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Self-Consistent Field, with Exchange, for Si IV and Si V

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Results of solutions of Fock's equations for the normal state of Si V and for 3*s*, 4*s*, 5*s*, 3*p*, 4*p*, 5*p*, 3*d*, 4*d*, 5*d*, 4*f*, and 5*g* states of Si IV are reported. Computed term values for the series electron are in satisfactory agreement with experimental values, although the agreement is no better than that obtained by McDougall who used a less elaborate method. Spin-orbit separations have been calculated from these wave functions. The agreement with observed value is satisfactory for the *p* states but not for the *d* and *f* states.

INTRODUCTION

IN ordinary self-consistent field calculations, the wave function for a many-electron atom is expressed as a product of one-electron wave functions. Starting with this assumption it is possible to set up the Schrödinger equation which each type of wave function must satisfy. A satisfactory technique of numerical solution of these equations has been developed and results for a number of atoms and ions have been obtained. The wave functions so obtained are satisfactory for many purposes but they do not satisfy the Pauli exclusion principle. Furthermore, the energy parameters for optical electrons obtained by this method correspond only very roughly with observed term values.

Slater[1] and Fock[2] have shown that by using determinantal wave functions the Pauli principle can be satisfied. Energy values calculated from the determinantal wave functions are usually in much better agreement with observed term values than the eigenvalues of self-consistent field calculations. When the determinantal wave functions are used, there occur additional terms in the expression for the energy of a given state. These additional contributions to the energy are known as exchange energies and can be expressed in terms of integrals over certain products of one-electron wave functions. McDougall[3] has calculated a number of term values in the spectrum of Si IV by substituting in these interaction integrals the one-electron wave functions found by standard self-consistent field methods. Similar calculations have been carried out by Hartree and Black[4] for O, O^+, O^{++}. In all cases the agreement with observed values was satisfactory, although the results for the more highly charged ions were in better agreement with experiment.

There is, however, an approximation involved in this method because the wave functions as well as the energies are affected by the exchange terms. Fock[5] was able to take this effect into account by applying the variational method to the complete expression for the energy. Numerical solutions of the equations were obtained by Fock and Petrashen for Na,[6] Li,[7] and Be.[8] Two of the present authors have developed a somewhat different method of calculation and applied to a number of atoms and ions.[9–17]

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* Most of the calculations reported in this paper were carried out by Mr. W. Hartree in consultation with Professor D. R. Hartree. Circumstances have made it impossible for Professor Hartree to prepare the material for publication. The undersigned has supplied the textual material and made a few supplementary calculations. Professor Hartree has read the manuscript but not the proof. Correspondence about this paper should be addressed to Millard F. Manning.—M.F.M.

[1] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

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[3] J. McDougall, Proc. Roy. Soc. **A138**, 550 (1932).

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[6] Na: V. Fock and M. Petrashen, Phys. Zeits. Sowjet. **6**, 368 (1934).

[7] Li: V. Fock and M. Petrashen, Phys. Zeits. Sowjet. **8**, 457 (1935).

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[9] Be: D. R. and W. Hartree, Proc. Roy. Soc. **A150**, 9 (1935).

[10] Be: D. R. and W. Hartree, Proc. Roy. Soc. **A154**, 588 (1936).

[11] Cl^-: D. R. and W. Hartree, Proc. Roy. Soc. **A156**, 45 (1936).

[12] Cu^+: D. R. and W. Hartree, Proc. Roy. Soc. **A157**, 490 (1936).

[13] Ca: D. R. and W. Hartree, Proc. Roy. Soc. **A164**, 167 (1938).

Partial solutions for Ne, F, and F^- have been obtained by Brown.[18] Solutions for neutral and ionized carbon have been obtained by Jucys[19] and solutions for Mg III have been obtained by Yost.[20]

FORMULATION OF FOCK'S EQUATIONS

The general method of formulation of Fock's equations is to set up the complete expression for the energy of an atomic system in terms of interaction integrals involving the different wave functions and to obtain the differential equation which each type of wave function must satisfy by application of the variational principle. The notation used in this paper is the same as that used in previous papers, but for convenience the defining equations for a number of functions which appear in the formulation and solution of Fock's equations are repeated here.

$$Z_K(\alpha\beta|r)=\int_0^r P_N(\alpha|r_1)P_N(\beta|r_1)(r_1/r)^k dr_1, \tag{1}$$

$$Y_K(\alpha\beta|r)=Z_K(\alpha\beta|r)+\int_0^\infty P_N(\alpha|r_1)P_N(\beta|r_1)(r/r_1)^{k+1}dr_1, \tag{2}$$

$$I(\alpha)=-\tfrac{1}{2}\int_0^\infty P_N(\alpha|r)\left[\frac{d^2}{dr^2}+\frac{2N}{r}-\frac{l(l+1)}{r^2}\right]P_N(\alpha|r)dr, \tag{3}$$

$$F_K(\alpha\beta|r)=\int_0^\infty P_N{}^2(\alpha|r)\,Y_K(\alpha\beta|r)r^{-1}dr, \tag{4}$$

$$=\int_0^\infty P_N{}^2(\beta|r)\,Y_K(\alpha\alpha|r)r^{-1}dr,$$

$$G_K(\beta\alpha|r)=\int_0^\infty P_N(\alpha|r)P_N(\beta|r)\,Y_K(\alpha\beta|r)r^{-1}dr. \tag{5}$$

