

Instabilities in the Iterative Solution of the Hartree-Fock Equations for Excited Electrons*†

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(Received 26 October 1970)

For many excited *d*- and *f*-electron configurations there exist instabilities in the iterative self-consistent solution of the Hartree-Fock (HF) equations which make it practically impossible to obtain HF solutions using standard methods. These instabilities are associated with the sudden contraction of the *d*- or *f*-electron wave function to smaller radii near the beginning of the corresponding transition or rare-earth series. The instabilities have been overcome by new methods of solving the HF problem which involve the temporary relaxation of the normalization condition and the application of techniques which search directly for that integral of the differential equation having the highest degree of self-consistency. Using these new methods, HF solutions have been obtained for excited *d*- and *f*-electron configurations throughout the transition and rare-earth series of elements, and the results of these calculations have been employed to study the nature of the solutions and of the associated instabilities.

I. INTRODUCTION

In an earlier paper¹ we carried out a detailed study of sudden changes in the binding energies and radial wave functions of *d* and *f* electrons preceding the onset of the transition and rare-earth series of elements, using the Hartree-plus-statistical-exchange method (HX).² We felt it desirable to verify the results of that paper using the theoretically more firmly based Hartree-Fock (HF) method. However, we found many configurations containing excited *d* and *f* electrons which could not be handled by either of two distinctly different and normally satisfactory HF programs.^{3,4} In investigating the reasons for these difficulties we found them to be due to extreme instabilities in the self-consistent iterative procedure which are of a very fundamental nature. It is the purpose of this paper to present methods for overcoming these instabilities and to discuss the nature of the instabilities with the aid of results computed by these methods.

For the most part, we shall consider the HF problem for the center-of-gravity energy of electronic configurations of neutral atoms. However, calculations for ions and for energies of specific *LS*-terms will also be discussed briefly.

II. NATURE OF INTEGRALS OF THE HF EQUATIONS

The HF method involves the self-consistent iterative solution of a set of coupled differential equations, each of which is of the form

$$\left(\frac{d^2}{dr^2} + f(r) - \epsilon\right) P(r) = g(r). \tag{1}$$

(We write all equations for radii in Bohr units and energies in rydbergs.) The desired integral $P(r)$

$= P_{n_l}(r)$ is that which satisfies the boundary conditions

$$P(0) = P(\infty) = 0, \tag{2}$$

the auxiliary condition is that the

$$\text{number of nodes} = n - l - 1, \tag{3}$$

and the normalization condition is⁵

$$\|P\| \equiv \left[\int_0^\infty P^2(r) dr\right]^{1/2} = 1. \tag{4}$$

For an orbital $P_i(r) = P_{n_i l_i}(r)$, corresponding to quantum numbers n_i, l_i , the term $f_i(r)$ (which for simplicity will be referred to as the potential term) is given by

$$f_i(r) = (2/r)[Z - Y_i(r)] - l_i(l_i + 1)/r^2, \tag{5}$$

where (for the configuration center of gravity)

$$\begin{aligned} Y_i(r) = & \sum_{n_j l_j \neq n_i l_i} q_j Y_0(n_j l_j; n_i l_i / r) \\ & + (q_i - 1) Y_0(n_i l_i; n_i l_i / r) \\ & - (q_i - 1) \sum_{k>0} \frac{2l_i + 1}{4l_i + 1} \begin{pmatrix} l_i & k & l_i \\ 0 & 0 & 0 \end{pmatrix}^2 \\ & \times Y_k(n_i l_i; n_i l_i / r); \end{aligned} \tag{6}$$

the term $g_i(r)$ (which for simplicity will be referred to as the exchange term) is given by

$$g_i(r) = -\frac{2}{r} X_i(r) + \sum_{n_j l_j \neq n_i l_i} \delta_{i_j} \epsilon_{i_j} P_j(r), \tag{7}$$

where (for the center of gravity)

$$X_i(r) = \sum_{n_j l_j \neq n_i l_i} \frac{q_j}{2} \sum_k \binom{l_i \quad l_j \quad k}{0 \quad 0 \quad 0}^2 \times Y_k(n_i l_i; n_j l_j / r) P_j(r); \quad (8)$$

and ϵ_i is the absolute value of the diagonal energy parameter. In the above equations q_i is the occupation number of the i th subshell, ϵ_{ij} is the off-diagonal energy parameter used to force orthogonality between the functions $P_i(r)$ and $P_j(r)$ for which $l_i = l_j$ and $n_i \neq n_j$, and $Y_k(n_i l_i; n_j l_j / r)$ is the integral

$$Y_k(n_i l_i; n_j l_j / r) = \int_0^r P_i(r') (r'/r)^k P_j(r') dr' + \int_r^\infty P_i(r') (r'/r)^{k+1} P_j(r') dr'. \quad (9)$$

In order to understand the self-consistent-field HF problem, it is helpful to first consider the nature of the integrals of Eq. (1) that satisfy only the boundary conditions of Eq. (2), as a function of the energy ϵ , for fixed $f(r)$ and $g(r)$. To this end we will need to consider integrals not only of the inhomogeneous equation (1), but also those of the homogeneous equation obtained by setting $g(r) \equiv 0$. The homogeneous equation will have nontrivial integrals $P_H(r)$ satisfying Eq. (2) only for a discrete set of eigenvalues $\{\epsilon_H^k, k=1, 2, 3, \dots, \infty\}$. For $\epsilon \neq \epsilon_H^k$ it is always possible to determine particular integrals of the homogeneous and inhomogeneous equations $P_H(r)$ and $P_I(r)$, respectively, such that $P_I(0) = P_H(0) = 0$, but $P_H(r)$ will not satisfy the boundary condition at $r = \infty$, and in general neither will $P_I(r)$. However, by forming the general solution of Eq. (1) from the linear combination

$$P(r) = P_I(r) + \alpha P_H(r), \quad (10)$$

we can force $P(\infty) = 0$ by choosing α appropriately. $P(r)$ then satisfies Eq. (2), and (for a given value of $\epsilon \neq \epsilon_H^k$) is unique. As ϵ approaches one of the homogeneous eigenvalues ϵ_H^k , $P_H(r)$ will approach a solution for which $P_H(\infty) = 0$; however, in general, $P_I(\infty)$ does not approach zero. Therefore, α will have to be very large in order to force $P(\infty) = 0$. Thus we would expect the norm of $P(r)$ to approach infinity as ϵ approaches ϵ_H^k .

