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Excited-State Wave Functions, Excitation Energies, and Oscillator Strengths for Argon $(3p^5 4s)$†

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Solutions of the Hartree-Fock equations for the ^3P and ^1P terms of argon $(3p^5 4s)$ have been obtained. Wave functions are tabulated and results of computations of excitation energies and oscillator strengths are presented. The former fall within 4% of experimental values. Predicted oscillator strengths for absorption at 1049 A and 1067 A are 0.20 and 0.05, respectively, with an estimated error of 10 to 20%.

1. INTRODUCTION

IN the course of an investigation into the electronic properties of the solid state of argon, it has been found necessary to compute numerical wave functions for the low-lying excited electronic states of the free argon atom. Since there has been a recent surge of interest in various properties of the solid rare gases,[1] it was thought advisable to make these intermediate results available at once. In addition, relatively few calculations of excitation energies have been performed[2] and the problem of computing wave functions and splittings for strongly spin-orbit coupled terms is of independent interest, for reasons which will now be discussed briefly.

One of the simplest problems in theoretical spectroscopy is that of an electronic sp configuration, or its p^5s counterpart, outside closed shells. The Russell-Saunders terms which arise are ^3P and ^1P, and even if the spin-orbit interaction of the p electron or hole is sizable, simple secular equations for the exact energies within the configuration obtain. The resulting wave functions will have lost their definite multiplicity, however, and it becomes difficult to obtain simple Hartree-Fock equations by using the variational principle on radial wave functions. In the low-lying p^5s configurations of the excited rare gas atoms, the spin-orbit interaction, which is set equal to zero in writing the Fock equations for terms of definite multiplicity, is of the order of magnitude of the purely electrostatic splitting of the ^1P and ^3P terms. Although the actual magnitude of the spin-orbit interaction is sufficiently small that relativistic equations need not be used, it is of interest to determine whether the spin-orbit interaction may be calculated accurately by the use of perturbation theory using wave functions computed for pure LS terms. It is possible to use a "center of gravity" wave function,[3] which is exact with regard to the spin-orbit energy in its Hamiltonian (the center-of-gravity of a configuration's term values contains no spin-orbit interaction), but then a separate description of the electronic charge densities of the singlet and triplet states of the atom is lost, however well the spin-orbit interaction and the center of gravity of the levels are predicted. Such a separate description is especially important if the wave functions are needed as trial functions to compute interactions of the excited atom with other systems. In the present calculation it is found that the spin-orbit interaction is predicted, by using pure-^3P trial functions, to be within 1% of the observed value, and it is thus concluded that pure-LS wave functions are good descriptions of the actual wave functions even near the nucleus where spin-orbit effects are largest.

In part 2(a) the Fock equations are written for $3p^5 4s$ $(^3P,^1P)$ argon, and in part 2(b) their numerical solution is discussed and tables of wave functions are given. Part 3 is devoted to the computation of excitation energies and term splittings, including comparisons with other work and estimates of errors; and in part 4, oscillator strengths, polarizability, and decay times are treated.

2. HARTREE-FOCK EQUATIONS FOR A$(3p^5 4s)$

(a) Formulation

A concise method of writing the Hartree-Fock equations[4] for configurations involving unfilled shells was given by Shortley.[3] His method was used in the present calculation and the resulting equations for argon $(3p^5 4s)$, transcribed into atomic units,[4] are as follows:

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[1] See, for example, the review by E. R. Dobbs and G. O. Jones, Reports on Progress in Physics (The Physics Society, London, 1957), Vol. 20, p. 516.

[2] For a listing of available computations of atomic functions, see R. S. Knox, author in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 413.

[3] G. H. Shortley, Phys. Rev. **50**, 1072 (1936).

[4] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 (1928); V. Fock, Z. Physik **61**, 126 (1930). For recent developments and standard notation, see D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley and Sons, Inc., New York, 1957).

s Functions $(n=1,2,3)$

$$\left\{\frac{d^2}{dr^2}+\frac{2}{r}\left[18-\sum_{n'l'=1s}^{4s}\eta_{n'l'}Y^0(n'l')+Y^0(ns)\right]\right\}P_{ns}(r)$$

$$+\frac{2}{r}[Y^0(ns,1s)P_{1s}(r)+Y^0(ns,2s)P_{2s}(r)$$

$$+Y^1(ns,2p)P_{2p}(r)+Y^0(ns,3s)P_{3s}(r)$$

$$+\tfrac{5}{6}Y^1(ns,3p)P_{3p}(r)+\tfrac{1}{2}Y^0(ns,4s)P_{4s}(r)$$

$$-Y^0(ns)P_{ns}(r)]=\sum_{n''=1}^{4}\epsilon_{ns,\,n''s}P_{n''s}(r).$$

4s Function $(M=1$ for ${}^1P$, $M=3$ *for* ${}^3P)$

$$\left\{\frac{d^2}{dr^2}+\frac{2}{r}\left[18-\sum_{n'l'=1s}^{3p}\eta_{n'l'}Y^0(n'l')\right]\right\}P_{4s}(r)$$

$$+\frac{2}{r}[Y^0(4s,1s)P_{1s}(r)+Y^0(4s,2s)P_{2s}(r)$$

$$+Y^1(4s,2p)P_{2p}(r)+Y^0(4s,3s)P_{3s}(r)$$

$$+\tfrac{1}{3}MY^1(4s,3p)P_{3p}(r)]$$

$$=\epsilon_{4s,\,4s}P_{4s}(r)+2\sum_{n''=1}^{3}\epsilon_{n''s,\,4s}P_{n''s}(r).$$

