Charge Distributions in Fluorine and Neon

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Hartree fields (modified to take account of exchange between $2p$ electrons) have been obtained for F, F$^-$, Ne. The energy parameters of the $1s$, $2s$ and $2p$ electrons are found to be 53.08, 2.40 and 1.09 for F; 52.38, 1.50 and 0.14 for F$^-$; and 65.68, 2.75, and 1.51 for Ne. The use of the fields for F and F$^-$ enable one to test the wave equation of the "hole" given by Heisenberg and Dirac. This equation is found to be equivalent to the Hartree equation for the corresponding electron and to give the wrong sign for the electron affinity of F. The $1s$, $2s$ and $2p$ functions have been represented by analytic expressions of the Slater type.

I. Introduction

In order to carry out any detailed atomic calculations accurate wave functions are essential. Good approximate functions can be obtained from antisymmetric combinations of products of single electron functions.

There are two general methods of obtaining the single electron functions. The variational method, developed mainly by Zener,[1] consists essentially in setting up wave functions with adjustable parameters for each electron, obtaining the energy expression for the entire atom in terms of these parameters and adjusting them to make the energy a minimum. The accuracy of the method depends on the form chosen for the single electron functions and the number of parameters at one's disposal.

The method of self-consistent fields was developed by Hartree[2] and refined to take account of exchange effects by Slater[3] and Fock.[4] The functions obtained by this method are more accurate but are available only in the form of a set of numerical values. It would be much more convenient to have these functions represented by analytic expressions of not too great complexity. The analytic functions[5] given by Slater are the best available at present.

Heisenberg[6] and Dirac[7] have set up a wave equation to describe the holes in a closed shell of an atom. For atoms containing almost closed shells the equation would appear to be much simpler than the equation for the electrons since it involves fewer coordinates.

Most of the work discussed in this paper was done to see if any practical use could be made of the wave equation of the hole for the determination of the energy levels and wave functions of atoms with almost closed shells. The necessary calculations have been carried out for the normal fluorine atom which lacks one electron of having all closed shells. As a further check on the accuracy of the work a self-consistent field for Ne was found.

II. Self-Consistent Fields

General method

In setting up the equation of the self-consistent field the method of Fock[4] has been used with slight modifications as suggested by Slater.[3] The wave function of the atom (in the case of F, F$^-$ and Ne) is written in the determinant form, and it is assumed that the single-electron wave functions may be written in the form

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[1] C. Zener, Phys. Rev. **36**, 51 (1930).

[2] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 and 111 (1928).

[3] J. C. Slater, Phys. Rev. **35**, 210 (1930).

[4] V. Fock, Zeits. f. Physik **61**, 126; **62**, 795 (1930).

[5] J. C. Slater, Phys. Rev. **42**, 33 (1932).

[6] W. Heisenberg, Ann. d. Physik **10**, 888 (1931).

[7] P. A. M. Dirac, Ann. de l'Inst. H. Poincare **1**, Pt. 4, 391 (1929).

$$u(n/xyz)=R(n/r)\,Y(\theta,\varphi), \tag{1}$$

which amounts to saying that they are the solutions of central field problems. The energy is then calculated by the method of Slater[8] and minimized with respect to the radial functions, subject to the condition of normality and orthogonality. This leads to a set of linear differential equations for the radial functions of each group of electrons with the same total and azimuthal quantum numbers. These equations are the Euler equations of the above variational problem. The radial functions are the factors which are varied, the coefficients of the arbitrary variations of each function separately being set equal to zero. The auxiliary conditions are taken account of by Lagrangian parameters in the Euler equations.

The notation of Slater's article is used as far as possible and the atomic units of Hartree are used throughout.

The Hamiltonian operator for a many-electron atom, neglecting relativity and all spin interactions, is

$$L=\sum_{k=1}^{N}H_k+\sum_{i>k=1}^{N}(1/r_{ik}),\qquad H_k=-\tfrac{1}{2}\Delta_k-(N/r_k). \tag{2}$$

Here Δ_k is the Laplacian operator acting on the coordinates of the kth electron, r_k is the distance of the kth electron from the nucleus, r_{ik} is the distance between electrons i and k and N is the atomic number.