A more detailed discussion of differential equations of the form of Eq. (1) is given by Courant and Hilbert⁶ using the theory of integral equations.

Many of the properties of the integrals of Eq. (1) discussed above can be very aptly displayed by plotting, for fixed potential and exchange terms, a curve of the norm of the integral $P(r)$ vs ϵ .⁷ A typical curve of this type is shown in Fig. 1. As discussed above, the homogeneous equation will have nontrivial integrals at certain discrete values of ϵ , four of which are indicated in the figure at ϵ_H^1 , ϵ_H^2 , ϵ_H^3 , and ϵ_H^4 . The inhomogeneous equation will

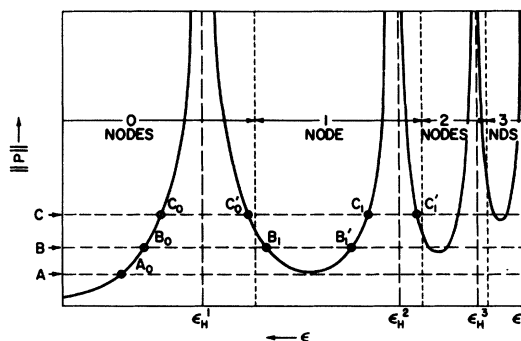


FIG. 1. Typical HF norm curve for an nl electron. The singularities at the energies ϵ_H^k ($k=1, 2, 3, 4$) correspond to the homogeneous integrals for $n=l+k$ (i. e., homogeneous integrals with 0, 1, 2, 3 nodes).

have integrals satisfying the boundary conditions (2) at every value of ϵ except at the energies ϵ_H^k , which is indicated in the figure by the singularities at these particular energies. However, if we now impose the other conditions [Eqs. (3) and (4)], the number of acceptable integrals is greatly reduced. Let us first consider the condition of the number of nodes in the integral. A typical arrangement of node count as a function of energy is also shown in Fig. 1. [The node count does not include the spurious nodes in the tail of the wave function due to $g(r)$ at large r .⁸] Although this particular node-count arrangement is not entirely general (excited f electrons in certain regions of the periodic system have a much more complex arrangement), it is typical for all core-electron wave functions as well as for outer-electron wave functions for $l \leq 2$.

We first discuss the case for which $n=l+1$ (e. g., a $3d$ electron). The possible acceptable integrals can occur only in that energy range where the node count is equal to zero. For illustrative purposes, consider three different cases for which $\|P\| = 1$ along the horizontal lines A, B, or C. For $\epsilon > \epsilon_H^1$, $\|P\|$ approaches zero monotonically as ϵ increases. Therefore, for either case A or B, there is one and only one acceptable normalized integral at A_0 or B_0 , respectively. For case C there appear to be two possible normalized integrals at C'_0 and C_0 ; however, the integral at C'_0 is unacceptable. For explanation of this refer to Fig. 2 where a plot of the "initial slope"

$$a_0 \equiv [P(r)/r^{l+1}] \quad \text{as } r \rightarrow 0$$

is shown as a function of ϵ corresponding to case C of Fig. 1. Note that the integral at C'_0 has a negative value of a_0 . This integral is not acceptable because the wave functions used to calculate the potential and exchange terms are, by convention, chosen to have positive initial slopes and therefore C'_0 cannot be close to a self-consistent result.⁹

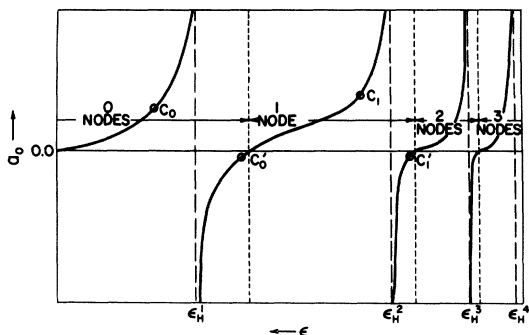


FIG. 2. Initial-slope curve corresponding to case C of Fig. 1. The circled points have unit norms.

For those electrons for which $n > l + 1$, the situation is quite different. To see this, let us assume that $n = l + 2$ (e. g., a $4d$ electron), and again consider the three different cases A, B, and C of Fig. 1. The possible acceptable integrals can occur only in the energy range where the node count equals 1. For A the norm of $P(r)$ is always greater than unity in the region of correct node count, and hence no acceptable normalized integral exists. For B there are two acceptable normalized integrals: a low-energy normalized integral at B_1' and a high-energy normalized integral at B_1 . For C there appear to be two acceptable normalized integrals at C_1' and C_1 , but the integral at C_1' is unacceptable because its initial slope is negative (see Fig. 2).

In summary, when $n = l + 1$, there is, in practice, always exactly one acceptable normalized integral of Eq. (1). However (contrary to a common misconception), this cannot be generalized, and for those cases for which $n > l + 1$ there may (at any given stage in the iterative search for self-consistent solutions) be zero, one, or two acceptable normalized integrals; when there are two such integrals the decision as to which one to choose has to be made on the basis of maximum self-consistency. Of course there is always one final self-consistent solution – a low-energy solution such as C_1 or B_1' if the effect of the exchange term $g(r)$ is small, or a high-energy solution such as B_1 if the effect of exchange is large.

III. SOLUTION OF HF EQUATIONS

A. Standard Methods

Let us first consider the methods developed by Hartree and co-workers¹⁰ to obtain self-consistent solutions to the HF equations. These methods have been successfully employed by numerous workers to obtain solutions for a large number of ground-state configurations and a relatively small number of excited configurations.

