Hartree-Fock Atomic Wave Functions from Cu^+ to Kr^{+8}

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Hartree-Fock atomic wave functions have been calculated and tabulated for the ground-state configurations of Cu^+ through Kr^{+8}. Interpolation functions for this configuration have also been tabulated.

INTRODUCTION

Atomic wave functions are of considerable interest not only for problems related to free atoms but also for certain investigations of molecular and crystalline aggregates of atoms. It was in connection with certain theoretical investigations of crystalline ZnS and ZnSe whose luminescent properties can be controlled by dilute substitutional impurities such as Cu, Ga, As, and Br that a need for atomic wave functions in this row of the periodic chart arose. Hartree-Fock wave functions were desired since they are well accepted as the best one-electron representation of many-electron atomic configurations. Since these functions had not appeared in the literature, a program for an IBM 650 computer was written to compute these functions.[1] Although the luminescent studies were not carried to a successful conclusion, the wave functions are of sufficient interest to be published.

In the Hartree-Fock scheme for a closed shell configuration, the total electronic wave function Ψ is a determinantal function made up of one-electron wave functions, $u(\zeta|i)$,

$$\Psi=(N!)^{-\frac{1}{2}}\sum_{p}(-1)^{p}\prod_{i=1}^{N}u(\zeta|i), \tag{1}$$

where N is the number of electrons in the configuration, p is the permutation operator for determinants, and

$$u(\zeta|i)=r_i^{-1}P(n_\zeta l_\zeta;r_i)S(l_\zeta m_\zeta;\theta_i,\phi_i)\chi(\zeta|i) \tag{2}$$

for the central-field case, where S is the spherical harmonic function and χ the spin function. If the energy expression

$$W=\int\Psi^*H\Psi d\tau \tag{3}$$

is minimized for an unrestricted radial wave function P after integrating over the angular and spin coordinates, then P is the Hartree-Fock radial wave function and, if r is measured in atomic units and $\epsilon_{\alpha\alpha}$ in rydbergs, is defined by an associated differential equation

$$\left[\frac{d^2}{dr^2}-\frac{l_\alpha(l_\alpha+1)}{r^2}+\frac{2Z}{r}\right]P_\alpha(r)$$
$$-\sum_{\nu}\sum_{k}\frac{2}{\eta_\alpha}(1+\delta_{\alpha\nu})A_{\alpha\nu}{}^{k}r^{-1}Y_{\nu\nu}{}^{k}(r)P_\alpha(r)$$
$$+\sum_{\nu}\sum_{k}\frac{2}{\eta_\alpha}(1+\delta_{\alpha\nu})B_{\alpha\nu}{}^{k}r^{-1}Y_{\alpha\nu}{}^{k}(r)P_\nu(r)$$
$$=\sum_{\nu}{}^{l}\,\epsilon_{\alpha\nu}P_\nu(r). \tag{4}$$

P_α is the radial wave function for all electrons in the shell $n=n_\alpha$ and $l=l_\alpha$, η_α is the number of electrons in this shell, and ν is the running index over all the shells in the configuration. Superscript l indicates the summation is limited to shells for which $l_\nu=l_\alpha$. Z is the nuclear charge. $A_{\alpha\nu}{}^{k}$ and $B_{\alpha\nu}{}^{k}$ are the appropriate sums of the Slater coefficients resulting from the angular integrations:

$$A_{\alpha\nu}{}^{k}=(1+\delta_{\alpha\nu})^{-1}\sum_{\zeta=\alpha,\xi=\nu}{}^{\prime}\;a^{k}(\zeta,\xi), \tag{5}$$

$$B_{\alpha\nu}{}^{k}=(1+\delta_{\alpha\nu})^{-1}\sum_{\zeta=\alpha,\xi=\nu}{}^{\pi\prime}\;b^{k}(\zeta,\xi), \tag{6}$$

where the prime denotes $\zeta\neq\xi$ and π limits the sum to electron pairs with parallel spins.

$$Y_{\alpha\nu}{}^{k}(r)=\int_0^r(\rho/r)^kP_\alpha P_\nu d\rho+\int_r^\infty(r/\rho)^{k+1}P_\alpha P_\nu d\rho. \tag{7}$$

For configurations containing only closed shells, $\epsilon_{\alpha\nu}=\epsilon_{\nu\alpha}$ and Hartree[2] has pointed out that there is a solution for which $\epsilon_{\alpha\nu}=0$ $(\alpha\neq\nu)$. He has suggested that this be called the standard solution. The standard solution is related to other solutions by an orthogonal transformation. Let $\mathbf{P}$ be an n vector whose components are the radial functions satisfying a set of Hartree-Fock equations:

$$\mathbf{P}^t=[P_{1s}(r),P_{2s}(r),P_{2p}(r),\cdots]. \tag{8}$$

The $\epsilon_{\alpha\nu}$'s associated with this solution may be written as a symmetric matrix

$$E=[\epsilon_{\alpha\nu}]. \tag{9}$$

There is always an orthogonal transformation Q which

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[1] W. W. Piper, Trans. Am. Inst. Elec. Engrs. **75** (1956), Part I (Communication and Electronics), p. 152.

[2] D. R. Hartree, *The Calculations of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957), p. 58.

TABLE I. Values of $C_{k\alpha\nu}$ for the configuration $(1s)^2\cdots(3d)^{10}$.

$\alpha\nu$ \ k	0	1	2	3
ss	2	0	0	0
sp	0	2	0	0
sd	0	0	2	0
ps	0	2/3	0	0
pp	2	0	4/5	0
pd	0	4/3	0	6/7
ds	0	0	2/5	0
dp	0	4/5	0	18/35

TABLE II. Values of $C_{k\alpha\alpha}$ for the configuration $(1s)^2\cdots(3d)^{10}$.

α \ k	2	4
s	0	0
p	2/5	0
d	2/7	2/7

will diagonalize E.

$$E'=Q^tEQ=\begin{bmatrix}\epsilon_{1s,1s} & 0 & \cdots \\ 0 & \epsilon_{2s,2s} & \cdots \\ \cdots & \cdots & \cdots\end{bmatrix}. \tag{10}$$

It can be easily shown that the standard solution $\mathbf{P}_s$ is

$$\mathbf{P}_s=Q\mathbf{P}. \tag{11}$$

The results reported in this paper have all been transformed to the standard solution.

NUMERICAL TECHNIQUES

The Hartree-Fock functions for a configuration with m closed shells are defined by m equations of the form

$$D^2P_\alpha(r)+g_\alpha(r)P_\alpha(r)=f_\alpha(r)+\sum_{\nu\neq\alpha}{}^{l}\,\epsilon_{\alpha\nu}P_\nu(r), \tag{12}$$

where

$$f_\alpha=-r^{-1}\sum_{k,\nu\neq\alpha}C_{k\alpha\nu}Y_{\alpha\nu}{}^k(r)P_\nu(r), \tag{13}$$

$$g_\alpha=2r^{-1}\Big[Z+\sum_{k\neq0}C_{k\alpha\alpha}Y_{\alpha\alpha}{}^k(r)-\sum_{\nu}(\eta_\nu-\delta_{\alpha\nu})Y_{\nu\nu}{}^0(r)\Big]$$
$$-r^{-2}[l_\alpha(l_\alpha+1)]-\epsilon_{\alpha\alpha}. \tag{14}$$

The values of the coefficients for the configuration $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}$ are given in Tables I and II. They may be derived from Eqs. (4)–(6) and are the appropriate ones for all of the configurations reported in this paper.

In order to solve the set of equations represented by Eq. (12), a set of starting functions P_α ($\alpha=1s, 2s, \cdots, 3d$) was assembled as a tabular array for a fixed list of values of the argument r. The computer program which was used requires that the increment of the argument is constant except that at the end of every s intervals (s = even integer) it doubles.

The set of wave functions was made self-consistent by choosing one of the functions to be improved. The coefficients were computed according to Eqs. (13) and (14) and a solution of Eq. (12) was obtained which replaced the input function for that shell. This procedure was repeated, selecting the wave function to be improved in a judicious sequence, until no significant change was obtained for any of the functions in the set.