A diagonal element of the energy matrix can be written in the form

$$E=\sum(n\text{'s})I(n)+\sum(\text{pairs of } n\text{'s})J(n;n')-\sum(\text{pairs of } n\text{'s} \parallel \text{spins})K(n;n'), \tag{3}$$

where

$$I(nlm_lm_s)=\int u^*(nlm_lm_s/k)H_ku(nlm_lm_s/k)dv_k. \tag{4}$$

On making the substitution (1) this reduces to

$$I(nlm_lm_s)=\int_0^\infty R(nl/r)[-\tfrac{1}{2}R''(nl/r)+(1/r)R'(nl/r)+(l(l+1)/2r^2)R(nl/r)-(N/r)R(nl/r)]r^2dr, \tag{5}$$

and, on the further substitution

$$f(nl/r)=rR(nl/r) \tag{6}$$

to

$$I(nlm_lm_s)=\int_0^\infty f(nl/r)[-\tfrac{1}{2}f''(nl/r)+\tfrac{1}{2}(l(l+1)/r^2)f(nl/r)-(N/r)f(nl/r)]dr,$$

which can be written in the form

$$I(nlm_lm_s)=\int_0^\infty\{\tfrac{1}{2}[f'(nl/r)]^2+f(nl/r)[\tfrac{1}{2}(l(l+1)/r^2)f(nl/r)-(N/r)f(nl/r)]\}dr. \tag{7}$$

The integral J has the value

$$\begin{aligned}J(nlm_lm_s;n'l'm_l'm_s')&=\int u^*(nlm_l/k)u^*(n'l'm_l'/j)(1/r_{kj})u(nlm_l/k)u(n'l'm_l'/j)dv_kdv_j\\&=\sum_k a^k(lm_l;l'm_l')F^k(nl;n'l'),\end{aligned} \tag{8}$$

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

where the a^k come from integration over the angular parts and are given in Slater's[8] tables. We can write

$$F^k(nl;n'l')=\int_0^\infty f^2(nl/r)(2k+1)F_k^{n'l';\,n'l'}dr, \tag{9}$$

where

$$F_k^{nl;\,n'l'}(r)=\int_0^\infty f(nl/r')f(n'l'/r')(1/(2k+1))(r^k(a)/r(b)^{k+1}). \tag{10}$$

The expression for the integral K is

$$\begin{aligned}K(nlm_lm_s;n'm_l'm_s')&=\delta(m_s;m_s')\int u^*(nlm_l/k)u^*(m'l'm_l'/j)(1/r_{kj})u(nlm_l/j)u(n'l'm_l'/k)dv_kdv_j\\&=\sum_k b^k(lm_l;l'm_l')G^k(nl;n'l'),\end{aligned} \tag{11}$$

where the b^k are given in the tables and

$$G^k(nl;n'l')=\int_0^\infty f(nl/r)f(n'l'/r)F_k^{nl;\,n'l'}(2k+1)dr. \tag{12}$$

These formulae allow one to obtain the energy of the atom in terms of radial integrals and are in a form especially convenient for carrying out the variational process.

Equations for atoms containing all closed shells

For the case of atoms with closed shells the equation for the radial functions can be immediately set down.

Heisenberg[6] and Shortley[9] have derived closed formulae for expressions of the type

$$\sum_{m_s'}\sum_{m_l'=-l'}^{l'}[J(nlm_lm_s;n'l'm_lm_s')-\delta(m_s;m_s')K(nlm_lm_s;n'l'm_l'm_s')]. \tag{13}$$

In the form given by Shortley the expression (16) is equal to

$$2(2l'+1)F^0(nl;\;n'l')-\frac{2l'+1}{2l+1}\sum_k C_{l'k}{}^lG^k(nl;n'l'), \tag{14}$$

where

$$C_{l'k}{}^\lambda=\frac{2\lambda+1}{2}\int_0^\pi P_\lambda(\cos w)P_{l'}(\cos w)P_k(\cos w)\sin w dw=\frac{2\lambda+1}{(2l'+1)^{\frac{1}{2}}(2k+1)^{\frac{1}{2}}}\{b^\lambda(l'0;k0)\}^{\frac{1}{2}}. \tag{15}$$

The energy of the atom can then be written in the form

$$E=W_1+W_2, \tag{16}$$

where

$$W_1=\sum(n'^s)I(n) \tag{17}$$

and

$$W_2=\sum_{nlm_lm_s}\sum_{n'l'}2(2l'+1)F^0(nl;n'l')-\sum_{nlm_lm_s}\frac{1}{2l+1}\sum_{n'l'}(2l'+1)\sum_k C_{l'k}{}^lG^k(nl;n'l'). \tag{18}$$

The energy is to be minimized subject to the conditions

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

$$\delta_{ll'} \int_0^\infty f(nl/r)f(n'l'/r)dr = \delta_{nl;\; n'l'}. \tag{19}$$