$(1/r)P_N(\alpha|r)$ is the normalized radial portion of the wave function, having quantum numbers represented by α.

The general expression for the energy of a configuration of closed shells in terms of these is (see reference 11, page 49)

$$E=\sum\nolimits_{nl}\left[2(2l+1)I_{nl}+(2l+1)(4l+1)F_0(nl,\,nl)-\sum\nolimits_k A_{lk}F_K(nl,\,nl)\right] \\ +\sum_{nl,\,n'l'}{}' 4(2l+1)(2l'+1)F_0(nl,\,n'l')-\sum_{nl,\,n'l'}{}' B_{ll'k}G_K(nl,\,n'l'). \tag{6}$$

The primes on the summations indicate that the term $nl=n'l'$ is to be omitted from the sum. Tables of the constants A_{lk} and $B_{ll'k}$ are published in reference 11 (page 48). Some of the values are repeated here in Table I. Discussions of the method of obtaining the constants are given in references 1, 3, and 11 and in chapter 6, Sec. 9 of Condon and Shortley.[21]

The differential equation which a particular nl type of wave function satisfies is found by formal differentiation of the expression

$$E'=E+\sum_{nn'l}\lambda_{nl,\,n'l}\int_0^\infty P_N(nl|r)P_N(n'l|r)dr. \tag{7}$$

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[14] K and A: D. R. and W. Hartree, Proc. Roy. Soc. **A166**, 450 (1938).

[15] Na^- and K^-: D. R. and W. Hartree, Camb. Phil. Soc. **34**, 550 (1938).

[16] O: D. R. and W. Hartree, and B. Swirles, Roy. Soc. Phil. Trans. **238**, 229 (1939).

[17] N and N^-: D. R. and W. Hartree (to be submitted to Phys. Rev.).

[18] F, F^-, N: F. W. Brown, Phys. Rev. **44**, 214 (1933).

[19] C, C^{++}, C^{++++}: A. Jucys, Proc. Roy. Soc. **A173**, 59 (1939).

[20] W. Jacque Yost, Phys. Rev. **58**, 557 (1940).

[21] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge, 1935).

The λ's are Lagrangian multipliers introduced because the variations are subject to the conditions that the final wave functions be normalized and orthogonal. The method of carrying out the differentiations is described in reference 10 and the results are quoted both there and in reference 11 and will not be repeated here. When the differentiations are carried out, the resulting differential equations can be expressed in the standard form

$$\sum_{n'l'} H'_{nl,\,n'l'} P_N(n'l'\,|\,r) = 0. \tag{8}$$

For the diagonal terms the operator $H'_{nl,\,nl}$ can be written in the form

$$H'_{nl,\,nl} = \frac{d^2}{dr^2} + \frac{2}{r}\Bigg[N - \sum_{n'l'} 2(2l'+1)\,Y_0(n'l',\,n'l'\,|\,r) + Y_0(nl,\,nl\,|\,r) + \frac{1}{2l+1}\sum_k A_{lk} Y_K(nl,\,nl\,|\,r)\Bigg] - \epsilon_{nl,\,nl} - \frac{l(l+1)}{r^2}. \tag{9}$$

The non-diagonal elements can be grouped into those for which $l'=l$ and those for which $l'\neq l$.

For $l'=l$

$$H'_{nl,\,n'l'} = \sum_k \frac{B_{ll'k}}{2l+1}\,\frac{Y_K(nl,\,n'l)}{r} - \epsilon_{nl,\,n'l}, \tag{10}$$

$l'\neq l$

$$H'_{nl,\,n'l'} = \sum_k \frac{B_{ll'k}}{2l+1}\,\frac{Y_K(nl,\,n'l')}{r}, \tag{11}$$

$$\epsilon_{nl,\,nl} = -\lambda_{nl,\,nl}/(2l+1),$$

$$\epsilon_{nl,\,n'l} = -\lambda_{nl,\,n'l}/2(2l+1), \quad n'=n.$$

To apply these equations to the $(1s)^2(2s)^2(2p)^6$ configuration of Si V, it is necessary to know the appropriate values of the A_{lk}'s and the $B_{ll'k}$'s. The only A_{lk} needed is A_{12} which is given in reference 11 as 6/5. The necessary values of $B_{ll'k}$ are given in Table I. These values, except those involving g functions, are taken from reference 11. The values for the g functions can be obtained from McDougall's paper[13] (Table V) by simple arithmetic.