The self-consistent iterative procedure consists

of a sequence of “potential cycles” each of which involves estimating trial radial wave functions, calculating the terms $Y(r)$ and $X(r)$ and the off-diagonal energy parameters, and then for each orbital in turn (in some prescribed order) repeatedly integrating the corresponding differential equation to find that integral which satisfies all boundary conditions. The potential-cycle iteration is continued until each integral is consistent with respect to the corresponding trial function.

Hartree developed two methods for determining the required integrals of the differential equations during any one potential cycle. His first method consists of a double-iterative procedure in which both the initial slope a_0 and the energy ϵ are adjusted until all conditions (2)–(4) are satisfied. His alternate procedure involves only a single iteration on the energy and, since it was employed here both to determine the appropriate integrals of the core electrons and as part of our new methods, we discuss it in more detail. A trial value for ϵ is chosen and, with an arbitrary value of a_0 , both the inhomogeneous and homogeneous differential equations are integrated; a linear combination (10) of the resulting integrals is then determined such that $P(r \rightarrow \infty) = 0$. [The condition that $P(r \rightarrow 0) = 0$ is automatically satisfied if a_0 is finite.] The initial slope and the norm of $P(r)$ are then calculated, and the entire process is repeated at new values of ϵ until an integral $P(r)$ is found for which $a_0 > 0$ and conditions (3) and (4) are satisfied.

Inherent in both of these methods is the assumption that there is one and only one normalized integral of the differential equation with the correct number of nodes and positive initial slope. However, for an excited d or f electron, there may be zero, one, or two normalized integrals which satisfy these conditions (cases A, C, B, respectively, of Fig. 1). It is obvious that the usual methods will not work when there is no acceptable normalized integral, and that when there are two acceptable normalized integrals these methods include no explicit way of determining which one of the integrals will lead to a self-consistent solution.

Even without the above complications Hartree found that the iterative process is not, in general, stable, and very often diverges if the final normalized integrals from one potential cycle are used as input to the next cycle. In general, it is therefore necessary to use some method to stabilize the over-all iterative procedure. One technique^{3,4} is to calculate the input wave function for the $m + 1$ potential cycle using the formula

$$P^{m+1}(\text{input}) = cP^m(\text{output}) + (1 - c)P^m(\text{input}) \quad (0 < c < 1), \quad (11)$$

where $P^{m+1}(\text{input})$ and $P^m(\text{input})$ are the input wave

functions for the $m+1$ and m cycles, respectively, and $P^m(\text{output})$ is the normalized integral obtained from the m th potential cycle. The majority of electrons (including all core electrons and all excited electrons with $l \leq 1$) have low-energy normalized HF solutions (e.g., C_1 or B'_1 of Fig. 1). For these cases, any instability which may arise in the self-consistent iterative procedure is oscillatory in nature and such oscillations can be controlled in the above manner by simply decreasing the constant c (i.e., decreasing the amount of the output wave function from the m th potential cycle used in the input wave function for the $m+1$ potential cycle).

However, we have found that when the self-consistent solution corresponds to a high-energy normalized integral (e.g., B_1 of Fig. 1), as is the case for many excited d and f electrons, the acceptance of the normalized integral (if one exists) or the use of any function (11) intermediate between the normalized integral and the input wave function appears to cause the iterative procedure to diverge in a monotonic fashion, [i.e., $P^m(\text{output})$ seems always to lead one away from the self-consistent function]. The situation is complex: Since the self-consistent function is unknown, the manner in which $P^m(\text{output})$ is leading one away from self-consistency is also unknown. But since use of the normalized integral of the differential equation is unsatisfactory, an obvious alternative is to temporarily relax the normalization condition and try using one of the unnormalized integrals; indeed, this is the only sort of integral available in case A of Fig. 1 where the minimum of the norm curve is greater than unity.

B. New Methods

Two new methods have been developed¹¹; they differ only in the technique used to select the particular un-normalized integral for the excited electron that will hopefully lead to a self-consistent normalized solution. In each method we perform (within each potential cycle) an additional iteration on the excited-electron wave function $P_i(r)$. During this iteration it is necessary to recalculate only $g_i(r)$ because, for singly occupied subshells (which are the only ones of practical importance for which these instabilities occur), $f_i(r)$ is independent of $P_i(r)$ —see Eqs. (5) and (6).

Method M2. The second technique developed is the more successful one, and we discuss it first. It selects an un-normalized integral on the basis of maximum self-consistency in the following sense: During each potential cycle the core-electron integrals are determined using one of the standard techniques, and values for the excited-electron potential and exchange terms are calculated. The potential term is then held fixed and the differential equation is repeatedly integrated for different values

of the diagonal-energy parameter ϵ_i to determine that (first-generation) integral $P_i^{(1)}(r)$ which is not normalized, but which satisfies the boundary conditions at zero and infinity, has the correct number of nodes, and when normalized, by dividing by the value of its norm, yields a new exchange term $g_i(r)$ with the following property: The differential equation formed from the original potential term and this new exchange term has a *normalized* second-generation integral $P_i^{(2)}(r)$ that satisfies the boundary conditions at zero and infinity, has the correct number of nodes, and is closest in form¹² to the normalized function $P_i^{(1)}(r)/\|P_i^{(1)}\|$; the determination of the normalized integral $P_i^{(2)}(r)$, of course, requires an additional iteration over the energy. At this point the norms and the diagonal energy parameters of the first- and second-generation integrals are not equal (i.e., the norm curves corresponding to the first- and second-generation integrals are not the same) and, since $\|P_i^{(1)}\| \neq 1$, $P_i^{(1)}(r)/\|P_i^{(1)}\|$ is not a solution of Eq. (1).⁵ Therefore, we replace the first-generation exchange term with the new exchange term, and repeat the entire process until the first-generation norm is equal to unity within some specified tolerance¹³; when this condition is satisfied the energies corresponding to the first- and second-generation integrals are necessarily equal (i.e., the two norm curves coalesce). Once such an integral is determined we go on to the next potential cycle, and continue the iterative process until all wave functions are simultaneously self-consistent within specified tolerances.