The variation of W_1 is carried out quite simply. In varying the integral W_2 we must note that the function to be varied also appears in the $F_k^{nl;\; n'l'}$. We can carry out two types of variation; a complete variation δW_2 in which both the $f(nl/r)$ and the $F_k^{nl;\; n'l'}$ are varied, or a partial variation $\delta' W_2$ in which only the $f(nl/r)$ are varied. It is easy to see that

$$W_2 = 2\delta' W_2. \tag{20}$$

Carrying out the variation and setting the coefficient of $f(nl/r)$ equal to zero, we have

$$\begin{aligned} -(2l+1)f''(nl/r) + 2(2l+1)[-(N/r)f(nl/r) + (1(l+1)/2r^2)f(nl/r) + \sum_{n'l'} 2(2l'+1)F_0^{n'l';\; n'l'}f(nl/r) \\ - \sum_{n'l'} [(2l'+1)/(2l+1)] \sum_k C_{l'k}{}^{l} G_k^{nl;\; n'l'} f(n'l'/r)] = \sum_{n'l'} \lambda_{nl;\; n'l'} \delta_{ll'} f_{(n'l'/r)}, \end{aligned} \tag{21}$$

where the $\lambda_{nl;\; n'l'}$ are Lagrangian parameters.

Equations for F, F⁻, Ne

For the normal electron configurations of F⁻ and Ne we can immediately write down the equations from the expression (21). If we write f_1, f_2, f_3 in place of $f(10/r), f(20/r), f(21/r)$, the equations become

$$-f_1'' + 2(-(N/r) + F_0^{11} + 2F_0^{22} + 6F_0^{33})f_1 - 2F_0^{22}f_2 - 6F_1^{31}f_3 = \lambda_{11}f_1 + \lambda_{22}f_2, \tag{22a}$$

$$-f_2'' + 2(-(N/r) + 2F_0^{11} + F_0^{22} + 6F_0^{33})f_2 - 2F_1^{12}f_1 - 6F_1^{32}f_3 = \lambda_{12}f_1 + \lambda_{22}f_2, \tag{22b}$$

$$-3f_3'' + 6(-(N/r) + 1/r^2 + 2F_0^{11} + 2F_0^{22} + 5F_0^{33} - 2F_2^{33})f_3 - 6F_1^{23}f_1 = \lambda_{33}f_3. \tag{22c}$$

For normal F_1

$$W_1 = \int_0^\infty \left[\left(\frac{df_1}{dr}\right)^2 + \left(\frac{df_2}{dr}\right) + \frac{5}{2}\left(\frac{df_3}{dr}\right)^2 + \frac{5}{r^2}f_3^2\right]dr - \int_0^\infty (2f_1^2 + 2f_2^2 + 5f_3^2)\frac{9}{r}\,dr \tag{23}$$

and

$$\begin{aligned} W_2 = \int_0^\infty [\tfrac{1}{2}(2f_1^2 + 2f_2^2 + 5f_3^2)(2F_0^{11} + 2F_0^{22} + 5F_0^{33} - f_1^2F_0^{11} - f_2^2F_0^{22} - (5/2)f_3^2(F_0^{33} + (8/5)F_2^{33}) \\ - 2f_1f_2F_0^{12} - 5f_1f_3F_1^{13} - 5f_2f_3F_1^{23})]dr. \end{aligned} \tag{24}$$

The variation equations, imposing the conditions

$$\int_0^\infty f_i^2 dr = 1 \quad (i = 1, 2, 3), \qquad \int_0^\infty f_1f_2 dr = 0 \tag{25}$$

are

$$-f_1'' + 2(-(9/r) + F_0^{11} + 2F_0^{22} + 5F_0^{33})f_1 - 2F_0^{21}f_2 - 5F_1^{31}f_3 = \lambda_{11}f_1 + \lambda_{21}f_2 \tag{26a}$$

$$-f_2'' + 2(-(9/r) + 2F_0^{11} + F_0^{22} + 5F_0^{33})f_2 - 2F_0^{12}f_1 - 5F_1^{32}f_3 = \lambda_{12}f_1 + \lambda_{22}f_2 \tag{26b}$$

$$-(5/2)f_3'' + 5(-(9/r) + 1/r^2 + 2F_0^{11} + 2F_0^{22} + 4F_0^{33} - (8/5)F_2^{33})f_3 - 5F_1^{13}f_1 - 5F_1^{23}f_2 = \lambda_{33}f_3. \tag{26c}$$

By multiplying (26a, b, c) by f_1, f_2, f_3, respectively, integrating over all r, and adding, one easily verifies that

$$\lambda_{11} + \lambda_{22} + \lambda_{33} = W_1 + 2W_2;$$

hence

$$E = \lambda_{11} + \lambda_{22} + \lambda_{33} - W_2. \tag{27}$$

In the solution of the Eqs. (22) and (26) the terms F_1^{ik}, $\lambda_{ik}(i \neq k)$ were neglected. The equations remaining after this simplification are essentially the Hartree equations except that enough of the exchange integral remains to make the equation for f_3 independent of the magnetic quantum number of the $2p$ electron under consideration. If this was not done the coefficient of F_2^{33} would be changed. In the method as originally developed by Hartree the coefficient of F_2^{33} will be zero in any case because of the method he used for averaging over the radius.

