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Iron Series Hartree-Fock Calculations*

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Seventy-six Hartree-Fock calculations have been completed for the iron series (Sc to Cu) atoms and ions. All calculations are for the $(3d)^n$ type of configuration (i.e., no $4s$ electrons are present). The results are discussed, but due to lack of space, are not presented here. Comparisons are made with the experimental ionization and multiplet spectra. Agreement is poor due to limitations in the Hartree-Fock formalism. The results are used in an effort to gain information concerning correlation energies.

I. INTRODUCTION

TRULY self-consistent Hartree-Fock solutions for the nonclosed shell iron series (Sc to Cu) ions have not been available until recently. This has been due to the large amount of work associated with the computations. The first such calculation was that of Worsely[1] for V III (V^{++}). There have also been calculations by Mayers,[2] by Piper,[3] and by the writer.[4,5] It seemed desirable to carry out a large number of Hartree-Fock calculations for the iron series so as to observe the properties of Hartree-Fock wave functions for this very interesting row of the periodic table. Seventy-six separate calculations have been completed with this purpose in mind. Unfortunately space considerations make it impossible to present the results here. These and discussion of the Hartree-Fock formalism and of the computational techniques used will be found elsewhere.[4,5] This paper will be limited to the results of a single sample calculation and to a discussion of the whole set of results.

The calculations are limited to the $3d^n$ configurations (by configuration we mean the assignment of the one-electron principal quantum numbers n and l to each electron). In other words no $4s$ electrons are present. These calculations were done on the Whirlwind computer at M.I.T. and the inclusion of the $4s$ shell would have necessitated a severe decline in numerical accuracy if the computations were to stay within Whirlwind's capacity. The $3d^n$ configuration is the most important one for doubly (III) and more highly ionized ions. It competes with the $3d^{n-1}4s$ in supplying the ground states for the singly ionized (II) ions and it provides high-lying states for the neutral (I) atoms. Many of the neutral atom $3d^n$ states, for which I have done calculations, are the lowest lying states of their particular symmetry.

The calculations which have been done are listed in Table I and *a* of *c* denotes a calculation for the average of all the multiplet states of a configuration,[6] i.e., a calculation where the variational principle is applied to the center of gravity of the configuration rather than to a single state.

The calculations have been done with the Roothaan procedure[7] as modified by Nesbet.[8] They yield analytic one-electron Hartree-Fock radial functions of the form:

$$U_i(r)=\sum_j C_{ij}r^{A_j+l+1}e^{-Z_jr}, \tag{I-1}$$

l is the angular quantum number of the particular one-electron function of which $U_i(r)$ is the radial part. The A_j's and Z_j's of the basis functions are supplied to the computer and the C_{ij}'s are determined by a variational calculation. One cannot do a calculation with a complete set of basis functions since one does not have a computer of infinite capacity. As a result, the Roothaan procedure has associated with it the problem of choosing good, incomplete sets of basis functions. To offset this disadvantage, the Roothaan procedure avoids the numerical integrations which introduce errors into the conventional numerical methods for solving Hartree-Fock equations. It is my belief that with the existing computers and computational techniques the Hartree-Fock solutions can be more economically and accurately obtained by analytic methods than by numerical techniques. There is one special feature of the version of the Roothaan procedure used by me which should be noted. It cannot handle nonzero off-diagonal Lagrange multipliers which are occasionally necessary if the final Hartree-Fock one-electron functions are to be orthogonal. This is no limitation here, for contrary to the belief of some workers, the

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[1] B. H. Worsley, Proc. Roy. Soc. (London) **A247**, 390 (1958).

[2] D. F. Mayers, Proc. Roy. Soc. (to be published).

[3] W. W. Piper (unpublished).

[4] R. E. Watson, Technical Report Number 12, June 15, 1959, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts (unpublished). Available on request.

[5] R. E. Watson, Ph.D. thesis, Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, February, 1959 (unpublished).

[6] J. C. Slater, Quarterly Progress Report No. 27, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, January, 1958 (unpublished), p. 3; G. H. Shortley, Phys. Rev. **50**, 1072 (1936).

[7] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).

[8] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 213 (1955); Quarterly Progress Report No. 15, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, January 1955, p. 10; ibid, No. 16, April, 1955, p. 38, p. 41; ibid, No. 18, October, 1955, p. 4; and forthcoming articles.

$3d^n$ configuration does not require such terms and as a result my calculations are, except for computational inaccuracies, solutions of Hartree-Fock equations of the form described by Hartree.[9]

One would like to know how the accuracy of these analytic Hartree-Fock solutions compares with numerical solutions. It is easy to obtain accurate values of the one and two-electron integrals and in turn the total energy for the analytic solutions but this is not the case for numerical solutions for which no total energies are available. Comparison of total energies would be one of the best measures of Hartree-Fock wave function accuracy but since this is impossible one must compare one-electron radial functions and the few available integrals. I have observed[4,5] that the analytic solutions agree best with the numerical solutions carried to greatest accuracy. One currently cannot say whether the best of the numerical results are or are not superior to the analytic results.

In the sections which follow one will find a sample set of results, then discussions concerning how well the Hartree-Fock solutions predict multiplet and ionization spectra and finally a description of an effort to gain some information about correlation energies (i.e., the differences between the Hartree-Fock total energies and the true total energies).

TABLE I. A list of states for which Hartree-Fock calculations have been done.

Sc I	d^3	^4F	Mn IV	d^4	^3H
Sc I	d^3	a of c	Mn IV	d^4	^3G
Sc II	d^2	^3F	Mn IV	d^4	a of c
Sc II	d^2	a of c	Mn V	d^3	^4F
Sc III	d^1	$^2D=a$ of c	Mn VI	d^2	^3F
Sc IV	d^0	$^1S=a$ of c	Fe I	d^8	^3F
Ti I	d^4	^5D	Fe I	d^8	a of c
Ti II	d^3	^4F	Fe II	d^7	^4F
Ti III	d^2	^3F	Fe II	d^7	a of c
Ti III	d^2	a of c	Fe III	d^6	^5D
Ti IV	d^1	$^2D=a$ of c	Fe III	d^6	a of c
Ti V	d^0	$^1S=a$ of c	Fe IV	d^5	^6S
V I	d^5	^6S	Fe IV	d^5	a of c
V I	d^5	a of c	Fe V	d^4	^5D
V II	d^4	^5D	Fe V	d^4	a of c
V II	d^4	a of c	Fe VI	d^3	^4F
V III	d^3	^4F	Co I	d^9	$^2D=a$ of c
V III	d^3	a of c	Co II	d^8	^3F
V IV	d^2	^3F	Co III	d^7	^4F
V V	d^1	$^2D=a$ of c	Co III	d^7	a of c
V VI	d^0	$^1S=a$ of c	Co IV	d^6	^5D
Cr I	d^6	^5D	Co IV	d^6	a of c
Cr II	d^5	^6S	Co V	d^5	^6S
Cr III	d^4	^5D	Co VI	d^4	^5D
Cr III	d^4	a of c	Ni I	d^{10}	$^1S=a$ of c
Cr IV	d^3	^4F	Ni II	d^9	$^2D=a$ of c
Cr IV	d^3	^4P	Ni III	d^8	^3F
Cr IV	d^3	^2G	Ni III	d^8	a of c
Cr IV	d^3	^2P	Ni IV	d^7	^4F
Cr IV	d^3	a of c	Ni IV	d^7	a of c
Cr V	d^2	^3F	Ni V	d^6	^5D
Cr V	d^2	a of c	Ni V	d^6	a of c
Cr VI	d^1	$^2D=a$ of c	Ni VI	d^5	^6S
Mn I	d^7	^4F	Cu II	d^{10}	$^1S=a$ of c
Mn II	d^6	^5D	Cu III	d^9	$^2D=a$ of c
Mn III	d^5	^6S	Cu IV	d^8	^3F
Mn III	d^5	a of c	Cu V	d^7	^4F
Mn IV	d^4	^5D	Cu VI	d^6	^5D