2p Function

$$\left\{\frac{d^2}{dr^2}+\frac{2}{r}\left[18-\frac{1}{r}\sum_{n'l'=1s}^{4s}\eta_{n'l'}Y^0(n'l')+Y^0(2p)\right.\right.$$

$$\left.\left.+\tfrac{2}{5}Y^2(2p)\right]\right\}P_{2p}(r)+\frac{2}{3r}\{Y^1(2p,1s)P_{1s}(r)$$

$$+Y^1(2p,2s)P_{2s}(r)+Y^1(2p,3s)P_{3s}(r)+[\tfrac{5}{2}Y^0(3p,2p)$$

$$+Y^2(3p,2p)]P_{3p}(r)+\tfrac{1}{2}Y^1(2p,4s)P_{4s}(r)\}$$

$$=\epsilon_{2p2p}P_{2p}(r)+\epsilon_{2p3p}P_{3p}(r).$$

3p Function $(M=1$ *for* ${}^1P$, $M=3$ *for* ${}^3P)$

$$\left\{\frac{d^2}{dr^2}+\frac{2}{r}\left[18-\frac{1}{r}\sum_{n'l'=1s}^{4s}\eta_{n'l'}Y^0(n'l')+Y^0(3p)\right.\right.$$

$$\left.\left.+(8/25)Y^2(3p)\right]\right\}P_{3p}(r)+\frac{2}{3r}\{Y^1(3p,1s)P_{1s}(r)$$

$$+Y^1(3p,2s)P_{2s}(r)+Y^1(3p,3s)P_{3s}(r)+[3Y^0(3p,2p)$$

$$+(6/5)Y^2(3p,2p)]P_{2p}(r)+\tfrac{1}{5}MY^1(3p,4s)P_{4s}(r)\}$$

$$=\epsilon_{3p3p}P_{3p}(r)+(6/5)\epsilon_{2p3p}P_{2p}(r).$$

In these equations $P_{nl}(r)$ is the square root of the radial charge density of one nl electron, i.e., $rR_{nl}(r)$ where $R_{nl}(r)$ is the radial part of the total wave function. Each P_{nl} is normalized to unity. The Y functions are defined by

$$Y^\kappa(nl,n'l';r)=\int_0^\infty(r_1{}^\kappa/r_2{}^{\kappa+1})P_{nl}(r')P_{n'l'}(r')dr',$$

where r_1 and r_2 are the smaller and larger of r and r', respectively. We write $Y^\kappa(nl,nl)=Y^\kappa(nl)$ and drop the argument, r, for simplicity. The Y's and ϵ's, which are now standard in the literature on atomic function calculations,[4] are related to Shortley's cgs quantities λ and T^κ as follows:

$$\lambda_{nl,\,n'l'}=-\eta_{nl}(e^2/a_0)\epsilon_{nl,\,n'l'},$$

$$rT^\kappa(nl,n'l')=(e^2/a_0)Y^\kappa(nl,n'l'),$$

where η_{nl} is the number of electrons in the nl shell and $e^2/a_0=27.21$ electron volts.

(b) Numerical Results

An IBM Type 650 Magnetic Drum Data Processing Machine was employed to solve the equations of part (*a*) with the use of a program written by Piper. The program has been used by him in connection with a number of atoms and ions,[5] and since the main features of the program are given elsewhere,[6] the present section will be devoted to particular aspects of the argon calculations.

Existing ground state $[3p^6({}^1S_0)]$ wave functions, computed by Hartree and Hartree with exchange,[7] were taken as initial estimates for the excited-state functions $1s^2\cdots3p^5$. A $4s$ function was computed without exchange and used as a trial function for the $4s({}^3P)$ calculation with exchange. After a dozen iterations the $4s$ function became reasonably self-consistent, i.e., there was no greater than $\frac{1}{2}\%$ difference between the values of the quantity $1-Z_0(r)$ computed from the input and output radial functions in the final iteration at all values of r. Here $1-Z_0(r)$ is the amount of charge lying outside a sphere of radius r.[8] The core was then allowed to relax and it was found that only the $3s$ and $3p$ functions were changed sensibly from their ground state forms. After several more iterations including orthogonalization of the $3s$ and $4s$ functions to each other and to the other s functions and of the $3p$ to the $2p$, computation was stopped with the $(1-Z_0)$-in and $(1-Z_0)$-out consistent to within 0.1% for all shells.

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[5] Mn^{4+}: W. W. Piper and J. S. Prener, Phys. Rev. **100**, 1250(A) (1955); Ge$({}^3P)$: W. W. Piper, Bull. Am. Phys. Soc. Ser. II, **2**, 265 (1957); Cu^+ through Kr^{8+}, isoelectronic sequence: W. W. Piper, Bull. Am. Phys. Soc. Ser. II, **2**, 132 (1957), and paper to be published.

[6] W. W. Piper, Trans. Am. Inst. Elec. Engrs. **75**, Part I, 152 (1956).

[7] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).