For other p electron configurations there is more than one state and the coefficient of F_2^{33} depends on the state chosen, the variation from state to state being as great as the value of the coefficient for some of the states. Hence, unless one wishes to go through separate calculations for the radial functions for each state of a configuration, it is just as well to neglect the coefficient entirely.

The order of magnitude of the change in the energy parameter of the equation for f_3, for the atoms on which calculations have been made, due to neglecting F_2^{33} would be around 0.05. For the case of F^- this would be an error of 35 percent. The change in the function itself would, however, be comparatively small. No estimate has been made of the other exchange terms, although Fock found that for Na they amounted to 3 percent of the total energy. With the solutions of the simplified equations at our disposal, it would not be difficult to get the accurate solutions.

Method of solution of equations

For convenience all equations are thrown into the form

$$f'' = [\epsilon - 2v + [1(1+1)/r^2]]f, \tag{28}$$

where $-v$ is the potential of the central field acting on the electron and ϵ is the energy parameter which gives the energy as a multiple of the ionization potential of hydrogen. The methods used in integration of this equation are essentially those described by Hartree.

Probably the only place in which any details further than those given by Hartree need be described is in the calculation of the potential. It is convenient to use the quantities

$$Z_{Vl}^{ik} = rF_l^{ik} \tag{29}$$

and

$$Z_l^{ik} = -r^2(dF_l^{ik}/dr). \tag{30}$$

The only cases to be considered are those for which $i=k$. For Hartree's method of averaging the only quantities entering would be those for which $1=0$, and the quantities (29) and (30) would then represent the charges which, when placed at the nucleus, would produce the same potential and field strength, respectively, as would be produced by the charge distribution of an electron.

For the case $1=0$

$$Z_0^{ii}(r) = \int_0^r f_i^2 dr \Big/ \int_0^\infty f_i^2 dr \tag{31}$$

and Z_{v0}^{ii} can be obtained by numerical integration of

$$dZ_{v0}^{ii}/dr = (Z_0^{ii} - Z_0^{ii})/r. \tag{32}$$

The integration of (32) is started inward from a large radius where the deviation from a coulomb field is neglible, with the initial values

$$Z_{v0}^{ii} = Z_0^{ii}, \quad dZ_{v0}^{ii}/dr = 0. \tag{33}$$

For $1=2$, Z_{v2}^{ii} can be obtained by successive numerical integration of

$$d\beta/dr = dZ_0^{ii}/dr - 2\beta/r \tag{34}$$

and

$$dZ_{v2}^{ii}/dr = (3Z_{v2}^{ii} - 5\beta/r), \tag{35}$$

where the integration of (34) is started at $r=0$ with initial values

$$\beta = 0, \quad \beta' = 0$$

and the integration of (35) is started inward at a large radius with the initial values

$$Z_{v2}^{ii} = \ , \quad dZ_{v2}^{ii}/dr = 0. \tag{36}$$

The successive approximations were carried out until the maximum variations of ΣZ_0^{ii} were 0.06, 0.06 and 0.05 for Ne, F, F^-, respectively.

Results

The results of the calculations are given in Tables I to IV inclusive. In the first three tables the normalized radial functions, the total effective nuclear charge and effective nuclear charge for potential, and total charge density are given for Ne, F and F^-. There is no differ-

TABLE I. *Effective nuclear charges, total charge distribution, and normalized radial functions for F.*

r	Z	Z_v	f_1	f_2	f_3	$-(dZ/dr)$
0	9.00	9.00	0	0	0	0
0.01	9.00	8.73	0.475	0.105	0.002	0.473
0.02	8.99	8.48	0.866	0.195	0.006	1.576
0.03	8.97	8.23	1.189	0.266	0.015	2.970
0.04	8.93	7.99	1.450	0.314	0.026	4.406
0.06	8.82	7.55	1.818	0.401	0.053	6.946
0.08	8.66	7.16	2.035	0.437	0.088	8.703
0.10	8.48	6.80	2.131	0.442	0.126	9.552
0.12	8.29	6.49	2.150	0.421	0.167	9.722
0.14	8.10	6.20	2.112	0.383	0.212	9.438
0.16	7.91	5.95	2.028	0.332	0.259	8.781
0.18	7.74	5.71	1.919	0.269	0.303	7.969
0.20	7.60	5.49	1.796	0.202	0.348	7.138
0.25	7.29	5.00	1.466	0.044	0.456	5.002
0.30	7.06	4.56	1.150	−0.176	0.553	4.236
0.35	6.85	4.16	0.881	−0.354	0.637	3.832
0.40	6.66	3.79	0.660	−0.507	0.709	3.899
0.5	6.25	3.13	0.359	−0.752	0.809	4.661
0.6	5.74	2.55	0.187	−0.908	0.862	5.434
0.7	5.17	2.07	0.091	−0.984	0.881	5.834
0.8	4.58	1.67	0.047	−1.003	0.877	5.862
0.9	4.02	1.34	0.024	−0.985	0.856	5.605
1.0	3.48	1.08	0.004	−0.942	0.819	5.129
1.2	2.56	0.69		−0.815	0.742	4.081
1.4	1.84	0.44		−0.677	0.653	3.049
1.6	1.31	0.28		−0.548	0.569	2.220
1.8	0.93	0.18		−0.437	0.490	1.543
2.0	0.64	0.12		−0.334	0.423	1.076
2.5	0.26	0.03		−0.185	0.285	0.474
3.0	0.10	0.01		−0.095	0.190	0.198
3.5	0.05			−0.048	0.126	0.084
4.0	0.02			−0.024	0.082	0.035
4.5	0.01			−0.011	0.052	0.014
5.0				−0.006	0.034	0.006
5.5				−0.003	0.021	0.002
6.0				−0.001	0.014	0.001
7.0					0.006	0
8.0					0.002	
9.0					0.001	

