The Magnetic Interaction of a Valence Electron with Inner Shells

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The magnetic interaction terms between two electrons are well known. By using antisymmetric wave functions the diagonal terms of the energy matrix for this interaction are calculated for an electronic configuration consisting of a valence electron and a closed shell. From the diagonal elements the doublet separation is easily obtained by applying the energy sum rule. The direct integrals, that is, terms which would occur even though the wave functions were not symmetrized for the Pauli principle, yield the expected contribution to the doublet separation; namely the interaction of the spin of the valence electron with the electric field produced by the closed shell. The exchange integrals give a contribution which decreases the doublet separation in the cases examined. They have been evaluated for the f terms of Cs I. Their effect is much too small to explain the inversion of the doublets in this spectrum.

INTRODUCTION

IN discussing the doublets of alkalies it is customary to consider the valence electron in a central field of force. The fact that the atom consists of a nucleus and many electrons is usually supposed to be taken care of by treating the closed inner electronic shells as spherically symmetrical distributions of charge. Their only effect in such a consideration is that of changing the central field of force in which the valence electron is moving. It is clear that there is no rigorous argument involved in such reasoning and that the only basis for its acceptance is the success of its results. Such results cannot be claimed, however, to be consequences of quantum mechanics because it does not follow from the general theory that the effect of inner shells is equivalent to a simple charge distribution derivable directly from Schroedinger's charge density. The results themselves are not always in agreement with experiment, for it is known that alkali doublets show inversion and it is also well known that such inversion can be explained on the above picture only if one supposes the effective electric field to be directed towards the nucleus at least in some region of space. Such an inversion of the electric field is inconsistent with the picture itself, as follows from simple electrostatics. We thought it of interest, therefore, to reconsider the problem. We shall see below that the usual central field picture is responsible for one of the terms in the result but that another exchange term is also present. The contributions to the doublet splittings due to the exchange term are usually very small and we may consider the central field picture as justifiable for ordinary cases. We have estimated the exchange terms for Cs f terms and we find that their effect is not sufficient to account for the inversion of these doublets. We are not prepared to state that no other inverted doublets can be accounted for by this effect of exchange.

1. THE INTERACTION ENERGY

Using the spin model for the electron and the Thomas correction factors, Heisenberg[1] has set up an expression for the spin-orbit and the spin-spin interactions of a pair of electrons with each other and with the nucleus. This interaction energy may be written (omitting the spin-spin interactions) as

$$H' = 2\mu_0^2(\mathbf{A}'_1 \cdot \mathbf{s}_1 + \mathbf{A}'_2 \cdot \mathbf{s}_2), \quad (1)$$

where

$$\mathbf{A}'_1 = Zr_1^{-3}\mathbf{l}_1 + r^{-3}[(\mathbf{r}_1 - \mathbf{r}_2) \times (2\mathbf{p}_2 - \mathbf{p}_1)] \quad (2)$$

and $\mathbf{A}'_2$ is obtained from the above by interchanging 1 and 2. Here $\mathbf{l}_1$, $\mathbf{s}_1$ are respectively the orbital and spin angular momenta of the first electron in units of $h/2\pi = \hbar$; $\mathbf{r}_1$, $\mathbf{p}_1$ are the

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[1] W. Heisenberg, Zeits. f. Physik 39, 499 (1927).

vector displacement from the origin and the linear momentum of this electron; Z is the atomic number and r is the distance between the two electrons. It should be noted that the matrices representing $\mathbf{s}$ are one-half of Pauli's σ's. This form of interaction energy may be justified by means of Dirac's equation.[2, 3, 4, 5, 6] This justification is itself not entirely free from speculation. It is, however, at least probable that to a sufficient approximation the interaction energy is given by

$$H' = -(e^2/2)[(\mathbf{a}^1\mathbf{a}^2)/r + (\mathbf{a}^1\mathbf{r})(\mathbf{a}^2\mathbf{r})/r^3] \quad (3)$$

which contributes the same amount to the spin-orbit interaction as the second part of (2)

$$\mathbf{A}_1 = r^{-3}[(\mathbf{r}_1 - \mathbf{r}_2) \times (2\mathbf{p}_2 - \mathbf{p}_1)] \quad (4)$$

in most of the configuration space. As long as one is treating the problem by means of radial functions satisfying Schroedinger's equation rather than by means of the radial equations of Darwin-Gordon, there is no advantage[7] in using Eq. (3) since then Eq. (4) is fully equivalent to Eq. (3). The additional terms due to spin-spin interactions which must be added to Eq. (4) are readily seen to have no effect on the interaction with closed shells. The calculation of this effect offers no difficulties and we leave it to the reader.