[8] The choice of this quantity as a measure of self-consistency is discussed in Hartree's book, reference 4, Chap. 5.

TABLE I. Normalized radial wave functions $P_{nl}(r)$, calculated with exchange for the terms ^3P and ^1P of the $3p^54s$ configuration of neutral argon. Unit of length: $a_0=0.5292\times10^{-8}$ cm. The 1*s*, 2*s*, and 2*p* functions are identical to those of the ground-state configuration (see text for eigenvalues).

r	$3s(^3P,^1P)$	$3p(^3P,^1P)$	$4s(^3P)$	$4s(^1P)$
		Values of $P_{nl}(r)/r^{l+1}$		
0.000	13.57	52.72	2.866	2.537
0.0075	11.87	49.68	2.498	2.205
0.0150	10.31	46.77	2.168	1.911
0.0225	8.902	44.08	1.872	1.649
0.0300	7.639	41.50	1.606	1.414
		Values of $P_{nl}(r)$		
0.000	0.000	0.000	0.000	0.000
0.0075	0.089	0.003	0.019	0.0165
0.0150	0.155	0.0105	0.0325	0.029
0.0225	0.200	0.022	0.042	0.037
0.0300	0.229	0.037	0.048	0.0425
0.0375	0.244	0.0545	0.051	0.045
0.0450	0.247	0.0735	0.052	0.046
0.0525	0.2405	0.094	0.0505	0.044
0.0600	0.226	0.115	0.047	0.042
0.0750	0.179	0.158	0.037	0.033
0.0900	0.117	0.200	0.024	0.021
0.105	0.046	0.240	0.0095	0.008
0.120	−0.027	0.276	−0.006	−0.005
0.135	−0.099	0.307	−0.021	−0.019
0.150	−0.168	0.334	−0.036	−0.031
0.165	−0.2305	0.356	−0.049	−0.043
0.18	−0.286	0.372	−0.060	−0.053
0.21	−0.374	0.391	−0.079	−0.069
0.24	−0.429	0.391	−0.090	−0.079
0.27	−0.454	0.375	−0.095	−0.083
0.30	−0.452	0.346	−0.094	−0.082
0.33	−0.427	0.306	−0.088	−0.077
0.36	−0.383	0.2575	−0.078	−0.068
0.39	−0.325	0.2025	−0.065	−0.057
0.42	−0.2565	0.143	−0.049	−0.044
0.48	−0.0985	0.016	−0.015	−0.013
0.54	0.070	−0.114	0.022	0.019
0.60	0.236	−0.239	0.057	0.050
0.66	0.389	−0.3555	0.089	0.078
0.72	0.525	−0.460	0.116	0.1015
0.78	0.641	−0.552	0.138	0.121
0.84	0.7365	−0.630	0.1545	0.135
0.90	0.8115	−0.695	0.166	0.1455
		Values of $P_{nl}(r)$		
1.02	0.907	−0.788	0.1735	0.153
1.14	0.9415	−0.837	0.165	0.146
1.26	0.932	−0.853	0.144	0.129
1.38	0.892	−0.844	0.114	0.104
1.50	0.834	−0.816	0.079	0.0735
1.62	0.765	−0.776	0.040	0.040
1.74	0.692	−0.729	−0.001	0.005
1.86	0.618	−0.6775	−0.042	−0.031
2.10	0.4815	−0.572	−0.122	−0.102
2.34	0.365	−0.471	−0.194	−0.169
2.58	0.272	−0.382	−0.2585	−0.230
2.82	0.200	−0.306	−0.313	−0.283
3.06	0.145	−0.243	−0.3585	−0.3285
3.30	0.1045	−0.191	−0.395	−0.367
3.54	0.075	−0.1495	−0.423	−0.3975
3.78	0.053	−0.117	−0.444	−0.421
4.26	0.026	−0.070	−0.466	−0.451
4.74	0.013	−0.042	−0.467	−0.460
5.22	0.006	−0.025	−0.453	−0.4525
5.70	0.003	−0.015	−0.428	−0.434
6.18	0.0015	−0.009	−0.397	−0.407
6.66	0.0005	−0.0055	−0.362	−0.376
7.14	0.000	−0.0035	−0.326	−0.342
7.62		−0.002	−0.290	−0.307
8.58		−0.001	−0.223	−0.241
9.54		0.000	−0.166	−0.184
10.50			−0.121	−0.1365
11.46			−0.086	−0.100
12.42			−0.060	−0.072
13.38			−0.041	−0.052
14.34			−0.0275	−0.037
15.30			−0.0185	−0.027
17.22			−0.0085	−0.015
19.14			−0.004	−0.0085
$\epsilon(^3P)$	3.007	1.676	0.285	...
$\epsilon(^1P)$	3.023	1.689	...	0.273

The resulting 3*s*, 3*p*, and 4*s* functions for ^3P are given in Table I. Values of ϵ for ^3P functions not included in the tables are $\epsilon_{1s}=237.5$, $\epsilon_{2s}=25.25$, and $\epsilon_{2p}=19.74$.