The quadratures required to compute tables of the coefficients g and f for each iteration are carried out by a modification of Simpson's rule.

$$\int_r^{r+h}Fdr=\tfrac{1}{12}h[5F(r)+8F(r+h)-F(r+2h)], \tag{15a}$$

$$\int_{r+h}^{r+2h}Fdr=\tfrac{1}{12}h[-F(r)+8F(r+h)+5F(r+2h)]. \tag{15b}$$

This is equivalent to fitting three points to a parabola and reduces to Simpson's rule at the end of each even interval.

Numerov's difference equation[3] is used to integrate Eq. (12). An associated function,

$$z_i=(1+\tfrac{1}{12}h^2g_i)P_i, \tag{16a}$$

is used to carry the integration forward step by step,

$$z_{i+1}=(2-G_i)z_i-z_{i-1}+F_i, \tag{16b}$$

where

$$G_i=(1+\tfrac{1}{12}h^2g_i)^{-1}h^2g_i, \tag{16c}$$

and

$$F_i=\tfrac{1}{12}h^2(f_{i+1}+10f_i+f_{i-1}). \tag{16d}$$

The first neglected term of this difference equation is $(1/240)\delta^6P$. Since z is a function of the interval size, it is adjusted at each change of interval. The integration begins at $r=0$ and for s functions

$$z_0=\tfrac{1}{6}h^2Z\lim_{r\to0}(P/r), \tag{17a}$$

for p functions

$$z_0=-\tfrac{1}{6}h^2\lim_{r\to0}(P/r^2), \tag{17b}$$

and for $l_\nu>1$, $z_0=0$.

The solution of Eq. (12) must satisfy the conditions that $P(0)=P(\infty)=0$ and that P be normalized and be orthogonal to all shells of the same orbital angular momentum. The last condition is satisfied by making use of the $\epsilon_{\alpha\nu}$'s. The $\epsilon_{\alpha\nu}$'s are initially considered to be zero. The integration is carried outward from $r=0$ and the boundary condition at infinity is replaced by $P(r_t)=0$. The value of r_t is chosen so that P is not large enough to influence the significant figures of the solution. In order to satisfy this modified boundary condition, the associated homogeneous equation is also in-

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[3] See D. R. Hartree, *Numerical Analysis* (Oxford University Press, New York, 1952), p. 132.

TABLE III. Coefficients of the screening-constant equation for $(3d)^{10}$ configurations.

nl	σ_{32}	A (a.u.)$^{-1}$	$\bar{r}_{32}$ (a.u.)
$1s$	0.641	1.785	0.0478
$2s$	3.839	3.848	0.2131
$2p$	4.999	4.014	0.1852
$3s$	10.666	3.552	0.6328
$3p$	12.752	2.282	0.6494
$3d$	17.166	−4.515	0.7078

TABLE IV. Reduced wave function $P^*(s)$ for Ge^{+4} as defined by Eq. (25).

s	$(1s)^2$	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3p)^2$	$(3d)^{10}$
0.00	0.000	0.000	0.000	0.000	0.000	0.000
0.01	0.037	0.102	0.001	0.174	0.011	0.000
0.02	0.072	0.190	0.005	0.280	0.039	0.001
0.03	0.107	0.265	0.011	0.331	0.080	0.003
0.04	0.140	0.329	0.019	0.341	0.128	0.006
0.05	0.172	0.382	0.030	0.320	0.180	0.011
0.06	0.204	0.425	0.041	0.277	0.234	0.018
0.07	0.234	0.460	0.055	0.217	0.287	0.027
0.08	0.264	0.486	0.069	0.146	0.338	0.038
0.09	0.292	0.504	0.085	0.070	0.385	0.050
0.10	0.320	0.516	0.102	−0.009	0.428	0.064
0.12	0.372	0.521	0.139	−0.165	0.498	0.098
0.14	0.421	0.506	0.178	−0.305	0.544	0.136
0.16	0.467	0.474	0.220	−0.420	0.568	0.180
0.18	0.510	0.430	0.263	−0.507	0.570	0.226
0.20	0.549	0.374	0.307	−0.564	0.552	0.275
0.22	0.586	0.311	0.351	−0.594	0.517	0.325
0.24	0.620	0.241	0.395	−0.597	0.467	0.376
0.26	0.652	0.167	0.438	−0.578	0.405	0.427
0.28	0.681	0.091	0.480	−0.538	0.334	0.477
0.30	0.708	0.014	0.522	−0.483	0.256	0.525
0.35	0.765	−0.178	0.618	−0.293	0.042	0.638
0.40	0.810	−0.360	0.704	−0.062	−0.177	0.736
0.45	0.845	−0.523	0.778	0.176	−0.383	0.817
0.50	0.870	−0.665	0.840	0.400	−0.567	0.880
0.55	0.887	−0.783	0.889	0.599	−0.722	0.927
0.60	0.897	−0.878	0.926	0.765	−0.846	0.960
0.70	0.899	−1.002	0.969	0.994	−1.010	0.987
0.80	0.884	−1.053	0.976	1.103	−1.077	0.976
0.90	0.855	−1.050	0.955	1.119	−1.075	0.940
1.00	0.817	−1.007	0.914	1.075	−1.028	0.889
1.10	0.773	−0.940	0.860	0.993	−0.952	0.829
1.20	0.726	−0.858	0.797	0.894	−0.864	0.765
1.40	0.627	−0.682	0.662	0.684	−0.678	0.638
1.60	0.531	−0.519	0.532	0.498	−0.511	0.520
1.80	0.444	−0.382	0.417	0.350	−0.374	0.418
2.00	0.366	−0.275	0.320	0.241	−0.269	0.332
2.20	0.299	−0.195	0.243	0.163	−0.190	0.261
2.40	0.243	−0.137	0.182	0.109	−0.133	0.204
2.60	0.196	−0.095	0.136	0.071	−0.092	0.158
2.80	0.157	−0.066	0.101	0.047	−0.063	0.122
3.00	0.125	−0.045	0.074	0.030	−0.043	0.093
3.20	0.100	−0.031	0.055	0.020	−0.029	0.071
3.40	0.079	−0.022	0.040	0.012	−0.020	0.054
3.60	0.063	−0.015	0.029	0.008	−0.013	0.041
3.80	0.049	−0.010	0.022	0.005	−0.009	0.031
4.00	0.039	−0.007	0.016	0.003	−0.006	0.023
4.50	0.021	−0.003	0.007	0.001	−0.002	0.011
5.00	0.012	−0.001	0.004	0.000	−0.001	0.005
5.50	0.006	−0.000	0.002		−0.000	0.002
6.00	0.003		0.001			0.001
6.50	0.002		0.000			0.000
7.00	0.001					
7.50	0.000					

TABLE V. Linear correction to the reduced wave function for Ge^{+4}, $Q^*(s)$, as defined by Eq. (28).