TABLE II. Mn III basis function parameters.

	j	l	A_j	Z_j
For the construction of s functions	1	0	0	26.0651
	2	0	1	22.7184
	3	0	1	11.4540
	4	0	2	10.5661
	5	0	2	6.0612
	6	0	2	3.8730
p functions	7	1	0	16.0787
	8	1	0	9.5095
	9	1	1	8.7370
	10	1	1	4.9595
	11	1	1	3.0743
d functions	12	2	0	2.0235
	13	2	0	3.9754
	14	2	0	7.4822
	15	2	0	13.4624

II. A SAMPLE SET OF RESULTS

The results of a calculation for the Mn III $3d^5$ ^6S state have been chosen as an illustration of the results which have been obtained. Hartree[10] did his pioneering calculation for this state. Due to the size of the computation, he used interpolated one-electron functions for the inner shells and solved Hartree-Fock (henceforth denoted as H-F) equations for the $3p$ and $3d$ alone. This led to results which differ[4,5] noticeably from mine.

The basis function parameters are listed in Table II. These and the parameters for the other calculations are the result of an extensive variational investigation which is described elsewhere.[5] Table III lists the results which consist of the total energy, the one-electron energies (i.e., the eigenvalues of the Hartree-Fock equations), the one-electron nuclear potential+kinetic energy integrals, the C_{ij}'s and all the two-electron integrals which contribute to the total energy. These are in the form of Slater F^k and G^k integrals.[11] It should be noted that due to the analytic form of the wave functions, the one and two-electron integrals are generally accurage to six digits for these functions. This does not mean that the Roothaan procedure converged this far.

III. COMPARISON OF RESULTS WITH THE OBSERVED MULTIPLETS

The energy expressions for the set of multiplet states for a single configuration differ in the two-electron integrals where both electrons are in nonclosed shells. Much work has been done on calculating the differences in the energy expressions. If one assumes a common set of radial functions for all the multiplet states, these

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[9] D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley & Sons, New York, 1957).

[10] D. R. Hartree, Proc. Cambridge Phil. Soc. **51**, 126 (1955).

[11] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1953) (in particular Chap. VI).

TABLE III. Mn III $3d^5\ {}^6S$ results (total energy $= -2298.2099$ ry).

Average one electron energies (H) and nuclear potential+kinetic energies (K) in rydbergs

H	K
$H(1s) = -482.3830$	$K(1s) = -624.7135$
$H(2s) = -59.51487$	$K(2s) = -152.6847$
$H(3s) = -8.921829$	$K(3s) = -58.48680$
$H(2p) = -50.92840$	$K(2p) = -151.3391$
$H(3p) = -6.261782$	$K(3p) = -54.89494$
$H(3d) = -2.583616$	$K(3d) = -45.90934$

Two electron F^k and G^k integrals (rydbergs)

$F^0(1s,1s) = +30.54914$	$F^0(1s,2p) = +10.12992$	$G^1(1s,2p) = +1.682690$
$F^0(1s,2s) = +9.055729$	$F^0(2s,2p) = +6.812214$	$G^1(2s,2p) = +3.938323$
$F^0(1s,3s) = +3.050969$	$F^0(3s,2p) = +2.779520$	$G^1(3s,2p) = +0.2184650$
$F^0(2s,2s) = +6.445168$	$F^0(1s,3p) = +2.959449$	$G^1(1s,3p) = +0.1844419$
$F^0(2s,3s) = +2.740247$	$F^0(2s,3p) = +2.641607$	$G^1(2s,3p) = +0.1518273$
$F^0(3s,3s) = +2.091190$	$F^0(3s,3p) = +2.034158$	$G^1(3s,3p) = +1.354236$
$G^0(1s,2s) = +0.8241432$	$F^0(1s,3d) = +2.365510$	$G^2(1s,3d) = +0.0030536$
$G^0(1s,3s) = +0.1029509$	$F^0(2s,3d) = +2.327156$	$G^2(2s,3d) = +0.2715640$
$G^0(2s,3s) = +0.1758411$	$F^0(3s,3d) = +1.853596$	$G^2(3s,3d) = +0.8144374$
$F^2(2p,2p) = +3.481113$	$G^2(2p,3p) = +0.2058069$	$G^3(2p,3d) = +0.1677535$
$F^0(2p,2p) = +7.378854$	$G^0(2p,3p) = +0.1968488$	$G^1(2p,3d) = +0.2956213$
$F^2(2p,3p) = +0.5173625$	$F^2(2p,3d) = +0.4183382$	$G^3(3p,3d) = +0.6482390$
$F^0(2p,3p) = +2.690531$	$F^0(2p,3d) = +2.336507$	$G^1(3p,3d) = +1.072835$
$F^2(3p,3p) = +0.9967973$	$F^2(3p,3d) = +0.8598438$	$F^4(3d,3d) = +0.4843713$
$F^0(3p,3p) = +1.981962$	$F^0(3p,3d) = +1.809526$	$F^2(3d,3d) = +0.7774090$
		$F^0(3d,3d) = +1.673131$

C_{ij} Combining Coefficients

$i=$	$1s$	$2s$	$3s$
$j=1$	$+244.9321$	-73.82540	$+27.19187$
2	$+280.1814$	-474.7808	$+165.9776$
3	-1.608468	$+389.7162$	-140.7843
4	$+3.639575$	$+625.4454$	-532.3601
5	-0.1279412	$+5.728098$	$+91.03777$
6	$+0.0057261$	-0.0693771	$+38.54133$