By substituting the numerical values for the A's and B's and then combining Eqs. (9), (10) and (11) with Eq. (8) the differential equations for the $(1s)$ and $(2p)$ functions are found to be

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\{T(r) + Y_0(1s,\,1s\,|\,r)\} - \epsilon_{1s,\,1s}\right] P_N(1s\,|\,r) + \left[\frac{2Y_0(1s,\,2s\,|\,r)}{r} - \epsilon_{1s,\,2s}\right] P_N(2s\,|\,r) + \left[\frac{2Y_1(1s,\,2p\,|\,r)}{r}\right] P_N(2p\,|\,r) = 0. \tag{12}$$

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\{T(r) + Y_0(2p,\,2p\,|\,r) + \tfrac{2}{5} Y_2(2p,\,2p\,|\,r)\} - \epsilon_{2p,\,2p} - \frac{2}{r^2}\right] P_N(2p\,|\,r) + \sum_{\alpha=1}^{2}\left[\frac{3}{2r} Y_1(\alpha s,\,2p\,|\,r)\right] P_N(\alpha s\,|\,r) = 0, \tag{13}$$

where $T(r)$ stands for

$$N - 2Y_0(1s,\,1s\,|\,r) - 2Y_0(2s,\,2s\,|\,r) - 6Y_0(2p,\,2p\,|\,r).$$

The differential equation for the $2s$ electron is the same as that for the $1s$ except that $1s$ and $2s$ are interchanged wherever they occur.

The method of setting up the differential equations when there is a single electron outside of closed shells is discussed in reference 13 (page 69). When the series electron is added there are additional terms in the energy. When there is only one electron outside of closed shells, there are no terms in the energy involving interactions within incomplete shells. It has been shown previously that each term in the interaction between a series electron and a closed shell is $1/(2l+1)$ times the interaction between closed shells. Hence the additional contribution to the energy due to the addition of an nl series electron is

$$E_b(nl)=I_{nl}+\sum_{n'l'}\left[2(2l'+1)F_0(nl,n'l')-\frac{1}{2(2l+1)}\sum_{k}B_{ll'k}G_K(nl,n'l')\right]. \tag{14}$$

Since these extra terms in the energy involve the core wave functions, the strict application of the variational principle would yield additional terms in the differential equations for each of the core functions. However, previous experience indicates that these additional terms will have a very small effect on the wave functions of the inner electrons. The effect is particularly small when, as in this case, the net nuclear charge is large. If this effect is neglected, the only equations that need to be considered are those for the series electron. The general expressions given in Eqs. (8), (9), (10), and (11) can be applied to the series electron wave functions; the necessary values of $B_{ll'k}$ are listed in Table I. In the present computations, wave functions for $3s$, $4s$, $5s$, $3p$, $4p$, $5p$, $3d$, $4d$, $5d$, $4f$ and $5g$ were obtained. The differential equations which $ns(n>2)$, $np(n>2)$, nd, nf, and ng functions satisfy are:

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}T(r)-\epsilon_{ns,\,ns}\right]P_N(ns\,|\,r)+\sum_{\alpha=1}^{2}\left[\frac{2}{r}Y_0(\alpha s,\ ns\,|\,r)-\epsilon_{\alpha s,\,ns}\right]P_N(\alpha s\,|\,r)$$
$$+\left[\frac{2}{r}Y_1(2p,\ ns\,|\,r)\right]P_N(2p\,|\,r)=0, \tag{15}$$

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}T(r)-\frac{2}{r^2}-\epsilon_{np,\,np}\right]P_N(np\,|\,r)+\sum_{\alpha=1}^{2}\left[\frac{2}{3r}Y_1(\alpha s,\ np\,|\,r)\right]P_N(\alpha s\,|\,r)$$
$$+\left[\frac{2}{r}Y_0(2p,\ np\,|\,r)+\frac{4}{5r}Y_2(2p,\ np\,|\,r)-\epsilon_{2p,\,np}\right]P_N(2p\,|\,r)=0, \tag{16}$$

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}T(r)-\frac{6}{r^2}-\epsilon_{nd,\,nd}\right]P_N(nd\,|\,r)+\sum_{\alpha=1}^{2}\left[\frac{2}{5r}Y_2(\alpha s,\ nd\,|\,r)\right]P_N(\alpha s\,|\,r)$$
$$+\left[\frac{4}{5r}Y_1(2p,\ nd\,|\,r)+\frac{18}{35r}Y_3(2p,\ nd\,|\,r)\right]P_N(2p\,|\,r)=0, \tag{17}$$

