PHYSICAL REVIEW VOLUME 119, NUMBER 6 SEPTEMBER 15, 1960

Iron Series Hartree-Fock Calculations. II*

R. E. Watson†
Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received May 9, 1960)

Analytic Hartree-Fock calculations have been carried out for the lowest neutral atom $3d^{n-2}4s^2$ states of Ti through Zn. Except for Cr and Cu, these calculations are for the neutral atom ground states. The results are compared with the earlier $3d^n$ state calculations. It is observed that the $4s$ electrons have little effect on the $3d$ and inner shells.

I. INTRODUCTION

Analytic Hartree-Fock calculations have been done for the neutral atom iron series (Ti to Zn) $3d^{n-2}4s^2$ configurations, where n denotes the number of electrons outside of the argon core. Except for Cr and Cu, the calculations are for the neutral atom ground states. In these two cases $3d^{n-1}4s$ states lie slightly lower than the computed states. The primary purpose of these calculations is to supplement an earlier series[1-3] of calculations which was done for $3d^n$ ion and neutral atom states. This latter work was done on the Whirlwind computer at MIT and the question of computer capacity necessitated either the exclusion of $4s$ electrons in the computations or a severe decline in the accuracy of the solutions. The restriction to the $3d^n$ type of state led to the neglect of three important types of states; they are: the $3d^{n-2}4s^2$ and $3d^{n-1}4s$ for neutral (I) atoms (these supply the low-lying neutral atom states) and the $3d^{n-1}4s$ for singly ionized (II) ions. When similar computer procedures became available on the IBM 704 computer at MIT, a computer of greater capacity than Whirlwind, it seemed desirable to do some calculations for iron series atoms with $4s$ electrons present. The calculations to be reported here are for just neutral atom $3d^{n-2}4s^2$ states. This restriction stems from the fact that the method used for solving the Hartree-Fock equations is particularly advantageous (and economical in computer time) if calculations are done for a series of elements for states of common ionization and configuration type. Of the three important types of states the neutral atom $3d^{n-2}4s^2$ was chosen for two reasons. First, it serves as a sort of bound on the effect of $4s$ electrons on the $3d$ and core electrons. Secondly, the $3d^{n-2}4s^2$ configuration does not have the off-diagonal Lagrange multiplier problem[3,4] which is associated with the conventional application of the Hartree-Fock formalism to the $3d^{n-1}4s$ type of configuration.

While the form and behavior of the $4s$ electrons is of interest, of perhaps greater interest is the effect of the $4s$ electron on the inner shells. We will see that the $4s$ electrons have almost no effect. In other words, the $3d$ and core electron wave functions of the neutral atom $3d^{n-2}4s^2$ states are very like those obtained earlier for the doubly ionized (III) $3d^{n-2}$ ions.

II. CALCULATIONS

The calculations have been done using the Roothaan[5] procedure as modified by Nesbet.[6] Normalized analytic one-electron radial functions [$U_i(r)$'s] are obtained as solutions of Hartree-Fock equations.[7] The $U_i(r)$'s have the form:

$$U_i(r)=\sum_j C_{ij}R_j(r), \tag{1}$$

their normalization condition is

$$\int_0^\infty |U_i(r)|^2dr=1, \tag{2}$$

and the basis functions (R_j's) are of the form,

$$R_j(r)=N_jr^{l+A_j+1}e^{-Z_jr}. \tag{3}$$

The l is the one-electron angular momentum appropriate for the one-electron function of which $U_i(r)$ is the radial part. The N_j is a normalization constant and is expressible in terms of the other parameters, i.e.,

$$N_j=\left[\frac{(2Z_j)^{2l+2A_j+3}}{(2l+2A_j+2)!}\right]^{\frac{1}{2}}. \tag{4}$$

It should be noted that here the combining coefficients (C_{ij}'s) are defined in terms of normalized R_j's. This is

---

* This work was supported in part by the Office of Naval Research.

† Now at AVCO, Research and Advanced Development Division, Wilmington, Massachusetts.

[1] R. E. Watson, Phys. Rev. **118**, 1036 (1960).

[2] R. E. Watson, Technical Report No. 12, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology (unpublished); for an account of some earlier and cruder work *including* Fe I $3d^64s^2$ and Ni I $3d^84s^2$ results see R. E. Watson, Quarterly Progress Report No. 27, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, January, 1958 (unpublished), p. 10.

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

[4] For an example of the simpler case for Li, see R. K. Nesbet and R. E. Watson, Ann. Phys. **9**, 260 (1960).

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

[6] R. K. Nesbet, Quarterly Progress Reports: No. 15, January, 1955, p. 10; No. 16, April, 1955, p. 38, p. 41; No. 18, October, 1955, p. 4, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology (unpublished). See also references 2 and 3.

[7] A good general reference for the Hartree-Fock formalism is D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley & Sons, New York, 1957).

TABLE I. Parameters (A_j and Z_j) which define the basis functions (R_j's).

