated iterations of a quadratic return map in one dimension (May 1976) have revealed a surprisingly complex structure of bifurcations which nevertheless display very interesting universal features (Feigenbaum 1980). These investigations and the studies motivated by them have, in recent years, opened up what has come to be called the period doubling route to "deterministic chaos". This Feigenbaum-like period doubling route to chaos has not only been seen in iterative calculations in comparatively higher dimensions but there has also been growing experimental evidence of the existence of such universal behaviour in actual physical systems with nonlinear dynamics.

The Hartree-Fock (HF) procedure is a well-known iterative scheme with a long history of application in molecular and nuclear calculations (Parr 1963*; Löwdin 1969; Ripka and Porneuf 1976). However there are many problems associated with this procedure. One of them is called the "symmetry-dilemma" which occurs in cases where the Hamiltonian of a system possesses a certain symmetry. It has been known for a long time (Delbrück 1930; Löwdin 1969) that symmetry-adapted starting iterates lead to symmetry-adapted final solutions which may not read the absolute minimum of the system. If one looks for the absolute minimum of the energy, one loses the symmetry property and if one restores the symmetry properties the associated energy may be

*This book contains reprints of important papers on the application of the Hartree-Fock technique to molecular structure calculations.

considerably higher. Additional problems can arise in systems possessing spin. Čížek and Paldus (1970) have shown that both "singlet"-and "triplet"-instabilities occur in singlet-HF solutions and these display different dynamical behaviour. Problems with the convergence of the HF iterative scheme are also well known and a number of techniques have been devised over the years to get around these difficulties and ensure improved convergence (Dalgaard and Jørgensen 1978). In addition, the occurrence of bifurcations in HF calculations has also been reported (Stanton 1968; King and Stanton 1969; Nyberg 1969; Natiello and Scuseria 1984) but this aspect has not been studied in any great detail. In this communication we wish to concentrate on the nature of possible bifurcations in an HF calculational scheme and examine whether they bear any resemblance to those that have been observed in lower dimensional iterative schemes involving nonlinear systems.

We therefore choose a model one-dimensional system consisting of a number of equidistant and equivalent lattice sites each carrying a positive charge, over which are distributed a number of negatively charged fermions which are taken to be spinless. This is done on grounds of simplicity and also because we wish to steer clear of any instabilities which may arise on account of the presence of spin. We study the ground state of such a system using the HF procedure. The equations of motion of the model are set up in § 2 and the calculations are described in § 3. As expected, these calculations indeed show bifurcations as the strength of the repulsion between the particles is increased. The details of the bifurcation scheme are described in § 4. However, unlike the period doubling bifurcations that are seen in lower dimensional systems, here we find stable solutions which are of either period one or period two. Stable solutions of higher periodicities are not observed, hence on the basis of the present work there seems to be no evidence for the existence of a period doubling route leading to chaotic solutions in the HF procedure. One must allow for the possibility, however, that this could be an artefact of the model we have chosen to investigate, particularly as we have restricted the number of sites to ten on grounds of computational tractability. There is need, therefore, for further investigations before one can make a categorical statement as to whether or not a HF procedure can lead to chaotic solutions.

2. The model

In order to keep the study as simple as possible, we consider a system consisting of N equidistant and equivalent lattice sites, each having just one orbital. M spinless charged fermions ($M \leqslant N$) are distributed over them. The model is described in a second quantized formalism (Languet-Higgins 1966) by a Schrödinger field $\Psi(\mathbf{r}, t)$ satisfying the anticommutation relation:

$$\{\Psi(\mathbf{r}, t), \Psi^{\dagger}(\mathbf{r}', t)\} = \delta^3(\mathbf{r} - \mathbf{r}'),$$

where † denotes Hermitian conjugation. We choose an approximate representation spanned by a set of N mutually orthogonal, real spatial functions $\{\phi_i(\mathbf{r})\}$ with $i = 1, 2, 3, \ldots, N$ such that

$$\Psi(\mathbf{r}, t) = a_i(t)\phi_i(\mathbf{r}).$$

Here a_i is the annihilation operator for a particle in the ith orbital and we are using the

convention that repeated indices imply a sum over the N lattice sites. These operators satisfy the usual anticommutation relations:

$$\{a_i^\dagger, a_j\} = \delta_{ij}, \quad \{a_i^\dagger, a_j^\dagger\} = 0, \quad \text{and} \quad \{a_i, a_j\} = 0.$$