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}T(r)-\frac{12}{r^2}-\epsilon_{nf,\,nf}\right]P_N(nf\,|\,r)+\sum_{\alpha=1}^{2}\left[\frac{2}{7r}Y_3(\alpha s,\ nf\,|\,r)\right]P_N(\alpha s\,|\,r)$$
$$+\left[\frac{18}{35r}Y_2(2p,\ nf\,|\,r)+\frac{8}{21r}Y_4(2p,\ nf\,|\,r)\right]P_N(2p/r)=0, \tag{18}$$

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}T(r)-\frac{20}{r^2}-\epsilon_{ng,\,ng}\right]P_N(ng\,|\,r)+\sum_{\alpha=1}^{2}\left[\frac{2}{9r}Y_4(\alpha s,\ ng\,|\,r)\right]$$
$$+\left[\frac{8}{21r}Y_3(2p,\ ng\,|\,r)+\frac{10}{33r}Y_5(2p,\ ng\,|\,r)\right]=0. \tag{19}$$

TABLE I. *Values of* $B_{ll'k}$ *(interactions between complete groups).*

GROUPS	l	l'	$k=0$	$k=1$	$k=2$	$k=3$	$k=4$	$k=5$
$(ns)^2(n's)^2$	0	0	2	—	—	—	—	—
$(ns)^2(n'p)^6$	0	1	—	2	—	—	—	—
$(ns)^2(n'd)^{10}$	0	2	—	—	2	—	—	—
$(ns)^2(n'f)^{14}$	0	3	—	—	—	2	—	—
$(ns)^2(n'g)^{20}$	0	4	—	—	—	—	2	—
$(np)^6(n'p)^6$	1	1	6	—	12/15	—	—	—
$(np)^6(n'd)^{10}$	1	2	—	4	—	18/7	—	—
$(np)^6(n'f)^{14}$	1	3	—	—	18/5	—	8/3	—
$(np)^6(n'g)^{20}$	1	4	—	—	—	24/7	—	30/11

TABLE II. *Values of* P_n/r^{l+1} *near origin for* Si V.

$r=$	0.00	0.01	0.02	0.03	0.04
1s	101.8	88.4	76.8	66.9	58.2
2s	27.1	23.5	20.3	17.4	14.9
2p	85.8	80.1	74.8	69.9	65.4

METHOD OF SOLUTION

The process of solution of Fock's equations is similar to that used in self-consistent field calculations in that it is necessary to start by making some initial estimates and use these estimates to calculate other values of the functions considered. New estimates are then made and the procedure repeated until initial and final values of the function show satisfactory agreement. In ordinary self-consistent field calculations and in the earlier solutions of Fock's equations, the initial estimates have usually been made in terms of the Z_k's. For Fock's equations there are such a large number of Z_k's to estimate and make consistent that it has proved more satisfactory to estimate the various $P_N(\alpha\beta|r)$'s directly and make the initial and final values consistent.

For the present calculations, the self-consistent field calculations of McDougall[3] were available as initial estimates. It was, however, possible to do somewhat better than these. By comparison of results with and without exchange for Be, Na, K, and Ca, it was possible to make an estimate of the changes in charge distribution which would be produced by introduction of the exchange terms. In general the effect of exchange terms is to make the whole structure more compact—shifting the maximum of the wave function toward the nucleus somewhat as an increased nuclear charge would. This effect was very small for the 1s functions and more pronounced for the 2s and 2p functions.

TABLE III. *Values of* P/r^{l+1} *near origin for series electrons in* Si IV.

r	s	p	d	f	g
0.00	10.00	100.0	100.0	10.00	10.00
0.01	8.68	93.3	95.5	9.66	9.73
0.02	7.50	87.0	91.3	9.34	9.47
0.03	6.44	81.3	87.3	9.04	9.22
0.04	5.50	76.0	83.6	8.75	8.99

TABLE IV. *Values of* P/r^{l+1} *between 0.06 and 0.20 for d, f, and g series electrons in* Si IV.

r	3d	4d	5d	∞d	4f	∞f	5g
0.06	76.7	76.7	76.7	76.7	8.22	8.22	8.56
0.08	70.7	70.7	70.7	70.6	7.74	7.74	8.16
0.10	65.3	65.3	65.3	65.2	7.31	7.30	7.80
0.12	60.4	60.4	60.4	60.3	6.91	6.90	7.46
0.14	56.1	56.1	56.0	55.9	6.55	6.54	7.15
0.16	52.1	52.1	52.0	52.0	6.21	6.20	6.87
0.18	48.6	48.5	48.4	48.4	5.91	5.90	6.60
0.20	45.3	45.2	45.2	45.1	5.63	5.61	6.36

For the series electron wave functions the nl wave function itself occurs only in exchange terms. In this case McDougall's results provided satisfactory initial estimates. These were then improved by a series of successive approximations until a satisfactory agreement was obtained.