R_j's used for the construction of	j	A_j					Z_j's for				
			Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
s functions ($l=0$)	1	0	22.8311	23.9091	24.9871	26.0651	27.1431	28.2211	29.2991	30.3771	31.4551
	2	1	19.5333	20.5950	21.6567	22.7184	23.7801	24.8418	25.9035	26.9652	28.0269
	3	1	9.5229	10.1666	10.8103	11.4540	12.0977	12.7414	13.3851	14.0288	14.6725
	4	2	8.7148	9.3319	9.9490	10.5661	11.1832	11.8003	12.4174	13.0345	13.6516
	5	2	4.7037	5.1562	5.6087	6.0612	6.5137	6.9662	7.4187	7.8712	8.3237
	6	2	3.3252	3.5078	3.6904	3.8730	4.0556	4.2382	4.4208	4.6034	4.7860
	7	3	3.6914	3.8742	4.0573	4.2404	4.4235	4.6066	4.7897	4.9728	5.1559
	8	3	1.8028	1.8764	1.9500	2.0236	2.0972	2.1708	2.2444	2.3180	2.3916
	9	3	1.1090	1.1462	1.1834	1.2206	1.2578	1.2950	1.3322	1.3694	1.4066
	10	3	0.7610	0.7800	0.7990	0.8180	0.8370	0.8560	0.8750	0.8940	0.9130
p functions ($l=1$)	11	0	13.9277	14.6347	15.3617	16.0787	16.7957	17.5127	18.2297	18.9467	19.6637
	12	0	7.9588	8.4757	8.9926	9.5095	10.0264	10.5433	11.0602	11.5771	12.0940
	13	1	7.3333	7.8012	8.2691	8.7370	9.2049	9.6728	10.1407	10.6086	11.0765
	14	1	3.8066	4.1909	4.5752	4.9595	5.3438	5.7281	6.1124	6.4967	6.8810
	15	1	2.4344	2.6477	2.8610	3.0743	3.2876	3.5009	3.7142	3.9275	4.1408
d functions ($l=2$)	16	0	1.7316	1.8289	1.9262	2.0235	2.1208	2.2181	2.3154	2.4127	2.5100
	17	0	3.4276	3.6102	3.7928	3.9754	4.1580	4.3406	4.5232	4.7058	4.8884
	18	0	6.4619	6.8020	7.1421	7.4822	7.8223	8.1624	8.5025	8.8426	9.1827
	19	0	11.9171	12.4322	12.9473	13.4624	13.9775	14.4926	15.0077	15.5228	16.0379

not the case with the earlier series of calculations[1–3] where the N_j's are incorporated into the C_{ij}'s. A set of R_j's is supplied for each l value for which Hartree-Fock solutions are to be obtained. $U_i(r)$'s of common l value are constructed from a common set of R_j's.

The strength of the Roothaan procedure lies in the fact that the necessary integrals are obtained analytically and the Hartree-Fock self-consistent procedure becomes a process of matrix manipulation and diagonalization. This process can be more rapidly and accurately carried out on a computer than can the conventional numerical methods of solving Hartree-Fock equations. The limitation of the analytic approach lies in the fact that we must use less than complete sets of basis functions. Thus we cannot obtain exact solutions. Currently good analytic calculations appear[8] to yield results which are as accurate as or more accurate than the best numerical results. One would like to compare the total energies of the two types of solutions but accurately evaluated total energies generally do not exist for numerical solutions. There are great advantages to having wave functions of analytic form for many quantities, such as expectation values of powers of r, can be easily, accurately, and analytically obtained.

The Roothaan procedure has associated with it the problem of choosing sets of basis functions. The sets used in these calculations were obtained in the following way. Earlier[2,3] it was noted that the free atom experimental spectra suggested that the $3d$ electrons (and hence also the core electrons) of the neutral atom $3d^{n-2}4s^2$ states behave very like the electrons of the doubly ionized $3d^{n-2}$ states. This suggested that the basis sets used in the earlier series of calculations for III states would be appropriate for the construction of all but the $4s$ one-electron functions of the current calculations. The earlier set, for any one particular element, has been supplemented by four s-like basis functions which contribute to the construction of the outer loop of the $4s$ function and the s-like basis functions already present for the $1s$, $2s$, and $3s$ are relied on for the construction of the inner loops of the $4s$ function. The V atom was taken and successive Hartree-Fock calculations were done, varying the Z_j's of the four additional s-like basis functions, until, with the total atom energy as a criterion, and optimum choice of these Z_j's was reached. Similar variations were not done with the other basis functions (based on the earlier $3d^{n-2}$III ion calculations). The same treatment was done with Ni and the Z_j's for the remaining atoms were obtained by having them vary linearly across the iron series. In the earlier calculations[3] it was observed that the Z_j's were linear to within the accuracy that they were established and it is reasonable to assume the same linearity for the "$4s$" Z_j's. The A_j's and Z_j's are to be found in Table I. The basis function normalization constants (N_j) are not listed but may be obtained by use of Eq. (4). We see that ten s-like R_j's are given for the construction of the $1s$, $2s$, $3s$, and $4s$ one-electron functions and there are five R_j's for the $2p$ and $3p$ and four for the $3d$. Due to limiting the basis function variation to R_7 through R_{10} one would expect the current calculations to be somewhat less accurate than the earlier set. The poorer ability of the R_j's to construct the $3d$ and inner electron $U_i(r)$'s for the atoms here rather than for the $3d^{n-2}$III ions produces a small