In computing ^1P functions, the ^3P solutions were used as trial functions and, as expected, self-consistency to within the 0.1% criterion was reached quite rapidly. It was found that only the 4*s* function changed appreciably, and so it is the only one given in Table I. Note that it moved away from the core. For all practical purposes, the $3p(^1P)$ function is identical to the one listed in Table I, but one may make the following changes if he wishes: add -0.001 to all values of $P_{3p}(r)$ for $r=0.72$ through 1.86; add 0.002 for $r=2.82$ through 5.70; add 0.0005 for $r=6.18$ through 8.58. Thus the 3*p* function actually contracted a very small amount when the 4*s* expanded. This is to be expected because the shielding of the nucleus by the 4*s* electron decreased slightly. Values of the ^1P eigenvalues not shown in Table I are $\epsilon_{1s}=237.5$, $\epsilon_{2s}=25.26$, and $\epsilon_{2p}=19.76$.

It should be remarked that the great spatial extent of the 4*s* electrons taxed the ability of the program (limited only by the memory of the IBM 650) to retain accuracy near the origin in all shells while covering a large range in *r*. The present form of the program requires that $r_{64}=2040r_1$, where r_{64} is the largest (i.e., the 64th) value of *r*, a point at which "boundary conditions at infinity" are imposed, and r_1 is the first value of *r* used in outward integrations from the origin, which must be kept as small as possible for accuracy in the inner nodes. With a choice of $r_1=0.0075a_0$, which is already fairly large, it was found that the $4s$ functions were not vanishingly small at $r_{64}=15.30a_0$. Hence an "exponential" boundary condition was employed. As the iterations progressed, the boundary value of $P_{4s}(r)$ was adjusted so that the values of the function on the tail ($r \geqslant 10a_0$) tended to remain stationary around an exponential curve, i.e., the last few functional values were allowed to "pull the boundary value around" until both self-consistency and an exponential form were obtained. Only an estimated 0.05% of the charge of the $4s$ electron lies outside this boundary, so no corrections to the standard normalizing routines and potential calculations were necessary. The values of $P_{4s}(r)$ at $r=17.22a_0$ and $19.14a_0$, included in Table I for convenience, are simply extensions of the exponential tails and do not represent computed points. In the asymptotic equation $(d^2/dr^2+2/r-\epsilon)P=0$, it is not possible to neglect $2/r$ in the case of the $4s$ functions because ϵ_{4s} is small. Therefore the exponential dependence is not $\exp(-\epsilon^{\frac{1}{2}}r)$ but is reasonably close to it.

From experience in watching the values of ϵ as the iterations progressed, we estimate that an optimistic statement of accuracy in the final results for ϵ is ±0.1%. For example, the Hartree's ground-state wave functions were recomputed for testing purposes. An excellently self-consistent $3p$ wave function was obtained from the first iteration but with $\epsilon=1.183$ as compared to the Hartrees' value 1.181. The values of ϵ obtained from our recomputation were used in obtaining energy differences: $\epsilon_{3p}=1.183$ and $\epsilon_{3s}=2.554$ (previously 2.555).

3. EXCITATION ENERGIES AND TERM SPLITTING

(a) Numerical Results

Since the $1s$, $2s$, and $2p$ radial functions did not change from their values in the ground state, it was possible to use an invariant $1s^22s^22p^6$ core for the argon $(3p^54s-3p^6)$ energy difference $E\equiv E(^3P)-E(^1S)$. In units of e^2/a_0, this quantity is given by[3,9,10]

$$\begin{aligned}E=&-(\bar{\epsilon}_{3s}-\epsilon_{3s})-(\tfrac{5}{2}\bar{\epsilon}_{3p}-3\epsilon_{3p})-\tfrac{1}{2}\bar{\epsilon}_{4s}\\&-[\bar{F}^0(3s,3s)-F^0(3s,3s)]-\{[10\bar{F}^0(3s,3p)\\&-(5/3)\bar{G}^1(3s,3p)]-[12F^0(3s,3p)-2G^1(3s,3p)]\}\\&-\{[10\bar{F}^0(3p,3p)-\tfrac{4}{5}\bar{F}^2(3p,3p)]-[15F^0(3p,3p)\\&-(6/5)F^2(3p,3p)]\}-[2\bar{F}^0(3s,4s)-\bar{G}^0(3s,4s)]\\&\qquad\qquad-[5\bar{F}^0(3p,4s)-\bar{G}^1(3p,4s)],\end{aligned}$$

where the ϵ are standard Hartree eigenvalues and the F and G are Slater Coulomb and exchange integrals (defined in reference 9). A dash over F or G means computation is to be carried out with radial functions belonging to the triplet term, the remaining ones to be done with ground state functions. A similar convention is used for ϵ. The computed value of E is $0.411\ e^2/a_0=11.18$ ev. The over-all computational error, estimated to be twice that incurred by the ϵ's, is $\pm 0.02\ e^2/a_0=\pm 0.54$ ev. The experimental value is 11.70 ev. (See below.) Thus the computed value is correct to within 4½%, which is about equal to the estimated computational error.