TABLE II. *Effective nuclear charges, total charge distribution and normalized radial functions for* F^-.

r	Z	Z_v	f_2	f_3	$-(dZ/dr)$
0	9.00	9.00	0	0	0
0.01	9.00	8.73	0.106	0.002	0.474
0.02	8.99	8.48	0.195	0.005	1.576
0.03	8.97	8.23	0.266	0.014	2.970
0.04	8.93	7.98	0.315	0.024	4.407
0.06	8.82	7.53	0.401	0.049	6.948
0.08	8.66	7.13	0.437	0.080	8.703
0.10	8.48	6.77	0.443	0.114	9.553
0.12	8.29	6.44	0.412	0.155	9.728
0.14	8.10	6.15	0.383	0.195	9.442
0.16	7.92	5.88	0.332	0.237	8.783
0.18	7.73	5.64	0.270	0.277	7.971
0.20	7.60	5.41	0.202	0.318	7.139
0.25	7.29	4.90	0.044	0.417	5.006
0.30	7.06	4.45	−0.176	0.506	4.243
0.35	6.86	4.03	−0.354	0.573	3.772
0.40	6.67	3.64	−0.508	0.647	3.899
0.5	6.25	2.93	−0.752	0.731	4.595
0.6	5.76	2.31	−0.899	0.794	5.469
0.7	5.20	1.77	−0.972	0.815	5.891
0.8	4.61	1.33	−0.981	0.813	5.895
0.9	4.03	0.95	−0.974	0.797	5.710
1.0	3.50	0.64	−0.932	0.772	5.313
1.2	2.52	0.17	−0.801	0.706	4.274
1.4	1.73	−0.16	−0.678	0.637	3.354
1.6	1.11	−0.38	−0.554	0.571	2.570
1.8	0.65	−0.54	−0.447	0.510	1.960
2.0	0.30	−0.66	−0.356	0.456	1.501
2.5	−0.26	−0.82	−0.201	0.348	0.807
3.0	−0.57	−0.90	−0.106	0.266	0.447
3.5	−0.74	−0.94	−0.060	0.207	0.264
4.0	−0.83	−0.96	−0.030	0.164	0.163
4.5	−0.90	−0.98	−0.018	0.130	0.102
5.0	−0.93		−0.010	0.105	0.066
5.5	−0.95	−0.99	−0.005	0.083	0.041
6.0	−0.96		−0.003	0.068	0.028
7	−0.97		−0.001	0.045	0.012
8	−0.98	−1.00		0.030	0.005
9	−0.99			0.020	0.002
10				0.013	0.001
11	−1.00			0.009	

ence between the functions f_1 for F and F^-, hence it is listed only once. A comparison of the approximate x-ray term values and ionization potentials as calculated by the method of self-consistent fields with the observed values, where those are known, is given in Table IV. Graphs of the functions and total charge distributions are given in Figs. 1, 2, 3. The value of the electron affinity of fluorine from this table is $+0.14$. The electron affinity of fluorine was also calculated, the difference in the functions of the atom and ion being taken into account by using the relation (32) (without exchange terms). The value obtained was -0.13. It seems strange that it should be negative. There are no measurements with which to compare it but the value obtained by extrapolation methods[10] is $+0.25$. One cannot be certain whether the polarization energy is actually so large or whether the discrepancy is due to inaccuracy in the method.

The energy of the K level of F was taken from the measurements of Södermann.[11] The ionization potentials are taken from the spectrographic data tabulated by Noyes and Beckman.[12]

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[10] J. H. Bartlett, Jr., Nature **125**, 459 (1930).