The Hamiltonian operator for the system can be written as

$$H = T_{ij} a_i^\dagger a_j + V_{ijlk} a_i a_j a_k a_l,$$

where T_{ij} and V_{ijlk}, the one- and two-particle operators, are given by

$$T_{ij} = \int \phi_i^*(\mathbf{r}) T_{\text{op}}(\mathbf{r}) \phi_j(\mathbf{r}) \, \mathrm{d}^3\mathbf{r},$$

$$V_{ijlk} = \int\int \phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2) V_{\text{op}}(\mathbf{r}_1, \mathbf{r}_2)\phi_l(\mathbf{r}_1)\phi_k(\mathbf{r}_2) \, \mathrm{d}^3\mathbf{r}_1 \, \mathrm{d}^3\mathbf{r}_2.$$

$T_{\text{op}}(\mathbf{r})$ is that part of the total Hamiltonian which depends only on single-particle coordinates while $V_{\text{op}}(\mathbf{r}_1, \mathbf{r}_2)$ is the particle–particle repulsion potential operator between two particles with coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$. The system then obeys the nonlinear equation of motion:

$$\begin{aligned} i\frac{\mathrm{d}}{\mathrm{d}t} a_m^\dagger(t) &= [H_1, a_m^\dagger] = a_k^\dagger (T_{km} + (V_{kjml} - V_{kjlm}) a_j^\dagger a_l) \\ &\equiv a_k^\dagger (T_{km} + \tilde{V}_{kjml} a_j^\dagger a_l). \end{aligned} \tag{1}$$

In the present study we restrict ourselves to only nearest neighbour interactions so that all the T_{ij} for $|i-j| > 1$ are zero. Since all the sites have been assumed to be equivalent, each diagonal element T_{ii} will have the same value and this we assume to be zero. This is equivalent to setting the zero of the energy. The $T_{i,i\pm1}$ corresponding to nearest neighbour interactions are chosen to be -1. This is equivalent to the choice of a scale for the energy.

Thus to summarize:

$$T_{ii} = 0 \qquad \text{for all } i = 1, 2, 3, \ldots, N,$$

$$T_{ij} = -1 \qquad \text{for all } |i-j| = 1,$$

and

$$T_{ij} = 0 \qquad \text{for all } |i-j| > 1.$$

We also assume that the inter-particle repulsion is of the screened Coulomb type and that there is no differential overlap. Therefore

$$\begin{aligned} V_{ijkl} &= 0 && \text{for all } i \neq k \text{ and } j \neq 1 \\ &= g \exp(\beta|i-j|)/|i-j| && \text{for all } i = k \text{ and } j = 1, \end{aligned}$$

where g is the overall coupling constant and β is the measure of the strength of the screening. These are the usual approximations made in molecular calculations (Pariser and Parr 1953). The terms corresponding to $i = j$ do not appear in V_{ijkl} because there is only one orbital at each site and two particles cannot occupy the same orbital.

3. The Hartree-Fock procedure as a self-referencing system

The HF approximation consists of linearizing (1) in the operator sense by replacing $a_j^\dagger a_l$ by its expectation value $\rho_{jl} = \langle a_j^\dagger a_l \rangle$ in the ground state of the system, so that:

$$i\frac{\mathrm{d}}{\mathrm{d}t}a_m^\dagger(t) = a_k^\dagger(T + \tilde{V}\rho)_{km}. \tag{2}$$

ρ is called the first order density matrix. The solution of (2) in terms of the normal modes of the system can be obtained by diagonalizing the HF matrix $(T + \tilde{V}\rho)$. This however requires that we know the density matrix ρ which implies that we know the ground state of the system, which in turn implies that the solution of (2) is itself known. Thus (1) cannot be solved directly and one therefore adopts an iterative procedure. Starting with some arbitrary initial configuration for the matrix ρ, one calculates the matrix $(T + V\rho)$ and its eigenvalues and eigenvectors:

$$(T + \tilde{V}\rho)_{jk}\psi_k^\alpha = \varepsilon_\alpha \psi_j^\alpha.$$

The eigenvalues ε_α of the HF matrix are the single particle energies and the corresponding eigenvectors are used to construct a new set of creation operators $\{b_m^\dagger\}$:

$$b_\alpha^\dagger = \psi_k^\alpha a_k^\dagger$$

such that

$$i\frac{\mathrm{d}}{\mathrm{d}t}b_\alpha^\dagger = \varepsilon_\alpha b_\alpha^\dagger.$$