$i=$	$2p$	$3p$		$3d$
$j=7$	$+190.7758$	-57.22179	$j=12$	$+2.225893$
8	$+273.5570$	-108.7043	13	$+29.24675$
9	$+4.259848$	-11.68352	14	$+65.10942$
10	$+2.247107$	$+72.44829$	15	$+23.89884$
11	-0.0907603	$+10.61107$		

differences give theoretical estimates of the multiplet splitting. Slater collected the existing published F^k and G^k integrals which had been obtained by fitting the observed iron series spectra. He then made additional fits using the method of least squares and the writer continued this work. Figure 1 shows the $F^2(3d,3d)$'s resulting for the $3d^n$ configurations. Only the $F^2(3d,3d)$ and $F^4(3d,3d)$ contribute to the $3d^n$ multiplet splitting if we assume common radial functions and neglect configuration interaction and other effects. The two $F^k(3d,3d)$'s stay moderately close to a fixed ratio, the $F^2(3d,3d)$ being larger and of more importance to the splitting. The figures shows points for different states of ionization and different atomic number. In several cases, fits supplied by several researchers for the same ion have been graphed. In some cases the resulting spread is considerable. The points do suggest curvature along the isoelectronic sequences. The points also show some structure in the lines of common ionization (appearing in the $F^4(3d,3d)/F^2(3d,3d)$ ratio as well). This structure is harder to pin down and it seems that straight lines are about all that can be reasonably drawn. The lines on the graph have been drawn so that they vary smoothly from one to another. Detailed fitting of the lines to the points has been neglected. This figure is of interest to us because if we assume hydrogenic $3d$ functions, the $F^2(3d,3d)$'s are proportional to the screening constants of the exponentials. This work emphasizes the linearity of functional variation along lines of common ionization rather than along isoelectronic sequences.

Fits for F^k's were made for other configurations. It is of interest to note that the $3d^{n-1}4s$ fits, for the $F^2(3d,3d)$, for the I states, fall on the II line of the figure and the $3d^{n-2}4s^2$(I) fits fall slightly below the III line. This tells us that the $4s$ electrons contribute almost no screening to the $3d$ electrons. Calculated and least square fit $F^2(3d,3d)$'s are presented in Fig. 2. The calculated values come from average of configuration H-F calculations. Individual multiplet state $F^2(3d,3d)$'s are not graphed. Lowest lying multiplet state values run larger than those for the averages of configuration (for the same atoms and states of ionization) with maximum increases of 0.001 rydberg. We see that there are violent differences between the calculated and the "experimental" $F^2(3d,3d)$'s. The neutral atom (I state) calculated $F^2(3d,3d)$'s are approximately twice as large as the "experimental" ones. This discrepancy decreases both in magnitude and in percent with increasing ionization. The calculated $F^2(3d,3d)$'s run large by approximately 20% for the IV state. More accurate H-F solutions would not appreciably change these discrepancies.

It is more convenient to consider the ratio $F^4(3d,3d)/F^2(3d,3d)$ rather than the $F^4(3d,3d)$ alone because the ratio gives some measure of how hydrogenic the $3d$ functions are. The value of the ratio for a hydrogenic $3d$ function is 0.649. Least square fit ratios flucuate

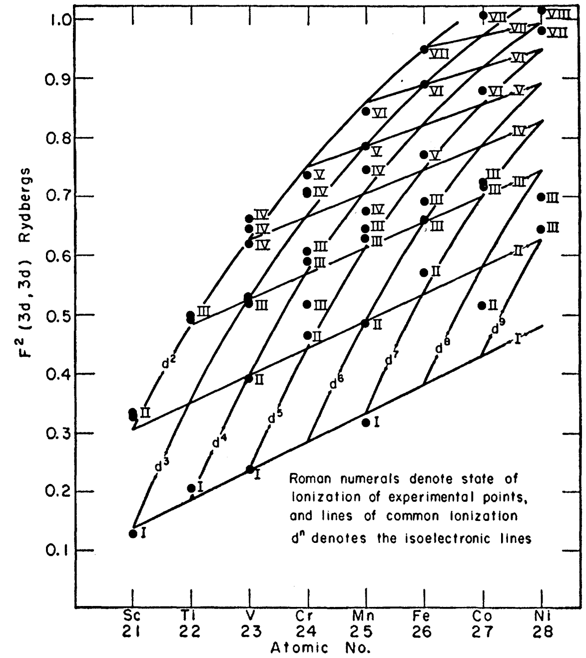

FIG. 1. $F^2(3d,3d)$ as a function of atomic number and ionization as determined by least square fits of the iron series $(3d)^n$ configuration spectra.

rather violently in value. For the most part they have values between 0.60 and 0.75 with an average of about 0.67. Any trend in the values is rather well hidden by the fluxuations so we will not try to generalize on this matter. The $F^4(3d,3d)/F^2(3d,3d)$ ratios for the H-F calculations are shown in Fig. 3. These values also represent the average of configuration solutions. All calculated values lie well below the hydrogenic ratio. What this implies in the shape of the functions can be seen in Fig. 4 which includes $U(r)$ as a function of r graphs for the Fe I average of configuration $3d$ function and for the hydrogenic $3d$ function with the same $F^2(3d,3d)$ value. The calculated ratios lie on smooth curves as do the calculated $F^2(3d,3d)$ values. This is not surprising since the average of configuration H-F equations vary smoothly with varying numbers of $3d$ electrons. Lowest lying multiplet state $F^4(3d,3d)/F^2(3d,3d)$ ratios do not vary as smoothly. This is due to less smoothly varying $3d$ H-F equations. These ratios lie within 0.001 of average of configuration values.

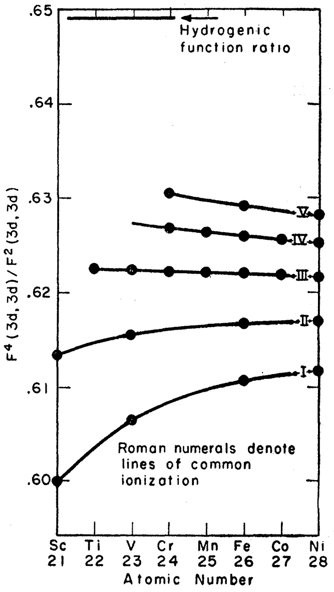

FIG. 3. The $F^4(3d,3d)/F^2(3d,3d)$ ratio as a function of atomic number and ionization as determined by Hartree-Fock average of configuration calculations for the iron series $(3d)^n$ configuration.