---

[8] While my iron series calculations appear to be as good as or better than numerical results, calculations for small atoms, with comparatively larger basis sets, better indicate the power of the analytic approach [see reference 4 and C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Revs. Modern Phys. **32**, 186 (1960)]. The iron series calculations represent an uneasy compromise between large basis sets for accurate solution of the Hartree-Fock equations and small sets so that the analytic form of the functions may be easily exploited. Having chosen the size of my basis sets, I believe that the actual sets represent good choices (see p. 24 of reference 2).

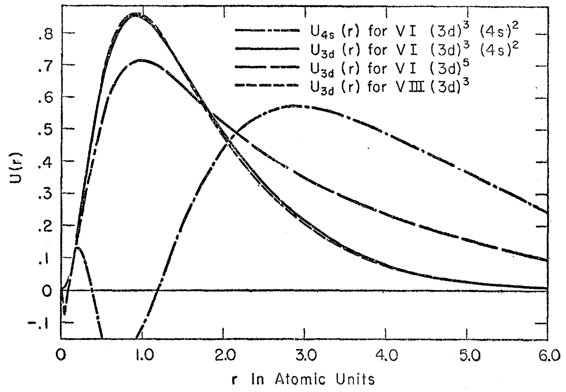

FIG. 1. Calculated $3d$ and $4s$ radial wave functions [$U(r)$'s] as a function of r for several states of atomic V.

error contribution of 0.001 a.u. (1 a.u. = 2 ry) or less. More serious is the fact that we rely on R_1 through R_6 for the construction of the three inner loops of the $U_{4s}(r)$ [see Fig. 1 for an illustration of a $U_{4s}(r)$] and we demand the four s-like $U_i(r)$'s to be orthogonal. The effect of this is harder to estimate. It might produce an error contribution of as much as 0.03 a.u. out of total energies of 1000 to 2000 a.u.

In practice the calculations have been carried to the point where the total energy is stabilized to 0.0001 a.u. The eigenvectors (C_{ij}'s) and the various one- and two-electron integrals obtained are less accurately established. The C_{ij}'s generally appear to be uniquely established to the third nonzero digit. The one- and two-electron integrals and one-electron energies which will be reported have been accurately evaluated *for* the final $U_i(r)$'s to as many or more digits than will be reported. The one-electron energies lie within approximately 0.01 a.u. of the true values. This is due to the limited basis sets.

Before leaving this section, I would like to point out to the reader that these are "conventional" Hartree-Fock calculations in the sense that the three restrictions

TABLE II. The eigenvectors (C_{ij}'s) defining the Hartree-Fock radial functions (U_i's) in terms of the basis functions (R_j's).