s	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3p)^6$	$(3d)^{10}$
0.00	0.00	0.00	0.000	0.000	0.000
0.01	0.01	0.00	0.007	0.007	0.000
0.02	0.01	0.00	−0.015	0.022	0.002
0.03	0.01	0.01	−0.052	0.041	0.007
0.04	0.00	0.01	−0.097	0.059	0.014
0.05	−0.01	0.02	−0.143	0.074	0.025
0.06	−0.02	0.02	−0.185	0.084	0.039
0.07	−0.04	0.03	−0.220	0.088	0.055
0.08	−0.06	0.04	−0.247	0.087	0.074
0.09	−0.08	0.05	−0.265	0.080	0.094
0.10	−0.10	0.05	−0.273	0.068	0.116
0.12	−0.14	0.07	−0.265	0.029	0.162
0.14	−0.18	0.08	−0.231	−0.024	0.209
0.16	−0.22	0.09	−0.171	−0.086	0.254
0.18	−0.25	0.10	−0.099	−0.153	0.296
0.20	−0.28	0.11	−0.019	−0.219	0.332
0.22	−0.31	0.12	0.064	−0.283	0.362
0.24	−0.33	0.12	0.145	−0.342	0.385
0.26	−0.34	0.13	0.221	−0.392	0.402
0.28	−0.34	0.13	0.288	−0.437	0.413
0.30	−0.35	0.13	0.348	−0.473	0.416
0.35	−0.34	0.12	0.450	−0.526	0.402
0.40	−0.31	0.10	0.493	−0.530	0.359
0.45	−0.28	0.08	0.488	−0.498	0.297
0.50	−0.23	0.06	0.448	−0.439	0.224
0.55	−0.17	0.04	0.376	−0.363	0.148
0.60	−0.12	0.01	0.310	−0.285	0.074
0.70	−0.04	−0.03	0.152	−0.124	−0.056
0.80	0.02	−0.05	0.022	0.006	−0.150
0.90	0.07	−0.07	−0.067	0.096	−0.208
1.00	0.07	−0.07	−0.118	0.147	−0.234
1.10	0.08	−0.07	−0.124	0.156	−0.237
1.20	0.06	−0.06	−0.122	0.157	−0.222
1.40	0.03	−0.03	−0.073	0.099	−0.160
1.60	−0.01	0.01	−0.003	0.024	−0.083
1.80	−0.03	0.02	0.051	−0.041	−0.009
2.00	−0.04	0.05	0.085	−0.087	0.052
2.20	−0.04	0.04	0.099	−0.113	0.099
2.40	−0.04	0.05	0.102	−0.125	0.132
2.60	−0.03	0.05	0.098	−0.124	0.152
2.80	−0.03	0.04	0.084	−0.114	0.160
3.00	−0.02	0.03	0.072	−0.103	0.161
3.20	−0.01	0.03	0.057	−0.087	0.155
3.40	−0.00	0.03	0.046	−0.074	0.146
3.60		0.02	0.035	−0.060	0.134
3.80		0.01	0.027	−0.049	0.121
4.00		0.00	0.020	−0.039	0.108
4.50			0.008	−0.020	0.077
5.00			0.005	−0.012	0.052
5.50			0.002	−0.006	0.034
6.00			0.001	−0.003	0.021
6.50			0.000	−0.002	0.013
7.00				−0.001	0.008
7.50				−0.000	0.004

tegrated. The two equations then are

$$D^2P' + g_\alpha P' = f_\alpha, \tag{18a}$$

$$D^2Q + g_\alpha Q = 0, \tag{18b}$$

so that

$$P = P' + xQ \tag{18c}$$

is a solution of Eq. (18a) and x can be chosen to satisfy

TABLE VI. Interpolated and final values of σ. The final value appears on the top line.

	Cu^+	Zn^{+2}	Ga^{+3}	Ge^{+4}	As^{+5}	Se^{+6}	Br^{+7}	Kr^{+8}
1*s*	0.634	0.637 0.637	0.641 0.640	0.644	0.646 0.647	0.647 0.649	0.653 0.650	0.658 0.654
2*s*	3.745	3.778 3.778	3.811 3.809	3.842	3.874 3.869	3.903 3.893	3.931 3.917	3.957 3.940
2*p*	4.909	4.941 4.941	4.971 4.971	5.000	5.029 5.024	5.056 5.048	5.081 5.070	5.105 5.091
3*s*	10.346	10.483 10.460	10.594 10.567	10.665	10.731 10.758	10.775 10.843	10.810 10.922	10.837 10.996
3*p*	12.505	12.624 12.595	12.706 12.678	12.752	12.790 12.821	12.811 12.883	12.824 12.941	12.832 12.994
3*d*	18.259	17.778 17.779	17.431 17.434	17.166	16.953 16.948	16.778 16.767	16.629 16.612	16.501 16.477

$P(r_t)=0$. The integral of P^2 is

$$\int P^2 dr = 1+\delta, \tag{19}$$

in general, $\epsilon_{\alpha\alpha}$ in g_α is adjusted until δ is made sufficiently small (in this case 10^{-5}) by assuming a linear relation between δ and $\epsilon_{\alpha\alpha}$ and reintegrating Eqs. (18) until the function is normalized within the δ limit. After P has been normalized it is made orthogonal to the other P_ν functions which have the value of $l=l_\alpha$. For s functions, each P_ν is treated in sequence as though it were the only one. This introduces a small error which disappears as the configuration approaches self-consistency.

If P_β must be made orthogonal to P_α, Eq. (18a) is subtracted from Eq. (12) and the result is divided by $\epsilon_{\alpha\beta}$ to give

$$(D^2+g_\alpha)S_\beta = P_\beta, \tag{20a}$$

where

$$S_\beta = (P_\alpha - P)/\epsilon_{\alpha\beta}. \tag{20b}$$

Equation (20a) is solved in the same fashion as was Eq. (18a), and the orthogonal solution is then

$$P_\alpha = P + \epsilon_{\alpha\beta} S_\beta, \tag{21}$$

where

$$\epsilon_{\alpha\beta} = -\int PP_\beta \Big/ \int S_\beta P_\beta. \tag{22}$$

At this point P_α is tested to ensure that it is sufficiently close to a normalized function. If it is not, the function is entirely reconstructed with an adjusted value of $\epsilon_{\alpha\alpha}$. The normalization test no longer occurs at the point described under Eq. (19) but instead after the orthogonalization routine.

In some cases of weakly bound shells it is desirable to take a linear combination of the input and output functions. This serves to damp any oscillations in successive approximations to a function and was found to be quite useful for the 3*d* shell.

In order to reduce the results to the standard solution, Jacobi's method was used to determine the transformation matrix.[4] A program for utilizing this method on the IBM 650 has already been described by the author.[5]

STARTING FUNCTIONS

Hartree[6,7] has proposed a technique for interpolating wave functions which was used in the computations reported in this paper and was found to work exceedingly well. The mean radius $\bar{r}$ was used as a scaling factor. The mean radius is defined by

$$\bar{r} = \int_0^\infty rP^2 dr, \tag{23}$$

if the radial wave function P is normalized. A screening constant, σ, is defined which equates $\bar{r}$ to the mean radius of a hydrogenlike function with a nuclear charge of $(Z-\sigma)$:

$$\bar{r} = \tfrac{1}{2}[3n^2 - l(l+1)]/(Z-\sigma). \tag{24}$$

A reduced wave function is defined by

$$P^*(s) = \bar{r}^{\frac{1}{2}} P(r), \tag{25}$$

where

$$s = r/\bar{r}. \tag{26}$$

For complete shells Hartree has made the observation that σ and $P^*(s)$ vary almost linearly as functions of $\bar{r}$. Thus a given complete shell of a configuration identified by its nuclear charge, Z, should be related to the same shell of a known configuration with nuclear charge Z_0 by

$$\sigma_Z = \sigma_{Z_0} - A(\bar{r}_Z - \bar{r}_{Z_0}), \tag{27}$$

$$P_Z^*(s) = P_{Z_0}^*(s) + (\bar{r}_Z - \bar{r}_{Z_0})Q^*(s). \tag{28}$$

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[4] See R. T. Gregory, Math. Tables Aids Comp. **7**, 215 (1953).

[5] W. W. Piper, General Electric Research Laboratory Report 56-RL-1503A, 1956 (unpublished).

[6] D. R. Hartree, Proc. Cambridge Phil. Soc. **51**, 684 (1955).

[7] D. R. Hartree, Revs. Modern Phys. **30**, 63 (1958).