[11] M. Södermann, Zeits. f. Physik **52**, 795 (1929).

[12] A. A. Noyes and A. D. Beckman, Chem. Rev. **5**, 85 (1928).

TABLE III. *Effective nuclear charges, total charge distributions and normalized radial functions for Ne.*

r	Z	Z_v	f_1	f_2	f_3	$-(dZ/dr)$
0	10.00	10.00	0	0	0	0
0.01	10.00	9.69	0.541	0.124	0.002	0.616
0.02	9.99	9.39	0.996	0.224	0.008	2.085
0.03	9.95	9.10	1.352	0.303	0.020	3.842
0.04	9.91	8.82	1.636	0.363	0.035	5.624
0.06	9.77	8.31	2.016	0.438	0.071	8.542
0.08	9.57	7.85	2.208	0.464	0.114	10.259
0.10	9.36	7.45	2.275	0.453	0.164	10.897
0.12	9.15	7.09	2.248	0.415	0.219	10.739
0.14	8.94	6.76	2.164	0.358	0.274	10.073
0.16	8.74	6.46	2.041	0.287	0.329	9.145
0.18	8.57	6.18	1.895	0.206	0.382	8.142
0.20	8.42	5.93	1.743	0.119	0.437	7.250
0.25	8.11	5.35	1.363	−0.105	0.550	5.552
0.30	7.84	4.83	1.016	−0.321	0.668	4.936
0.35	7.59	4.34	0.745	−0.511	0.756	5.061
0.40	7.31	3.90	0.534	−0.672	0.826	5.567
0.5	6.67	3.11	0.264	−0.897	0.916	6.773
0.6	6.00	2.46	0.128	−1.013	0.952	7.523
0.7	5.22	1.94	0.057	−1.049	0.950	7.618
0.8	4.48	1.52	0.028	−1.032	0.922	7.231
0.9	3.81	1.19	0.001	−0.983	0.881	6.590
1.0	3.22	0.93		−0.916	0.829	5.801
1.2	2.24	0.57		−0.761	0.718	4.251
1.4	1.55	0.36		−0.610	0.607	2.955
1.6	1.08	0.22		−0.478	0.508	2.005
1.8	0.74	0.13		−0.369	0.413	1.301
2.0	0.52	0.09		−0.283	0.349	0.891
2.5	0.20	0.03		−0.143	0.214	0.316
3.0	0.07	0.01		−0.069	0.130	0.111
3.5	0.03			−0.033	0.076	0.037
4.0	0.01			−0.015	0.045	0.012
4.5				−0.007	0.026	0.004
5.0				−0.003	0.015	0.001
5.5				−0.001	0.009	0.000
6.0					0.005	
7.0					0.002	
8.0					0.001	

TABLE IV. *Comparison of term values obtained from self-consistent field with the observed values.*

	F		F$^-$		Ne	
Level	ϵ	$\frac{\nu}{R}$ obs.	ϵ	$\frac{\nu}{R}$ obs.	ϵ	$\frac{\nu}{R}$ obs.
K	53.08	49.74	52.38	—	65.68	—
L	2.40	—	1.50	—	2.75	—
Ionization potential	1.09	1.248	0.14	—	1.51	1.587

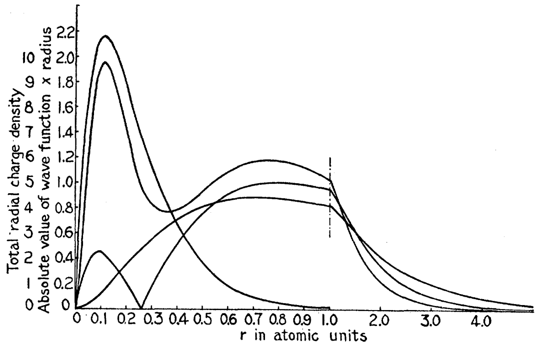

FIG. 1. Total radial charge density and absolute value of functions f_1, f_2, f_3 for F.

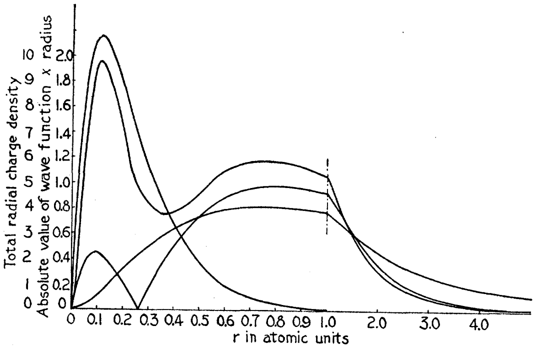

FIG. 2. Total radial charge density and absolute value of functions f_1, f_2, f_3 for F$^-$.