Using Eqs. (1) and (4) we calculate the doublet splitting using the method of sums. We deal with the states of the valence electron appropriate to strong fields and we describe them by assigning the orbital and spin magnetic quantum numbers m', μ'. We suppose that the atomic wave functions may be described sufficiently well as an antisymmetric combination of products of single electron functions, there being one kind of function for each electron in the atom. The first-order perturbation energy is then

$$W = \sum'_{ab}\{(ab|H'|ab) - (ab|H'|ba)\},$$

where a, b are the electronic states present and the summation is restricted to pairs. For the calculation of doublet splittings the pairs of electrons in inner shells do not matter and we may restrict the summation to

$$W = \sum_b\{(ab|H'|ab) - (ab|H'|ba)\}, \quad (5)$$

where a refers to the valence electron and b to the closed shells so that:

$$a = m', \mu', \quad b = m, \mu. \quad (5')$$

The closed shells are specified here by the principal quantum number n, the azimuthal number l, and the orbital and spin magnetic numbers m, μ. The energy (5) may be broken up into parts, each part referring to a shell with given n, l. We shall suppose that it has been thus broken up and we shall consider the contribution to (5) due to such a shell. In order not to complicate the notation we will call this also W. We have, using (1)

$$\sum_b(ab|H'|ab) = 4\mu_0^2\mu' I_{m'}; \quad \sum_b(ab|H'|ba) = 6\mu_0^2\mu' J_{m'} \quad (6)$$

where

$$I_{m'} = \sum_m \int w_{m'}^*(1) u_m^*(2) A_{1z} w_{m'}(1) u_m(2) d\tau_1 d\tau_2$$

$$J_{m'} = \sum_m \int w_{m'}^*(1) u_m^*(2) B_z w_{m'}(2) u_m(1) d\tau_1 d\tau_2 \quad (6')$$

$$\mathbf{B} = [(\mathbf{r}_1 - \mathbf{r}_2) \times (\mathbf{p}_2 - \mathbf{p}_1)]/r^3 = (\mathbf{A}_1 + \mathbf{A}_2)/3 \quad (6'')$$

and $w_{m'}$, u_m are the Schroedinger orbital wave functions for the valence and shell electron, respectively. The matrix vector character of $\mathbf{A}$, $\mathbf{B}$ shows that

[2] J. A. Gaunt, Phil. Trans. Roy. Soc. **A228**, 151 (1929).
[3] G. Breit, Phys. Rev. **34**, 553 (1929).
[4] G. Breit, Phys. Rev. **39**, 616 (1932).
[5] Fock and Podolsky, Phys. Zeits. d. Sow. **1**, 798 (1932).
[6] Bethe and Fermi, Zeits. f. Physik **77**, 296 (1932).

[7] Since this work was practically completed there arrived a paper by Fock in Zeits. f. Physik **81**, 195 (1933). His considerations are closely related to ours and are in many respects more general. Thus he goes into the influence of exchange on the effective central field which we leave

$$I_{m'}=m'I, \quad J_{m'}=m'J \tag{7}$$

and a simple application of the method of sums shows that the difference in the energies of the two doublet states due to the influence of inner shells is

$$\Delta w=2\mu_0^2(2l'+1)(I-3J/2) \tag{8}$$

where l' is the azimuthal quantum number of the valence electron. In addition the nucleus exerts its usual effect.

