TRANSITION INTEGRALS FOR Si IV AND Ca II

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Received 13 July 1961

ABSTRACT. Atomic wave functions calculated using the Hartree–Fock equation and a polarization potential are used to obtain mean square radii of atomic orbitals for the ions Si^{3+} and Ca^{+}, and transition integrals for the Si IV and Ca II spectra. A table of radial wave functions for Ca^{+} is given. Our results are compared with those obtained from other wave functions, and in one case with an experimental value, and generally good agreement is obtained.

1. *Introduction.* In a previous paper (3) by one of us (A. S. D.) a method was described for improving the approximate calculation of energy levels for atomic configurations consisting of a set of closed shells and a single series electron. In the course of that work new radial wave functions were obtained for various states of the ions Si^{3+} and Ca^{+}. These ions are of considerable astrophysical interest, and we have therefore calculated transition integrals from the wave functions for various spectroscopic transitions (denoted in the customary way as Si IV and Ca II, respectively).

2. *Results for* Si IV. Wave functions were calculated for the ground state $1s^2\,2s^2\,2p^6\,3s$ of Si^{3+} and for the excited states $3p$, $3d$, $4s$, $4p$ and $4d$. Wave functions for these states had previously been calculated including exchange by Hartree, Hartree and Manning (5). The differences between our functions and theirs are quite small. The maximum differences (in the sense Douglas *minus* Hartree) between the normalized wave functions are: $3s$, $+0{\cdot}012$; $3p$, $-0{\cdot}014$; $3d$, $+0{\cdot}016$; $4s$, $-0{\cdot}015$; $4p$, $+0{\cdot}013$; $4d$, $-0{\cdot}017$. The general effect is a slight contraction of the wave functions, including of course a slight contraction in the positions of the maxima of the wave functions. As a further test of the effect of the introduction of a polarization potential on the wave functions we have computed the mean square radii of the orbitals from our wave functions. The results are given in Table 1, together with values of $\overline{r^2}$ calculated from

Table 1. *Mean square radii in* Si^{3+}

Series electron	$\overline{r^2}$ This paper	$\overline{r^2}$ S.C.F. with exchange	$\overline{r^2}$ Coulomb approximation
$3s$	3·89	3·99	3·78
$3p$	4·92	5·00	4·68
$3d$	6·86	7·03	7·03
$4s$	17·0	17·2	17·0
$4p$	20·9	21·4	20·8
$4d$	27·8	29·0	28·8

the Coulomb approximation of Bates and Damgaard ((2), footnote, p. 111). The largest change introduced by the present work is about 5 % in $\overline{r^2}$. In view of the smallness of these changes we are not publishing the detailed tables of radial wave functions.

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https://doi.org/10.1017/S0305004100036574 Published online by Cambridge University Press

The transition integrals are given in Table 2. The tabulated quantity is σ^2, where

$$\sigma^2 = \frac{1}{4l^2-1}\left(\int_0^\infty rP_iP_f dr\right)^2,$$

l is the greater of the two azimuthal quantum numbers involved in the transition, and P_i/r and P_f/r are the normalized radial wave functions. Transition probabilities and oscillator strengths may be obtained from σ^2 in the usual way ((1), pp. 51–62). Our results are compared with those given by Hartree, Hartree and Manning (5), and with results we have computed from the Coulomb approximation of Bates and Damgaard (2). The results obtained for the three methods are in very close agreement. This agreement gives some confidence in the reliability of the results, although it does not of course constitute strict proof of their accuracy.

Table 2. *Transition integrals for* Si IV

	σ^2		
Transition	This paper	S.C.F. with exchange	Coulomb approximation
$3s$–$3p$	1·23	1·26	1·19
$3p$–$3d$	0·31	0·32	0·30
$3s$–$4p$	0·017*	0·018	0·012
$3p$–$4s$	0·33	0·32	0·29
$3p$–$4d$	0·0015*	0·00078	0·00073
$3d$–$4p$	0·14	0·14	0·14
$4s$–$4p$	5·29	5·37	5·20
$4p$–$4d$	1·24	1·27	1·25

* Substantial cancellation occurs.

3. *Results for* Ca II. Wave functions were calculated for the ground state $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s$ of Ca^+ and for the excited states $4p$ and $3d$. Wave functions for these states had previously been calculated by Hartree and Hartree (4) with exchange. The differences between our radial functions and those of Hartree and Hartree are rather larger than for Si^{3+}. Their maximum values are (in the sense Douglas *minus* Hartree): $4s$, $-0{\cdot}036$; $4p$, $+0{\cdot}029$; $3d$, $-0{\cdot}044$. There is an appreciable contraction of the wave functions and a contraction in the positions of the maxima of the wave functions. The wave functions for Ca^+ have become something in the nature of a test case: the $3d$ wave function in particular is unusually sensitive to the assumptions made in the calculation. The wave functions are given in Table 3. Wave functions, including both exchange and polarization, have also been given by Trefftz and Biermann (10). Their $4s$ and $4p$ wave functions are very similar to ours, differing at most by a few units in the third decimal. Their $3d$ function is appreciably different from ours, being more compact, and differing from ours by up to 0·022. The values of $\overline{r^2}$ from our wave functions are given in Table 4, together with those from the wave functions of Trefftz and Biermann, and of Hartree and Hartree, and with values from the Coulomb approximation ((2), footnote, p. 111). The change in $\overline{r^2}$ for the $3d$ electron on introducing polarization is proportionally much greater than for the $4s$ and $4p$ electrons.