TABLE VII. Normalized self-consistent radial wave functions for Cu^+. The argument r is given in atomic units of length and the eigenvalues are in rydbergs.

r	$(1s)^2$	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3p)^6$	$(3d)^{10}$
0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.005	1.3280	0.4074	0.0164	0.1522	0.0061	0.0000
0.010	2.2984	0.6995	0.0613	0.2610	0.0225	0.0002
0.015	2.9841	0.8952	0.1284	0.3335	0.0472	0.0007
0.020	3.4447	1.0109	0.2127	0.3756	0.0780	0.0016
0.030	3.8761	1.0564	0.4159	0.3888	0.1520	0.0050
0.040	3.8805	0.9260	0.6435	0.3347	0.2341	0.0108
0.050	3.6454	0.6858	0.8766	0.2386	0.3167	0.0193
0.060	3.2902	0.3835	1.1021	0.1192	0.3946	0.0306
0.070	2.8894	0.0535	1.3115	−0.0098	0.4643	0.0447
0.080	2.4876	−0.2804	1.4993	−0.1384	0.5237	0.0613
0.090	2.1098	−0.6016	1.6629	−0.2599	0.5713	0.0804
0.100	1.7686	−0.8995	1.8010	−0.3697	0.6068	0.1017
0.120	1.2109	−1.4026	2.0017	−0.5434	0.6413	0.1499
0.140	0.8085	−1.7699	2.1106	−0.6501	0.6308	0.2039
0.160	0.5305	−2.0073	2.1425	−0.6918	0.5820	0.2618
0.180	0.3438	−2.1327	2.1137	−0.6761	0.5025	0.3218
0.200	0.2209	−2.1677	2.0397	−0.6135	0.3999	0.3825
0.220	0.1410	−2.1339	1.9339	−0.5145	0.2810	0.4427
0.240	0.0896	−2.0502	1.8076	−0.3893	0.1520	0.5014
0.260	0.0568	−1.9327	1.6697	−0.2466	0.0179	0.5578
0.280	0.0360	−1.7944	1.5271	−0.0942	−0.1169	0.6113
0.300	0.0224	−1.6462	1.3854	0.0613	−0.2491	0.6614
0.350	0.0073	−1.2709	1.0539	0.4369	−0.5538	0.7707
0.400	0.0024	−0.9395	0.7769	0.7567	−0.8042	0.8558
0.450	0.0008	−0.6744	0.5602	1.0009	−0.9929	0.9178
0.500	0.0003	−0.4740	0.3976	1.1686	−1.1224	0.9591
0.550	0.0001	−0.3283	0.2790	1.2677	−1.2000	0.9828
0.600	0.0000	−0.2252	0.1943	1.3103	−1.2348	0.9920
0.700		−0.1040	0.0930	1.2752	−1.2123	0.9785
0.800		−0.0479	0.0446	1.1475	−1.1153	0.9377
0.900		−0.0225	0.0217	0.9838	−0.9856	0.8825
1.000		−0.0109	0.0110	0.8171	−0.8481	0.8212
1.100		−0.0055	0.0058	0.6640	−0.7166	0.7585
1.200		−0.0030	0.0032	0.5311	−0.5977	0.6973
1.400		−0.0011	0.0013	0.3290	−0.4049	0.5845
1.600		−0.0005	0.0006	0.1981	−0.2682	0.4871
1.800		−0.0002	0.0004	0.1172	−0.1753	0.4047
2.000		−0.0001	0.0002	0.0686	−0.1136	0.3358
2.200		0.0000	0.0001	0.0399	−0.0733	0.2782
2.400			0.0000	0.0231	−0.0471	0.2302
2.600				0.0133	−0.0302	0.1902
2.800				0.0077	−0.0195	0.1570
3.000				0.0045	−0.0125	0.1294
3.200				0.0026	−0.0081	0.1065
3.400				0.0015	−0.0053	0.0875
3.600				0.0009	−0.0035	0.0718
3.800				0.0006	−0.0023	0.0588
4.000				0.0003	−0.0015	0.0481
4.500				0.0001	−0.0006	0.0289
5.000				0.0000	−0.0002	0.0173
5.500					−0.0001	0.0102
6.000					0.0000	0.0060
6.500						0.0035
7.000						0.0020
7.500						0.0012
8.000						0.0007
8.500						0.0004
9.000						0.0002
9.500						0.0001
10.000						0.0000
$\epsilon_{\alpha\alpha}$	658.278	82.252	71.856	10.645	7.283	1.621
$\lim_{r\to 0}\left(\frac{P}{r^{l+1}}\right)$	307.	94.	710.	35.	258.	243.

TABLE VIII. Normalized self-consistent radial wave functions for Zn^{+2}. The argument r is given in atomic units of length and the eigenvalues are in rydbergs.

r	$(1s)^2$	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3p)^6$	$(3d)^{10}$
0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.005	1.3910	0.4283	0.0180	0.1614	0.0067	0.0000
0.010	2.3954	0.7313	0.0669	0.2753	0.0250	0.0003
0.015	3.0947	0.9302	0.1399	0.3495	0.0521	0.0009
0.020	3.5547	1.0432	0.2311	0.3909	0.0860	0.0020
0.030	3.9604	1.0718	0.4498	0.3974	0.1666	0.0061
0.040	3.9260	0.9164	0.6927	0.3328	0.2552	0.0131
0.050	3.6519	0.6490	0.9391	0.2250	0.3434	0.0234
0.060	3.2639	0.3212	1.1751	0.0946	0.4255	0.0370
0.070	2.8384	−0.0308	1.3918	0.0438	0.4978	0.0538
0.080	2.4199	−0.3817	1.5839	−0.1797	0.5580	0.0736
0.090	2.0325	−0.7149	1.7486	−0.3059	0.6049	0.0962
0.100	1.6874	−1.0199	1.8851	−0.4179	0.6380	0.1213
0.120	1.1332	−1.5239	2.0762	−0.5892	0.6640	0.1778
0.140	0.7423	−1.8786	2.1695	−0.6857	0.6412	0.2405
0.160	0.4779	−2.0949	2.1826	−0.7119	0.5777	0.3072
0.180	0.3040	−2.1950	2.1342	−0.6777	0.4826	0.3757
0.200	0.1917	−2.2038	2.0414	−0.5952	0.3643	0.4444
0.220	0.1201	−2.1449	1.9186	−0.4768	0.2307	0.5118
0.240	0.0750	−2.0388	1.7777	−0.3334	0.0885	0.5768
0.260	0.0467	−1.9024	1.6278	−0.1749	−0.0569	0.6385
0.280	0.0291	−1.7489	1.4760	−0.0092	−0.2010	0.6964
0.300	0.0178	−1.5892	1.3277	0.1568	−0.3402	0.7500
0.350	0.0055	−1.1988	0.9888	0.5463	−0.6538	0.8640
0.400	0.0018	−0.8668	0.7140	0.8648	−0.9021	0.9490
0.450	0.0006	−0.6092	0.5047	1.0970	−1.0807	1.0070
0.500	0.0002	−0.4196	0.3513	1.2463	−1.1954	1.0417
0.550	0.0000	−0.2851	0.2420	1.3243	−1.2559	1.0569
0.600		−0.1920	0.1656	1.3455	−1.2732	1.0568
0.700		−0.0857	0.0767	1.2729	−1.2186	1.0237
0.800		−0.0384	0.0358	1.1181	−1.0967	0.9638
0.900		−0.0176	0.0171	0.9380	−0.9497	0.8912
1.000		−0.0084	0.0085	0.7631	−0.8015	0.8144
1.100		−0.0043	0.0045	0.6079	−0.6645	0.7383
1.200		−0.0023	0.0025	0.4767	−0.5437	0.6655
1.400		−0.0008	0.0010	0.2837	−0.3543	0.5345
1.600		−0.0004	0.0005	0.1638	−0.2252	0.4249
1.800		−0.0002	0.0003	0.0928	−0.1409	0.3351
2.000		−0.0001	0.0002	0.0519	−0.0872	0.2627
2.200		0.0000	0.0001	0.0288	−0.0536	0.2049
2.400			0.0001	0.0158	−0.0327	0.1590
2.600			0.0000	0.0086	−0.0198	0.1228
2.800				0.0047	−0.0121	0.0946
3.000				0.0026	−0.0073	0.0725
3.200				0.0014	−0.0045	0.0554
3.400				0.0008	−0.0027	0.0422
3.600				0.0004	−0.0017	0.0320
3.800				0.0002	−0.0010	0.0242
4.000				0.0001	−0.0006	0.0183
4.500				0.0000	−0.0002	0.0090
5.000					−0.0001	0.0043
5.500					0.0000	0.0020
6.000						0.0010
6.500						0.0005
7.000						0.0002
7.500						0.0001
8.000						0.0000
$\epsilon_{\alpha\alpha}$	708.185	90.197	79.336	12.767	9.186	3.068
$\lim_{r\to 0}\left(\frac{P}{r^{l+1}}\right)$	323.	100.	777.	37.	290.	303.