The HF ground state for the system with M particles is obtained by filling the lowest M of these energy levels. Thus

$$|\psi\rangle_0 = b_M^\dagger b_{M-1}^\dagger b_{M-2}^\dagger \cdots b_1^\dagger |0\rangle$$

and the expectation value of the density operator in this state is therefore

$$\rho_{ij} = {}_0\langle\psi|a_i^\dagger a_j|\psi\rangle_0 = \sum_{\alpha=1}^{M} \psi_i^\alpha \psi_j^\alpha. \tag{3}$$

Thus (3) gives a new configuration for the density matrix. We can therefore summarise the HF procedure as:

(i) Start with some initial configuration for the density matrix ρ.
(ii) Calculate $(T + \tilde{V}\rho)$ and diagonalize it.
(iii) Construct a new ρ using the lowest M orbitals, compare this with the previous ρ used in the calculation of $\tilde{V}\rho$ in step (ii).
(iv) Steps (ii) and (iii) are repeated until the nth and the $(n+1)$th iterates ρ_n and ρ_{n+1} converge.

The criterion for convergence one uses is that the inequality

$$|(\rho_{ij})_n - (\rho_{ij})_{n+1}| < \delta$$

should be satisfied for each element ρ_{ij} of the density matrix. In our calculations we have taken $\delta = 10^{-6}$.

Formally therefore, we may represent the HF procedure as the discrete mapping of the space of N-dimensional real matrices on to itself, i.e.

$$\rho_{n+1} = \mathscr{HF}(\rho_n)$$

where $\mathscr{HF}$ denotes the full HF operation for one cycle. Then provided the procedure converges, it yields the correct density matrix of the system.

The results of our calculations for the HF ground state density distribution for a system of ten sites ($N = 10$) with the number of particles varying from one to ten ($M = 1$ to 10) are shown in figure 1. Figure 2 shows the variation, with the coupling constant g, of the probability density distribution for the case of five particles distributed on the ten sites.

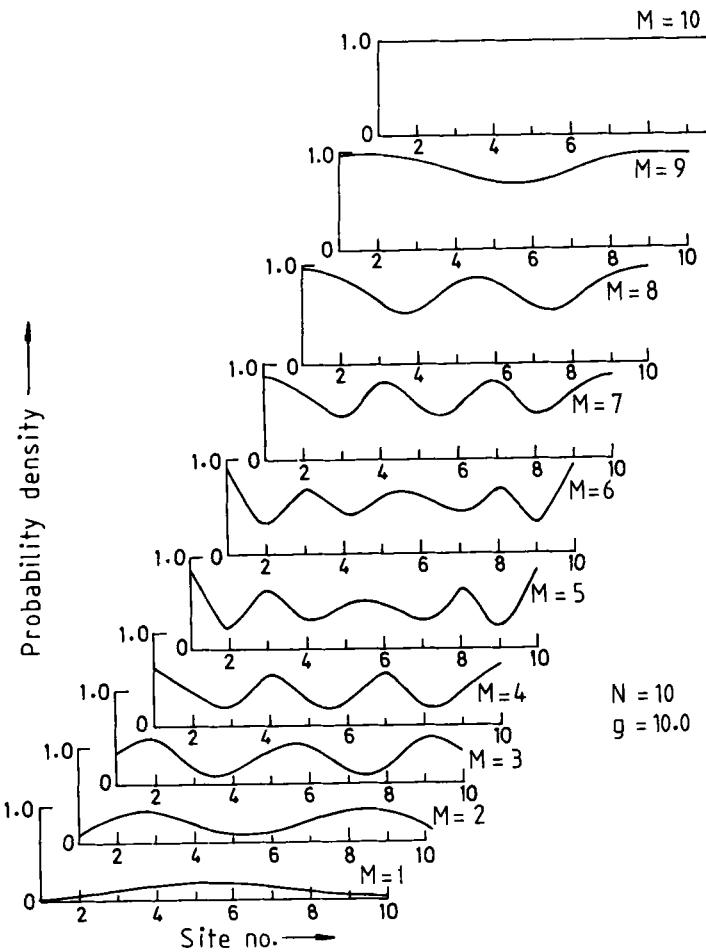


Figure 1. The Hartree-Fock ground state density distributions over the 10 sites for the number of particles varying from 1 to 10. The coupling strength is kept fixed at $g = 10$. The density distributions have been shown as smooth curves between sites although they are meaningful only over the location of each site.