During the search for the appropriate normalized second-generation integral there are often two normalized integrals which satisfy all conditions (e.g., B'_1 and B_1 of Fig. 1). In principle, both of these integrals should be determined and compared with the first-generation integral; however, this approximately doubles the time required to determine the appropriate second-generation integral, and in some cases can also lead to complications in the search procedure. For this reason we have determined, by trial and error methods, the ranges of Z over which excited d and f electrons of atoms and ions have high- or low-energy self-consistent integrals; the decision as to which normalized integral to choose is then made on the basis of the atomic number and ionization stage of the case at hand. However, for excited electrons at or very near the sudden contraction of the d -electron wave function¹ (e.g., the nd electron of Ca I $4s\ nd$) the most nearly self-consistent integral tends to oscillate between the low- and high-energy normalized integrals during the iterative procedure. *M2* will not work for such cases. Because of this, we briefly discuss our first method which, although not nearly as successful on the whole as *M2*, is

free from the above difficulty.

Method M1. This method makes the decision as to which unnormalized integral to choose on the basis of the norms of the first- and second-generation integrals determined at the same value of ϵ . That is, an energy search is carried out to determine that first-generation (un-normalized) integral which satisfies the boundary conditions at zero and infinity, has the correct number of nodes, and when normalized, by dividing by the value of its norm, yields a new exchange term with the following property: The differential equation formed from the original potential term and the new exchange term has an integral at the *same energy* which satisfies the boundary conditions at zero and infinity, has the correct number of nodes, and is more nearly normalized than the first-generation integral. (In practice, the decision as to *how much* closer to unity the norm of the second-generation solution should be is quite critical and varies from case to case, and this is one of the major difficulties of the method.) Once such an integral is obtained, the first-generation exchange term is replaced by the new exchange term and the process is repeated until both the first- and second-generation integrals have norms of unity within a specified tolerance.¹³ We then go on to the next potential cycle, and continue the iterative process until all wave functions are simultaneously self-consistent.

Comparison of M1 and M2. Even though M2 requires many more integrations of the differential equation than does M1 (because of the required iteration on ϵ to determine a normalized second-generation integral), it provides such good control over the search for the self-consistent integral that it usually converges more rapidly than does M1. Indeed, there exist many high-energy solutions (lying very close to a singularity in the curve) for which the nature of the wave function varies so rapidly with energy that M2 is the only workable method of the two. M1 is useful mainly for those cases in which the minimum of the norm curve in the region of correct node count lies close to unity, where there is a tendency for the iteration to oscillate between the two possible normalized integrals of nearly equal energy.

By employing these new methods self-consistent solutions have been determined for a large number of excited configurations for which the usual method (11) will not work. The results of some of these calculations are given in Sec. IV where we consider the nature of the solutions and of the associated self-consistent instabilities.

IV. HF SOLUTIONS AND ASSOCIATED INSTABILITIES

A. Nature of the Solutions

We wish to consider the effects of the wave-function contractions,¹ at the onset of the various

transition series, on the nature of the corresponding HF solutions. As discussed in connection with Fig. 1, when $n-l-1=0$ there is always exactly one acceptable normalized integral of the differential equation; therefore, the wave-function contraction has no qualitative effect on the appearance of the norm curve nor on the nature of the HF problem. However, when $n-l-1>0$, the wave-function contractions are accompanied by important changes.

We first discuss the situation for d electrons. As an example, we show in Fig. 3 the $4d$ norm curves for the self-consistent integrals of $_{19}\text{K}14d$, $_{20}\text{Ca}14s4d$, and $_{22}\text{Ti}14s3d^24d$. In each case there are two normalized integrals with positive initial slope and the correct number of nodes; however, only one of these integrals corresponds to the self-consistent solution. As, with increasing Z , the $4d$ wave function contracts to smaller radii and begins to resemble a $3d$ wave function (so far as its mean radius and eigenvalue are concerned), the HF $4d$ solution changes from a low-energy normalized integral for $_{19}\text{K}$ to a high-energy normalized integral for $_{22}\text{Ti}$; $_{20}\text{Ca}$ is intermediate between K and Ti and, although the self-consistent solution is a low-energy case, the $4d$ integral tends to oscillate between the high- and low-energy cases during the iterative procedure. Note that in passing from a low- to a high-energy solution, the minimum of the norm curve rises to unity and falls again. The situation for all nd electrons with $n \geq 5$ is similar. For simplicity, we shall refer to the low-energy solutions as type 1 and to the high-energy solutions as type 2.

In Fig. 4 the results of extensive calculations for excited d electrons of neutral atoms are shown in the form of plots of the effective quantum numbers n^* and n_H^* vs Z ; n^* has been calculated from the formula

$$n^* = \epsilon_i^{-1/2},$$

where ϵ_i is the HF eigenvalue, and n_H^* has been calculated from the formula

$$n_H^* = (\epsilon_H^i)^{-1/2},$$

where ϵ_H^i is the eigenvalue corresponding to the integral of the homogeneous equation for quantum numbers $n_i l_i$. Note that n^* undergoes sudden drops at $Z=20$ and $Z=38$, preceding the onset of the transition series of elements, as was also the case for the effective quantum numbers calculated with the HX method in Ref. 1. However, n_H^* for the nd electrons with $n \geq 4$ throughout the first transition series and n_H^* for the nd electrons with $n \geq 5$ throughout the second transition series remain virtually unchanged, their drops not occurring until $Z=33$ and $Z=50$, respectively.¹⁴ These different behaviors of n^* and n_H^* indicate large energy separations between the HF eigenvalues and the eigen-