TABLE IX. Normalized self-consistent radial wave functions for Ga^{+3}. The argument r is given in atomic units of length and the eigenvalues are in rydbergs.

r	$(1s)^2$	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3p)^6$	$(3d)^{10}$
0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.005	1.4546	0.4496	0.0197	0.1710	0.0074	0.0000
0.010	2.4925	0.7633	0.0729	0.2900	0.0276	0.0003
0.015	3.2041	0.9649	0.1519	0.3658	0.0574	0.0011
0.020	3.6621	1.0747	0.2504	0.4060	0.0945	0.0024
0.030	4.0399	1.0850	0.4848	0.4052	0.1822	0.0073
0.040	3.9658	0.9037	0.7430	0.3296	0.2776	0.0157
0.050	3.6528	0.6086	1.0027	0.2098	0.3715	0.0279
0.060	3.2324	0.2552	1.2488	0.0680	0.4577	0.0440
0.070	2.7838	−0.1179	1.4722	−0.0796	0.5323	0.0637
0.080	2.3505	−0.4849	1.6676	−0.2224	0.5929	0.0870
0.090	1.9556	−0.8285	1.8324	−0.3527	0.6385	0.1134
0.100	1.6074	−1.1394	1.9665	−0.4663	0.6688	0.1425
0.120	1.0589	−1.6412	2.1462	−0.6333	0.6849	0.2077
0.140	0.6804	−1.9806	2.2225	−0.7180	0.6484	0.2795
0.160	0.4298	−2.1738	2.2160	−0.7270	0.5691	0.3551
0.180	0.2684	−2.2474	2.1476	−0.6730	0.4574	0.4321
0.200	0.1654	−2.2300	2.0364	−0.5702	0.3232	0.5084
0.220	0.1017	−2.1466	1.8972	−0.4321	0.1748	0.5825
0.240	0.0624	−2.0189	1.7424	−0.2708	0.0195	0.6533
0.260	0.0381	−1.8653	1.5819	−0.0971	−0.1367	0.7197
0.280	0.0234	−1.6978	1.4218	0.0811	−0.2895	0.7813
0.300	0.0143	−1.5275	1.2677	0.2567	−0.4352	0.8374
0.350	0.0042	−1.1265	0.9246	0.6563	−0.7547	0.9536
0.400	0.0012	−0.7978	0.6545	0.9693	−0.9977	1.0357
0.450	0.0004	−0.5488	0.4533	1.1870	−1.1641	1.0873
0.500	0.0001	−0.3705	0.3095	1.3161	−1.2621	1.1130
0.550	0.0000	−0.2469	0.2093	1.3717	−1.3042	1.1180
0.600		−0.1631	0.1406	1.3713	−1.3033	1.1069
0.700		−0.0706	0.0632	1.2616	−1.2160	1.0516
0.800		−0.0303	0.0284	1.0825	−1.0705	0.9715
0.900		−0.0136	0.0133	0.8876	−0.9072	0.8808
1.000		−0.0064	0.0065	0.7067	−0.7498	0.7887
1.100		−0.0032	0.0034	0.5509	−0.6087	0.6999
1.200		−0.0017	0.0019	0.4226	−0.4875	0.6168
1.400		−0.0006	0.0008	0.2405	−0.3039	0.4719
1.600		−0.0003	0.0004	0.1324	−0.1843	0.3557
1.800		−0.0001	0.0002	0.0715	−0.1098	0.2649
2.000		−0.0001	0.0001	0.0379	−0.0644	0.1953
2.200		0.0000	0.0001	0.0198	−0.0374	0.1428
2.400			0.0000	0.0103	−0.0215	0.1036
2.600				0.0054	−0.0124	0.0747
2.800				0.0028	−0.0071	0.0535
3.000				0.0014	−0.0040	0.0381
3.200				0.0007	−0.0022	0.0269
3.400				0.0003	−0.0012	0.0189
3.600				0.0002	−0.0007	0.0134
3.800				0.0001	−0.0004	0.0093
4.000				0.0000	−0.0002	0.0065
4.500					−0.0001	0.0026
5.000					0.0000	0.0010
5.500						0.0004
6.000						0.0001
6.500						0.0000
ϵ_{aa}	760.178	98.748	87.418	15.195	11.396	4.818
$\lim_{r\to 0}\left(\frac{P}{r^{l+1}}\right)$	340.	105.	849.	40.	322.	365.

Hartree's wave functions[8] for Cu$^+$ were first verified with the program here described, and the result is listed in Table VII. Wave functions for Mn^{+2} were also available.[9] The mean radius for each shell of these two

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[8] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

[9] D. R. Hartree, Proc. Cambridge Phil. Soc. **51**, 126 (1954).

TABLE X. Normalized self-consistent radial wave functions for Ge^{+4}. The argument r is given in atomic units of length and the eigenvalues are in rydbergs.

r	$(1s)^2$	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3p)^6$	$(3d)^{10}$
0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.005	1.5185	0.4708	0.0214	0.1811	0.0082	0.0001
0.010	2.5890	0.7947	0.0791	0.3054	0.0304	0.0004
0.015	3.3116	0.9983	0.1644	0.3827	0.0631	0.0013
0.020	3.7663	1.1040	0.2703	0.4217	0.1037	0.0028
0.030	4.1139	1.0946	0.5210	0.4128	0.1988	0.0086
0.040	3.9984	0.8861	0.7947	0.3253	0.3013	0.0185
0.050	3.6468	0.5631	1.0673	0.1928	0.4010	0.0328
0.060	3.1960	0.1844	1.3231	0.0395	0.4913	0.0516
0.070	2.7255	−0.2093	1.5525	−0.1176	0.5679	0.0745
0.080	2.2788	−0.5912	1.7503	−0.2670	0.6286	0.1014
0.090	1.8772	−0.9444	1.9146	−0.4012	0.6724	0.1318
0.100	1.5285	−1.2588	2.0452	−0.5156	0.6991	0.1653
0.120	0.9878	−1.7553	2.2119	−0.6768	0.7041	0.2396
0.140	0.6228	−2.0767	2.2698	−0.7477	0.6526	0.3206
0.160	0.3861	−2.2449	2.2430	−0.7380	0.5564	0.4052
0.180	0.2366	−2.2911	2.1545	−0.6629	0.4273	0.4905
0.200	0.1437	−2.2465	2.0246	−0.5386	0.2763	0.5742
0.220	0.0869	−2.1388	1.8696	−0.3802	0.1129	0.6547
0.240	0.0523	−1.9911	1.7022	−0.2012	−0.0552	0.7306
0.260	0.0314	−1.8209	1.5319	−0.0125	−0.2218	0.8010
0.280	0.0189	−1.6417	1.3652	0.1771	−0.3824	0.8653
0.300	0.0111	−1.4638	1.2073	0.3605	−0.5331	0.9231
0.350	0.0032	−1.0549	0.8620	0.7675	−0.8562	1.0390
0.400	0.0009	−0.7302	0.5975	1.0730	−1.0917	1.1158
0.450	0.0003	−0.4922	0.4058	1.2723	−1.2428	1.1586
0.500	0.0000	−0.3258	0.2719	1.3785	−1.3221	1.1734
0.550		−0.2131	0.1806	1.4105	−1.3444	1.1665
0.600		−0.1385	0.1194	1.3874	−1.3242	1.1430
0.700		−0.0578	0.0519	1.2416	−1.2045	1.0641
0.800		−0.0245	0.0229	1.0382	−1.0350	0.9627
0.900		−0.0108	0.0105	0.8314	−0.8575	0.8545
1.000		−0.0050	0.0051	0.6465	−0.6927	0.7483
1.100		−0.0025	0.0027	0.4922	−0.5495	0.6488
1.200		−0.0013	0.0015	0.3688	−0.4300	0.5580
1.400		−0.0005	0.0006	0.1998	−0.2553	0.4051
1.600		−0.0002	0.0003	0.1046	−0.1471	0.2884
1.800		−0.0001	0.0001	0.0535	−0.0829	0.2021
2.000		0.0000	0.0001	0.0269	−0.0461	0.1399
2.200			0.0000	0.0134	−0.0253	0.0957
2.400				0.0065	−0.0137	0.0649
2.600				0.0031	−0.0073	0.0435
2.800				0.0015	−0.0039	0.0290
3.000				0.0007	−0.0021	0.0192
3.200				0.0004	−0.0011	0.0127
3.400				0.0002	−0.0006	0.0083
3.600				0.0001	−0.0003	0.0054
3.800				0.0000	−0.0002	0.0035
4.000					−0.0001	0.0023
4.500					0.0000	0.0007
5.000						0.0002
5.500						0.0001
6.000						0.0000
$\epsilon_{\alpha\alpha}$	813.890	107.874	96.066	17.931	13.894	6.838
$\lim_{r\to 0}\left(\frac{P}{r^{l+1}}\right)$	356.	111.	927.	43.	357.	432.