2. The Direct Term

According to Eq. (8), part of the doublet splitting is due to the direct integrals I. The term

$$2\mu_0^2(2l'+1)I \tag{8'}$$

in (8) we call the direct term because it would be present even if there were no Pauli principle. We shall now calculate (8') and we shall see that its value is the same as one would expect from simple charge density considerations. We resolve the orbital functions of the valence and the shell electron into their angle and radial factors:

$$w_{m'}=Y_{l'}{}^{m'}F(r); \quad u_m=Y_l{}^m f(r) \tag{9}$$

and we normalize each factor to unity:

$$\int_0^{\pi}\int_0^{2\pi}|Y_l{}^m|^2\sin\theta d\theta d\varphi=\int_0^{\infty}|f(r)|^2r^2dr=1. \tag{10}$$

We have the summation theorem formula for spherical harmonics:

$$\sum_m Y_l{}^{m*}(1)\,Y_l{}^m(2)=(2l+1)P_l(\cos\theta_{12})/4\pi \tag{11}$$

where P_l is the Legendre function of order l and θ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. The summation theorem is applied to the first Eq. (6'). It must be remembered that the operator $\mathbf{p}_2$ in Eq. (4) applies only to $u_m(2)$ and not to $u_m{}^*(2)$. Thus we introduce a third point 3, use Eq. (11) for $\sum_m u_m{}^*(3)u_m(2)w_{m'}(1)$ apply the operator A_{1z} to the result and then we let the point 3 approach the point 2 as a limit. We have

$$I_{m'}=[(2l+1)/4\pi]\int w_{m'}{}^*(1)\{r^{-3}[(\mathbf{r}_1-\mathbf{r}_2)\times(2\mathbf{p}_2-\mathbf{p}_1)]_z P_l(\cos\theta_{23})f_2f_3w_{m'}(1)\}_{3\to 2}d\tau_1d\tau_2.$$

We note that $\lim[(\mathbf{r}_1-\mathbf{r}_2)\times\mathbf{p}_2]_z\cos\theta_{23}=0$ and also that the operation $\mathbf{p}_2$ on f_2 gives rise to a term which disappears on integration over 2. We are left with

$$I_{m'}=\frac{2l+1}{4\pi}\int w_{m'}(1)\left\{\frac{[(\mathbf{r}_2-\mathbf{r}_1)\times\mathbf{p}_2]_2}{r^3}f_2{}^2d\tau_2\right\}w_{m'}(1)d\tau_1. \tag{12}$$

out of account. Fock considers two cases: (a) the non-relativistic, nonspin case in which the electrostatic interaction is considered. This has to do with the calculation of term values irrespective of multiplet structure. (b) He works also with the Diracian form modified by Eq. (3). He shows that in interactions with closed shells only the exchange part of Eq. (3) gives a non-vanishing contribution. Neglecting this he obtains the usual doublet-splitting formula, making use of the Darwin-Gordon radial equations and approximating the solutions of these by means of the Schroedinger radial functions. He also gives a tentative form for the effect of exchange on the doublet splitting which involves the smaller of the Darwin-Gordon functions. This form he regards as uncertain. In this respect we have a more definite result, for we believe that as long as the Darwin-Gordon functions are approximated in the usual way by Schroedinger's function, one may use Eq. (4) instead of Eq. (3). It is furthermore likely that the use of the exact relativistic radial functions matters only for p electrons and even there we expect the difference to be small because the difference between these exact functions and their non-relativistic approximations disappears in regions where the wave functions of the shell and valence electron overlap.

We interpret $(\mathbf{r}_2-\mathbf{r}_1)f_2^2/r^3$ as the electric field at the point 1 due to a charge $-f_2^2 d\tau_2$ at the point 2. Expression (12) is thus the diagonal matrix element with respect to $w_{m'}$ of the quantity $(2l+1)[\mathcal{E}\times\mathbf{p}]_z/4\pi$ where $\mathcal{E}$ is the electric intensity at the valence electron due to a spherically symmetrical distribution of charge having a charge density $-f^2$. This contribution thus corresponds to the central field picture. The interaction of the valence electron spin with the electric field of the nucleus gives rise to a perturbing energy: $2\mu_0^2 Z[\mathbf{r}_1\times\mathbf{p}_1]\cdot\mathbf{s}_1/r_1^3$, which contributes to the doublet splitting the amount $2\mu_0^2(2l'+1)I_N$, where $I_N=I_{Nm'}/m'$.