	j	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$i=1s$	1	0.92434949	0.92286952	0.92152229	0.92029233	0.91916088	0.91811986	0.91715694	0.91626600	0.91543924
	2	0.09550157	0.09666839	0.09770646	0.09863051	0.09946303	0.10021035	0.10089690	0.10151104	0.10207042
	3	−0.00524901	−0.00449059	−0.00378558	−0.00311760	−0.00249126	−0.00189259	−0.00135619	−0.00082029	−0.00031407
	4	0.00420564	0.00344379	0.00279550	0.00220845	0.00169418	0.00121451	0.00082668	0.00042420	0.00005423
	5	−0.00680665	−0.00276855	−0.00118750	−0.00032341	0.00015486	0.00050214	0.00065184	0.00084513	0.00099400
	6	0.01443288	0.00474490	0.00121263	−0.00053900	−0.00135820	−0.00187408	−0.00195346	−0.00214153	−0.00224333
	7	−0.00932989	−0.00299967	−0.00065975	0.00051805	0.00106818	0.00141961	0.00145943	0.00158712	0.00165507
	8	−0.00011424	−0.00005689	−0.00005589	−0.00006884	−0.00007872	−0.00009045	−0.00008941	−0.00009666	−0.00010203
	9	0.00006986	0.00004114	0.00004267	0.00005173	0.00005769	0.00006496	0.00006304	0.00006722	0.00007017
	10	−0.00002805	−0.00001734	−0.00001825	−0.00002197	−0.00002432	−0.00002725	−0.00002630	−0.00002796	−0.00002911
$i=2s$	1	−0.27340501	−0.27487263	−0.27621054	−0.27743642	−0.27857079	−0.27961313	−0.28057440	−0.28146591	−0.28229729
	2	−0.16768250	−0.16770390	−0.16737480	−0.16675505	−0.16590205	−0.16489727	−0.16378101	−0.16257869	−0.16133612
	3	0.85585825	0.82020464	0.78805113	0.75879582	0.73199046	0.70741223	0.68478499	0.66386708	0.64453485
	4	0.29187281	0.32998156	0.36219277	0.38999564	0.41438741	0.43573467	0.45456581	0.47130886	0.48620591
	5	0.03449514	0.01058850	0.00895228	0.01232114	0.01705462	0.02258262	0.02827951	0.03390105	0.03943004
	6	−0.03985789	0.02345770	0.03230426	0.03023658	0.02579648	0.02053685	0.01572351	0.01163536	0.00813704
	7	0.02369412	−0.01880418	−0.02496034	−0.02359647	−0.02050309	−0.01675300	−0.01327490	−0.01027788	−0.00767897
	8	0.00095331	0.00119682	0.00146399	0.00159765	0.00163453	0.00158306	0.00149504	0.00138714	0.00126795
	9	−0.00062933	−0.00087898	−0.00106493	−0.00115189	−0.00117378	−0.00113270	−0.00106913	−0.00099185	−0.00090645
	10	0.00025613	0.00036911	0.00044550	0.00048194	−0.00049236	0.00047551	0.00044994	0.00041808	0.00038258
$i=3s$	1	0.09779690	0.09949267	0.10094000	0.10216117	0.10337843	0.10441708	0.10533365	0.10615378	0.10689175
	2	0.06209759	0.06218400	0.06190374	0.06130461	0.06064672	0.05980181	0.05883479	0.05780579	0.05669787
	3	−0.32280647	−0.31011743	−0.29754559	−0.28510578	−0.27369636	−0.26257991	−0.25189598	−0.24175670	−0.23201149
	4	−0.24943759	−0.26955085	−0.28819359	−0.30543152	−0.32131696	−0.33582523	−0.34914628	−0.36126087	−0.37262275
	5	0.52534796	0.37353041	0.30781252	0.27334487	0.24844592	0.23215177	0.22045579	0.21116110	0.20442268
	6	0.47357794	0.87140454	1.0474006	1.1384088	1.2103673	1.2553498	1.2861447	1.3094038	1.3250123
	7	0.16834296	−0.08912278	−0.20390093	−0.26216834	−0.31095634	−0.34063747	−0.36041406	−0.37510133	−0.38430314
	8	0.02638413	0.02246560	0.02214272	0.02297385	0.02400116	0.02539019	0.02687978	0.02846597	0.02990454
	9	−0.01366745	−0.01160526	−0.01165952	−0.01232595	−0.01317665	−0.01417407	−0.01519006	−0.01625641	−0.01719750
	10	0.00526820	0.00448393	0.00454126	0.00483371	0.00521841	0.00564478	0.00608119	0.00653700	0.00693516
$i=4s$	1	−0.02253651	−0.02244797	−0.02227506	−0.02200447	−0.02186079	−0.02163745	−0.02139245	−0.02113253	−0.02084909
	2	−0.01415968	−0.01390591	−0.01360171	−0.01318160	−0.01287018	−0.01249183	−0.01209688	−0.01171079	−0.01130232
	3	0.07394358	0.06962484	0.06554930	0.06141911	0.05812634	0.05484490	0.05174739	0.04889635	0.04614937
	4	0.06518462	0.06773727	0.06956041	0.07107415	0.07237351	0.07330565	0.07402881	0.07441423	0.07468274
	5	−0.15938476	−0.09707771	−0.06972038	−0.05625998	−0.04561736	−0.03902859	−0.03464830	−0.03102298	−0.02846875
	6	−0.08842540	−0.24620956	−0.31160921	−0.33751142	−0.36116049	−0.37103106	−0.37400107	−0.37455462	−0.37180036
	7	−0.06709239	0.04411542	0.09461933	0.11794874	0.14035277	0.15238676	0.15883110	0.16320048	0.16487185
	8	0.34890168	0.36068942	0.36670105	0.36731683	0.37133716	0.37164519	0.37059331	0.36854132	0.36527582
	9	0.61639804	0.60899600	0.60360450	0.60067753	0.59660660	0.59397020	0.59219320	0.59063630	0.58928552
	10	0.15200055	0.14868524	0.14847761	0.15102187	0.15142512	0.15424094	0.15771451	0.16213607	0.16775410
$i=2p$	1	0.17468309	0.16962715	0.16408591	0.15932740	0.15485609	0.15065397	0.14669353	0.14295312	0.13940445
	2	0.85685407	0.85322176	0.85159110	0.84955079	0.84788172	0.84647611	0.84530003	0.84432092	0.84357168
	3	−0.01495638	−0.00702005	−0.00080121	0.00517974	0.01057164	0.01542382	0.01980733	0.02377867	0.02732136
	4	0.01995576	0.01951532	0.01954484	0.01960539	0.01965743	0.01984658	0.02012295	0.02046241	0.02085625
	5	−0.00647378	−0.00552515	−0.00485359	−0.00425450	−0.00371777	−0.00326805	−0.00288007	−0.00253932	−0.00224156
$i=3p$	1	−0.04510348	−0.04640618	−0.04692006	−0.04703533	−0.04704417	−0.04667367	−0.04602592	−0.04514848	−0.04407400
	2	−0.34690544	−0.34321622	−0.34096384	−0.33939238	−0.33876045	−0.33873259	−0.33927654	−0.34034620	−0.34190392
	3	0.04667642	0.02392674	0.00490181	−0.01092733	−0.02530600	−0.03715640	−0.04696666	−0.05501376	−0.06148085
	4	0.72111908	0.68637253	0.65597158	0.62778671	0.60696303	0.58666591	0.56757590	0.54966016	0.53280611
	5	0.36257120	0.41366107	0.45779257	0.49732397	0.52841968	0.55720384	0.58333906	0.60706566	0.62864967
$i=3d$	1	0.56543798	0.52430835	0.49449168	0.46745960	0.46070536	0.45090539	0.44241698	0.43489993	0.42635360
	2	0.46809864	0.49893811	0.51800585	0.53460897	0.53112786	0.53160811	0.53162760	0.53136516	0.53254284
	3	0.10026656	0.11312810	0.12594570	0.13747322	0.15129696	0.16300657	0.17347120	0.18294501	0.19148700
	4	0.00528159	0.00545223	0.00533546	0.00529102	0.00445566	0.00393326	0.00350603	0.00315215	0.00291818