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Table 3. *Normalized radial wave functions for* Ca^+

r	$P(4s)$	$P(4p)$	$P(3d)$	r	$P(4s)$	$P(4p)$	$P(3d)$
0·01	0·042	0·002	—	1·4	+0·009	−0·082	0·614
0·02	0·068	0·007	0·0002	1·6	−0·125	+0·005	0·613
0·03	0·081	0·015	0·0006	1·8	−0·250	0·096	0·603
0·04	0·084	0·023	0·0013	2·0	−0·357	0·182	0·587
0·05	0·079	0·033	0·0024	2·2	−0·444	0·261	0·565
0·06	0·069	0·043	0·0040	2·4	−0·510	0·331	0·540
0·07	0·055	0·053	0·0059	2·6	−0·556	0·390	0·512
0·08	0·038	0·063	0·0083	2·8	−0·585	0·438	0·482
				3·0	−0·599	0·476	0·452
0·10	0·000	0·080	0·0145	3·2	−0·600	0·504	0·421
0·12	−0·038	0·095	0·022	3·4	−0·591	0·523	0·392
0·14	−0·072	0·106	0·032	3·6	−0·575	0·534	0·363
0·16	−0·102	0·113	0·043	3·8	−0·552	0·538	0·334
0·18	−0·124	0·117	0·055	4·0	−0·524	0·535	0·308
0·20	−0·140	0·117	0·069				
0·22	−0·150	0·114	0·083	4·5	−0·446	0·507	0·246
0·24	−0·153	0·108	0·098	5·0	−0·363	0·459	0·194
0·26	−0·151	0·100	0·114	5·5	−0·289	0·403	0·151
0·28	−0·144	0·090	0·130	6·0	−0·224	0·344	0·115
0·30	−0·133	0·078	0·147	6·5	−0·170	0·288	0·087
				7·0	−0·127	0·236	0·066
0·35	−0·092	0·044	0·189				
0·40	−0·038	0·005	0·231	8	−0·069	0·152	0·036
0·45	+0·019	−0·034	0·272	9	−0·035	0·094	0·020
0·50	0·076	−0·072	0·311	10	−0·018	0·056	0·010
0·55	0·128	−0·107	0·348	11	−0·009	0·032	0·005
0·60	0·172	−0·137	0·383	12	−0·004	0·018	0·003
				13	−0·002	0·010	0·002
0·7	0·237	−0·183	0·444	14	−0·001	0·005	0·002
0·8	0·266	−0·208	0·494	15	—	0·003	0·001
0·9	0·265	−0·215	0·533	16	—	0·001	0·001
1·0	0·239	−0·207	0·563	17	—	0·001	—
1·1	0·195	−0·187	0·584				
1·2	0·139	−0·158	0·599				

Table 4. *Mean square radii in* Ca^+

	$\overline{r^2}$			
Series electron	This paper	Trefftz and Biermann	S.C.F. with exchange	Coulomb approximation
$4s$	14·5	14·6	15·8	13·7
$4p$	21·8	21·7	22·9	20·4
$3d$	6·79	6·33	8·42	6·52

The transition integrals for Ca II spectral transitions are listed in Table 5. Both the dipole length and dipole velocity formulae have been used by Trefftz and Biermann and by ourselves. The values for self-consistent fields with and without exchange are taken from Hartree and Hartree (4) and from Bates and Damgaard (2); Zwann's results (12) are based on the use of an approximate core potential, and the Coulomb approximation tables ((2), together with a normalization correction due to Seaton (9))

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had to be judiciously extrapolated to obtain the $4p$–$3d$ value. Varsavsky's results (11) are based on Layzer's screening theory (6). The value by Ostrovskii and Penkin (8) is experimental, one of the relatively few absolute intensity measures for lines in the second spectrum of an atom. Finally, we have collected in Table 6 values of the radial integral needed in calculating the probability of the $4s$–$3d$ quadrupole transition.

Table 5. *Transition integrals for* Ca II

	σ^2			
	$4s$–$4p$		$4p$–$3d$	
	Length	Velocity	Length	Velocity
This paper	4·74	4·45	0·35	0·095
Trefftz and Biermann	4·76	4·47	0·31	0·11
S.C.F. with exchange	5·15	4·1	0·46	—
S.C.F. without exchange	6·11	—	1·11	—
Zwann	4·81	—	0·42	—
Coulomb approximation	4·38	—	0·25	—
Varsavsky	5·41	—	0·019	—
Ostrovskii and Penkin	5·14	—	—	—

Table 6. *Quadrupole integral in* Ca II

	$\int_0^\infty r^2 P(4s)\, P(3d)\, dr$
S.C.F. with exchange	−10·8
This paper	− 9·1
Trefftz and Biermann	− 8·6

Osterbrock (7) used the Hartree and Hartree wave functions for this purpose, and we have quoted his result together with those obtained from our wave functions and from the wave functions of Trefftz and Biermann. As usual it is difficult to assess the reliability of the transition integrals. One is tempted to select a representative value $\sigma^2 = 4{\cdot}9$ for the $4s$–$4p$ transition. It does seem as if in this case the Coulomb approximation gives a result below the true value. The value of σ^2 for the $4p$–$3d$ transition is obviously still rather uncertain. An experimental determination of this quantity is greatly desired.

The authors are indebted to the late Prof. D. R. Hartree for his interest and guidance during the earlier stages of this work. One of us (A. S. D.) is grateful to the Director and Staff of the University Mathematical Laboratory, Cambridge, for the use of their facilities.

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