$$I_{Nm'}=(Z/2)\int w_{m'}^*(1)[\mathbf{r}_1\times\mathbf{p}_1]_z r_1^{-3} w_{m'}(1)d\tau_1. \tag{13}$$

Comparing this with Eq. (12) we see also that the numerical factors are precisely such as one would expect on the charge density picture. The effect of the shell is to decrease the effect of the nucleus. It is convenient to divide the action of the nucleus into parts, each part belonging to a shell. The total nuclear charge Z is then divided into $2(2l+1)$ parts and the contribution of any part to Eq. (13) is combined with the corresponding I as given by Eq. (12). The electric field due to the charge density $-f^2$ in Eq. (12) may be broken up into contributions due to charges $-4\pi f_2^2 r_2^2 dr_2$ at $r_1=0$ for $r_2<r_1$. The sum of the contributions to I due to the shell and the corresponding nuclear charge then becomes, by Eq. (9),

$$(I_N+I)_s=(2l+1)\int_{r_1>r_2}(F_1r_1)^2 f_2 r_2)^2/r_1^3 dr_1 dr_2. \tag{14}$$

This contribution added to $-3J/2$ and multiplied by $2\mu_0^2(2l'+1)$ gives the doublet splitting due to the closed shell together with the positive charge $2(2l+1)$ on the nucleus. According to Eq. (14) the effect of $2(2l+1)$ charges on the nucleus is modified by the presence of the shell to the extent of obliterating $1/r^3$ outside the shell.

3. The Exchange Term

We evaluate next $J_{m'}$ as given by the second Eq. (6'). Various forms can be given to the result. We first derive a form which involves only the radial functions f, F and the derivative of the valence electron function F. To obtain this we transform the part of $J_{m'}$ due to $\mathbf{p}_1$ in (6''). We integrate by parts, thus transferring the differential operator $\mathbf{p}_1$ from $u_m(1)$ to $w_{m'}^*(2)$. In the result we interchange the variables 1 and 2 and we combine this result with the part of $J_{m'}$ due to $\mathbf{p}_2$ of Eq. (6''). We have

$$J_{m'}=(2l+1)/4\pi\int f_1 f_2 P_l(12)\{[(\mathbf{r}_1-\mathbf{r}_2)\times\mathbf{p}_2]_z/r^3\}[w_{m'}^*(1)w_{m'}(2)-w_{m'}(1)w_{m'}(2)]d\tau_1 d\tau_2.$$

Using the second Eq. (7) and the summation theorem (11) we have

$$[(l'(l'+1)(2l'+1))/6]J=\sum_{m'}m'J_{m'}$$
$$=[(2l+1)(2l'+1)/8\pi^2]\int f_1 f_2 P_l(12)\{[(\mathbf{r}_1-\mathbf{r}_2)\times\mathbf{p}_2]_z/r^3\}[\mathbf{r}_2\times\mathbf{p}_2]_z F_1 F_2 P_{l'}(12)d\tau_1 d\tau_2. \tag{15}$$

By symmetry we may replace the product of the two z components of the vector products in the above integral by their scalar product provided we divide the result by three. We then note that

$$[(\mathbf{r}_1-\mathbf{r}_2)\times\mathbf{p}_2]\cdot[\mathbf{r}_2\times\mathbf{p}_2]=-(\mathbf{r}_1\cdot\mathbf{r}_2)\Delta_2+2(\mathbf{r}_1\cdot\nabla_2)+(\mathbf{r}_2\cdot\nabla_2)(\mathbf{r}_1\cdot\nabla_1)-l_2^2,$$

where $\mathbf{l}_2=[\mathbf{r}_2\times\mathbf{p}_2]$ and we find by means of Eq. (15) that

$$J=\frac{2l+1}{8\pi^2 l'(l'+1)}\int f_2 f_2 P_l r^{-3}\left\{l'(l'+1)\left(\frac{r_1}{r_2}\cos\theta-1\right)F_1F_2P_{l'}+\frac{r_1}{r_2}\sin^2\theta P_{l'}'F_1\frac{d}{dr_2}(F_2r_2)\right\}d\tau_1 d\tau_2.$$