The calculated F^k's predict multiplet splittings which are much too large. There are two ways to improve on these predictions. First, one can do H-F calculations for individual multiplet states and use the differences in total energies to predict multiplet splittings. Secondly, one can go on to wave functions which are superior to H-F wave functions. For example, one could superimpose configuration interaction on the H-F solutions. This would also require individual calculations for individual multiplet states when predicting multiplet splitting. We will shortly consider these approaches but let us first consider the spectra which we wish to predict. Inspection of Moore's[12] tables shows that in general the order of the observed multiplets for any single configuration is somewhat different from the order predicted by the multiplet energy expressions. Further study shows that the observed order changes as one moves along an isoelectronic sequence. In the iron series, one of the extreme examples of this occurs for the $(3d)^3$ configuration. We have listed the predicted order and the observed orders from Sc I to Ni VIII for

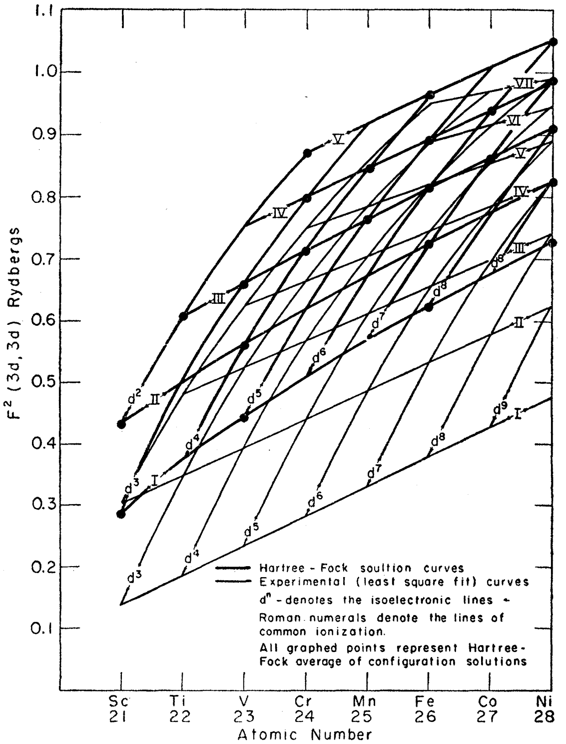

FIG. 2. Comparison between experimental and Hartree-Fock average of configuration values for $F^2(3d,3d)f$ as a function of atomic number and ionization for the iron series $(3d)^n$ configurations.

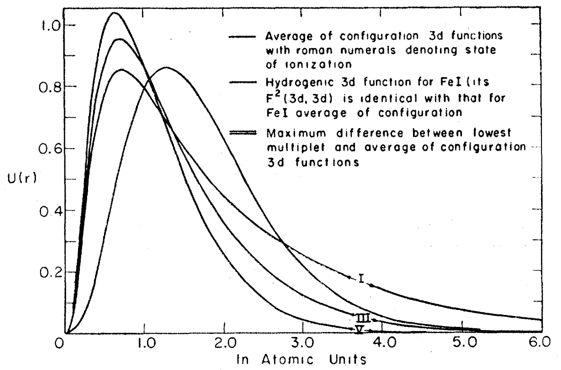

FIG. 4. Fe$3d$ wave functions [$U(r)$'s] for the $(3d)^n$ configurations.

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[12] C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. I–III; and for some corrections to the iron series ionization spectra see, M. A. Catalán and R. Velasco, Anales real soc. españ. fís. y quím A48, 247 (1952).

TABLE IV. $3d^3$ predicted and observed multiplet state orders.

	Observed							
Predicted	Sc I	Ti II	V III	Cr IV	Mn V	Fe VI	Co VII	Ni VIII
^4F	^4F	^4F	^4F	^4F	^4F	^4F	^4F	^4F
^4P	^2D	^2G	^2P	^2P	^4P	^4P	^4P	^4P
^2G	^4P	^4P	^4P	^4P	^2G	^2G	^2G	^2G
$\{{}^2P$		^2P	^2G	^2G	^2P	^2P	^2D	^2D
${}^2H\}$		^2D	^2D	^2D	^2D	^2D	^2H	^2H
^2D		^2H	^2H	^2H	^2H	^2H		
^2F		^2F		^2F				
^2D		^2D						

$(3d)^3$ in Table IV. The lowest levels are listed at the top of the columns and the bracket in the "predicted" column signifies that these two multiplet states are supposed to have identical energy levels. Not one ion has a multiplet state order which is in agreement with the "predicted." The ^2G falls lower than the ^4P in violation of the predicted order for Ti II. All other violations are due to the ^2P and one of the ^2D's taking on lower level positions than predicted.

The writer has run computations for the average of configuration and the four lowest multiplet states of Cr IV. This is of interest in light of the above discussion on ordering but is of greater interest since it gives an indication of how much the predicted multiplet splittings can be improved through the use of individual multiplet state calculations. This ion was chosen for two reasons. First, it has a $(3d)^3$ configuration and secondly because for IV states, the $(3d)^n$ multiplet states lie well below all other observed multiplet states. This assures us that any configuration interaction would lower energies. Let us first consider Table V which lists the total energies and a number of integrals which are interesting to compare. We see that the variations in the $K(3d)$'s (one-electron kinetic plus nuclear potential energies) are of the order of the energy differences between multiplet states and that the $K(3p)$ and $K(3s)$ variations are about 0.1 and 0.05 of the energy differences, respectively. The writer would say that these represent important variations in the functions. The results of greatest interest are to be seen in Table VI. This table gives the multiplet splittings in terms of the ground ^4F whose energy is set to zero. The first column gives the experimentally observed values. The second is obtained by putting the results of least squares fits back into the multiplet splitting equations. We should note that the least square fits gave values of F^2, F^4 and an average energy for the configuration. These three values were inserted into the energy expressions and the *energy scale was shifted* so that the ^4F energy equaled zero. Thus the zero of the second (and also those for the third and fifth) column is not strictly the zero of the first. The third column was calculated using the F^2 of Fig. 1 and an assumed F^4/F^2 value of 0.649 (the hydrogenic value). The fourth column gives the energy differences resulting from the four multiplet state calculations and the fifth column was calculated using the F^2 and F^4 from the authors' average of configuration calculation. The F^2 and F^4 values associated with the various columns are listed underneath the spectra.

TABLE V. Cr IV total energies and K(f) values (all are in rydbergs).

State	Total energy	$K(3d)$	$K(3p)$	$K(2p)$
av of config.	−2082.7414	−43.35800	−50.67848	−139.1392
^4F (ground)	−2082.9435	−43.54521	−50.65748	−139.1382
^2P	−2082.7289	−43.34633	−50.67985	−139.1393
^4P	−2082.7844	−43.39908	−50.67391	−139.1390
^2G	−2082.7919	−42.39416	−50.67441	−139.1389

State	$K(3s)$	$K(2s)$	$K(1s)$
av of config.	−54.00450	−140.4926	−575.7166
^4F	−53.99000	−140.4919	−575.7167
^2P	−54.0054	−140.4927	−575.7166
^4P	−54.00134	−140.4926	−575.7167
^2G	−54.00168	−140.4924	−575.7166

Table VI Comparision of experimental and calculated multiplet spectra for Cr IV $(3d)^3$ (all energies are in rydbergs).

	Exptl.[a]	Exptl. fits of F^2 and F^4	F^2 and F^4 from figure	Based on individual calculations	Using av of config. F^4 and F^2
^4F	0	0	0	0	0
^2P	0.12462	0.19020	0.18032	0.2056	0.21383
^4P	0.12548	0.13833	0.12978	0.1501	0.15865
^2G	0.13399	0.14409	0.13706	0.1526	0.16094
^2D(one of two)	0.18164	0.20769	0.19725	···	0.23265
^2H	0.18827	0.19020	0.18032	···	0.21383
^2F	0.32971	0.32853	0.31010	···	0.37248
F^2	0.70202		0.663		0.79608
F^4	0.45026		0.4303		0.49826
F^4/F^2	0.6414		0.649		0.6267

[a] $L\cdot S$ splitting is ~0.003 rydberg for these states.