If one takes an invariant core of $1s^2\cdots 3p^5$ in the computation of the electrostatic splitting parameter $\Delta\equiv E(^1P)-E(^3P)$, the result is simply[11] $-\frac{1}{2}(\tilde{\epsilon}_{4s}-\bar{\epsilon}_{4s})=0.17$ ev. If, on the other hand, an invariant core of $1s^2\cdots 3s^2$ is assumed and the very slight difference of the ^3P and ^1P $3p$ radial functions is taken into account, one obtains, with

$$\begin{aligned}\Delta=&-\tfrac{5}{2}(\tilde{\epsilon}_{3p}-\bar{\epsilon}_{3p})-\tfrac{1}{2}(\tilde{\epsilon}_{4s}-\bar{\epsilon}_{4s})-\{[15\tilde{F}^0(3p,3p)\\&-(6/5)\tilde{F}^2(3p,3p)]-[15\bar{F}^0(3p,3p)\\&\quad-(6/5)\bar{F}^2(3p,3p)]\}-\{[5\tilde{F}^0(3p,4s)-\tfrac{1}{3}\tilde{G}^1(3p,4s)]\\&\qquad\qquad-[5\bar{F}^0(3p,4s)-\bar{G}^1(3p,4s)]\},\end{aligned}$$

the value $\Delta=0.0054\ e^2/a_0=0.15$ ev. It is to be noted, however, that this "improvement" of -0.02 ev in the computed value of Δ is actually a small difference between two larger quantities, i.e., $-\frac{5}{2}(\tilde{\epsilon}_{3p}-\bar{\epsilon}_{3p})$ and the Slater integrals, each of which is again a small difference between still larger quantities. The last quantities, even if correct to within 0.1%, cannot help producing a large uncertainty in the correction to Δ, and this uncertainty is in fact much larger than the correction itself in this case. Therefore, the best computed value of Δ is taken to be 0.17 ev, best in the sense that large unavoidable errors have been eliminated. If the computational error is taken to be that incurred by the ϵ's, we obtain $\Delta=(0.17\pm 0.01)$ ev. This result is in agreement with the observed value $\Delta=0.18$ ev. (See below.) Table II shows the values of the F and G used in computing E and Δ.

Matrix elements of the spin-orbit interaction[12] contain certain integrals involving the singlet and

TABLE II. Slater integrals computed from the wave functions of Table I. Units: $e^2/a_0=27.21$ ev. The designation ^1S refers to $3p^6$ argon and ^3P and ^1P refer to LS terms of the $3p^54s$ configuration.

	^1S	^3P	^1P
$F^0(3s,3s)$	0.6353	0.6529	0.6529
$F^0(3s,3p)$	0.5865	0.6121	0.6121
$F^0(3p,3p)$	0.5467	0.5778	0.5789
$F^2(3p,3p)$	0.2719	0.2911	0.2920
$F^0(3s,4s)$	⋯	0.2158	0.2054
$F^0(3p,4s)$	⋯	0.2144	0.2043
$G^1(3s,3p)$	0.3855	0.4066	0.4066
$G^0(3s,4s)$	⋯	0.00616	0.00492
$G^1(3p,4s)$	⋯	0.01008	0.00808

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[9] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), Chaps. 6 and 13.

[10] When the wave functions of a particular shell are the same for two different atomic states, the ϵ of that shell may be different in the two states. However, it may be shown quite easily that this change is cancelled identically by the Slater integrals[9] involving that shell. The use of an "invariant core" is especially essential when changes in ϵ are so small, relative to ϵ, as to be incapable of computation within the accuracy of the Hartree-Fock solutions.

[11] For singlet quantities a tilde is used, e.g., $\tilde{\epsilon}_{3p}\equiv\epsilon_{3p}(^1P)$.

[12] Reference 9, p. 120.

triplet functions and charge distributions. Hence the parameters ζ_p and λ, defined as follows, were evaluated:

$$\zeta_p=(\hbar^2e^2/2m^2c^2)\int_0^\infty r^{-3}\bar{Z}(r)[\bar{P}_{3p}(r)]^2dr,$$

$$\lambda\zeta_p=(\hbar^2e^2/2m^2c^2)\int_0^\infty r^{-3}Z'(r)\tilde{P}_{3p}(r)\bar{P}_{3p}(r)dr.$$

Again a dash signifies association of a quantity with the triplet term and a tilde the singlet. $\bar{Z}(r)$ is the total charge inside a sphere of radius r excluding the $3p$ electron, and $Z'(r)$ is essentially the same as $\bar{Z}(r)$ but the contribution of each electron to the radial charge density is of the form $\tilde{P}\bar{P}$ instead of $\bar{P}^2$. The quantity $r^{-3}\bar{Z}(r)$ is the usual $r^{-1}(\partial V/\partial r)$ appearing in the Thomas-Frenkel expression[12] for the spin-orbit interaction. Numerical results were $\zeta_p=0.1157$ ev and $\lambda=1.001$, the latter computed with $Z'(r)=\bar{Z}(r)$ since the principal contribution to ζ_p and $\lambda\zeta_p$ was from the region $r\approx0.1a_0$, where $\bar{Z}(r)$ was of the order of 16 and unaffected by slight changes in $3p$ and $4s$ wave functions.