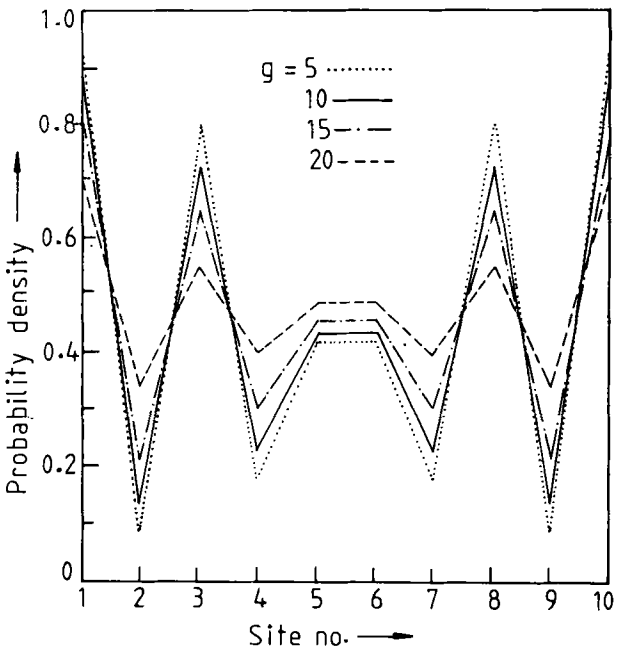


Figure 2. The variation of the Hartree-Fock ground state density distribution with the coupling strength g for the case of 5 particles distributed over 10 sites.

The variation of the independent particle energy eigenvalues ε_α with g in this case is shown in figure 3. All these results are evidently in conformity with what we would expect from physical intuition.

4. Bifurcations and periodic solutions

The existence of convergence difficulties in HF molecular calculations is well known and various techniques have been devised for achieving or speeding up convergence (Dalgaard and Jørgensen 1978). Bifurcations in the HF procedure have been reported earlier by Natiello and Scuseria (1984); they however only mention that in certain situations a two-cycle bifurcation takes place. In this communication we have tried to study the different non-convergent situations in detail to present a clearer picture of the nature of these bifurcations, using our model system as a testing ground.

Although our results are qualitatively similar for all values of the particle number M lying between 1 and 10, the richest behaviour is seen for $M = 5$. Consequently, for the rest of this paper we shall report specific details only for the case of 5 particles distributed over the 10 sites.

Our calculations show that after about 200 iterations, arbitrary initial configurations lead to a converged ρ^*, i.e.

$$\rho^*(g) = \mathscr{H}\mathscr{F}[\rho^*(g)]$$

provided the coupling constant g is less than a critical value g_1, which we have found to