In carrying out the integrations for the core wave functions, it was found to be practicable to start with values of P's at small values of r found by series expansion and integrate outward. Different values of the parameters $\epsilon_{nl,\,nl}$, $\epsilon_{n'l,\,nl}$ and the arbitrary multiplicative constant in

TABLE V. *Values of* P_n *for* Si V.

r	$(1s)^2$	$(2s)^2$	$(2p)^6$	r	$(1s)^2$	$(2s)^2$	$(2p)^6$
0.00	0.000	0.000	0.0000	0.6	0.025	−1.245	1.118
0.01	0.883	0.235	0.008	0.7	0.0085	−1.062	0.960
0.02	1.537	0.406	0.030	0.8	0.003	−0.870	0.801
0.03	2.006	0.523	0.063	0.9	0.001	−0.693	0.656
0.04	2.329	0.597	0.105	1.0	0.0005	−0.540	0.529
				1.1		−0.414	0.421
0.06	2.652	0.639	0.206	1.2		−0.314	0.332
0.08	2.689	0.582	0.322				
0.10	2.559	0.461	0.443	1.4		−0.174	0.201
0.12	2.341	0.301	0.564	1.6		−0.094	0.119
0.14	2.085	+0.121	0.679	1.8		−0.050	0.069
0.16	1.820	−0.065	0.787	2.0		−0.026	0.040
0.18	1.566	−0.250	0.886	2.2		−0.0135	0.023
0.20	1.333	−0.426	0.974	2.4		−0.007	0.013
				2.6		−0.0035	0.0075
0.25	0.859	−0.806	1.146	2.8		−0.002	0.0045
0.30	0.535	−1.084	1.255	3.0		−0.001	0.0025
0.35	0.327	−1.263	1.309	3.2		−0.0005	0.0015
0.40	0.197	−1.359	1.320	3.4			0.001
0.45	0.118	−1.390	1.298	3.6			0.0005
0.50	0.070	−1.372	1.252				

TABLE VI. *Values of* P *for s and p valence electrons in* Si IV (*not normalized*).

r	$3s$	$4s$	$5s$	∞s	$3p$	$4p$	$5p$	∞p
0.00	0.000				0.0000			
0.01	0.087				0.0093			
0.02	0.150				0.0348			
0.03	0.193				0.0732			
0.04	0.220				0.1215			
0.06	0.234	0.234	0.234	0.234	0.239	0.239		
0.08	0.211	0.210	0.210	0.210	0.373	0.373		
0.10	0.164	0.163	0.163	0.162	0.512	0.511		
0.12	0.102	0.101	0.101	0.100	0.648	0.647		
0.14	+0.033	+0.031	+0.031	+0.030	0.777	0.775		
0.16	−0.038	−0.040	−0.041	−0.042	0.894	0.892		
0.18	−0.107	−0.109	−0.111	−0.112	0.999	0.995		
0.20	−0.173	−0.175	−0.176	−0.177	1.088	1.082	1.08	1.075
0.25	−0.309	−0.311	−0.311	−0.312	1.245	1.23	1.225	1.22
0.30	−0.399	−0.399	−0.399	−0.398	1.31	1.29	1.28	1.265
0.35	−0.444	−0.440	−0.438	−0.435	1.295	1.265	1.245	1.225
0.40	−0.448	−0.439	−0.435	−0.429	1.21	1.17	1.145	1.12
0.45	−0.419	−0.404	−0.398	−0.389	1.08	1.02	0.99	0.955
0.50	−0.366	−0.344	−0.335	−0.323	0.90	0.825	0.79	0.75
0.6	−0.209	−0.173	−0.159	−0.139	+0.475	+0.365	+0.32	+0.265
0.7	−0.018	+0.030	+0.047	+0.072	−0.01	−0.14	−0.19	−0.26
0.8	+0.178	0.232	0.251	0.278	−0.50	−0.65	−0.70	−0.77
0.9	0.363	0.414	0.432	0.456	−0.97	−1.12	−1.16	−1.225
1.0	0.527	0.566	0.578	0.592	−1.40	−1.53	−1.56	−1.60
1.1	0.666	0.680	0.681	0.680	−1.79	−1.86	−1.87	−1.87
1.2	0.777	0.753	0.740	0.718	−2.12	−2.11	−2.09	−2.04
1.4	0.920	0.787	0.732	0.654	−2.61	−2.37	−2.25	−2.05
1.6	0.972	0.689	0.581	0.440	−2.88	−2.30	−2.05	−1.67
1.8	0.956	0.494	0.336	+0.138	−2.98	−1.97	−1.58	−1.02
2.0	0.896	+0.241	+0.041	−0.189	−2.93	−1.44	−0.91	−0.21
2.2	0.809	−0.036	−0.260	−0.488	−2.78	−0.78	−0.15	+0.63
2.4	0.710	−0.311	−0.532	−0.717	−2.56	−0.06	+0.63	1.39
2.6	0.610	−0.564	−0.754	−0.851	−2.31	+0.66	1.36	1.99
2.8	0.513	−0.782	−0.911	−0.882	−2.04	1.34	1.98	2.36
3.0	0.426	−0.960	−0.997	−0.813	−1.78	1.96	2.46	2.51
3.2	0.349	−1.095	−1.013	−0.658	−1.53	2.49	2.78	2.40
3.4	0.282	−1.187	−0.964	−0.437	−1.30	2.92	2.93	2.07
3.6	0.226	−1.241	−0.859	−0.175	−1.09	3.25	2.92	1.56
3.8	0.180	−1.261	−0.708	+0.102	−0.91	3.49	2.76	0.93
4.0	0.142	−1.253	−0.523	0.372	−0.75	3.63	2.47	+0.22
4.5	0.077	−1.142	+0.014	0.881	−0.455	3.66	+1.33	−1.51
5.0	0.039	−0.962	0.552	1.014	−0.265	3.37	−0.10	−2.64
5.5	0.020	−0.764	0.998	0.754	−0.15	2.90	−1.53	−2.80
6.0	0.010	−0.581	1.306	+0.225	−0.085	2.37	−2.74	−2.01
6.5	0.005	−0.427	1.473	−0.379	−0.045	1.87	−3.62	−0.59
7.0	0.0025	−0.305	1.517	−0.871	−0.025	1.43	−4.16	+1.01
8	0.0005	−0.146	1.352	−1.079	−0.005	0.78	−4.33	3.08
9		−0.065	1.036	−0.286		0.39	−3.75	+2.41
10		−0.028	0.717	+0.760		0.19	−2.88	−0.22
11		−0.012	0.462	1.247		0.085	−2.04	−2.73
12		−0.005	0.281	+0.881		0.04	−1.35	−3.42
13		−0.002	0.164	−0.047		0.015	−0.86	−1.99
14		−0.001	0.092	−0.954		0.005	−0.52	+0.59
15		−0.0005	0.050	−1.346			−0.31	2.88
16			0.027	−1.051			−0.175	3.73
17			0.014				−0.09	
18			0.0075				−0.055	
19			0.004				−0.03	
20			0.002				−0.015	
21			0.001				−0.010	
22							−0.005	