(b) Comparison with Experiment

Diagonalization of the complete Hamiltonian matrix for p^5s terms[13] yields the following set of energies [measured relative to $3p^6(^1S_0)$]:

$$\begin{aligned}
&E(^1P_1)=E+\tfrac{1}{2}\Delta+\tfrac{1}{4}\zeta_p+[(\tfrac{1}{2}\Delta-\tfrac{1}{4}\zeta_p)^2+\tfrac{1}{2}\lambda^2\zeta_p{}^2]^{\frac{1}{2}},\\
&E(^3P_0)=E+\zeta_p,\\
&E(^3P_1)=E+\tfrac{1}{2}\Delta+\tfrac{1}{4}\zeta_p-[(\tfrac{1}{2}\Delta-\tfrac{1}{4}\zeta_p)^2+\tfrac{1}{2}\lambda^2\zeta_p{}^2]^{\frac{1}{2}},\\
&E(^3P_2)=E-\tfrac{1}{2}\zeta_p.
\end{aligned}\tag{1}$$

E and Δ are the electrostatic energy parameters of the unperturbed (pure LS) states which were computed in part (a). Here a slight generalization of the formulas of reference 9 has been made[14] by the inclusion of λ, which multiplies ζ_p in the $^1P_1-{}^3P_1$ off-diagonal matrix element only. If the ^1P and ^3P radial functions of each electron are identical, then $\lambda=1$. King and Van Vleck first introduced $\lambda\neq1$ as an adjustable parameter rather than as a computed quantity. If one knows experimental values of the four energies (1), he may obtain unique values of E, Δ, ζ_p, and λ. This involves the reasonable assumption that higher combining terms do not appreciably upset the splitting of the low-lying levels (an energy separation of combining terms of the order of $2\frac{1}{2}$ ev exists in argon). The four parameters have been computed from experimental term values[15] for four rare gases and the results are given in Table III. Lines 2 and 3 of the table give a comparison between our computations of energy parameters and the values derived from the spectrum. As we have already seen, E and Δ are predicted within the estimated computational errors. The results for ζ_p and λ are in excellent agreement, both being predicted to within less than 1%.

TABLE III. Energy parameters of the lowest ^1P and ^3P terms of four of the rare gases. Notation: E, Δ, ζ_p, and λ are the pure-^3P excitation energy, electrostatic splitting factor, spin-orbit interaction, and King-Van Vleck parameter, respectively. $E(^1P_1)$ and $E(^3P_1)$ are actual term energies in the argon atom [see Eqs. (1)] and δ is their difference. All energies are measured in ev. S indicates derivation from the spectrum, and C, direct computation using Hartree-Fock wave functions.

Atom	Z	E	Δ	ζ_p	λ	$E(^1P_1)$	$E(^3P_1)$	δ	Source
Ne	10	16.743	0.1844	0.0642	0.9976	16.848	16.695	0.153	S
A	18	11.696	0.1801	0.1165	0.9962	11.828	11.601	0.227	S
A	18	11.18	0.169	0.1157	1.001	11.39	11.19	0.20	C
Kr	36	10.230	0.1984	0.4314	1.0013	10.643	10.032	0.611	S
Xe	54	8.814	0.2437	0.7546	1.0545	9.569	8.436	1.133	S

Most calculations of term energies from Hartree-Fock solutions have been concerned with absolute term values, and since few atoms have as high a fundamental excitation energy as argon, no direct comparisons are possible. In two calculations on $sp\,^1P$ and ^3P terms, namely, those for the Be and Ca atoms, Hartree and Hartree[16] obtained agreement in various energy differences ranging from 3 to 50%; these errors represent the cumulative effect of discrepancies of 10% or less in absolute term energies. Similar remarks hold for the term values and splittings in the O$^+$ and O^{++} computations by Hartree and Black.[17] The argon $^3P-{}^1S$ term difference is several-fold larger than any in the atoms just mentioned, so one might expect higher accuracy in the computation, say, on the order of $\frac{1}{2}$ to 5%. Thus our $4\frac{1}{2}$% error seems not to be unreasonable.

The good agreement between computed and observed values of ζ_p, the spin-orbit parameter, is encouraging and justifies the use of separate Hartree-Fock solutions of the uncoupled LS terms as trial functions, as discussed in the introduction. Other direct computations of spin-orbit splittings with Hartree-Fock functions have been in good agreement with experiment.[18] Both experiment and computation indicate that λ is practically unity in argon. This fact indicates that the wave functions which are important in the determination of ζ_p differ very little between the two terms and should therefore be practically as good as a center-of-gravity solution, which is "exact" with respect to spin-orbit interactions in the wave equation.

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[13] See reference 9, pp. 268, 271, 299, and 304.

[14] G. W. King and J. H. Van Vleck, Phys. Rev. **56**, 464 (1939).

[15] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1948), Vol. 1, p. 212.

[16] Be: D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A154**, 588 (1936); Ca: D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A164**, 167 (1938).

[17] D. R. Hartree and M. Black, Proc. Roy. Soc. (London) **A139**, 311 (1933). Their results are summarized in reference 9, p. 364.

[18] For example, 7% in the work of Hartree, Hartree, and Manning on Si^{+++} [Phys. Rev. **60**, 857 (1941)], and 7% in a computation on Fe by J. H. Wood and G. W. Pratt, Jr. [Phys. Rev. **107**, 995 (1957)] using wave functions computed with exchange by M. F. Manning and L. Goldberg [Phys. Rev. **53**, 662 (1938)]. These figures are the best of those reported by the authors; agreement is not as good for higher states of Si^{+++}, and Wood and Pratt found that "unrestricted" Hartree-Fock solutions gave a result 30% too large.

The excitation energies $E(^1P_1)$ and $E(^3P_1)$ have been calculated by using Eqs. (1) and are compared with experiment at the right side of Table III. The values agree to within 4%.