configurations was computed, σ calculated from Eq. (24), and P^* determined according to Eq. (25). With $Z_0=29$ (Cu^+) and $Z=25$ (Mn^{+2}), the constant A and the function Q^* were determined in Eqs. (27) and (28). The values of $\bar{r}$ were next determined for Ge^{+4} by substituting $Z=32$ into Eq. (24) and simultaneously solving this equation and Eq. (27) by an iterative process. This result was then used to calculate $(P^*)_{Ge}$ by Eq.

TABLE XI. Normalized self-consistent radial wave functions for As^{+5}. The argument r is given in atomic units of length and the eigenvalues are in rydbergs.

r	$(1s)^2$	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3p)^6$	$(3d)^{10}$
0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.005	1.5831	0.4922	0.0232	0.1914	0.0091	0.0001
0.010	2.6857	0.8262	0.0855	0.3208	0.0334	0.0005
0.015	3.4184	1.0314	0.1775	0.3995	0.0692	0.0015
0.020	3.8684	1.1323	0.2911	0.4369	0.1133	0.0033
0.030	4.1837	1.1021	0.5582	0.4192	0.2162	0.0101
0.040	4.0268	0.8659	0.8474	0.3193	0.3258	0.0216
0.050	3.6366	0.5145	1.1327	0.1739	0.4312	0.0382
0.060	3.1555	0.1108	1.3976	0.0091	0.5253	0.0599
0.070	2.6649	−0.3025	1.6322	−0.1571	0.6035	0.0863
0.080	2.2066	−0.6981	1.8317	−0.3125	0.6637	0.1171
0.090	1.8005	−1.0588	1.9943	−0.4495	0.7049	0.1517
0.100	1.4515	−1.3761	2.1207	−0.5641	0.7274	0.1897
0.120	0.9200	−1.8642	2.2727	−0.7175	0.7199	0.2735
0.140	0.5689	−2.1653	2.3113	−0.7728	0.6522	0.3640
0.160	0.3460	−2.3071	2.2636	−0.7430	0.5381	0.4576
0.180	0.2081	−2.3252	2.1550	−0.6458	0.3911	0.5510
0.200	0.1234	−2.2546	2.0076	−0.5000	0.2237	0.6417
0.220	0.0732	−2.1239	1.8377	−0.3218	0.0456	0.7280
0.240	0.0433	−1.9568	1.6584	−0.1256	−0.1347	0.8083
0.260	0.0254	−1.7724	1.4797	0.0766	−0.3107	0.8818
0.280	0.0152	−1.5824	1.3072	0.2766	−0.4781	0.9480
0.300	0.0089	−1.3972	1.1458	0.4670	−0.6332	1.0065
0.350	0.0024	−0.9849	0.8014	0.8766	−0.9560	1.1195
0.400	0.0006	−0.6680	0.5445	1.1695	−1.1801	1.1886
0.450	0.0001	−0.4409	0.3625	1.3487	−1.3140	1.2205
0.500	0.0000	−0.2862	0.2384	1.4308	−1.3730	1.2227
0.550		−0.1836	0.1553	1.4387	−1.3747	1.2025
0.600		−0.1169	0.1008	1.3937	−1.3353	1.1659
0.700		−0.0475	0.0426	1.2131	−1.1836	1.0625
0.800		−0.0192	0.0181	0.9898	−0.9934	0.9408
0.900		−0.0084	0.0082	0.7733	−0.8035	0.8163
1.000		−0.0038	0.0039	0.5869	−0.6338	0.6980
1.100		−0.0019	0.0020	0.4359	−0.4908	0.5903
1.200		−0.0010	0.0011	0.3184	−0.3745	0.4945
1.400		−0.0003	0.0004	0.1638	−0.2111	0.3396
1.600		−0.0001	0.0002	0.0810	−0.1150	0.2278
1.800		0.0000	0.0001	0.0393	−0.0613	0.1500
2.000			0.0000	0.0186	−0.0320	0.0972
2.200				0.0087	−0.0164	0.0621
2.400				0.0043	−0.0084	0.0393
2.600				0.0023	−0.0043	0.0246
2.800				0.0010	−0.0021	0.0153
3.000				0.0004	−0.0010	0.0093
3.200				0.0002	−0.0005	0.0056
3.400				0.0000	−0.0002	0.0033
3.600					−0.0001	0.0020
3.800					0.0000	0.0012
4.000						0.0007
4.500						0.0002
5.000						0.0000
$\epsilon_{\alpha\alpha}$	870.306	117.552	105.274	20.917	16.645	9.120
$\lim_{r\to 0}\left(\frac{P}{r^{l+1}}\right)$	373.	116.	1008.	45.	394.	514.

(28) and P_{Ge} by Eq. (25) for each shell except the $3d$. For the $3d$ shell, σ was taken the same for Cu^+ and Ge^{+4}, Eq. (24) was solved for $\bar{r}$, and P was obtained directly from Eq. (25) and $P^*(3d,Cu^+)$.

The starting functions for Ge^{+4} were made self-consistent according to the program outlined above. With the final functions for Ge^{+4} and Cu^+, $Q^*(s)$ and A were calculated for all shells including the $(3d)$ shell.

Table XII. Normalized self-consistent radial wave functions for Se^{+6}. The argument r is given in atomic units of length and the eigenvalues are in rydbergs.