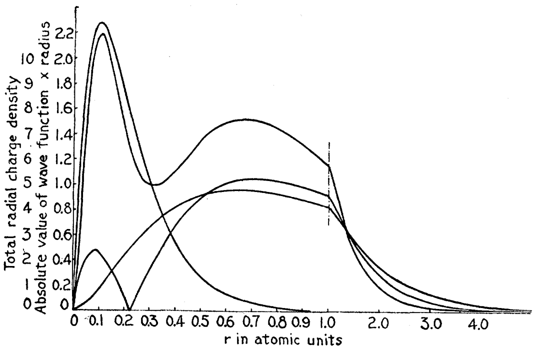

FIG. 3. Total radial charge density and absolute value of functions f_1, f_2, f_3, for Ne.

THE WAVE EQUATION OF THE HOLE

The method used by Heisenberg to derive a wave equation describing the holes in a closed shell will be described briefly. Starting from the energy operator of an atom in terms of the non-commutative amplitudes a_i as given by Jordan and Wigner[13]

$$E=\sum_{i,\ k=1}^{k} a_i^* a_k(\delta_{ik}E_i+H_{ik})+\tfrac{1}{2}\sum_{ikrs} a_i^* a_k^* a_r a_s H_{ik;\ rs} \tag{37}$$

where

$$a_i a_i^* = N_i \text{ (number of electrons in state } i=0,\ 1), \tag{38}$$

K is the total possible number of states an electron may have, the E_i are the unperturbed energy levels of the single electrons, and the other matrix elements are defined by

$$H_{ik}=\int u_i^*(l)Hu_k(l)dv_l \tag{39}$$

$$H_{ik;\ rs}=\int u_i^*(l)u_k^*(m)(1/r_m)u_r(m)u_s(l)dv_l dv_m, \tag{40}$$

and making the assumption that the probability of transitions to states outside a closed shell are negligible (i.e., $K=n$, where n is the number of electrons in a closed shell), he transforms to a new set of amplitudes a_i' obeying the same commutation relations as the a_i and satisfying the relations

$$a_i'^* a_i'=(1-N_i)=N_i' \text{ (number of holes in state } i=0,\ 1) \tag{41}$$

$$a_i'=a_i^*, \tag{42}$$

to obtain a new energy operator

$$E=\sum_{i=1}^{n}(H_{ii}+E_i)+\tfrac{1}{2}\sum_{i,\ k=1}^{n}(H_{ik;\ ki}-H_{ik;\ ik})-\sum_{i,\ k=1}^{n} a_i'^* a_k'[\delta_{ik}E_i+H_{ki}$$

$$+\tfrac{1}{2}\sum_{r}(H_{kr;\ ri}-H_{rk;\ ri}-H_{kr;\ ir}+H_{rk;\ ir})]+\tfrac{1}{2}\sum_{ikrs=1}^{n} a_i'^* a_k'^* a_r' a_s' H_{rs;\ ik}. \tag{43}$$

The H^l can be any perturbation on acting on the lth electron. A special case would be the spin-orbit interaction for a single electron.

The essential difference between (37) and (43) is in the factor of $a_i'^* a_k'$ which represents the perturbation energy acting on a hole. The sign is reversed and there are additional terms which arise from the interactions of the electrons and represent the difference in the central fields acting on the electrons and holes. The matrix element H_{ik} becomes H_{ki}. There is also an added term

$$\sum_{i}(E_i+H_{ii})+\tfrac{1}{2}\sum_{i,\ k}(H_{ik;\ ki}-H_{ik;\ ik})=A, \tag{44}$$

which represents the energy of the closed shell.

If we set $H_{ik}=H_{ki}$ and $H_{ik;\ rs}=H_{rs;\ ik}$ the wave equation of the hole becomes

$$\left\{\sum_{l=1}^{n-N}\tfrac{1}{2}\Delta^l+U^l+\sum_{l>m}\frac{1}{r_{lm}}+A-E\right\}\psi=0. \tag{45}$$

U^l is a central field which we shall later discuss in detail. If one wishes to use the equation to calculate the term values of the lowest states of atomic spectra, the perturbation H can be considered as the

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[13] P. Jordan and E. Wigner, Zeits. f. Physik **47**, 631 (1928).

interaction between spin and orbit for each electron. For the remaining discussion we shall neglect the spin-orbit interaction.

For the case of one hole in a closed shell there is only one a_i' different from zero in the energy expression (43), hence $i=k$ and the expression which represents the energy due to the additional central field

$$\tfrac{1}{2}\sum_r (H_{kr;\,ri}-H_{rk;\,ri}-H_{kr;\,ir}+H_{rk;\,ir})$$

reduces to

$$\sum_r (H_{ir;\,ri}-H_{ri;\,ri})=\sum_{n'} J(n;n')-\sum_{n'} K(n;n'), \tag{46}$$

where n' is summed over the closed shells.