The first thing to note is that the individual calculations did not change the predicted order of the spectra. It is impossible for this to happen since the H-F equations are derived from expressions for the total energy which involve this order. The second factor to note is that the individual multiplet calculations do give appreciably better predictions than one obtains using the average of configuration F^2 and F^4 values (column 5). The last factor of some interest is that the experimental fits give a fair but not very good reproduction of the spectrum.

The predicted multiplet splittings from the individual calculations are 20 percent high for the ^4P and 14% high for the ^2G. The ^2P which does not lie in the predicted position shows a 65 percent error. These results and the large calculated F^k's are typical of what one finds if one studies other cases, for example the unfilled $2p$ or $3p$ shell spectra. More accurate or less restricted H-F solutions might produce better multiplet splitting predictions, but the improvements would not be great.

It is apparent that configuration interaction (or some other technique for wave function improvement) is necessary if we wish to accurately predict multiplet spectra. The need for configuration interaction is greater than had been previously thought. We should note that our discrepancies are in a direction which configuration interaction will improve. Any randomly chosen, single excited configuration is *more likely* to contain a multiplet state with low L and S values than a state with higher L and S values. This suggests that configuration interaction will have its greatest effect on states with low S and L values. We have seen that the experimental $(3d)^3$ spectra show the ^2D and ^2P terms lying lower than expected. These are the terms of lowest L and S. One should also note that the lowest lying multiplet states generally have the largest S and L values (witness Hund's rule). This suggests that these terms would be least affected by configuration interaction and thus that a H-F predicted spectrum would be more widely spaced than the experimental one. This means that the calculated F^2 and F^4 integrals should run large and this is what we observe.

The writer does not believe that the configuration interaction can be restricted to the contributions of just a few configurations and produce good results. This matter will be discussed shortly.

IV. Fe CALCULATIONS FOR VARIOUS STATES OF IONIZATION

In the last section, we discussed both the fitting of the multiplet spectra and the variations in one-electron wave functions produced by obtaining solutions for different multiplet states. We will now discuss the discrepancies between observed and predicted ionization energies and the variation in $3d$ wave functions when going from one state of ionization to the next. We will use Fe as our example.

Let us first consider the variations in Fe $3d$ functions. Figure 4 is a plot of the $3dU(r)$'s as a function of r for the Fe I, III, and V average of configuration solutions. A hydrogenic $3d$ function, with an $F^2(3d,3d)$ which is equal to that for the Fe I function, is also plotted. Let us note the fact that the $3d$ screening constant values have a dependence on atomic number and ionization which roughly parallels the calculated $F^2(3d,3d)$ values. With this in mind, it is interesting to see that although all the Fe V $3d$ screening constants [and to a less extent the $F^2(3d,3d)$] are roughly twice those for Fe I, the Fe V and Fe I $U(r)$ maxima lie close together. The Fe I maximum is not twice as far out as the Fe V one, although this is what the change in screening constants would suggest. We see that the changes in the $3d$ function are primarily matters of shape. The $3d$ functions for states of higher ionization are more nearly hydrogenic.

TABLE VII. The $K(i)$'s and total energies for the Fe I, II, III, and IV lowest $(3d)^n$ multiplet calculations in rydbergs.

	Fe I	Fe II	Fe III	Fe IV
$K(1s)=$	-675.7103	-675.7103	-675.7100	-675.7094
$K(2s)=$	-165.3840	-165.3819	-165.3782	-165.3781
$K(3s)=$	-63.25324	-63.30455	-63.61446	-64.01641
$K(2p)=$	-164.0475	-164.0456	-164.0416	-164.0429
$K(3p)=$	-59.51367	-59.63822	-59.93252	-60.43305
$K(3d)=$	-44.42264	-47.69708	-50.27814	-52.60767
Total energy $=$	-2524.3137	-2524.2856	-2523.3041	-2521.2214

This agrees with the F^4/F^2 trend shown on Fig. 3. Some of the readers may have felt that an F^4/F^2 ratio of 0.61 was really not far from the hydrogenic value of 0.649. Figure 4 shows that this difference represents a rather pronounced change in the shape of the function. The last thing to note, concerning Fig. 4, is that the differences between average of configuration and lowest multiplet state $3d$ functions are so small that it is impractical to include both on the figure. The maximum difference for the Fe functions is illustrated on the figure.

Let us now consider Table VII. Here we have listed the $K(i)$'s (one-electron kinetic+nuclear potential energies) for the Fe I, II, III, and IV lowest multiplet state calculations. The writer has also included the total energies. The variations in the $K(3d)$ are greater than the total energy differences. The $K(3s)$ and $K(3p)$ variations are generally between one-quarter and one-half the total energy differences. From this, the author concludes that the $3s$, $3p$, and $3d$ wave function variations are significant when going from one state of ionization to the next. Table VII also enables us to trace the variations of the functions, because $K(i)$ increases when $U(i)$ moves in toward the nucleus and vice-versa. Although the writer finds these shifts interesting, he will not discuss them but let the reader study the table instead.

Let us now compare the observed $(3d)^n$ configuration ionization energies with the calculated values. Table VIII gives the comparison. The first column lists the observed values and the second is obtained by taking the differences in calculated total energies. The third column lists the (individual) one-electron energy of the electron being removed from the lower energy state as given by the calculation for the lower state and the

TABLE VIII. Comparison of observed and calculated $\mathrm{Fe}(3d)^n$ ionization energies in rydbergs.

	Experimental	Differences in calculated total energies	Lower state one-electron energy	Higher state one-electron energy
Fe I ^3F → Fe II ^4F	$+0.29938$	$+0.0281$	$+0.35594$	-0.34014
Fe II ^3F → Fe III ^5D	$+1.17127$	$+0.9815$	$+1.23847$	$+0.69713$
Fe III ^5D → Fe IV ^6S	$+2.249$—	$+2.0827$	$+2.3212$	$+1.8308$
Fe IV → Fe V	not observed			

last column gives the (individual) one-electron energy of the same electron as given by the calculation for the higher state. We see that the differences in total energies give poorer results than do the third column one-electron energies. This is in contrast to the case of multiplet splitting where differences in total energies gave better results than did splitting estimates based on single calculations. The reason for the poor "difference in total energy" results, is that the various calculations are for systems with differing number of electrons.

When H-F solutions have been obtained for small atoms where the total energy has been observed experimentally, comparison of experimental and H-F total energies has shown that the magnitude of error in the H-F total energy increases when the number of electrons is increased. This appears to be happening here. We can use the discrepancies between the observed ionization energies and the differences in calculated total energies to give crude estimates of the error in the H-F total energy contributed by the electrons which are being removed. Doing this, we can say that for Fe, there is a H-F total energy error of 0.27 rydberg associated with the 28th electron, 0.19 rydberg with the 27th and 0.16 rydberg with the 26th. We will make use of these figures shortly.