TABLE VII. *Values of P for d, f, and g series electrons in* Si IV (*not normalized*).

r	$3d$	$4d$	$5d$	∞d	$4f$	∞f	$5g$
0.20	0.36	0.36	0.36	0.36	0.0090	0.9909	0.0020
0.25	0.60	0.60	0.595	0.595	0.0195	0.0195	0.0057
0.30	0.885	0.88	0.88	0.875	0.0364	0.0362	0.0130
0.35	1.21	1.205	1.20	1.19	0.0609	0.0605	0.0260
0.40	1.57	1.555	1.55	1.53	0.0945	0.0938	0.0472
0.45	1.96	1.935	1.925	1.90	0.1387	0.1372	0.0796
0.50	2.37	2.33	2.315	2.28	0.1946	0.1919	0.1266
0.6	3.24	3.16	3.13	3.05	0.347	0.340	0.281
0.7	4.15	4.01	3.95	3.82	0.560	0.544	0.548
0.8	5.08	4.85	4.74	4.53	0.842	0.810	0.972
0.9	6.01	5.64	5.48	5.16	1.20	1.14	1.60
1.0	6.91	6.38	6.13	5.68	1.63	1.52	2.48
1.1	7.78	7.02	6.68	6.07	2.14	1.97	3.68
1.2	8.59	7.55	7.09	6.30	2.72	2.46	5.23
1.4	10.0	8.25	7.5	6.25	4.1	3.55	9.6
1.6	11.05	8.4	7.3	5.5	5.7	4.7	15.9
1.8	11.75	8.0	6.5	4.2	7.4	5.8	24.4
2.0	12.1	7.1	5.2	2.5	9.25	6.7	35.2
2.2	12.1	5.75	3.5	+0.5	11.1	7.35	48.3
2.4	11.85	4.1	+1.6	−1.55	12.8	7.65	63.6
2.6	11.4	2.25	−0.45	−3.5	14.5	7.6	80.9
2.8	10.75	+0.3	−2.45	−5.1	15.9	7.1	100
3.0	10.0	−1.65	−4.3	−6.3	17.2	6.3	120
3.2	9.2	−3.55	−5.95		18.2		141
3.4	8.35	−5.35	−7.3		19.0		163
3.6	7.5	−6.95	−8.3		19.5		185
3.8	6.7	−8.35	−8.95		19.8		207
4.0	5.95	−9.55	−9.2		19.9		228
4.5	4.25	−11.55	−8.35		19.4		275
5.0	2.95	−12.25	−5.85		17.9		312
5.5	2.0	−12.0	−2.3		15.9		337
6.0	1.3	−11.05	+1.6		13.6		349
6.5	0.8	−9.7	5.3		11.4		349
7.0	0.5	−8.25	8.5		9.3		339
8	0.2	−5.45	12.45		5.8		297
9	0.05	−3.35	13.45		3.45		240
10		−1.9	12.3		1.95		183
11		−1.05	10.15		1.05		132
12		−0.55	7.75		0.55		92
13		−0.3	5.6		0.3		62
14		−0.15	3.85		0.15		40
15		−0.1	2.55		0.1		25
16		−0.05	1.6		0.05		16
18			0.6				6
20			0.2				2