Making use of the relation (14) and neglecting the exchange terms for which $n,\ l\neq n',\ l'$ we see immediately that the added central field

$$\sum_{n'l'} 2(2l'+1)F_0{}^{n'l';\,n'l'}-\sum_K C_{Kl}{}^l G_K{}^{nl;\,nl} \tag{47}$$

and the equation for the radial part of the function of the hole is

$$f''+2\left[\frac{N}{r}-\frac{l(l+1)}{2r^2}+\sum_{n'l'} 2(2l'+1)F_0{}^{n'l';\,n'l'}-\sum_K C_{lK}{}^l G_K{}^{nl;\,nl}\right]f=2(E-A)f. \tag{48}$$

Neglecting the exchange terms for which $n\neq n'l'$ in (21) we obtain

$$f''(nl/r)+2[(N/r)-l(l+1)/2r^2-\sum_{n'l'} 2(2l'+1)F_1{}^{n'l';\,n'l'}+\sum_k C_{lk}{}^l G_k{}^{nl;\,nl}f(nl/r)]=\lambda f(nl/r),$$

which is exactly equivalent to (48).

From this it is seen that the equation of the hole in a closed shell is exactly equivalent to the equation of an electron in the closed shell when one neglects the exchange terms for which $nl\neq n'l'$. If one takes into account all the exchange terms, expression (46) does not represent an energy due to a central field alone, but also includes exchange terms of the same form as those entering into Fock's modified Hartree equations. From the method of deviation it is not, however, obvious how these added terms enter into the equation of the hole. In Heisenberg's derivation of the wave equation of the hole these exchange terms did not enter because he considered only one (nl) group.

The term value obtained from a solution of the wave equation of the hole is then correct to the extent to which the energy parameters in the Hartree equations actually represent the term values. There is no account taken of the difference of the wave functions of the electrons in the closed shell and those in a shell lacking one electron. For fluorine this difference was found to be large enough to change the sign of the electron affinity.

If there is more than one hole present in the closed shells one can carry out a process of obtaining a self-consistent field for the holes in the same manner as for electrons. For the holes, however, the field U^l would be used as the basic field to which the potentials due to the charge distribution of the holes would be added, whereas in the case of electrons the potentials due to the charge distributions of the electrons are subtracted from (N/r). The radial parts of the hole functions would again be the same as those of the electrons except that the polarization of the part of the atom not included in the particular (nl) group containing the hole would not be taken into account.

Heisenberg has shown that in order for the multiplets to be inverted in cases where there are fewer holes than electrons in a configuration the angular part of the hole function must be the complex conjugate of that for the electron. Hence we can say that the wave functions of the holes in a closed shell are simply the complex conjugates of the functions of the electrons.

It is obvious that there is no particular advantage in using the wave equation of the hole to calculate the term values, since it is equivalent to the Hartree method.

IV. The Analytic Expressions for the Functions

The functions obtained from the self-consistent field can be represented approximately by the following expressions

$$\begin{aligned}
\text{F}:\ 1s&: f_1=51.77re^{-8.75r},\\
2s&: f_2=11.30[re^{-7.25r}-r^2(1.00e^{-3.31r}+0.341e^{-1.98r})],\\
2p&: f_3=13.76r^2(e^{-3.85r}+0.202e^{-1.66r}),\\
\text{F}^-:\ 1s&: f_1=51.77re^{-8.75r},\\
2s&: f_2=11.55[re^{-7.25r}-r^2(1.03e^{-3.33r}+0.300e^{-1.90r})],\\
2p&: f_3=13.57r^2(e^{-3.86r}+0.133e^{-1.36r}),\\
\text{Ne}:\ 1s&: f_1=60.70re^{-9.73r},\\
2s&: f_2=13.60[re^{-8.22r}-r^2(1.08e^{-3.69r}+0.350e^{-2.15r})],\\
2p&: f_3=20.13r^2(e^{-4.48r}+0.198e^{-1.91r}),
\end{aligned}$$

which are of the form suggested by Slater. The curves were fitted by the method outlined by Slater. The analytic expressions for f_1 and f_2 are not exactly orthogonal. The values of the integrals of their products are 0.0000203 for Ne, 0.0000251 for F, and 0.0000292 for F^-. The agreement between the curves and the analytic expression is good for ranges in which the functions are large but in other ranges the discrepancy may be as much as 0.02.

The functions as given are probably not accurate enough for many calculations. To get an accurate fit would probably require several more exponentials. It seems to be just as convenient to carry out the numerical integrations as to use the analytic expressions, if great accuracy is desired.

In conclusion the author wishes to thank Professor J. H. Bartlett, Jr., for suggestions and assistance in this research.