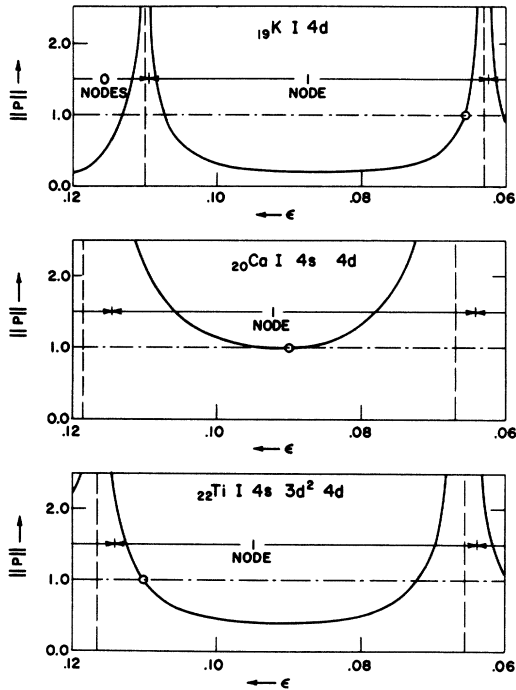


FIG. 3. Norm curves for the $4d$ electrons of ${}_{19}\text{K}$, ${}_{20}\text{Ca}$, and ${}_{22}\text{Ti}$. In each curve the low-energy singularity corresponds to the $4d$ homogeneous integral and the high-energy singularity corresponds to the $3d$ homogeneous integral. The circled points correspond to the $4d$ self-consistent normalized integrals.

values of the corresponding homogeneous integrals from $Z = 20$ to $Z = 32$ and from $Z = 38$ to $Z = 49$. These separations are large enough that nd electrons with $n \geq 4$ from $Z = 21$ to $Z = 32$ and with $n \geq 5$ from $Z = 40$ to $Z = 49$ have type 2 solutions. ${}_{38}\text{Sr}$ and ${}_{39}\text{Y}$, like ${}_{20}\text{Ca}$, have type 1 solutions which occur very close to the corresponding high-energy normalized integrals and tend to oscillate, during the iterative procedure, between the high- and low-energy normalized integrals. The magnitude of the drop in n^* for nd electrons ($n \geq 6$) at the onset of the first rare-earth series is smaller than those at the onset of the two preceding transition series; as a result, the excited nd electrons of the lanthanides have type 1 solutions with the exception of those configurations having a $5d$ core electron (e.g., $\text{La I } 6s 5d nd$), which have type 2 solutions. A similar situation occurs for the excited nd electrons ($n \geq 7$) of the neutral actinides. However, the relative separation between n^* and n_H^* increases preceding the onset of the $5d$ transition series, and the nd electrons with $n \geq 6$ have type 2 solutions from $Z = 71$ to $Z = 81$.

Unlike n_H^* for the nd electrons with $n \geq 5$, n_H^* for the $4d$ electron decreases at $Z = 38$ and $Z = 39$ (where the $4d$ -electron wave function contracts into

the core) by an amount which is large enough that the $4d$ self-consistent solutions remain of type 1. It is indeed generally true that once a wave function has collapsed into the core, the HF solution for that wave function will become a type 1 solution and will remain so for all higher values of Z .¹⁵

The behavior of HF solutions for excited f electrons is somewhat different from that for d electrons. In Fig. 5 are shown the norm curves for the $5f$ electrons of $\text{Ba I } 6s 5f$ and $\text{La I } 6s^2 5f$ corresponding to the self-consistent solutions. For ${}_{56}\text{Ba}$ there are two normalized integrals with the correct number of nodes and positive initial slopes, but the $5f$ self-consistent solution is the normalized integral having an eigenvalue just to the high-energy side of the $5f$ singularity (i.e., the singularity which corresponds to the $5f$ homogeneous integral). However, with the very abrupt collapse of the $5f$ wave function to smaller radii in going from Ba to La, the eigenvalue of the self-consistent solution shifts all the way to the high-energy side of the $4f$ singularity. Besides the abruptness of this change in solution type and the different relative energy position of the high-energy f -electron solution, there are several other differences which distinguish the f -electron case from those of d electrons (compare the norm curve for ${}_{57}\text{La}$ with that of ${}_{22}\text{Ti}$ in Fig. 3). The node-count arrangement corresponding to excited d electrons

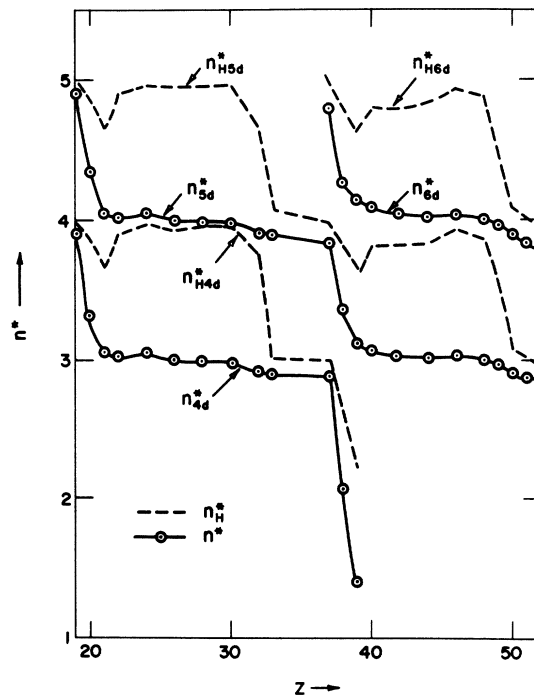


FIG. 4. Computed HF effective quantum number curves for d electrons, where $n^* = (\epsilon_{nd})^{-1/2}$ and $n_H^* = (\epsilon_H^d)^{-1/2}$.

with type 2 solutions is identical to that of Figs. 1 and 2. However, we see from Fig. 5 that the $5f$ electron of La has a node-count arrangement which is quite different; the most striking features are the change from two nodes to zero nodes at $\epsilon \approx 0.055$ Ry and the reoccurrence of one node to the high-energy side of the $4f$ singularity. Second, it should be noted, in contrast to the nd -electron cases, how rapidly the norms of the integrals change in the vicinity of the singularities, and how very small and constant the norms are in the energy range between the singularities. Another interesting feature of this case is that, unlike the typical initial-slope curve shown in Fig. 2, the initial slopes of these integrals *increase* with energy between two adjacent singularities. Finally, for this f -electron case, like many of the nd -electron cases, there are two normalized integrals with positive initial slopes and the correct number of nodes; however, here the low-energy normalized integral occurs at an energy which is on the *low*-energy side of the $5f$ singularity. The above-mentioned properties are characteristic of all excited nf electrons for which the self-consistent solution occurs to the high-energy side of the $(n-1)f$ singularity. In order to