TABLE III. Hartree-Fock one-electron energies (ϵ_i), one-electron nuclear potential + kinetic energies (K_i), total energies and assorted Slater two-electron integrals (F^k and G^k) for the iron series neutral atoms. All energies are in atomic units (1 a. u. = 2 ry).

Element State	Ti $4s^23d^2\ ^3F$	V $4s^23d^3\ ^4F$	Cr $4s^23d^4\ ^5D$	Mn $4s^23d^5\ ^5D$	Fe $4s^23d^6\ ^5D$	Co $4s^23d^7\ ^4F$	Ni $4s^23d^8\ ^3F$	Cu $4s^23d^9\ ^2D$	Zn $4s^23d^{10}\ ^1S$
ϵ_{1s}	−183.2640	−201.4934	−220.5827	−240.5235	−261.3544	−283.0401	−305.5911	−329.0036	−353.2608
ϵ_{2s}	−21.4147	−23.8663	−26.4308	−29.1005	−31.9179	−34.8441	−37.8902	−41.0536	−44.3189
ϵ_{3s}	−2.8648	−3.1752	−3.4911	−3.8084	−4.1541	−4.5033	−4.8624	−5.2306	−5.5997
ϵ_{4s}	−0.2189	−0.2288	−0.2379	−0.2461	−0.2550	−0.2633	−0.2711	−0.2787	−0.2855
ϵ_{2p}	−17.7829	−20.0141	−22.3569	−24.8037	−27.3962	−30.0961	−32.9144	−35.8483	−38.8822
ϵ_{3p}	−1.7870	−2.0117	−2.2413	−2.4719	−2.7278	−2.9866	−3.2539	−3.5287	−3.8035
ϵ_{3d}	−0.4379	−0.5057	−0.5634	−0.6334	−0.6359	−0.6595	−0.6868	−0.7155	−0.7505
K_{1s}	−241.8631	−264.3608	−287.8587	−312.3568	−337.8549	−364.3532	−391.8517	−420.3502	−449.8488
K_{2s}	−58.7985	−64.3982	−70.2468	−76.3441	−82.6911	−89.2869	−96.1317	−103.2257	−110.5693
K_{3s}	−22.1405	−24.4246	−26.8006	−29.2661	−31.8503	−34.5254	−37.2968	−40.1669	−43.1356
K_{4s}	−6.7477	−7.3686	−7.9971	−8.6242	−9.2987	−9.9731	−10.6590	−11.3563	−12.0596
K_{2p}	−58.1051	−63.7118	−69.5662	−75.6688	−82.0204	−88.6203	−95.4685	−102.5656	−109.9120
K_{3p}	−20.4905	−22.7167	−25.0306	−27.4305	−29.9552	−32.5690	−35.2785	−38.0874	−40.9962
K_{3d}	−16.1548	−18.2952	−20.4729	−22.7537	−24.9512	−27.2831	−29.7024	−32.2123	−34.8422
Total energy	−848.4011	−942.8803	−1043.3036	−1149.8620	−1262.4367	−1381.4045	−1506.8569	−1638.9310	−1777.8234
$F^0(3d,3d)$	0.644777	0.706916	0.765631	0.824758	0.873262	0.924215	0.974859	1.025351	1.077205
$F^2(3d,3d)$	0.297950	0.326784	0.353965	0.381624	0.402854	0.425674	0.448408	0.471119	0.494694
$F^4(3d,3d)$	0.185279	0.203240	0.220158	0.237432	0.250384	0.264423	0.278420	0.292412	0.306990
$F^0(4s,3d)$	0.302562	0.317390	0.331172	0.343815	0.356952	0.369179	0.380946	0.392287	0.403105
$G^2(4s,3d)$	0.035761	0.034008	0.032726	0.031311	0.031489	0.031216	0.030922	0.030613	0.030134
$F^0(4s,4s)$	0.238268	0.248546	0.258125	0.266818	0.276207	0.284804	0.293062	0.300982	0.308459