The argument of the Legendre function is $\mu=\cos\theta_{12}$. We have

$$\begin{aligned}\int_{-1}^{+1}(1-\mu^2)P_lP_{l'}'r^{-3}d\mu&=\int_{-1}^{+1}(1-\mu^2)P_lP_{l'}'r_1^{-1}r_2^{-1}(\partial/\partial\mu)r^{-1}d\mu\\&=-r_1^{-1}r_2^{-1}\int_{-1}^{+1}r^{-1}[-l'(l'+1)P_lP_{l'}+(1-\mu^2)P_{l'}'P_l']d\mu\\&=[l'(l'+1)/r_1r_2]\int_{-1}^{+1}r^{-1}\{P_lP_{l'}+P_{l'}[(P_{l'+1}-P_{l'-1})/(2l'+1)]\}d\mu\end{aligned}$$

and thus

$$J=\frac{2l+1}{8\pi^2}\int f_1f_2F_1\left\{r_2^{-1}\left(\frac{\partial}{\partial r_2}r^{-1}\right)P_lP_{l'}F_2+\left[\frac{P_lP_{l'}}{r}+P_{l'}\frac{P_{l'+1}-P_{l'-1}}{(2l'+1)r}\right]r_2^{-2}\frac{\partial}{\partial r_2}(F_2r_2)\right\}d\tau_1d\tau_2. \tag{16}$$

Here the angular integrations can be performed by means of Gaunt's integrals for products of three spherical harmonics since

$$P_l'=(2l+1)P_{l-1}+(2l-5)P_{l-3}+\cdots. \tag{16'}$$

By means of the expansion

$$1/r=\sum_0^\infty(r_2^n/r_1^{n+1})P_n\quad r_1>r_2$$

the expression (16) reduces to

$$\begin{aligned}J=(2l+1)\sum_\tau\int_{r_1>r_2}\Bigg\{(l_1l_1'\tau)\Bigg[\left(\tau\frac{r_2^{\tau-2}}{r_1^{\tau+1}}-(\tau+1)\frac{r_2^\tau}{r_1^{\tau+3}}\right)F\\+G_{12}\frac{r_2^{\tau-2}}{r_1^{\tau+1}}+G_{21}\frac{r_2^\tau}{r_1^{\tau+3}}\Bigg]+[l_1l_1'\tau]\left(G_{12}\frac{r_2^{\tau-2}}{r_1^{\tau+1}}+G_{21}\frac{r_2^\tau}{r_1^{\tau+3}}\right)\Bigg\}dr_1dr_2,\end{aligned} \tag{17}$$

where

$$\begin{aligned}(l,m,n)&=\int_{-1}^{+1}P_lP_mP_nd\mu\\&=2\frac{[((l+m+n)/2)!]^2(m+n-l)!(l+m-n)!(l+n-m)!}{(l+m+n+1)![((m+n-l)/2)!]^2[((l+m-n)/2)]^2[((l+n-m)/2)]^2}\end{aligned} \tag{17'}$$

is Gaunt's integral[8] while

$$[l_1\,l_1'\,\tau]=\int_{-1}^{+1}P_l'[(P_{l'+1}-P_{l'-1})/(2l'+1)]P_\tau d\mu=[l(l+1)/l'(l'+1)][l_1'\,l_1\,\tau] \tag{17''}$$

can be calculated by means of Gaunt's integrals or usually more simply by using the expression for P_l' as a polynomial in μ and applying the recurrence formula

$$(2n+1)\mu P_n=(n+1)P_{n+1}+nP_{n-1}$$

to express the integrand as a sum of products involving two Legendre functions at a time. In particular for an f electron outside a p shell we have $l=1$, $l'=3$ and

[8] See reference 2, Eq. (14). Note that Gaunt's P_l is l' times the Legendre function used here. Thus Gaunt's form has been divided by l' m' n' for use here.