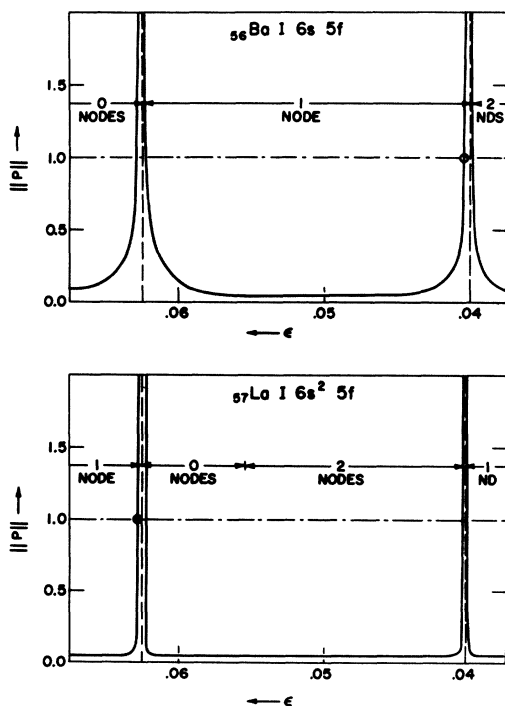


FIG. 5. Norm curves for the $5f$ electrons of ${}_{56}\text{Ba}$ and ${}_{57}\text{La}$. In each curve the low-energy singularity corresponds to the $5f$ homogeneous integral and the high-energy singularity corresponds to the $4f$ homogeneous integral. The circled points correspond to the $5f$ self-consistent normalized integrals.

distinguish these cases from the type 2 high-energy solutions, they will be referred to as type 3 solutions. Of the many HF calculations that have been carried out for excited nf -electron configurations of neutral atoms, $\text{Ac I } 7s^2 nf$ and $\text{Ac I } 7s 6dnf$ are the only cases we have found for which the nf electron has a type 2 self-consistent solution. However, there are several cases for which the most nearly self-consistent solution oscillates between type 2 and type 3 solutions during the iterative process. Further HF calculations of excited nf -electron configurations indicate that the nf electrons of neutral atoms have high-energy solutions (type 3 with the exception of the two cases just noted) for $n \geq 5$ from $Z = 57$ to $Z = 76$ and for $n \geq 6$ from $Z = 89$ throughout and beyond the second rare-earth series.¹⁶

All of the above discussion pertains only to neutral atoms. For excited electrons in ions the situation is quite different. With increasing ionization stage, cancellation between the terms $2Z/r$ and $-2Y_i(r)/r$ in the potential term $f_i(r)$ [Eq. (5)] decreases, the exchange term $g_i(r)$ tends to become of less importance relative to $f_i(r)$, and the inhomogeneous integral tends to become more like the homogeneous one. Thus the nd electrons of singly ionized atoms have type 2 solutions over smaller ranges of Z (e.g., for $n \geq 4$, from $Z = 22$ to 31), while the nd electrons of doubly ionized atoms appear to have only type 1 solutions. For excited f electrons of singly ionized atoms, the high-energy solutions are of type 2, except for $71 \leq Z \leq 75$ which remain type 3. The doubly ionized f -electron solutions closely resemble the neutral d -electron solutions (i.e., the high-energy solutions are all of type 2 and the norm curves resemble those of Fig. 3). In atoms which are more than doubly ionized, all f -electron solutions appear to be of type 1.

These remarks refer to the effect of ionization in elements for which the d - or f -wave-function collapse has already occurred in the neutral atom. For elements of lower Z the wave-function collapse may still occur upon ionization of a core electron¹⁷; this can increase (rather than decrease) the importance of $g_i(r)$ relative to $f_i(r)$. Thus, for example, the $5f$ electron has a type 1 solution in $\text{Cs I } 5f$ and $\text{Ba I } 6s 5f$, but a type 2 solution in $\text{Cs III } 5p^4 5f$ and $\text{Ba III } 5p^5 5f$. $\text{Ba II } nf$ appears to be a unique borderline case in which the degree of collapse (and the value of the quantum defect $\delta \equiv n - n^*$)¹⁸ increase gradually with n ; as a result, the nf solutions are of type 1 for $n \leq 7$ but of type 2 for $n \geq 8$.

So far we have been concerned with calculations for the center of gravity of a configuration. We now wish to consider modifications which result when HF calculations are made for a specific LS term. For such calculations, $f_i(r)$ and $g_i(r)$ in general contain additional terms beyond those given in Eqs.

(5)–(8). The effect of these added terms is to shift the solution from type 3 or type 2 toward type 1, or vice versa, depending on the signs of the added terms. For example, the $4d$ electron of $\text{Ca I } 4s \ 4d$ is seen in Fig. 3 to have a type 1 solution for a center-of-gravity calculation; however, for the 3D term the solution is of type 2, lying very slightly to the high-energy side of the minimum in the norm curve. Conversely, for $\text{Cu II } 3d^9 \ 4d$, the $4d$ electron for the center-of-gravity calculation is distinctly of type 2 (the norm-curve minimum being 0.70), but for the 1S term the solution lies very nearly at the minimum of the norm curve.

B. Discussion of Instabilities

Because of the complex mathematical form of the exchange term we shall not attempt to describe the nature of the instabilities beyond a few qualitative remarks. The first of these concerns the high sensitivity of the computed value of the excited-electron exchange term $g_i(r)$ to small variations in the low-radius portion of the excited-electron integral $P_i(r)$. In elements which precede a transition or rare-earth series, there exists a node in $P_i(r)$ which lies just outside the region of appreciable core-electron density. In elements following one of the wave-function collapses, this node has moved into the core-electron region. Therefore, both positive and negative portions of $P_i(r)$ contribute in an important fashion to the integrals $Y_k(n_i l_i; n_j l_j / r)$ of the exchange term $g_i(r)$. This leads to cancellation effects which cause the computed magnitude of the exchange term to be quite sensitive to the position of the node. Test calculations indicate that serious cancellation occurs for all high-energy solutions, and also for a few low-energy solutions in elements immediately following the sudden drop in n_H^* (e.g., the $4d$ electron of ${}_{33}\text{As I } 4p^2 \ 4d$).