which are commonly applied to the Hartree-Fock formalism[9] have been applied here. These restrictions are (1) that the Hartree-Fock one-electron functions have an angular dependence which is a spherical harmonic—this lets us turn the three-dimensional Hartree-Fock equations into one-dimensional radial equations, (2) that the $U_i(r)$'s be independent of the one-electron quantum number m_l, and (3) that the $U_i(r)$'s be independent of the one-electron spin quantum number m_s. Abandonment of any or all of these restrictions causes the collapse of the conventional electron shell description of atoms. While many of the properties of the many-electron, total atom wave function are little affected by these restrictions, their relaxation has interesting effects on theoretical predictions concerning such phenomena as hyperfine effects and the magnetic scattering in neutron diffraction.[10]

III. RESULTS

The eigenvectors (C_{ij}'s) appear in Table II, and Table III contains the eigenvalues of the one-electron Hartree-Fock equations otherwise known as the one-electron energies (ϵ_i), the one-electron nuclear potential plus kinetic energy integrals (K_i), the atom total energies, and some Slater two-electron integrals.[11] Due to space considerations, the two-electron integrals have been restricted to those involving the $3d$ and $4s$ one-electron functions. A Slater F^k integral is defined to be:

$$F^k(m,n)=\int_0^\infty\int_0^\infty [U_m(r)]^2[U_n(r')]^2\frac{r_<^k}{r_>^{k+1}}drdr', \quad (5)$$

and the Slater exchange integral is:

$$G^k(m,n)=\int_0^\infty\int_0^\infty U_m(r)U_n(r)U_m(r')U_n(r')\times\frac{r_<^k}{r_>^{k+1}}drdr'. \quad (6)$$

Complex conjugate signs do not appear here since the $U_i(r)$'s are real. These integrals are of interest since the Racah parameterization[12] of the multiplet spectra is in terms of these.

Comparison with the few existing numerical Hartree-Fock solutions for these states will not be made. A comparison of total energies is the true test of wave function superiority but the lack of accurate estimates of the total energies for the numerical solutions makes this impossible. This leaves one with the comparison of one- and two-electron integrals (except for one-electron energies these are rare) and the one-electron wave functions themselves. Such comparisons are rather uninformative but it has been my experience that my functions and their one-electron energies agree most

TABLE IV. The one-electron nuclear potential + kinetic energy integrals (K_i's) for several states of V, in atomic units.

	Neutral (I) $3d^34s^2\ ^4F$	Doubly ionized (III) $3d^3\ ^4F$	Singly ionized (II) $3d^4\ ^5D$
K_{1s}	−264.3608	−264.3608	−264.3610
K_{2s}	−64.3982	−64.3968	−64.3975
K_{3s}	−24.4246	−24.4276	−24.2771
K_{4s}	−7.3686	...	...
K_{2p}	−63.7118	−63.7127	−63.7130
K_{3p}	−22.7167	−22.7465	−22.5460
K_{3d}	−18.2952	−18.5264	−17.1873

---

[9] See Chap. II of reference 3 and also C. C. J. Roothaan, Revs. Modern Phys. **32**, 179 (1960), for an extension of the analytic method for cases where the restrictions introduce difficulties in the formalism.

[10] G. W. Pratt, Phys. Rev. **102**, 1303 (1956); L. M. Sachs (to be published); and reference 14.

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

[12] While the energy expressions for the unfilled d shell multiplet spectra had been obtained previously the classic papers are those of G. Racah, Phys. Rev. **61**, 186 (1942); **62**, 438 (1942); **63**, 367 (1943).

TABLE V. $F^2(3d,3d)$'s for Ti through Ni. Theoretical and experimental $3d^{n-2}4s^2$ neutral atom values and theoretical values for neutral, singly ionized, and doubly ionized $3d^n$ configurations are given, in atomic units.

	Theoretical I $3d^n$	Theoretical II $3d^{n-1}$	Theoretical III $3d^{n-2}$	Theoretical I $3d^{n-2}4s^2$	Experimental I $3d^{n-2}4s^2$
Ti	0.193018	0.256680	0.306864	0.297950	0.18391, 0.20093
V	0.231686	0.287822	0.334714	0.326784	0.22600, 0.23804
Cr	0.258094	0.318443	0.361688	0.352965	0.28164, 0.29024
Mn	0.286019	0.340879	0.388705	0.381624	0.29498, 0.29917
Fe	0.311244	0.364548	0.409388	0.402854	0.31486, 0.31576, 0.31926
Co	0.338938	0.386988	0.431936	0.425674	0.33601, 0.33980, 0.32150
Ni	0.363110	0.410765	0.454481	0.448408	0.36906, 0.33464, 0.38611

closely with the best of the numerical solutions.[2,3] A review of the existing iron series numerical solutions and some comparisons of numerical solutions with the earlier set of calculations may be found in reference 2.