If we *ignore* the discussion of the preceding paragraph, we can quite easily understand the rather good predictions of the individual one-electron energies. Koopmans[13] theorem tells us that the individual one-electron energies are just the energies gained or lost by adding or removing an electron, providing that both states of ionization have the same one-electron radial functions. We have seen that the radial functions do vary noticeably with changing ionization. We would expect that the calculations for the lower state would predict a large ionization energy since the resulting functions would be poor for the higher state (thus raising its energy). Similar reasoning would suggest that the higher state calculation should predict an ionization energy which is small. We might then expect an observed ionization energy to fall below the value given by the lower state one-electron energy and above the value for the higher state one-electron energy. We see this happens in all three cases. We might note that the average of the one-electron energy values is close to the value of the total energy difference in each case.

The behavior of the calculated Fe$(3d)^n$ ionization energies is typical of that for the other iron series elements. An exception occurs for the Cr I to Cr II ionization where the H-F total energies say that Cr II lies lower than Cr I by 0.087 rydberg. This is easy to explain. The observed ionization energy is 0.174 rydberg which is the smallest of the observed ionization energies of interest to us. It is smaller than the 0.20 or 0.25 rydberg penalty (in H-F total energy error) that Cr I pays for possessing one more electron than Cr II. With an observed 0.174 rydberg ionization energy, we should expect that H-F results would predict that Cr II lies lower than Cr I.

We can use the crude H-F total energy discrepancy estimate for Fe's 26th, 27th, and 28th electrons to give an even cruder estimate of the total error in the H-F total energy. The writer believes that at the very minimum this error is 1.0 rydberg (the three 3d electrons contributed 0.6 ry) and that very likely the error is more than 4 rydbergs. We might hope to use configuration interaction to improve the total wave function and the total energy. Earlier the writer[14] applied configuration interaction to Ni I$^3F(3d)^8(4s)^2$. The effects of single configurations on the ground state were considered and second order perturbation theory was used. This gave energy improvements of:

$$\Delta E=\frac{\left|\int \Psi^*(\text{ground})H\Psi(\text{perturbing})d\tau\right|}{E(\text{ground})-E(\text{perturbing})}. \quad \text{(IV-1)}$$

The writer considered some of the perturbing configurations which produce the smallest denominators (in IV-1) and thus possibly the largest ΔE's. The availability of integrals limited what configurations could be considered, for example, configurations with f and g electrons could not be used (some workers believe such configurations are important). The largest ΔE obtained was 0.005 rydberg. It is possible that a few very important configurations were overlooked but the result does suggest that effective iron series atom configuration interaction requires the use of more than a few (say less than 50) strongly interacting configurations.

V. IRON GROUP ONE-ELECTRON ENERGIES

We have seen that there was remarkable agreement between Fe's calculated lower state one-electron energies and its observed ionization energies. We will now make further comparisons between calculated iron series one-electron energies and observed ionization energies. The tables to be discussed are in large part due to Slater.

Let us apply Koopmans' theorem to the average of configuration energies ($E_{a\text{ of }c}$). If we do this, we can utilize the work of Slater[15] where he discussed the the experimental energy differences between average of configuration energies of atoms in their normal states and of ions with one electron removed. These experimental values are not appropriate for the 3d electrons here since $3d^{n-2}4s^2$ or $3d^{n-1}4s$ rather than $3d^n$ configura-

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[13] T. Koopmans, Physica 1, 104 (1933).

[14] Ni I$(3d)^8(4s)^2\,{}^3F$ was a somewhat special case in that the two near lying configurations, the $(3d)^9$, $4s$ and $(3d)^{10}$, have no multiplets of the same symmetry. One would expect the strongest interactions to be between the $(d)^n$, $(d)^{n-1}4s$ and $(d)^{n-2}(4s)^2$. See R. E. Watson, Quarterly Progress Report No. 27, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, January, 1958 (unpublished); p. 10.

[15] J. C. Slater, Phys. Rev. **98**, 1039 (1955).

tions were considered. We would like to recompute $E_{a\text{ of }c}$'s for $3d^n$ configurations. One would like to do this by finding the weighted mean of the observed multiplet state energies of *all* the multiplet states of any given configuration. Unfortunately there are very few cases where all the multiplet states of a configuration have been observed. Slater and the author have computed the $3d^n$ $E_{a\text{ of }c}$'s from the experimental data in the following way. We took values of $F^2(3d,3d)$ from Fig. 1 and obtained $F^4(3d,3d)$'s by assuming the $F^4(3d,3d)/F^2(3d,3d)$ ratio to be the hydrogenic value of 0.649 (variations of the ratio within the range observed in the original fittings would have little effect on our conclusions). These F's were then used in computations for the energies of the multiplet states of the atoms and ions of interest. These computations utilized a program set up for this purpose on the 704 computer. The computed energies lack the $E_{a\text{ of }c}$ terms which are of interest. The computed multiplet state energies were then subtracted from the observed values giving a different value of $E_{a\text{ of }c}$ for each observed multiplet state. Whatever the choice of F^2 and F^4, one will never obtain a common value of $E_{a\text{ of }c}$ for all the multiplet states of a configuration because the experimental $3d^n$ multiplet spectra cannot be exactly fitted by Racah's expressions for the multiplet splittings. A weighted average of the $E_{a\text{ of }c}$'s was obtained for each configuration. The $E_{a\text{ of }c}$ of each multiplet state was weighted by the degree of that multiplet state's degeneracy.

TABLE IX. Comparison of experimental average of configuration ionization energies with calculated one-electron energies for ionization processes involving the removal of $3d$ electrons. Computed values refer to average of configuration solutions, except those in parentheses, which are computed for the lowest multiplet of a configuration.

Transition	Experimental ionization energy	Calculated (lower state of ionization) one-electron energy
Sc I $d^3 \rightarrow$ II d^2	0.22873 rydberg	0.23072
Ti I $d^4 \rightarrow$ II d^3	0.26713	(0.32043)
Ti II $d^3 \rightarrow$ III d^2	0.96081	(1.04643)
Ti III $d^2 \rightarrow$ IV d	1.9580	(2.04648)
V I $d^5 \rightarrow$ II d^4	0.31937	0.32280
V II $d^4 \rightarrow$ III d^3	1.0497	1.08397
V III $d^3 \rightarrow$ IV d^2	2.0874	2.13157
V IV $\rightarrow$ V d	3.48695	(3.48145)
Cr I $d^6 \rightarrow$ II d^5	0.36333	(0.39748)
Cr II $d^5 \rightarrow$ III d^4	1.14523	(1.29980)
Cr III $d^4 \rightarrow$ IV d^3	2.21000	2.27563
Mn I $d^7 \rightarrow$ II d^6	0.38753	(0.41532)
Mn II $d^6 \rightarrow$ III d^5	1.21696	(1.32693)
Mn III $d^5 \rightarrow$ IV d^4	2.35802	2.41948
Fe I $d^8 \rightarrow$ II d^7	0.39888	0.41946
Fe II $d^7 \rightarrow$ III d^6	1.28721	1.35454
Fe III $d^6 \rightarrow$ IV d^5	2.46869	2.55251
Co I $d^9 \rightarrow$ II d^8	0.40277	0.44547
Co II $d^8 \rightarrow$ III d^7	1.36365	(1.46752)
Ni I $d^{10} \rightarrow$ II d^9	0.43246	0.50065
Ni II $d^9 \rightarrow$ III d^8	1.42955	1.52535

Table X. Calculated one-electron energies compared with observed ionization energies involving the removal of an electron from any shell from neutral iron series atoms. Both calculated and observed values are for the averages of configuration, except for the calculated values in parentheses, which are computed for the lowest multiplet state of a configuration.