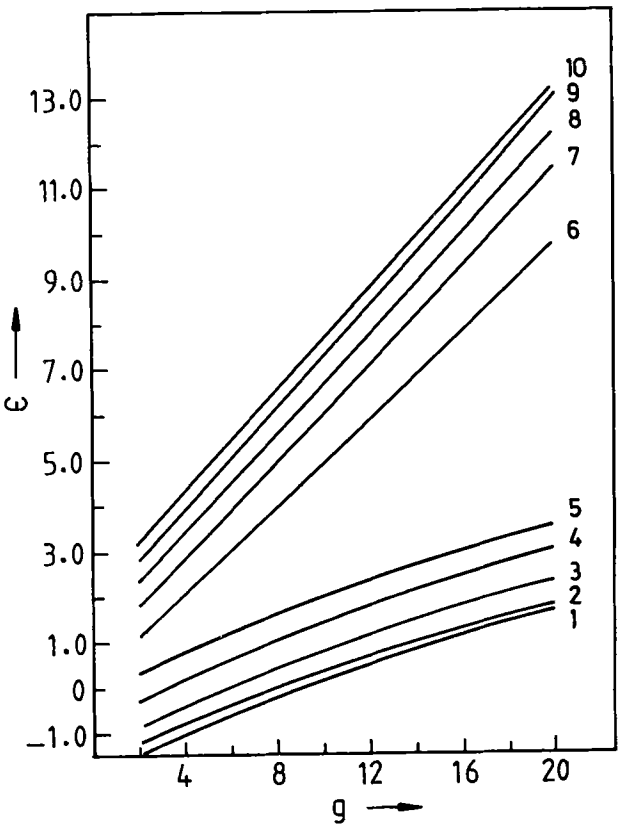


Figure 3. The variation of the 10 independent particle energy eigenvalues ε_α, for $\alpha = 1, 2, 3, \ldots 10$ with the coupling strength g for the case of 5 particles distributed over 10 sites.

be 10·1167. However, if g is increased beyond g_1, then whereas for most initial configurations the HF procedure still leads to a unique stable solution $\rho^*(g)$, now there exist some initial configurations for which the iterations do not converge to a single final density distribution. Instead the iterations oscillate between two dissimilar density distributions $\rho_1^*(g)$ and $\rho_2^*(g)$ such that

$$\rho_2^*(g) = \mathscr{H}\mathscr{F}[\rho_1^*(g)]$$

and

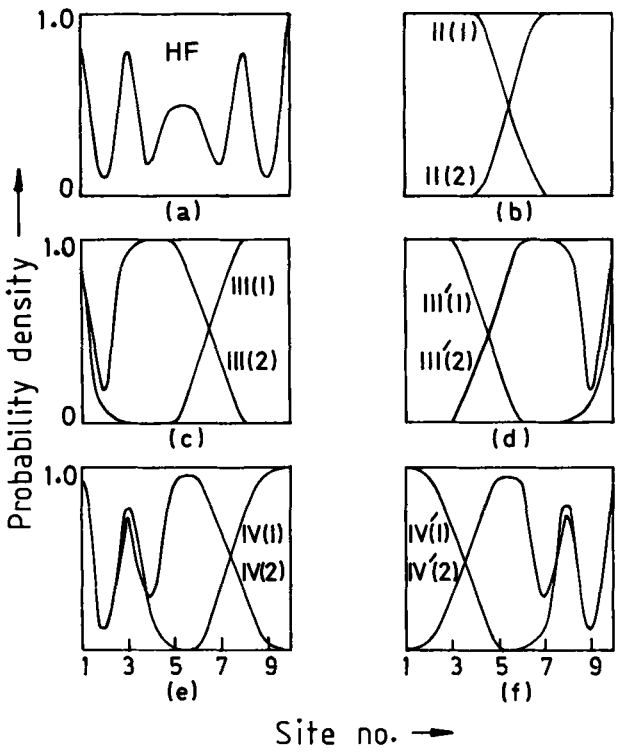
$$\rho_1^*(g) = \mathscr{H}\mathscr{F}(\rho_2^*(g)).$$

This implies the existence of a stable two-attractor for $g \geqslant g_1$. As g is increased further, different initial configurations show bifurcations at different values of g and not necessarily into the same stable two-cycle configuration—thus indicating the existence of more than one stable two-attractor. We emphasize that for all values of g that we have studied (i.e. up to $g = 80$) along with these two-period solutions there always exist initial configurations that lead to the converged HF solution, i.e. the stable one- and two-attractors coexist.

Ideally one would like to investigate the behaviour of the system for all possible initial configurations. However even the simple system that we have chosen has a ten by ten dimensional configuration space associated with it as ρ is specified by a 10×10 matrix. This is too large a space to allow an exhaustive search of the behaviour of the system for all possible initial configurations. Thus we have adopted a Monte-Carlo approach which consists of choosing randomly a set of M orthogonal vectors in a 10 $\times$ 10 dimensional space, assigning these as the wavefunctions for the M particles and using them to construct the density matrix ρ for this initial configuration. The details of this procedure are explained in the appendix.

In all the cases that we have investigated, repeated iterations either converge to a simple fixed density distribution giving the HF solution of the problem, or show a limit 2-cycle behaviour of the kind explained above. The appearance of non-HF 2-cycle solutions may be connected with the failure of the aufbau method reported by King and Stanton (1969), but this needs further investigation. All these solutions (HF and 2-cycle) can be grouped into one of the four classes which are described below and displayed in figure 4.