Table IV lists the one-electron K_1 integrals for the V solution and compares them with the solutions obtained for the II $3d^{n-1}$ and III $3d^{n-2}$ states of the atom from the earlier set of calculations. It should be noted that the K_i's offer a rather sensitive way to compare one-electron wave functions. The table indicates that the $3d$ and core electron K_i's of the neutral V ground state ($3d^34s^2\,{}^4F$) differ from the doubly (III) ionized $3d^3\,{}^4F$ K_i's by less than one fifth of the differences observed for going between $3d^n$ states of adjacent stages of ionization. The apparent tendency of the $2s$ and $2p$ not to follow this rule very likely follows from the fact that the $2s$ is to be orthogonal to the $4s$ and this perturbs the $2s$ and in turn the $2p$ functions by small amounts (note that the K_i pertubations are of opposite signs). The $U_{3d}(r)$'s for the V I $3d^34s^2$, I $3d^5$, and III $3d^3$ calculations are graphed in Fig. 1. This emphasizes how very little the $4s$ electrons have perturbed the $3d$ and core electrons. The $U_{4s}(r)$ has been graphed on the same figure. The results we see here for V are typical of similar comparisons which can be made for the other atoms.

The $F^k(3d,3d)$'s are of interest since they also give evidence of $3d$ functional behavior. The $F^2(3d,3d)$ is of particular interest since it plays the prominent role in the unfilled $3d$ shell multiplet spectra as predicted by the Racah type of formalism. The calculated neutral atom $3d^{n-2}4s^2$ $F^2(3d,3d)$'s are listed for Ti through Ni in Table V. The theoretical values for the earlier d^n I, II, and III states and the values obtained by fitting the experimental multiplet spectra are also listed. In each case more than one experimental value is given. The collection of experimental values represents fits by Slater and the author and the published values already in the literature. We see that the "experimental" $F^2(3d,3d)$ values are rather dependent on who does the fitting, and what way it was done. Comparing the theoretical $3d^{n-2}4s^2$ values with the others we see that again the $3d$ function is most like that for the ion obtained by removing the two $4s$ electrons. We also see that the experimental $F^2(3d,3d)$'s are systematically smaller than the theoretical ones. Similar deviations were earlier observed for the $3d^n$ solutions. These deviations are not due to the Hartree-Fock $3d$ functions having different radial behavior than some "true" $3d$ one-electron functions but are instead due to the fact that the experimental $F^2(3d,3d)$'s are not true $F^2(3d,3d)$ integrals but in fact are affected by many-electron (correlation) effects which are outside of the scope of the Hartree-Fock, F^k type of description of an atom.

We cannot compare the total energies with experimental total energies since the latter do not exist for atoms of this size. We can compare ionization energies and in Table VI we list both the theoretical and experimental values for the transition from the neutral $3d^{n-2}4s^2$ atom to the doubly ionized $3d^{n-2}$ ion. The theoretical ionization is obtained by taking the difference in calculated total energies, i.e., $E(3d^{n-2})-E(3d^{n-2}4s^2)$. The former energy is obtained from the earlier set of calculations. In the third column are listed the differences between the theoretical and experimental values. The differences are an estimate of the $4s$ "correlation energy" or energy error associated with the $4s$ electrons in a Hartree-Fock rather than exact description of an atom. It should be noted that we believe the $3d^{n-2}4s^2$ solutions to be less accurate than the $3d^{n-2}$ solutions. Improved $3d^{n-2}4s^2$ solutions would lower $E(3d^{n-2}4s^2)$, increase the theoretical ionization energy and decrease the estimated $4s$ "correlation energy." Thus the estimates of Table VI are, at best, upper bounds on the "correlation energies." These estimates are roughly one-half those observed for the two $3d$ electrons involved in the neutral $3d^n$ atom to $3d^{n-2}$ ion transition (observe the final figure of references 1 or 2). The structure in the $4s$ "correlation energies" is typical of what has been seen for the $3d^n$ case.

IV. CONCLUSIONS

The primary purpose of these calculations was to provide wave functions which could be used for further purposes. X-ray scattering factors have already been calculated using these functions.[13] Concerning the results themselves, of interest is the fact that the $4s$

TABLE VI. Theoretical and experimental neutral atom lowest $d3^{n-2}4s^2$ state to doubly ionized $3d^{n-2}$ ground-state ionization energies and the differences between theoretical and experimental values for Ti through Cu $E(\text{III } 3d^{n-2})-E(3d^{n-2}4s^2)$, in atomic units.

	Theoretical	Experimental	Experimental-theoretical
Ti	0.6749	0.7497	0.0748
V	0.7043	0.7864	0.0821
Cr[a]	0.7295	0.8196	0.0902
Mn	0.7571	0.8480	0.0909
Fe	0.7848	0.8851	0.1003
Co	0.8107	0.9086	0.0980
Ni	0.8358	0.9387	0.1029
Cu[a]	0.8604	0.9711	0.1108

[a] In these two cases the lowest I $3d^{n-2}4s^2$ state is not the neutral atom ground state.

