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THE FINE STRUCTURE OF He AS A TEST OF THE SPIN INTERACTIONS OF TWO ELECTRONS

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Abstract

A tentative expression for the quantum Hamiltonian of two electrons has been set up in a previous paper. The equation is discussed again. It is shown that the last term in it is subject to doubt. The Hamiltonian is tested by applying it to the calculation of the fine structure of the He 2^3P level. It is found that the above mentioned term in e^4 is in contradiction with experiment. Removing the term from the equation one is left essentially with Heisenberg's old Hamiltonian. The spin interaction in it is shown to agree well with experiment. The calculation has been applied also to Li^+.

The essential improvements on previous work are: (1) an increase in the precision of the unperturbed eigenfunctions; (2) a determination from experimental data of a constant D which depends directly on spin—spin interactions (see Eq. (1) below) and which can be calculated with fair accuracy. Comparing the theoretical and empirical values of D a clearer test of the magnitude of spin—spin interactions can be obtained than by calculating the relative positions of the three components of the triplet. The reason for this is that the relative positions of the lines depend also on another constant C which is a difference of two approximately equal numbers and is more difficult to calculate accurately.

§I Purpose of Work and Results

The motion of one electron in an external field is treated very satisfactorily by the Dirac equation. It is desirable to have a similar treatment of the two or many electron problem. A partial attempt in this direction has been made by the writer.[1] Considerations in configuration space and also the application of the Heisenberg-Pauli[2] wave field theory led to the Eq. (6) of the above paper. This equation appeared at the time as a likely one, but it was impossible to give a rigorous derivation. The writer has used the first form of the Heisenberg-Pauli theory. Because of the indefiniteness due to the infinite self interactions of point charges with themselves a certain amount of

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[1] Breit, Phys. Rev. **34**, 553 (1929).

[2] W. Heisenberg and W. Pauli Jr., Zeits. f. Physik **56**, 1, 1929, Zeits. f. Physik **59**, 168 (1930).

arbitrariness was necessary in removing the infinite terms of the total energy. Also the interaction was derived only to the first approximation in e^2. The same problem has been treated in more detail by Oppenheimer[3] who showed that even to higher powers of e^2 the writer's Eq. (6) could be derived if certain infinite terms of the interaction energy are systematically neglected. However, Oppenheimer also shows that a strict application of the wave field theory leads to infinite relative displacements of the atomic energy levels. The failure of quantum mechanics to give a satisfactory account of the electromagnetic interaction of two particles appears to be connected with two difficult questions: (1) the size of the electron i.e. whether the electron can be located at a point and (2) the Dirac jumps to states of negative energy which make it impossible to have normal states for a finite number of particles. Neither of these questions can be answered at present and it seems that no satisfactory purely theoretical solution of the two electron problem can be obtained before this is done.

The derivation of (6) in configuration space was obtained by using Darwin's classical Hamiltonian function. The choice of quantum symbols has been made in such a way as to obtain equations of motion in agreement with the classical ones. This however was not sufficient to establish the validity of the equation. In fact a discussion in configuration space enables one to see a fault in the equation. In order to explain this unsatisfactory feature we explain first in somewhat more detail the satisfactory side of it. With (6) as it stands we have, omitting the external field, the following equations of motion:

$$(A)\quad \dot{x}_k{}^{\mathrm{I}} = -c\alpha_k{}^{\mathrm{I}};\ \dot{p}_k{}^{\mathrm{I}} = -e_{\mathrm{I}}e_{\mathrm{II}}\frac{\partial}{\partial x_k{}^{\mathrm{I}}}\left\{r^{-1} - \frac{1}{2}[(\boldsymbol{\alpha}^{\mathrm{I}}\boldsymbol{\alpha}^{\mathrm{II}})r^{-1} + r^{-3}(\boldsymbol{\alpha}^{\mathrm{I}}\boldsymbol{r})(\boldsymbol{\alpha}^{\mathrm{II}}\boldsymbol{r})]\right\}$$