4. OSCILLATOR STRENGTHS

Eigenfunctions corresponding to the "$^1P_1$" and "$^3P_1$" terms of Eqs. (1) are really mixtures of pure $^1P_1$ and $^3P_1$ eigenfunctions. Therefore, each may be optically excited, according to the extent to which the pure $^1P_1$ function is mixed into it. Dipole matrix elements connecting the ground state of the atom, $\Psi(^1S_0)$, to any of the three singlet or three triplet $J=1$ states are readily found to be, respectively.

$$^1\mathbf{M}\equiv\int\Psi(^1S_0)^*\textstyle\sum_i e\mathbf{r}_i\Psi(^1P_1)d\tau$$
$$=(1+\zeta_p{}^2\mathfrak{F}^{-2})^{-\frac{1}{2}}(\tfrac{2}{3})^{\frac{1}{2}}KeR\mathbf{u},$$

and

$$^3\mathbf{M}\equiv\int\Psi(^1S_0)^*\textstyle\sum_i e\mathbf{r}_i\Psi(^3P_1)d\tau$$
$$=(1+\mathfrak{F}^2\zeta_p{}^{-2})^{-\frac{1}{2}}(\tfrac{2}{3})^{\frac{1}{2}}KeR\mathbf{u},$$

where $2^{-\frac{1}{2}}\lambda\mathfrak{F}\equiv\frac{1}{2}\Delta-\frac{1}{4}\zeta_p+[(\frac{1}{2}\Delta-\frac{1}{4}\zeta_p)^2+\frac{1}{2}\lambda^2\zeta_p{}^2]^{\frac{1}{2}}$, R is the radial factor $\int_0^\infty rP_{3p}(r)\tilde{P}_{4s}(r)dr$ of the dipole matrix element, $\sum_l$ runs over all electrons in the atom, and K is a correction factor which differs from unity because the ground- and excited-state radial functions "overlap," in the sense that the integral $\int_0^\infty P_{nl}(r)\tilde{P}_{n'l}(r)dr$ is not proportional to $\delta_{nn'}$. Finally $\mathbf{u}$ is a unit vector whose direction depends on which of the three P states is chosen for the dipole matrix element. Numerical values computed from the wave functions of part 2 are $K=0.939$, $R=0.699a_0$, and $\zeta_p\mathfrak{F}^{-1}=0.53$. The oscillator strengths[19] for absorption to the three degenerate states of the $^1P_1$ and $^3P_1$ terms are thus

$$^1f=\frac{8\pi^2m\nu(^1P_1,{}^1S_0)}{3h}\left(\frac{2K^2R^2}{1+\zeta_p{}^2\mathfrak{F}^{-2}}\right),$$

$$^3f=\frac{8\pi^2m\nu(^3P_1,{}^1S_0)}{3h}\left(\frac{2K^2R^2}{1+\mathfrak{F}^2\zeta_p{}^{-2}}\right),$$

where $\nu(B,A)$ is the transition frequency from state A to state B. If the transition energies $W_1=h\nu(^1P_1,{}^1S_0)$ and $W_3=h\nu(^3P_1,{}^1S_0)$ are expressed in electron volts and R in units of a_0, one obtains

$$^1f=\tfrac{4}{3}W_1K^2R^2/[(27.21)(1+\zeta_p{}^2\mathfrak{F}^{-2})],$$
$$^3f=\tfrac{4}{3}W_3K^2R^2/[(27.21)(1+\mathfrak{F}^2\zeta_p{}^{-2})].$$

These oscillator strengths have been computed on both an absolute basis (from wave functions alone) and on a semiempirical basis, i.e., from energy parameters obtained from the atomic spectrum in conjunction with the value of KR computed from wave functions. Results, along with predicted values of decay times, are given for these two cases in columns 2 and 3 of Table IV. To the author's knowledge, no experimental results are available to enable comparisons to be made. Probable errors of 20 and 40% have been estimated for the absolute calculations of oscillator strengths for the singlet and triplet terms, respectively. The latter figure is larger because of a stronger dependence of ^3f on the square of $\zeta_p\mathfrak{F}^{-1}$, which depends largely on Δ for its accuracy.

In view of the success[14] of the King-Van Vleck method in predicting oscillator strength ratios, it is felt that in the computation of strengths using spectral data, the radial factor of the dipole matrix element is the principal source of probable error. Although an exhaustive analysis of this error along the lines of that of Villars[20] will not be attempted, it is pertinent to compute the contributions of the $3p^54s$ configuration to the static polarizability, α, of the argon atom. The results of the computation are shown in Table IV along with the experimental value of α.[21] As in the case of oscillator strengths both an absolute and a semi-empirical computation were done. It is seen that the contribution to α by the $3p^54s$ configuration is 13% of the total, which is less than one-third of the fraction contributed by the first excited configuration of the hydrogen atom to its total polarizability. One might expect a result resembling that of the case of hydrogen, since all states of argon lying below the first ionization limit arise from $3p^5nl$ configurations and the distribution of configurations resembles that of a one-electron system.[9,15] On the other hand, Wolf and Herzfeld[22] concluded, from an analysis of the argon dispersion curve between 2400 A and 5800 A, that the resonance transitions contribute very little to dispersion, having a combined oscillator strength of about 0.03. They found that an effective transition of strength 4.6 to an energy slightly above

TABLE IV. Absorption oscillator strengths (f), decay times (τ), and static polarizability (α) associated with argon ($3p^6-3p^54s$). Theoretical values: (1) based solely on wave functions; (2) semi-empirical, based on experimental energies and a dipole matrix element computed from wave functions. The prefixed superscripts 1 and 3 refer to the "singlet" and "triplet" levels which give rise to lines at 1049 A and 1067 A, respectively.