	Sc	Ti	V	Cr
$1s$ calc	331.50 ry	(366.08)	402.55	(440.62)
obs	331.1	366.1	402.9	441.6
$2s$ calc	37.80	(42.32)	47.23	(52.24)
obs	37.3	42.0	46.9	51.9
$2p$ calc	37.99	(35.07)	39.59	(44.11)
obs	30.0	34.0	38.3	43.0
$3s$ calc	4.77	(5.23)	5.85	(6.37)
obs	4.2	4.8	5.3	6.0
$3p$ calc	2.82	(3.12)	3.56	(3.91)
obs	2.6	2.9	3.2	3.6
$3d$ calc	0.23	(0.32)	0.32	(0.42)
obs	0.23	0.27	0.32	0.36
	Mn	Fe	Co	Ni
$1s$ calc	(480.47)	522.05	565.34	610.46
obs	482.0	524.3	568.3	614.1
$2s$ calc	(57.56)	63.11	68.88	74.97
obs	57.7	63.0	69.0	75.3
$2p$ calc	(48.97)	54.08	59.40	65.04
obs	47.8	52.8	58.2	63.7
$3s$ calc	(6.97)	7.60	8.22	8.91
obs	6.6	7.3	8.0	8.7
$3p$ calc	(4.34)	4.80	5.24	5.75
obs	4.0	4.4	4.9	5.4
$3d$ calc	(0.42)	0.42	0.45	0.50
obs	0.39	0.40	0.40	0.43

Let us now compare the calculated and experimental results. In Table IX, we consider the ionization energies associated with the removal of $3d$ electrons and compare the experimental average of configuration ionization energies with the calculated one-electron energies for the lower states of ionization. The experimental ionization energies are $E_{a\text{ of }c}$'s of the more highly ionized states minus the $E_{a\text{ of }c}$'s of the less ionized states. In Table X, we consider the removal of electrons of any shell from the neutral atoms. The second table's observed ionization energies are those found in Slater's article,[15] supplemented by the newly calculated values for the $3d$ electrons. Calculated values in parentheses, in both tables, refer to calculations in which the calculated one-electron energies for the lowest multiplet state were used (due to the lack of an average of configuration calculation). Such calculated results differ somewhat from calculated average of configuration values.

Agreement between calculated and experimental values is remarkably good in both tables. This is due to a cancellation of errors as was indicated in the last section. In the case of Fe, discussed in the last section, the calculated (lower state) one-electron energies were always larger in magnitude that the observed ionization energies. There are many cases where this is not so in the section. This occurs once in Table IX and is due to an experimental error. This will be discussed in the next section. In Table X the apparently small one-electron energies occur for 1*s* and 2*s* functions. The 1*s* functions are just the ones which require relativistic corrections to the one-electron energies. With these corrections, the resultant one-electron energies are larger than the observed ionization energies. We might note that the magnitude of these corrections increases rapidly with increasing nuclear charge. This is just what is needed here.

VI. CORRELATION ENERGY

Let us now consider what information we can obtain concerning "correlation energy." By "correlation energy" the author means the difference between the true (i.e., experimental) total energy of an electronic system and the system's H-F energy, that is,

$$E_{\text{corr}} = E_{\text{obs}} - E_{\text{H-F}}. \qquad \text{(VI-1)}$$

This definition differs from the normal in that one usually subtracts relativistic correction terms from E_{obs} and uses the resultant value in the equation.

Unfortunately, total energies have not been observed for atoms for more than ten electrons so we must again turn to considerations of energy differences. Let us consider the change in correlation energy (ξ) during ionization processes, i.e.:

$$\begin{aligned}\xi \equiv\; & E_{\text{corr}}(\text{state of higher ionization}) \\ & \quad - E_{\text{corr}}(\text{state of lower ionization}) \\ =\; & E_{\text{obs}}(\text{higher}) - E_{\text{obs}}(\text{lower}) \\ & \quad - E_{\text{H-F}}(\text{higher}) + E_{\text{H-F}}(\text{lower}) \\ =\; & \Delta E_{\text{obs}} - \Delta E_{\text{calc}}. \qquad \text{(VI-2)}\end{aligned}$$

One might expect that ξ is, for the most part, a correlation error "associated" with the electron which is being removed. It is particularly convenient to consider ξ for ionization processes between lowest multiplet states since such are single determinants. Then the electron which is being removed has definite n, l, m_l, and m_s assignments. We will shortly consider ionization processes involving the removal of 3*d* electrons from single determinants. One would expect that relativistic corrections would be almost identical for both states and thus that ξ can be interpreted as the difference in correlation energies as conventionally defined.

TABLE XI. Net changes in correlation energy (ξ) during ionization processes involving iron series lowest $3d^n$ multiplets.

Ionization process	ΔE_{obs} ry	$\Delta E_{\text{H-F}}$ ry	$\xi(=\Delta E_{\text{obs}} - \Delta E_{\text{H-F}})$ ry
Sc I $d^3 \rightarrow$ II d^2	0.2170	0.1186	0.0984
Sc II $d^2 \rightarrow$ III d	0.8972	0.8335	0.0637
Sc III $d \rightarrow$ IV d^0	1.8197	1.7543	0.0654
Ti I $d^4 \rightarrow$ II d^3	0.2480	0.1208	0.1273
Ti II $d^3 \rightarrow$ III d^2	0.9902	0.9110	0.0792
Ti III $d^2 \rightarrow$ IV d	2.0194	1.9651	0.0543
Ti IV $d \rightarrow$ V d^0	3.1577	3.1203	0.0374
V I $d^5 \rightarrow$ II d^4	0.3132	0.1819	0.1313
V II $d^4 \rightarrow$ III d^3	1.0771	0.9806	0.0965
V III $d^3 \rightarrow$ IV d^2	2.1521	2.0886	0.0635
V IV $d^2 \rightarrow$ V d	3.56—	3.3846	~0.18—
V V $d \rightarrow$ VI d^0	4.8—	4.7413	~0.05—
Cr I $d^6 \rightarrow$ II d^5	0.1738	−0.0874	0.2612
Cr II $d^5 \rightarrow$ III d^4	1.2125	1.1208	0.0917
Cr III $d^4 \rightarrow$ IV d^3	2.277-	2.2049	0.072-
Cr IV $d^3 \rightarrow$ V d^2	3.6—	3.5515	~0.05—
Cr V $d^2 \rightarrow$ VI d	5.319	5.0637	0.255-
Mn I $d^7 \rightarrow$ II d^6	0.2687	0.0102	0.2585
Mn II $d^6 \rightarrow$ III d^5	1.0166	0.8211	0.1955
Mn III $d^5 \rightarrow$ IV d^4	2.482-	2.4077	0.074-
Mn IV $d^4 \rightarrow$ V d^3	not observed		
Mn V $d^3 \rightarrow$ VI d^2	5.573-	5.2762	0.297-