(a) The HF solution: A typical HF solution is shown in figure 4(a). The density distribution in such a case is always symmetric about the centre of the linear chain. Such solutions exist for all values of g.



Figures 4 (a)–(f). Plots of the four different classes of density distributions that arise for the coupling strength $g = 20$ as a result of Hartree-Fock iterations for the case of 5 particles distributed over 10 sites.

(b) Class II solution: Such solutions arise for some initial configurations for $g \geqslant g_1 = 10{\cdot}1167$. An example is shown in figure 4(b). In such cases the iterations oscillate between configurations labelled II and II′ which are mirror reflections of each other about the centre of the chain (a prime denotes a mirror image).

(c) Class III solution: For $g \geqslant g_2 = 11{\cdot}8739$ some initial configurations give rise to a two-period solution which is distinct from II and II′ (see figure 4(c)). The iterations oscillate between configurations labelled III(1) and III(2) which are not mirror reflections of each other. However, as is to be expected from the symmetry of the problem, another set which is the mirror image of III(1) and III(2) is also an independent two-period solution (figure 4(d)). We denote these as III(1)′ and III(2)′.

(d) Class IV solution: For $g \geqslant g_3 = 19{\cdot}2316$ some initial configurations give rise to yet another two-period solution, which is distinct from solutions II and III. The iterations now oscillate between two density distributions IV(1) and IV(2) which are shown in

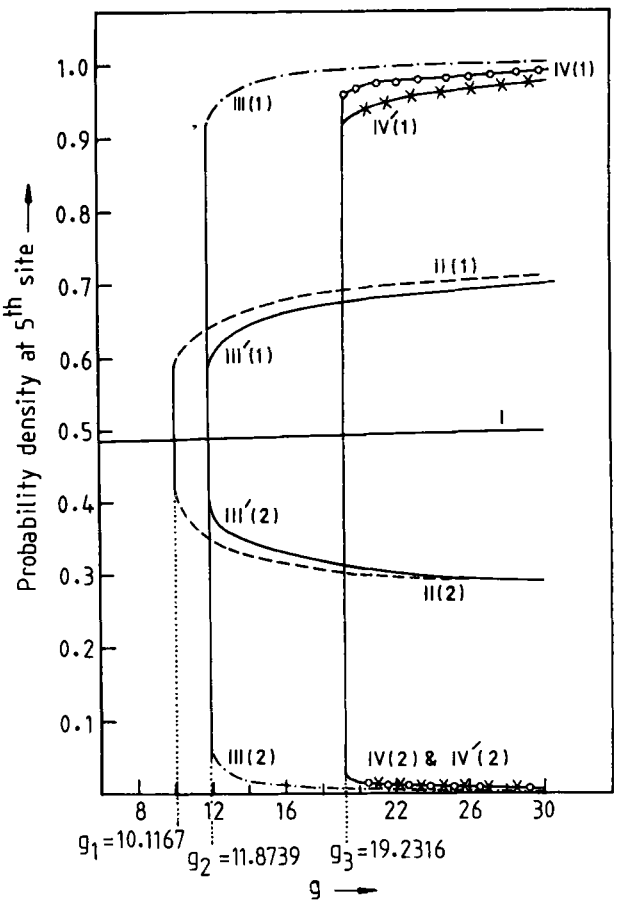


Figure 5. Bifurcation diagram arising from a plot of the probability density at the fifth site as a function of the coupling strength g for the case of 5 particles distributed over the 10 sites. Note that the Hartree-Fock solution (labelled I) persists for all values of the coupling strength g.

figure 4(e). These are again not mirror images of each other so that a set of mirror reflected density distributions IV(1)′ and IV(2)′ is also an independent two-period solution. These solutions possess more structure than the class III solutions.