Quantity	Theory (1)	Theory (2)	Experiment
^1f	0.17	0.200	...
$^1\tau$ (10^{-8} sec)	0.30	0.25	...
^3f	0.052	0.049	...
$^3\tau$ (10^{-8} sec)	1.05	1.02	...
α (due to ^1P, ^3P)	$1.38a_0{}^3$	$1.33a_0{}^3$	...
α (total)	...	...	$11.04a_0{}^3$

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[19] See, e.g., F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 643.

[20] D. S. Villars, J. Opt. Soc. Am. **42**, 552 (1952).

[21] The static polarizability was obtained by M. Born and W. Heisenberg [Z. Physik **23**, 388 (1924)] by extrapolation from data of C. Cuthbertson and M. Cuthbertson [Proc. Roy. Soc. (London) **A84**, 13 (1911)].

[22] K. L. Wolf and K. F. Herzfeld, *Handbuch der Physik* (Verlag-Julius Springer, Berlin, 1928), Vol. 20, Chap. 10, pp. 490 and 626.

the ionization limit gave a best fit to the dispersion curve. The reason for the discrepancy between their results and ours for the resonance oscillator strengths is not immediately clear. However, the Wolf-Herzfeld curve fitting covers only a relatively small region of the spectrum, and some clarification might result from an extension of their analysis toward the resonance energies.[23]

One final independent check on the wave functions used in this calculation should be mentioned. The ground state functions were found by the Hartrees[7] to give as accurate a prediction of the diamagnetic susceptibility as could be checked by existing experiments, i.e., to within 5 or 10%.

In view of the foregoing facts, the predicted absorption oscillator strengths as derived from a computed dipole matrix element and spectral term values, i.e., $^1f(1049\text{ A})=0.20$ and $^3f(1067\text{ A})=0.05$, may be considered reliable probably to within 10 or 20%.

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[23] The region covered is such that the denominator of the polarizability expression, $\nu_0^2-\nu^2$, varies by only 10% from one end of the region to the other, where ν_0 is the resonance frequency used in the analysis

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K Capture—Positron Ratios for First-Forbidden Transitions: Sb^{122}, Rb^{84}, I^{126}, As^{74}†

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The theory for the relative probabilities of *K*-electron capture and of positron emission is reinvestigated in the cases of allowed and first-forbidden transitions. Effects of screening and of finite nuclear size are discussed and calculated. Careful comparison is made between theory and available experimental results for allowed and "unique" first-forbidden transitions; details and results of a new measurement for the transition $\text{Sb}^{122}\rightarrow\text{Sn}^{122}$ ($\Delta J=2$, yes) are presented. Other types of first-forbidden transitions are analyzed in terms of the relative contributions of the various matrix elements which appear in the interaction combinations *S*, *T*, *P* and *V*, *A*; and the experimental results for the $\Delta J=0$, yes transitions in As^{74}, Rb^{84}, and I^{126} are discussed. Simple formulas are presented for the evaluation of the coefficients of the several matrix elements.

INTRODUCTION

THE study of the shapes of beta spectra has been used to gain insight into the nature of beta decay. Another valuable tool of similar nature is the study of the relative probabilities of *K* capture and positron emission in effecting transitions between characterized nuclear states. In this paper special emphasis will be placed on the comparison between theory and experiment for first-forbidden transitions. New experimental data will be presented for a first-forbidden transition with spin change two which occurs in the decay of Sb^{122}.

The compilations of theoretical beta-decay probabilities for the well-known five types of interactions, pure and mixed,[1] provide a simple basis from which one may easily calculate the theoretical *K*-capture probabilities. Using Pursey's notation for cross terms, the probability of *n*th-forbidden positron decay[2] is given by

$$P_{+}=\frac{1}{2\pi^3}\sum_{X,Y}G_XG_Y\tfrac{1}{2}(1+\delta_{XY})\times\int_1^{W_0}pW(W_0-W)^2F_0(W,Z)C_n(X,Y)dW$$

$$=\frac{1}{2\pi^3}\sum_{X,Y}G_XG_Y\tfrac{1}{2}(1+\delta_{XY})\mathcal{C}_n(X,Y)\times\int_1^{W_0}pW(W_0-W)^2F_0(W,Z)L_0dW,\quad(1)$$

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[1] E. J. Konopinski and G. E. Uhlenbeck, Phys. Rev. **60**, 308 (1941); E. Greuling, *ibid.* **61**, 568 (1942); A. M. Smith, *ibid.* **82**, 955 (1951); D. Pursey, Phil. Mag. **42**, 1193 (1951); M. E. Rose and R. K. Osborne, Phys. Rev. **93**, 1315 (1954).

[2] S. R. De Groot and H. A. Tolhoek, Physica **16**, 456 (1950).