The quantities ΔE_{obs}, $\Delta E_{\text{H-F}}$ and ξ will be found in Table XI. As indicated above, these are for the lowest multiplet states of configurations and *not* for the averages of configurations. In Fig. 5, ξ is graphed as a function of the numbers of 3*d* electrons in the pairs of states. The most important feature of the figure is the break in the curves between the $d^6 \rightarrow d^5$ and $d^5 \rightarrow d^4$ transitions. The former involves the removal of an electron whose spin is antiparallel to the spins of the other 3*d* electrons while the latter transition involves the removal of an electron of parallel spin. One would expect the break in the curves since the H-F formalism has some built in correlation (the "exchange hole") between electrons of parallel spin. Another prominent feature is the set of high lying points on the left-hand side of the figure. Most of these points rely on ΔE_{obs}'s which the experimenters obtained by extrapolation rather than direct measurement. This is the case for a sizable fraction of the ΔE_{obs}'s used here. This suggests that the positions of these points are due to errors in ΔE_{obs} values. More and better ΔE_{obs}'s are needed.

One might be tempted to analyse the curves further. This is dangerous due to the possibility of systematically varying errors in the $E_{\text{H-F}}$'s. Random errors would raise one ξ and lower an adjacent one for the same element. Systematic errors could shift, compress or even rotate the curves. For this reason, the writer will attempt no further analysis other than noting the suggestion of structure on the right hand side of the figure (as indicated by the dashed curves) and the possibility of similar structure on the left-hand side.

We could define an ξ^* where the $\Delta E_{\text{H-F}}$ of ξ has been replaced by the lower state one-electron energy for the

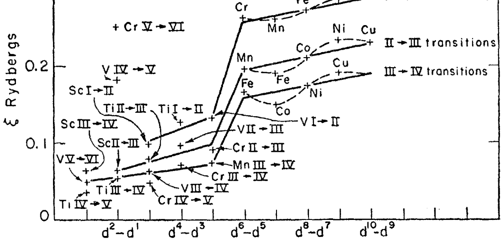

FIG. 5. Change in correlation energy (ξ) for ionization progresses involving lowest iron series $3d^n$ multiplet states.

electron being removed. A graph of ξ^* would show breaks in its curves between the $d^6 \longrightarrow d^5$ and $d^5 \longrightarrow d^4$ transitions. The graph would also show that most of the ξ^*'s are negative (i.e., $\Delta E_{\text{obs}} < \Delta E_{\text{one electron}}$). The exceptions occur for the high-lying point cases of Fig. 5. Inspection of Table IX shows that the one case of an apparently small average of configuration $\Delta E_{\text{one electron}}$ is for a high-lying point transition (V IV → V). The fact that the ξ's and ξ^*'s are generally out of line for the same transitions suggests that experimental rather than computational errors are the cause. The writer reran the pertinent H-F calculations as a check. No errors were uncovered.

VII. CONCLUSION

We have seen that the Hartree-Fock results are generally in poor agreement with experiment. While the total energies are accurate to better than one percent, the observables we are trying to predict by taking total energy differences are even smaller and thus poorly predicted. The calculated F^k $(3d,3d)$ integrals poorly predict the multiplet spectra. This is in large part due to the inadequacies of the Hartree-Fock formalism and to a lesser part due to the assumption of common radial functions for all the multiplet states of a configuration. The lower state one-electron energies are found to be in very good agreement with ionization energies. This is due to a remarkable cancellation of errors. Finally we have the unsurprising behavior of the 3d electron "correlation" energy with its sudden increase for more than half filled shells.

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Range-Energy Relations for Protons in Various Substances*

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An expression is obtained for the range-energy relation $R(T_p)$ for protons (T_p=proton kinetic energy) as a function of the mean excitation potential I which enters into the Bethe-Bloch formula for the ionization loss dE/dx. The expression for $R(T_p)$ is obtained by an interpolation of the previously calculated range-energy relations for Be, Al, Cu, and Pb. The resulting expression for $R(T_p)$ can be used for any substance, provided an appropriate value of I is assumed. Values are also obtained for the quantity $q=(I/R)(dR/dI)$ which gives the fractional change of R for a small variation of the excitation potential I.

I. INTRODUCTION

Range-energy relations for protons[1] have been recently calculated for six substances (Be, C, Al, Cu, Pb, and air). These range-energy relations are based on values of the ionization loss dE/dx which include the shell corrections at low proton energies and the density effect correction which becomes important in the high-energy region. The values of dE/dx depend mainly on the value of the mean excitation potential I of the atoms of the substance considered. The following values of I were used in the previous calculations: $I_{\text{Be}}=64$ ev, $I_{\text{C}}=78$ ev, $I_{\text{Al}}=166$ ev, $I_{\text{Cu}}=371$ ev, $I_{\text{Pb}}=1070$ ev, and $I_{\text{air}}=94$ ev.

In the present paper, we will obtain an expression which gives the range $R(T_p)$ for an arbitrary value of I, as a function of the proton kinetic energy T_p, and which can therefore be used to obtain the range-energy relation for any substance, if an appropriate value of I is assumed. The general expression for $R(T_p)$ is obtained by an interpolation of the previous results[1] for Be, Al, Cu, and Pb. It is estimated that the resulting range-energy relation is accurate to $\lesssim 1\%$ for values of I lying in the range from $I_{\text{Be}}=64$ ev to $I_{\text{Pb}}=1070$ ev.

II. EXPRESSION FOR $R(T_p)$

In order to obtain the interpolation formula for $R(T_p)$, we note that the Bethe-Bloch formula for dE/dx can be written as follows:

$$-\frac{1}{\rho}\frac{dE}{dx}=\frac{Z}{A}M(\beta)\left[\ln\frac{N(\beta)}{I^2}-2\beta^2-\delta-U\right], \qquad (1)$$

where ρ is the density of the medium (in g/cm^3), A is the atomic weight, $M(\beta)$ and $N(\beta)$ are functions of the

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[*] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[1] R. M. Sternheimer, Phys. Rev. **115**, 137 (1959). This paper will be referred to as I.