The sensitivity produced by the cancellation effects is particularly serious because it occurs in cases for which the exchange term has a large effect on the integral of the differential equation; i.e., for which the eigenvalue ϵ^k of the inhomogeneous equation lies far from the corresponding eigenvalue ϵ_H^k of the homogeneous equation. Moreover, the nature of the sensitivity changes at the energy ϵ_m where the norm curve has a minimum (and which divides the low-energy from the high-energy region) – this can be seen from the following plausibility argument: Suppose that the exchange term $g_i(r)$ is scaled down by some constant factor which is made to gradually approach zero. Then the inhomogeneous equation approaches the homogeneous equation as a limit. At the same time, it may be seen from Eq. (1) that, for all ϵ , the solution $P_i(r)$ is scaled down by this same factor, so that each section of the norm curve decreases everywhere

and approaches the limiting form of a square well (i.e., $\|P\| = 0$ everywhere except at ϵ_H^k and ϵ_H^{k-1}). In any low-energy case $\epsilon^k < \epsilon_m$, the lowering of the norm curve forces the eigenvalue ϵ^k of the normalized integral to decrease in magnitude (as is to be expected physically for smaller exchange), with ϵ^k tending to ϵ_H^k and with the normalized integral approaching the proper solution of the homogeneous equation. For the high-energy case $\epsilon^k > \epsilon_m$, however, both ϵ^k and the normalized integral are forced to change in the *wrong* direction, with ϵ^k increasing toward ϵ_H^{k-1} and the integral tending to the homogeneous solution with $k-2$ nodes instead of $k-1$ nodes.

Further evidence that the use of the normalized integral tends to carry one away from the self-consistent integral in the high-energy cases was obtained through test calculations in which very nearly self-consistent d - and f -electron wave functions, obtained through application of method M2, were used as input to the “standard method” [Hartree’s alternate method plus Eq. (11)], all core-electron wave functions being held fixed. All high-energy solutions diverge monotonically regardless of the degree of self-consistency of the input – higher degrees of self-consistency merely decreasing the initial rate of divergence. The results of one of these test calculations for the $5f$ electron of $\text{Os I } 6s 5d^6 5f$ are shown in Table I. Here we give the initial slopes of the integrals of the $5f$ electron as a function of the iteration cycle of the standard

TABLE I. Monotonic divergence of the $5f$ electron of $\text{Os I } 6s 5d^6 5f$ as a function of the standard iterative cycle^a with two different nearly self-consistent input wave functions.^b

Iterative cycle	a_o (case 1)	a_o (case 2)
0 -input	7.363 945 4	7.363 951 9
1	7.363 940 0	7.363 959 5
2	7.363 923 5	7.363 984 7
3	7.363 871 5	7.364 013 7
4	7.363 705 7	7.364 142 1
6	7.361 968 8	7.365 476 3
8	7.347 832 6	7.376 298 2
10	7.233 027 8	7.464 280 5
12	6.300 665 0	8.178 708 0
14	no acceptable normalized solution	13.980 752 3
16	...	61.103 443 7
18	...	no acceptable normalized integral

^aThe value $c=0.10$ was used in Eq. (11) for both cases in order to slow down the divergence.

^bBoth $5f$ input wave functions were self-consistent to approximately 2 parts in 10^8 . The frozen-core wave functions were the same in both cases, but were only approximately self-consistent.

method for two different input wave functions which differ only slightly – and in opposite directions – from the self-consistent function. We see that with these two input wave functions, which for all practical purposes are identical, the iterative procedure diverged monotonically in different directions.

Both the plausibility argument and the results in Table I suggest that these unstable cases might be controllable by using a modification of the standard method with, in Eq. (11), a negative value of c ; i. e., by using a new input function obtained by extrapolating from the output integral backward beyond the old input function. Actually, the situation is much more complex than this and a radially dependent function $c(r)$ is needed, frequently (but by no means always) with negative $c(r)$ at small r and positive $c(r)$ at large r . The appropriate function can in principle be predicted with the aid of Pratt's improvement scheme¹⁹ applied to the input and output functions $P_i(r)$ for the two preceding cycles. However, this functional extrapolation proves to be highly erratic and unreliable; even when the predicted function $c(r)$ is artificially limited to values near zero and carefully smoothed, its use tends to cause the growth of gross irregularities in the trial input function. Instead of trying to use some function $c(r)$, we have found it much better to improve the trial function alternately at small and at large radii in the following way: As in methods $M1$ and $M2$, we carry out an iteration on $P_i(r)$ – with $f_i(r)$ fixed but with $g_i(r)$ recomputed each time – using $c = -0.05$ to -0.50 (depending on the configuration) for two or more cycles [until the Pratt-predicted value of $c(r)$ at $r \approx 0.1$ becomes positive] followed by $c = +1$ for one cycle, and then repeating; a total of 10 to 30 cycles may be required, depending on the desired degree of self-consistency.

We have not yet tested this method extensively, but it appears to be capable of working well. However, the choice of the negative value of c is rather critical: If the magnitude is too small, convergence is very slow, and if it is too large, the iteration

oscillates and may diverge. If we consider the necessity for trial-and-error adjustment of the value of c , the required computing time is usually greater than that of method $M2$. Moreover, it must be remembered that there are many excited-electron cases for which it is difficult to find an initial trial wave function for which there exists any acceptable normalized output integral; this is true not only of type 2 and type 3 cases, but also of some "stable" (type 1) cases – including p electrons as well as d and f electrons. For such cases, the most practical procedure is to employ method $M2$ or $M1$ for at least the first cycle; having had to use such a method at all, it is simplest to continue to use it exclusively.