These are the only four types of stable solutions that we have encountered in our investigations. They appear at different values of g. The complete bifurcation diagram for the probability density at the fifth site (ρ_{55}) is shown in figure 5. This bifurcation scheme has been obtained by the following procedure. Suppose we have obtained a two-period class IV solution at a particular value of g from one of our random initial configurations. We then use this class IV two-period solution as the initial configuration for subsequent calculations for progressively lower values of g. Starting with $g = 80$ as we go lower we find that as long as $g \geqslant g_3$ a class IV type initial configuration leads to a class IV solution, however for $g < g_3$ it leads to the HF solution. On further lowering g we see that as long as $g \geqslant g_2$ class III initial configurations lead to class III solutions, but for $g < g_2$ a class III initial configuration converges to the HF solution. Similarly, class II solutions are seen only for $g \geqslant g_1$ and not for lower values of g.

Our investigations would lead us to believe that there exist a maximum of four attractors in the system of five particles distributed over ten lattice sites—only one of which is a one-attractor, the other three being two-attractors. The HF solution is of course given by the one-attractor. Starting with 100 randomly distributed initial configurations, we show in table 1 how many of them lead to the different classes of solutions for different values of g. These results indicate that the one-attractor has the largest basin so that random initial configurations lead, in the majority of cases, to the HF solution for arbitrary values of g. As we change the value of g the size of the basins of the different attractors change. Consequently, the probability that an initial configuration will fall in the basin of a particular attractor changes with g. This can be seen from the statistics shown in table 1. At $g = 20$ all the four types of solutions can be seen but the probabilities of obtaining the different classes of solutions are different. As we reduce g the basins corresponding to the non-HF solutions shrink and as g is progressively lowered, at certain critical values i.e. g_3, g_2, g_1 the basins for class IV, class III and class II solutions, in turn, disappear completely.

Table 1. Statistics of the number of solutions of various classes to be found at different coupling strengths $10 < g < 20$, starting from 100 randomly chosen initial configurations.

	Number of solutions of each class			
g	I	II	III	IV
10·0	100	0	0	0
11·0	100	0	0	0
13·0	99	0	1	0
15·0	97	0	3	0
18·0	91	1	8	0
20·0	85	3	8	4

5. Discussion

We would like to conclude with a number of observations. In the first place, although we have reported the detailed bifurcation scheme for a system of five particles distributed over ten lattice sites, the situation for a smaller or larger number of particles (< 10) is qualitatively similar. Secondly, similar bifurcations are also seen if we vary the screening strength β instead of varying g—the strength of the mutual repulsion between the particles.

We have already remarked that in the present study we find no evidence of a Feigenbaum-like period doubling sequence of bifurcations in which as the coupling strength is increased, repeated iterations lead successively from a stable one-cycle to a stable two-cycle, to a stable four-cycle,... and so on. Note that these transitions are by flip bifurcations so that a stable $2n$-cycle develops at precisely that value of the coupling constant at which the n-cycle becomes unstable. The most complex situation that has been observed in the present study, on the other hand, is one in which there are three independent stable two-cycle solutions coexisting with a stable one-cycle solution. One other feature is worth stressing. In systems displaying a period doubling scenario all possible initial states converge either to the one-attractor or to the two-attractor, or to the four-attractor,... as the coupling is increased. Thus at a given coupling strength, the entire configuration space is the basin of the stable attractor which exists at that value of the coupling strength. On the other hand, in the HF procedure although for a sufficiently low value of g the entire configuration space is again the basin of the one-attractor, as the value of g is increased, at certain critical values the basin fractures such that although the major part of it yet remains the basin of the one-attractor, small portions of the configuration space now become the basin of a new two-attractor. We have tried to illustrate this situation schematically in figure 6. The distinction to be made is that at any value of the coupling strength, during the Feigenbaum period doubling sequence the entire configuration space is the basin of a single n-attractor whose periodicity n depends on the coupling strength, whereas in the HF procedure a

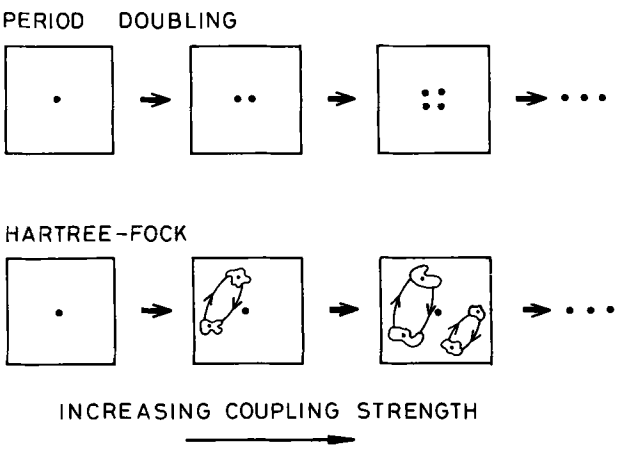


Figure 6. Schematic representation contrasting the bifurcation schemes in the Feigenbaum period doubling scenario with that encounterd in the present study.