r	$(1s)^2$	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3p)^6$	$(3d)^{10}$
0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.005	1.6481	0.5137	0.0251	0.2020	0.0100	0.0001
0.010	2.7820	0.8574	0.0923	0.3366	0.0366	0.0005
0.015	3.5233	1.0635	0.1910	0.4164	0.0756	0.0017
0.020	3.9674	1.1590	0.3125	0.4519	0.1235	0.0039
0.030	4.2485	1.1066	0.5965	0.4248	0.2344	0.0117
0.040	4.0490	0.8417	0.9012	0.3119	0.3514	0.0250
0.050	3.6208	0.4618	1.1989	0.1531	0.4625	0.0441
0.060	3.1110	0.0335	1.4724	−0.0233	0.5600	0.0689
0.070	2.6017	−0.3986	1.7116	−0.1983	0.6394	0.0990
0.080	2.1333	−0.8067	1.9119	−0.3593	0.6985	0.1339
0.090	1.7238	−1.1737	2.0720	−0.4986	0.7366	0.1730
0.100	1.3763	−1.4920	2.1932	−0.6123	0.7542	0.2158
0.120	0.8555	−1.9689	2.3290	−0.7560	0.7327	0.3093
0.140	0.5190	−2.2474	2.3472	−0.7940	0.6476	0.4094
0.160	0.3097	−2.3614	2.2782	−0.7425	0.5148	0.5119
0.180	0.1827	−2.3510	2.1496	−0.6224	0.3495	0.6132
0.200	0.1062	−2.2543	1.9850	−0.4545	0.1653	0.7105
0.220	0.0617	−2.1013	1.8010	−0.2565	−0.0271	0.8020
0.240	0.0358	−1.9165	1.6112	−0.0438	−0.2190	0.8861
0.260	0.0206	−1.7190	1.4252	0.1711	−0.4035	0.9619
0.280	0.0121	−1.5201	1.2482	0.3801	−0.5765	1.0290
0.300	0.0069	−1.3298	1.0848	0.5757	−0.7343	1.0872
0.350	0.0017	−0.9166	0.7429	0.9842	−1.0538	1.1950
0.400	0.0003	−0.6084	0.4946	1.2617	−1.2640	1.2541
0.450	0.0000	−0.3934	0.3229	1.4178	−1.3781	1.2733
0.500		−0.2505	0.2084	1.4741	−1.4151	1.2614
0.550		−0.1577	0.1334	1.4572	−1.3955	1.2270
0.600		−0.0987	0.0851	1.3902	−1.3366	1.1767
0.700		−0.0388	0.0349	1.1768	−1.1541	1.0487
0.800		−0.0152	0.0144	0.9356	−0.9448	0.9075
0.900		−0.0065	0.0064	0.7124	−0.7454	0.7688
1.000		−0.0029	0.0030	0.5270	−0.5734	0.6411
1.100		−0.0014	0.0015	0.3814	−0.4327	0.5281
1.200		−0.0007	0.0008	0.2713	−0.3215	0.4305
1.400		−0.0002	0.0003	0.1322	−0.1716	0.2791
1.600		−0.0001	0.0001	0.0617	−0.0882	0.1760
1.800		0.0000	0.0000	0.0282	−0.0444	0.1087
2.000				0.0125	−0.0218	0.0659
2.200				0.0054	−0.0105	0.0393
2.400				0.0023	−0.0050	0.0232
2.600				0.0010	−0.0024	0.0135
2.800				0.0004	−0.0011	0.0078
3.000				0.0002	−0.0005	0.0044
3.200				0.0001	−0.0002	0.0024
3.400				0.0000	−0.0001	0.0013
3.600					0.0000	0.0008
3.800						0.0004
4.000						0.0002
4.500						0.0000
$\epsilon_{\alpha\alpha}$	928.417	127.771	115.011	24.167	19.652	11.647
$\lim_{r\to 0}\left(\frac{P}{r^{l+1}}\right)$	391.	122.	1093.	48.	433.	605.

Equations (27) and (28) were then used to determine starting functions for the remaining configurations reported in this paper. Tables III–V summarize the constants and functions used in Eqs. (27) and (28). Table VI compares the final value of σ with the screening constant obtained initially by linear interpolation.

A final aid for the initial iteration of each shell was a good estimate for the eigenvalue $\epsilon_{\alpha\alpha}$. Slater's tabulation of one-electron energies of free atoms[10] was found to be quite useful. The neutral atom energies were

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

TABLE XIII. Normalized self-consistent radial wave functions for Br^{+7}. The argument r is given in atomic units of length and the eigenvalues are in rydbergs.

r	$(1s)^2$	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3p)^6$	$(3d)^{10}$
0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.005	1.7133	0.5357	0.0271	0.2128	0.0109	0.0001
0.010	2.8777	0.8890	0.0994	0.3526	0.0399	0.0006
0.015	3.6265	1.0955	0.2051	0.4333	0.0824	0.0020
0.020	4.0633	1.1851	0.3348	0.4666	0.1342	0.0045
0.030	4.3084	1.1094	0.6358	0.4293	0.2534	0.0135
0.040	4.0658	0.8150	0.9560	0.3027	0.3777	0.0288
0.050	3.6002	0.4063	1.2658	0.1305	0.4943	0.0505
0.060	3.0631	−0.0461	1.5473	−0.0576	0.5950	0.0786
0.070	2.5368	−0.4962	1.7902	−0.2410	0.6751	0.1126
0.080	2.0599	−0.9155	1.9905	−0.4070	0.7325	0.1520
0.090	1.6485	−1.2876	2.1472	−0.5476	0.7668	0.1958
0.100	1.3035	−1.6053	2.2624	−0.6595	0.7788	0.2435
0.120	0.7949	−2.0683	2.3807	−0.7916	0.7420	0.3470
0.140	0.4732	−2.3223	2.3776	−0.8105	0.6384	0.4569
0.160	0.2772	−2.4075	2.2870	−0.7361	0.4861	0.5682
0.180	0.1606	−2.3685	2.1388	−0.5923	0.3022	0.6771
0.200	0.0916	−2.2464	1.9576	−0.4022	0.1015	0.7805
0.220	0.0524	−2.0721	1.7606	−0.1849	−0.1046	0.8764
0.240	0.0299	−1.8711	1.5613	0.0434	−0.3072	0.9634
0.260	0.0170	−1.6621	1.3691	0.2698	−0.4991	1.0406
0.280	0.0098	−1.4560	1.1888	0.4861	−0.6763	1.1078
0.300	0.0056	−1.2621	1.0244	0.6852	−0.8355	1.1647
0.350	0.0014	−0.8508	0.6871	1.0886	−1.1482	1.2649
0.400	0.0003	−0.5528	0.4482	1.3474	−1.3415	1.3120
0.450	0.0001	−0.3502	0.2869	1.4781	−1.4339	1.3168
0.500	0.0000	−0.2188	0.1818	1.5075	−1.4478	1.2898
0.550		−0.1351	0.1142	1.4657	−1.4064	1.2405
0.600		−0.0831	0.0716	1.3773	−1.3283	1.1762
0.700		−0.0317	0.0285	1.1336	−1.1169	1.0243
0.800		−0.0121	0.0114	0.8776	−0.8911	0.8654
0.900		−0.0050	0.0050	0.6508	−0.6851	0.7150
1.000		−0.0022	0.0023	0.4688	−0.5134	0.5809
1.100		−0.0011	0.0012	0.3302	−0.3771	0.4656
1.200		−0.0006	0.0006	0.2285	−0.2726	0.3689
1.400		−0.0002	0.0002	0.1052	−0.1375	0.2253
1.600		−0.0001	0.0001	0.0462	−0.0666	0.1335
1.800		0.0000	0.0000	0.0199	−0.0315	0.0773
2.000				0.0082	−0.0145	0.0438
2.200				0.0033	−0.0065	0.0244
2.400				0.0014	−0.0029	0.0134
2.600				0.0006	−0.0013	0.0073
2.800				0.0002	−0.0006	0.0039
3.000				0.0001	−0.0002	0.0021
3.200				0.0000	−0.0001	0.0010
3.400					0.0000	0.0005
3.600						0.0003
3.800						0.0001
4.000						0.0000
$\epsilon_{\alpha\alpha}$	988.513	138.513	125.275	27.665	22.903	14.417
$\lim_{r\to 0}\left(\frac{P}{r^{l+1}}\right)$	408.	128.	1183.	51.	476.	699.

adjusted for an ionized configuration by shifting the energy of each shell the same amount. The estimates so obtained were usually well within the bounds beyond which the program would not converge to an appropriate solution.