V. CONCLUSIONS

The new methods $M1$ and $M2$ described above for solving the HF problem appear to be workable for all cases for which the usual methods are impractical or impossible. Though time consuming they have been used successfully to make an extensive survey of configurations containing an excited d or f electron throughout the various transition and rare-earth series up to $Z \approx 95$. The computed binding energies of excited electrons agree well both with experimental values (where known) and with the results of our previous calculations employing a statistical approximation for exchange (cf. Fig. 4 of this paper with Fig. 1 of Ref. 1). In particular, the values of Z at which the sudden binding-energy jumps are computed to occur are identical with those found previously by the HX method – specifically, $Z = 20, 38, 56$, and 88 for d electrons, and $Z = 57$ and 89 for f electrons.

ACKNOWLEDGMENTS

The authors are indebted to Dr. Charlotte Fischer for providing them with a copy of her HF computer program, upon which our present program was based, and to Dr. George Pimbley for helpful discussions.

* Paper based on a portion of a Ph.D. thesis submitted by D. C. Griffin to Purdue University, 1970, and upon subsequent work.

† Work done jointly under the auspices of the U. S. Atomic Energy Commission, the National Aeronautics and Space Administration, and the National Science Foundation.

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¹D. C. Griffin, K. L. Andrew, and R. D. Cowan, *Phys. Rev.* **177**, 62 (1969).

²R. D. Cowan, *Phys. Rev.* **163**, 54 (1967).

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⁴J. B. Mann, Jr., Los Alamos Scientific Laboratory Reports Nos. LA-3690 and LA-3691 (unpublished).

⁵It should be recalled that for an inhomogeneous equa-

tion (unlike a homogeneous equation) the normalization condition cannot be satisfied simply by dividing a specific integral $P(r)$ by its norm $\|P\|$.

⁶R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1953), Vol. I, pp. 358-362.

⁷This technique was first suggested to the authors by Dr. George Pimbley of Los Alamos.

⁸D. C. Griffin, Ph. D. thesis, Purdue University, 1970 (unpublished).

⁹It is conceivable that the input wave function might be so far from the self-consistent solution that the signs of all slopes would be opposite to those shown in Fig. 2, so that there would be no acceptable integrals for cases A or B , and for C the only acceptable integral would be C_0 ; however, this appears never to occur in practice.

¹⁰D. R. Hartree, *The Calculation of Atomic Structures* (Wiley, New York, 1957).

¹¹A complete description of these methods along with flow diagrams and computer listings are given in Ref. 8.

¹²We have found the initial slope a_0 to be the most practical criterion for comparing the form of the first- and second-generation integrals.

¹³In practice, the tolerance on normalization is quite loose on the first few potential cycles but is gradually tightened on later cycles.

¹⁴It is important not to confuse the homogeneous integral, to which corresponds the effective quantum number n_H^* , with the self-consistent integral of the Hartree model; the former is the integral of the homogeneous equation with the HF potential term while the latter is the integral of the homogeneous equation with the Hartree potential term. These potential terms are analytically

identical (when $q_i = 1$) but numerically quite different because of the different wave functions used to compute them; therefore, the effective quantum numbers calculated using these two potential terms will undergo drops at different values of Z —see Ref. 1, Table II.

¹⁵It is for this reason that *all* orbitals involved in ground-state configurations can be readily handled with Hartree's standard methods.

¹⁶The detailed variation of solution type with Z does depend somewhat on the assumed core-electron configuration.

¹⁷R. D. Cowan, *J. Opt. Soc. Am.* **58**, 924 (1968).

¹⁸This behavior of quantum defect is in qualitative agreement with experiment, and is explained in Ref. 1 with the aid of HX effective potentials.

¹⁹G. W. Pratt, Jr., *Phys. Rev.* **88**, 1217 (1952).

Length and Velocity Formulas in Approximate Oscillator-Strength Calculations^{*†}

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(Received 5 October 1970)

The matrix element for electric dipole transitions is correctly given by the length formula in the Hartree-Fock, configuration-interaction, and related approximations, which involve the diagonalization of an approximate, but nonlocal, Hamiltonian.

INTRODUCTION

Fano and Cooper¹ have emphasized the lack of a consistent theoretical formula for calculating transition matrix elements and their contributions to the Thomas-Reiche-Kuhn sum rule with approximate wave functions. It is generally known that there exist three alternative forms for the electric dipole transition matrix element, called the length, velocity, and acceleration formulas.² These formulas are equivalent when one uses exact eigenfunctions of either the complete spin-independent Hamiltonian or of an independent-electron central-field-model Hamiltonian. However, they disagree whenever the eigenfunctions of a central-field model are improved by including some correlation, even by only the Hartree-Fock procedure.¹⁻⁵ In practice, the disagreement among the alternative formulas is less bothersome than the lack of some criterion to choose among them. Indeed, there are cases^{3,5} in which length and velocity formulas using improved wave functions differ by a factor of 2 and yet *either* would be more accurate than a central-field-model calculation, in which all alternative formulas give the same result.

This paper identifies a class of approximations

in which the length formula is the physically correct one for calculating the transition matrix element for electric dipole processes. This class encompasses all those procedures which solve for the exact eigenfunction of an approximate Hamiltonian. Two examples are the Hartree-Fock and the configuration-interaction approximations. Explicitly excluded from this class are those variational procedures which do not give exact solutions to an approximate Hamiltonian; for these, qualitative considerations must be used to determine which of the alternative formulas are likely to be most accurate.^{2,6} For conciseness we shall compare only the length and velocity formulas.

THEORY

The difficulty that arises in the interpretation of the length and velocity formulas stems from the occurrence of nonlocal potentials, which is implied by some common approximation procedures, as shown in the next section. Here, therefore, we discuss the properties of nonlocal potentials. Consider first the ordinary case of a local potential V . In coordinate representation V is given by $V(\vec{r})$, and the effect of operating with $V(\vec{r})$ on a wave function $\psi(\vec{r})$ is just the product $V(\vec{r})\psi(\vec{r})$. However, this is a special case. In general, the