$P(nl|r)$ were tried until the proper behavior at large values of r was obtained simultaneously with the fulfillment of the normalization and orthogonality conditions. The wave function so found was compared with that initially assumed and a new wave function estimated. The process of successive approximations was continued until initial and final values of each P_N checked to within 0.003.

The integrations for the outer wave functions are best carried out to some convenient radius (usually near the outer inflection point). For the same $\epsilon_{nl,\,nl}$ an inward integration is started from some large radius where an asymptotic expansion can be found. The values of $\epsilon_{nl,\,nl}$ are then adjusted until the values of $(1/P)(dP/dr)$ as found by outward and inward integration are equal. The details of the method of inward integration are described in reference 9. In theory the non-diagonal multipliers should be taken into account, but as was found[13] for Ca$^+$, the wave functions found are already orthogonal to the core functions.

TABLE VIII. *Values of* $[\int_0^\infty P^2 dr]^{\frac{1}{2}}$, ϵ, ν, *and* q.

		$[\int_0^\infty P^2 dr]^{\frac{1}{2}}$	ϵ	ν_c(cm^{-1})	ν_c(J.M.)	ν_0	q_c	q_0
Si V	1*s*	1	141.6					
	2*s*	1	16.17					
	2*p*	1	12.41					
Si IV	3*s*	1.185	3.275	359,400	360,400	364,098	0.79	0.804
	4*s*	2.09	1.538	168,800	169,200	170,116	0.775	0.787
	5*s*	3.13	0.893	98,000	98,500	98,677	0.765	0.782
	∞*s*	—	0				0.765	
	3*p*	3.91	2.639	289,600	289,600	292,655	0.535	0.550
	4*p*	6.49	1.319	144,100	145,100	145,774	0.515	0.529
	5*p*	9.45	0.793	87,000	87,300	87,566	0.505	0.521
	∞*p*	—	0				0.500	
	3*d*	18.45	1.839	201,800	202,200	203,721	0.05	0.064
	4*d*	23.9	1.033	113,400	113,500	114,087	0.065	0.077
	5*d*	31.3	0.658	72,200	72,300	72,599	0.07	0.082
	∞*d*	—	0				0.071	
	4*f*	37.7	1.0004	109,800	109,800	109,968		0.004
	f	—	0					
	5*g*	782	0.6401	70,240	—	70,258		0.001

RESULTS

The wave functions for the core electrons are listed in Tables II and V. The greatest discrepancy in the P_N's between these results and those obtained by McDougall is 0.006 for the 1*s*, 0.05 for the 2*s*, and 0.03 for the 2*p* functions. In all cases the effect of exchange is to contract the wave functions toward the nucleus. As tabulated, the 1*s*, 2*s* and 2*p* functions are normalized and orthogonal.

The wave functions for the series electron in Si IV are listed in Tables III, IV, VI, VII. The columns headed ∞*s*, ∞*p*, etc., give the wave functions for $\epsilon_{nl,\,nl}=0$. As tabulated, these functions are orthogonal to the core functions, but are not normalized. The normalization integrals are given in the first column of Table VIII. In the second column of this table are listed the $\epsilon_{nl,\,nl}$ values for the series electron in the different states. It has been proved previously[13] that when the perturbation of the core is neglected the energy parameters for a single electron outside of filled shells are the same as the term values. In the next column the corresponding values of the energy expressed in cm^{-1} instead of Rydbergs are listed. In the fourth column are the corresponding values calculated by McDougall[3] using the wave functions found by self-consistent field methods neglecting exchange but including exchange terms in the expression for the energy. The fifth column lists the observed values as given by Edlén and Soderquist.[22] The discrepancy between observed and calculated values is not more than two percent and is smaller for the higher n and l values. It is perhaps surprising to note that the more elaborate calculations reported here do not agree as well with experiment as those obtained by McDougall.[3] The reason for this would be difficult to assign without a detailed comparison of all of the terms appearing in the expression for the energy. The neglect of exchange in calculating the wave functions has two opposite effects which might well counteract each other. The neglect of exchange decreases the charge density due to the series electron in the regions near the nucleus, but on the other hand, it causes an expansion of the core wave functions. The expansion of the core functions decreases the screening action at a particular radius and hence increases the computed term value of the series electron.