$$J=\int_{r_1>r_2}\left\{\left(\frac{36}{35r_1^3}-\frac{2r_2^2}{105r_1^5}-\frac{40r_2^4}{21r_1^7}\right)F+\left(\frac{12}{35r_1^3}+\frac{10r_2^2}{21r_1^5}\right)G_{12}+\left(\frac{12r_2^2}{35r_1^5}+\frac{10r_2^4}{21r_1^7}G_{21}\right)\right\}dr_1dr_2, \quad (18)$$

while for an f electron outside a d shell $l'=3$, $l=2$, and

$$J=\int_{r_1>r_2}\left\{\left(\frac{6}{7r_2r_1^1}-\frac{4}{7}\frac{r_2}{r_1^4}+\frac{444r_2^3}{693r_1^7}-\frac{200r_2^5}{77r_1^8}\right)F+\left(\frac{2}{7r_2r_1^2}+\frac{2r_2}{7r_1^4}+\frac{50r_2^3}{77r_1^6}\right)\left(G_{12}+\frac{r_2^2}{r_1^2}G_{21}\right)\right\}dr_1dr_2. \quad (19)$$

4. $5p$ Shell of Caesium

We begin with the outer shells of Cs for we expect the largest exchange effects will come from these shells. We have to evaluate the integral J of Eq. (18). This is done in three ways. The first is a calculation with a hydrogenic wave function for the $4f$ electron and an approximate nodeless function for $5p$. The second makes use of the same function for $4f$ but an improved $5p$ function having nodes. The third uses Hartree's $5p$ function and a wave function for $4f$ obtained using Hartree's field by a numerical procedure.

The nodeless function is so chosen as to fit the Hartree $5p$ function[9] at large distances for we expect that in this region the maximum overlapping between the shell and the valence electron will occur, and hence we expect that the biggest contributions to our integral will be due to this region.

Thus

$$F(x)=2.20\times10^{-4}a_H^{-\frac{3}{2}}x^3e^{-\frac{1}{4}x},$$

$$f(x)=0.418a_H^{-\frac{3}{2}}x^4e^{-1.82x},$$

$$x=r/a_H,\quad a_H=h^2/4\pi^2me^2.$$

Our integral then contains terms of the type

$$J_{nm}=\int_{x_1>x_2}x_1^nx_2^me^{-\gamma(x_1+x_2)}dx_1dx_2,$$

$$\gamma=1.82+.25=2.07.$$

On rotating the coordinate system through 45° the double integral becomes

$$J_{nm}=2\int_0^\infty x^{n+m+1}e^{-2\gamma x}\int_0^x(1-y/x)^m(1+y/x)^ndy/x.$$

Changing variables to $z=y/x$ in the second integral, we find

$$J_{nm}=[2(n+m+1)!/(2\gamma)^{n+m+2}]H_{nm},$$

$$H_{nm}=\int_0^1(1+z)^n(1-z)^mdz.$$

In this way the terms of J are readily evaluated and we find that the doublet splitting[10] due to exchange is decreased by an amount 5×10^{-4} cm^{-1}.

In order to test the error in our approximation to the Hartree function, we have used other approximations in which the part of the function for large r is unchanged but nodes are introduced in the inner part of the function. This is done by replacing x^4 in $f(x)$ by a polynomial in such a way that the inner loops are about the same size as the actual Hartree function. We find that the contribution to the doublet separation is not significantly affected by this change.

Finally we have examined the effect of the charge distribution of the inner shells on the wave function for the valence electron. From Hartree's Z for the various shells, the potential in which the valence electron moves is found by integration. For $x>4$ this potential is inappreciably different from the Coulomb potential. Starting with the hydrogenic solution at $x=4$ we have continued the solution in to $x=1.5$ by means of the method of Wentzel-Kramers-Brillouin. At this point the actual solution is about twice as large as the hydrogenic solution. Since the important contributions to the integral all come from the region where x is large (about $x=3$ or 4) it is probable that this correction cannot alter the order of magnitude of the contribution to the doublet splitting. The point has been examined by means of numerical calculations and it has been found that no important change is produced by using the improved wave function.

[9] We are indebted to Professor Slater for communicating to us tables of the Hartree function for caesium.

[10] The actual doublet separations in the f series of Cs are of the order of 10^{-1} cm^{-1}, since the contribution of the direct integrals I to the doublet splitting is necessarily positive, the exchange integrals must be at least as great as the actual doublet separations if the inversions are due to this effort.