number of different two-attractors can coexist with the one-attractor, the one-attractor being present for all values of the coupling stength. Finally the question as to whether the bifurcation scheme we have reported is generic to the HF procedure or not is moot and is currently being investigated as is the question of any possible connection between the appearance of non-HF solutions and the failure of the aufbau principle.

Appendix: Generation of random initial configurations

The choice of the initial configuration is sought to be made uniformly over an orthogonal ensemble by utilising the fact that if **A** is a real symmetric matrix then the matrix ensemble defined by the probability function

$$P(\mathbf{A}) \prod_{i>j} d\mathbf{A}_{ij} = F(\mathrm{TrA}, \mathrm{TrA}, \mathrm{TrA}, .., .., ..) \prod_{i>j} d\mathbf{A}_{ij}$$

is invariant under an orthogonal transformation (Mehta 1967). In other words, if two matrices **A** and **A**′ are related to each other by an orthogonal transformation, i.e.

$$\mathbf{A} = O\mathbf{A}'O,$$

then **A** and **A**′ have the same probability of being members of this ensemble. We have as a consequence the result that if **D** is the diagonalizing transformation of **A**, the diagonalizing transformation of **A**′ is **DO**. Thus both **D** and **DO** will be selected with the same probability for all orthogonal transformations **O**. Therefore all **D**'s in this sense are uniformly distributed. The initial configuration for the HF calculations, which we require to be uniformly distributed over the 10×10 dimensional configuration space, may therefore be obtained by picking matrices in the above ensemble and diagonalizing them. The diagonalizing matrix then gives the required initial configuration.

In general, however, it is not a simple matter to generate the members of this ensemble. However for a particular choice of the function F, known as the Wigner ensemble:

$$P(\mathbf{A}) \prod_{i>j} d\mathbf{A}_{ij} = \exp(-\mathrm{TrA}^2) \prod_{i>j} d\mathbf{A}_{ij} = \prod_{i>j} \exp(-2\mathbf{A}_{ii}^2) \exp(-\mathbf{A}_{ij}^2) d\mathbf{A}_{ij}$$

the matrix elements themselves turn out to be independent Gaussian variates with the variance for the off-diagonal elements differing from that of the diagonal ones by a factor of $2^{1/2}$. We therefore use the matrices of such an ensemble, generating them with the help of the SSP routine GAUSS and obtain the diagonalizing matrix D using the routine EIGEN.

References

Čížek J and Paldus J 1970 *J. Chem. Phys.* **53** 821

Dalgaard E and Jørgensen P 1978 *J. Chem. Phys.* **69** 3833

Delbrück M 1930 *Pro. R. Soc. (London)* **A129** 686

Feigenbaum M J 1980 *Los Alamos Science* **1** 4; reprinted in Cvitanovic P (ed.) 1984 *Universality in chaos* (Bristol: Adam Hilger)

King H F and Stanton R E 1969 *J. Chem. Phys.* **50** 3789
Languet-Higgins H C 1966 in *Quantum theory of atoms, molecules and solids* (ed.) P O Löwdin (New York: Academic Press)
Löwdin P O 1969 *Adv. Chem. Phys.* **14** 283
Mehta M L 1967 *Random matrices and statistical theory of energy levels* (New York: Academic Press)
May R M 1976 *Nature (London)* **261** 459
Natiello M A and Scuseria G E 1984 *Int. J. Quantum Chem.* **26** 1039
Nyberg J 1969 *Lett. Al. Nuovo Cimento* **1** 687
Pariser R and Parr R G 1953 *J. Chem. Phys.* **21** 767
Parr R G 1963 *The quantum theory of molecular structure* (New York: Benjamin)
Ripka G and Porneuf N (eds) 1976 *Proceedings of the international conference on nuclear self-consistent fields* (Amsterdam: North Holland)
Stanton R E 1968 *J. Chem. Phys.* **48** 257