A fairer estimate of the correctness of a set of wave functions is obtained by comparing not the energy values but the departures from the hydrogenic values which are measured by the constant q in the formula:

$$\epsilon_{nl,\,nl}=C^2/(n-q)^2, \tag{20}$$

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[22] B. Edlén and J. Soderquist, Zeits. f. Physik **87**, 217 (1933).

where $\epsilon_{nl,\,nl}$ is the term value in Rydbergs, C is the net charge of the core, and n is the principal quantum number. The values of q as computed by the present method and the q as found from experimental values of ϵ are listed in columns six and seven of Table VIII. It is interesting to note that the discrepancies in energy vary in both absolute and relative values from one state to another, but that the discrepancies in the q's are nearly the same for all levels although slightly less for the higher l values.

The spontaneous transition probabilities between two states can be found from formulas given in reference 13 and by Condon and Shortley.[23] Since the experimental data on Si IV are meager, the spontaneous transition probabilities have not been calculated. However, the integrals $\int_0^\infty rP_N(\alpha|r)P_N(\beta|r)dr$ for $s-p$ and $p-d$ transitions are listed in Table IX.

Spin-Orbit Interaction

The energy levels in a one-electron spectrum are known to be double with the two levels corresponding to $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$. Normally the level with the smaller value of j has the larger term value. The formula for the difference in wave number is[24]

$$\Delta W_{nl}=R\alpha^2(l+\tfrac{1}{2})\int_0^\infty \frac{Z(r)}{r^3}P_N{}^2(nl|r)dr, \qquad (21)$$

where R is the Rydberg constant, α is the fine structure constant, Z is the effective nuclear charge at radius r, and $P_N{}^2(nl|r)$ is the radial charge density for the type of wave function under consideration. If energies are measured in cm^{-1}, the constant $R\alpha^2$ has the numerical value of 5.822.

Table IX. *Values of the integrals* $\int_0^\infty rP_N(\alpha)P_N(\beta)dr$.

	3*s*	4*s*	5*s*	3*d*	4*d*	5*d*
3*p*	−1.944	0.975		−2.176	0.108	0.134
4*p*	0.223	−4.015	2.090	1.451	−4.36	−0.055
5*p*	0.133	0.321		0.293	3.08	−7.13

$\int_0^\infty rP(3s)P(\infty p)dr=1.123.$ $\int_0^\infty rP(4s)P(\infty p)dr=3.975.$
$\int_0^\infty rP(4p)P(\infty s)dr=6.395.$

Table X. *Spin-orbit separation.*

	3*p*	4*p*	5*p*	3*d*	4*d*	4*f*
Observed	460	162	75	1.57	0.08	1.3
Calculated	430	149	70	19	9	2.3

The integral occurring in Eq. (21) has been evaluated numerically, from the values tabulated in Tables V, VI, and VII. In Table X the computed and observed values are given. The experimental values are due to Edlén and Soderquist,[22] except the d levels which are taken from Bowen and Millikan.[25] For the p states the agreement between observed and computed separations is quite satisfactory but for the d and f levels the agreement is not even qualitative.[26] The cause of the small values of the separations in Si IV is presumably the same as the cause of the inverted doublets in the spectra of Na I, Mg II and Al III which are iso-electronic with Si IV. White[27] and Phillips[28] have suggested that the inverted doublets in these spectra can be accounted for by configuration interaction. Because of the effect of the valence electron, the core will not be spherically symmetric and besides the wave functions for the $2p^6$ configuration, a linear combination, including $2p^53p$, $2p^54p$, etc. must be used. Because the energies of these excited states are so high, their coefficients in the linear combination will be small. The important point for the present discussion is that the spin-orbit interaction for these states is large and negative,[29] so that even a small admixture of these states can give a comparatively large negative contribution to the spin-orbit interaction.

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[23] See reference 21, Chapter V, Sec. 9.

[24] See reference 21, Chapter V, Sec. 4.

[25] I. Bowen and R. A. Millikan, Phys. Rev. **25**, 301 (1925).

[26] The spin-orbit separations for Ca$^+$ 3d and 4p states have been computed from the wave functions reported in reference 13. The computed values were 85 cm^{-1} and 159 cm^{-1} for the 3d and 4p levels, respectively, compared with 60.8 and 222.8 as given by R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932).

[27] H. E. White, Phys. Rev. **40**, 316 (1932).

[28] Melba Phillips, Phys. Rev. **44**, 644 (1933). The authors wish to thank Dr. E. U. Condon for calling references 27 and 28 to their attention.

[29] G. H. Shortley, Phys. Rev. **40**, 185 (1932).