5. 4*d* Shell of Caesium

Since the valence electron function decreases rapidly as x decreases we expect our exchange integrals to be smaller for the 4*d* than for the 5*p* shell. (See Fig. 1 for the 4*d* and 5*p* functions.) If we calculate as before, using the hydrogenic wave function for the valence electron, we find that the effect of the 4*d* shell is about 1/100 that of the 5*p* shell. However if we examine the effective potential energy for the 4*f* valence electron, we find (Fig. 2) that there is a second region of classical motion between $x=0.8$ and

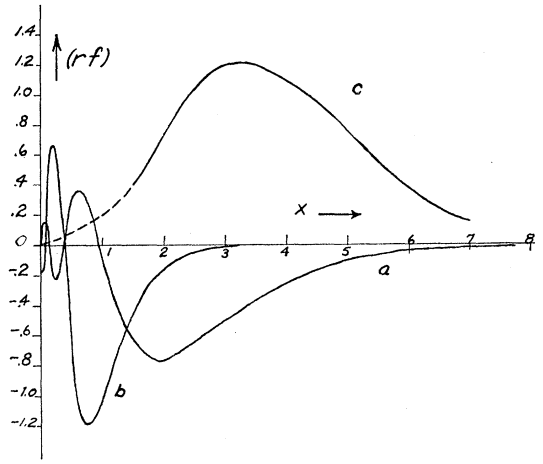

FIG. 1. a, Hartree 5*p* function for Cs1. b, Hartree 4*d* function for Cs1. c, $[(rf)(rF)/r^3]_0\int^r(rf)(rF)dr$ where f is the Hartree 5*p* function and F is the wave function of the valence electron (see Fig. 2c). The arc under this curve is the contribution of the first term of Eq. (18) to the integral J. The numbers from the graph must be multiplied by 7.18×10^{-7}.

$x=0.3$. We therefore have continued the valence electron function into the origin in the following way. For the region $2>x>0.3$ the effective potential is approximated by the dotted lines in the figure. For the region $0.30>x>0.15$ we assume a constant effective nuclear charge of $Z=32.5$, while for the region $0.15>x>0$ we

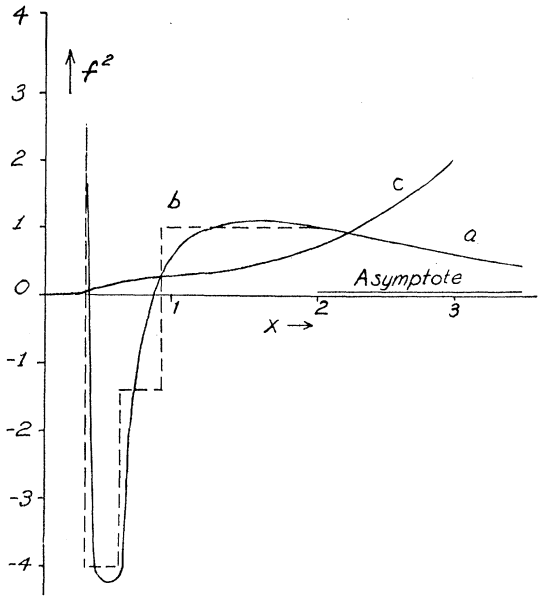

FIG. 2. a, Effective potential energy for the 4*f* electron of Cs1 as computed from Hartree's Z. b, The approximation to the effective potential energy used in the inner region of classical motion. c, Wave function for the 4*f* valence electron of Cs as computed from the above effective potential energy. The figures given by the graph must be multiplied by 4.34×10^{-3} to give the actual wave function.

assume an effective nuclear charge of $Z=54$. The above Z is that used by Hartree. Our use of two different Z's thus introduces a discontinuity only in the derivative of the potential but not in the potential itself. With the solution obtained in this way we have made a numerical estimate of our integrals. This modification increases the effect of the 4*d* shell so that it is of the same order of magnitude as the 5*p* shell.

From these calculations we conclude that for the caesium atom the magnetic exchange effects are unimportant. Though they are of the right sign, they are about a thousand times too small to explain the inversion of the *f* terms in this spectrum.