---

[13] A. J. Freeman and R. E. Watson, Acta Cryst. (to be published).

electrons have almost no effect on the inner electrons. This result is not unexpected. Less expected is the fact that the 4*s* perturbation on the 3*d* and inner electrons is less than that suffered by an iron series ion when it is inserted into a crystalline environment.[14,15]

ACKNOWLEDGMENTS

Thanks are due to Professor J. C. Slater for his interest and support, to Professor R. K. Nesbet who supplied many of the computer programs and to the MIT Computation Center on whose IBM 704 the major portion of the computation was done.

---

[14] A. J. Freeman and R. E. Watson, Phys. Rev. **118**, 1168 (1960).

[15] R. E. Watson and A. J. Freeman (to be published).

PHYSICAL REVIEW VOLUME 119, NUMBER 6 SEPTEMBER 15, 1960

Collisions of Electrons with Hydrogen Atoms. V. Excitation of Metastable 2*S* Hydrogen Atoms*

R. F. Stebbings, Wade L. Fite, David G. Hummer,† and R. T. Brackmann
John Jay Hopkins Laboratory for Pure and Applied Science, General Atomic, San Diego, California

(Received May 9, 1960)

Ground-state hydrogen atoms produced by thermal dissociation in a tungsten furnace were excited by collision with electrons having energies up to 600 ev. Those atoms which were excited to the metastable 2*S* state were subsequently quenched in an electrostatic field, and the resulting Lyman-alpha radiation was detected with an iodine-vapor-filled photon counter. In order to assign absolute cross-section values to the excitation function obtained in this way, the ratio of the 2*S* to the 2*P* excitation cross sections was determined. From previously obtained knowledge of the cross section for excitation to the 2*P* state, the absolute 2*S* cross section was evaluated. Agreement with the Born approximation was observed at high energies. The angular distribution of the scattered 2*S* atoms was also investigated for electron energies up to 600 ev.

I. INTRODUCTION

THE cross section for excitation of ground-state hydrogen atoms to the metastable 2*S* state on electron impact has been the subject of extensive theoretical investigation.[1–7] The fact that both the initial and final states have zero angular momentum, so that the wave functions are extremely simple in addition to being precisely known, makes this inelastic collision process particularly amenable to a variety of scattering-theory approximations.

However, the predictions of the various scattering-theory approximations differ quite widely, and it is difficult, on theoretical grounds, to select with any confidence the approximation that most closely describes the transition. It seems possible, therefore, that insight into the problem may be gained more directly from a laboratory study of this process and that preference for a particular approximation may be indicated by the results of an accurate experiment. Prior to the present work, experimental evidence on the form of this cross section near threshold was provided by the relative measurements of Lamb and Retherford[8] and by the more recent work of Lichten and Schultz,[9] who used energies up to 40 ev. In the present measurements, the use of modulated-atomic-beam techniques enabled the range of measurements to be extended to considerably higher values of the electron energy.

II. APPARATUS AND PROCEDURE

A schematic view of the apparatus which was employed in the present work is shown in Fig. 1. Atomic hydrogen flowing from a tungsten furnace in the first of three differentially pumped vacuum chambers was modulated at 100 cps by a motor-driven, toothed chopper wheel located in the second chamber. The hydrogen atoms were then excited by a beam of electrons from a gun that was placed in the third chamber with its axis normal to the direction of the atomic beam. After passing through the gun, the atoms entered a "quench" region throughout which an electrostatic field could be established. An iodine-vapor-filled ultraviolet photon counter[10] was mounted on a movable

---

* This research was supported in part by the Advanced Research Projects Agency through the Office of Naval Research, and in part under a joint General Atomic—Texas Atomic Energy Research Foundation program on controlled thermonuclear reactions.

† Present address: Department of Physics, University College, London, England.

[1] D. R. Bates, A. Fundaminsky, J. W. Leech, and H. S. W. Massey, Phil. Trans. Roy. Soc. London **A243**, 93 (1950).

[2] G. A. Erskine and H. S. W. Massey, Proc. Roy. Soc. (London) **A212**, 521 (1952).

[3] H. S. W. Massey and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A66**, 406 (1953).

[4] B. H. Bransden and J. S. C. McKee, Proc. Phys. Soc. (London) **A69**, 422 (1956).

[5] R. Marriott, Proc. Phys. Soc. (London) **A72**, 121 (1958).

[6] R. Akerib and S. Borowitz, Research Report CX-34, New York University, 1958 (unpublished).

[7] A. E. Kingston, B. Skinner, and B. L. Moiseiwitsch (private communication).

[8] W. E. Lamb, Jr., and R. C. Retherford, Phys. Rev. **81**, 227 (1951).

[9] W. Lichten and S. Schultz, Phys. Rev. **116**, 1132 (1959).

[10] R. T. Brackmann, W. L. Fite, and K. E. Hagen, Rev. Sci. Instr. **29**, 125 (1958).