RESULTS AND DISCUSSION

The final self-consistent wave functions are listed in Tables VII–XIV. They have been interpolated to convenient values of r and rounded to four decimal places. The integrations were made either for an initial increment of $\Delta r = 0.002$ a.u. (atomic unit) which doubled at the end of every six intervals, or for an increment of 0.005 a.u. doubling after every eight intervals. In some cases both interval schemes were used and the differences were found to be insignificant. Maximum deviation of P was a few digits in the fourth decimal place

TABLE XIV. Normalized self-consistent radial wave functions for Kr^{+8}. The argument r is given in atomic units of length and the eigenvalues are in rydbergs.

r	$(1s)^2$	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3p)^6$	$(3d)^{10}$
0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.005	1.7789	0.5577	0.0291	0.2238	0.0119	0.0001
0.010	2.9730	0.9203	0.1067	0.3687	0.0435	0.0007
0.015	3.7280	1.1267	0.2197	0.4500	0.0894	0.0023
0.020	4.1564	1.2097	0.3577	0.4808	0.1453	0.0051
0.030	4.3637	1.1094	0.6761	0.4326	0.2730	0.0155
0.040	4.0776	0.7849	1.0118	0.2919	0.4048	0.0328
0.050	3.5753	0.3475	1.3334	0.1059	0.5267	0.0574
0.060	3.0123	−0.1285	1.6221	−0.0935	0.6302	0.0891
0.070	2.4704	−0.5954	1.8681	−0.2849	0.7104	0.1273
0.080	1.9867	−1.0248	2.0674	−0.4551	0.7655	0.1712
0.090	1.5746	−1.4003	2.2199	−0.5963	0.7952	0.2200
0.100	1.2331	−1.7160	2.3282	−0.7055	0.8009	0.2728
0.120	0.7378	−2.1626	2.4277	−0.8239	0.7474	0.3866
0.140	0.4309	−2.3903	2.4027	−0.8219	0.6243	0.5062
0.160	0.2477	−2.4459	2.2904	−0.7235	0.4521	0.6262
0.180	0.1410	−2.3783	2.1229	−0.5554	0.2495	0.7423
0.200	0.0788	−2.2315	1.9259	−0.3433	0.0327	0.8511
0.220	0.0443	−2.0372	1.7168	−0.1074	−0.1865	0.9509
0.240	0.0249	−1.8214	1.5092	0.1354	−0.3986	1.0400
0.260	0.0139	−1.6025	1.3120	0.3718	−0.5967	1.1177
0.280	0.0079	−1.3907	1.1294	0.5939	−0.7768	1.1839
0.300	0.0044	−1.1944	0.9650	0.7948	−0.9359	1.2386
0.350	0.0011	−0.7876	0.6339	1.1890	−1.2383	1.3290
0.400	0.0002	−0.5009	0.4051	1.4259	−1.4122	1.3622
0.450	0.0000	−0.3110	0.2543	1.5292	−1.4809	1.3513
0.500		−0.1906	0.1582	1.5311	−1.4710	1.3083
0.550		−0.1155	0.0976	1.4646	−1.4078	1.2438
0.600		−0.0698	0.0601	1.3556	−1.3110	1.1656
0.700		−0.0258	0.0232	1.0847	−1.0731	0.9910
0.800		−0.0095	0.0090	0.8172	−0.8339	0.8168
0.900		−0.0039	0.0039	0.5897	−0.6242	0.6575
1.000		−0.0017	0.0018	0.4133	−0.4552	0.5198
1.100		−0.0008	0.0009	0.2831	−0.3253	0.4050
1.200		−0.0004	0.0005	0.1904	−0.2286	0.3117
1.400		−0.0001	0.0002	0.0828	−0.1088	0.1792
1.600		0.0000	0.0001	0.0341	−0.0495	0.0996
1.800			0.0000	0.0138	−0.0221	0.0540
2.000				0.0054	−0.0095	0.0286
2.200				0.0020	−0.0040	0.0149
2.400				0.0008	−0.0017	0.0076
2.600				0.0003	−0.0007	0.0039
2.800				0.0001	−0.0003	0.0020
3.000				0.0000	−0.0001	0.0009
3.200					0.0000	0.0004
3.400						0.0002
3.600						0.0001
3.800						0.0000
$\epsilon_{\alpha\alpha}$	1050.847	149.791	136.062	31.405	26.394	17.426
$\lim_{r\to 0}\left(\dfrac{P}{r^{l+1}}\right)$	426.	134.	1274.	54.	520.	817.

and the eigenvalues differed by a few thousandths of a rydberg.

Another indication of the magnitude of the error in these solutions is given by the results obtained when a hydrogenlike configuration is integrated. For a $1s$ function with $Z=30$, the exact eigenvalue is 900 ry. The deviation for each of the interval sizes described above was $+0.06$ ry. The wave function was also compared with the exact solution and the maximum deviation was 0.0003. A similar test was made for a $3s$ function with $Z=20$. In this case, the maximum deviations were -0.01 ry and $\Delta P=0.0001$.

For Cu^+ it is possible to compare the present results with Watson's recently published Hartree-Fock functions for the Fe series[11] which were obtained by varying

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[11] R. E. Watson, Tech. Rept. No. 12, 1959, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts (unpublished).

an analytical expression (Roothaan procedure). None of the eigenvalues differ by more than 0.01 ry except for a difference of 0.02 ry for $\epsilon_{3s,3s}$ and 0.06 ry for $\epsilon_{1s,1s}$. The sum of one-electron energies of the configuration for the present results is 1993.418 rydbergs compared to Watson's 1993.144. In view of the deviations of our numerical results for hydrogenlike configurations, no better agreement could be expected.

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"Repulsion of Energy Levels" in Complex Atomic Spectra

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Rosenzweig and Porter have shown a "repulsion of energy levels" in spacing distributions determined from energy levels in complex atomic spectra. The present paper extends their work by showing that these spacing distributions can be determined from calculated positions of the levels in these spectra. Since calculated data are available for spectra where the observed data are scarce or incomplete, this partially overcomes limitations imposed by statistical inaccuracy when direct use is made of the observed data. The equivalence of the two approaches is demonstrated by showing that calculated data for Ta II yield the same spacing distribution as obtained from observed data for Ta II and Re I combined. These are complex spectra in which a fully developed repulsion effect is present. A similar demonstration of equivalence is carried out for spectra of Ru I and Mo I, where the repulsion effect is in an intermediate state of development. The results also indicate that numbers easily evaluated from the radial parameters of the theory will indicate roughly the degree of repulsion, replacing to some extent the need for an explicit calculation of the spacing distribution.

1. INTRODUCTION

STATISTICAL models are often used to interpret nuclear data. Usually, mean values of the observables are calculated, but recent increases in the quantity and quality of observed data have dictated a need for calculating distributions about the mean. Wigner has suggested a formula for the distribution of nearest-neighbor level spacings (between levels of the same total angular momentum and parity), S, when the average spacing of such pairs is D.[1] Expressed in terms of the ratio $x=S/D$, this formula is

$$P(x)=\tfrac{1}{2}\pi x\exp(-\tfrac{1}{4}x^2). \qquad (1)$$

The distinguishing feature of formula (1) is the "repulsion effect." If levels occurred randomly, with the probability the same per unit energy interval over a given range of energy, then the distribution of nearest-neighbor level spacings would follow instead the Poisson formula,

$$P(x)=e^{-x}. \qquad (2)$$

Formula (1) predicts zero probability for zero spacing, whereas formula (2) makes the zero spacing most probable. If spacings in the first one-third-interval are counted (i.e., the number of spacings between zero and a third of D), then formula (1) predicts that about 9% of all the spacings will be in this interval, while formula (2) predicts 28%. In the first two-thirds-interval the predictions still differ considerably, being 30% and 50% of all spacings for formulas (1) and (2), respectively. For large values of x there is also a difference between the formulas; 5% and 15% of the spacings are greater than $2D$ according to formulas (1) and (2), respectively. In this paper, it is considered that a spacing distribution shows a "full" repulsion effect only when there is close agreement with the predictions of formula (1) for the first one-third-interval, the first two-thirds-interval, and the number of spacings greater than $2D$. For convenience, all the spacing distributions are normalized to a total of 74 spacings. The corresponding spacing distributions from formulas (1) and (2) are given in Table I.

The deficiency of small spacings can be understood intuitively as a "repulsion effect" by considering the well-known interpretation of a second-order perturbation as a mutual repulsion between two levels. The deficiency of large spacings can be interpreted as a secondary result of this, if it is assumed that the expansion of short intervals is preferentially (when possible) at the expense of an adjacent large interval,

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[1] E. P. Wigner, Proceedings of the Conference on Neutron Physics by Time of Flight, Gatlinburg, Tennessee, 1956 [Oak Ridge National Laboratory Report ORNL-2309 (unpublished), p. 59].