The classical expressions obtained from Darwin's Hamiltonian are:

$$(B)\ \dot{x}_k{}^{\mathrm{I}} = v_k = \frac{p_k{}^{\mathrm{I}}}{m_{\mathrm{I}}} - \frac{p_k{}^{\mathrm{I}}p_{\mathrm{I}}{}^2}{2c^2m_{\mathrm{I}}{}^3} - \frac{e_{\mathrm{I}}e_{\mathrm{II}}}{2m_{\mathrm{I}}m_{\mathrm{II}}c^2}[p_k{}^{\mathrm{II}}r^{-1} + r^{-3}(x_k{}^{\mathrm{II}} - x_k{}^{\mathrm{I}})(\boldsymbol{p}_{\mathrm{II}}\boldsymbol{r})]$$

$$(C)\ \dot{p}_k{}^{\mathrm{I}} = -e_{\mathrm{I}}e_{\mathrm{II}}\frac{\partial}{\partial x_k{}^{\mathrm{I}}}\{r^{-1} - (1/2m_{\mathrm{I}}m_{\mathrm{II}}c^2)[r^{-1}(\boldsymbol{p}^{\mathrm{I}}\boldsymbol{p}^{\mathrm{II}}) + r^{-3}(\boldsymbol{p}^{\mathrm{I}}\boldsymbol{r})(\boldsymbol{p}^{\mathrm{II}}\boldsymbol{r})]\}.$$

The first equation (A) is an exact relation between the velocity and α_k. Equation (B) connects the velocities with the momenta. It was supposed that, in the sense of the correspondence principle, (B) is also true in the quantum theory. It then followed that (C) agrees with the second equation (A) to within terms in $(v/c)^2$. The $p_k{}^I$ of Eq. (6) therefore replaces Darwin's $p_k{}^I$ because they have the same rate of change. The employment of equation (B) in the quantum theory is, of course, questionable. All that can be said is that the correct quantum equation should give (B) as an effective equation holding for wave packages. This has to be proved for whatever equation is finally devised.

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[3] J. R. Oppenheimer, Phys. Rev. **35**, 461 (1930).

For the discussion of positive energy levels we can use the writer's Eq. (48) which is equivalent to (6). Here if terms in h are dropped the Hamiltonian becomes exactly the classical one with the exception that the last term does not disappear. This shows that (B) and (C) are not satisfied consistently in Eq. (6) the error being of the order of e^4/mc^2r^2. The writer is very grateful to Professors Pauli and Heisenberg for emphasizing the fact that this last term does not contain h.

There is another unsatisfactory property of Eq. (6). Equation (B) gives p_k^I, p_k^{II} in terms of v_κ^I, v_k^{II}. Thus

$$\boldsymbol{p}_{\mathrm{I}} = m_{\mathrm{I}}\boldsymbol{v}_{\mathrm{I}} + m_{\mathrm{I}}\boldsymbol{v}_{\mathrm{I}}(v_{\mathrm{I}}^2/2c^2) + (e_{\mathrm{I}}e_{\mathrm{II}}/2c^2)\,[r^{-1}\boldsymbol{v}_{\mathrm{II}} + r^{-3}\boldsymbol{r}(\boldsymbol{v}_{\mathrm{II}}\boldsymbol{r})]$$

This is a purely classical relation. In (6) $\boldsymbol{p}_I$ is replaced by $(h/2\pi i)\nabla_I$. For a single particle of charge e_I in an external field of vector potential $\boldsymbol{A}_I$ we replace $m_I\boldsymbol{v}_I(1-\beta_I^2)^{-1/2}$ by $(h/2\pi i)\nabla_I-(e_I/c)\boldsymbol{A}_I$ In this case, to a sufficient approximation $\boldsymbol{A}_I=e_{II}\boldsymbol{v}_{II}/cr$. We should expect that a correct theory will replace $m_I\boldsymbol{v}_I(1-\beta_I^2)^{-1/2}\cong m_I\boldsymbol{v}_I+m_I\boldsymbol{v}_I(v_I^2/2c^2)$ by $\boldsymbol{p}_I-(e_Ie_{II}\boldsymbol{v}_{II}/c^2r)$. We have identified however the quantum operator $(h/2\pi i)\nabla_I$ with Darwin's $\boldsymbol{p}_I$. We see therefore that $\boldsymbol{p}_I$ in (6) replaces the classical

$$\left[\frac{m_{\mathrm{I}}\boldsymbol{v}_{\mathrm{I}}}{(1-\beta_{\mathrm{I}}^2)^{1/2}}+\frac{e_{\mathrm{I}}e_{\mathrm{II}}\boldsymbol{v}_{\mathrm{II}}}{c^2r}\right]+\frac{e_{\mathrm{I}}e_{\mathrm{II}}}{2c^2}\left[-\frac{\boldsymbol{v}_{\mathrm{II}}}{r}+\frac{\boldsymbol{r}(\boldsymbol{v}_{\mathrm{II}}\boldsymbol{r})}{r^3}\right]$$

while it would be more satisfactory if it replaced only the first part of that expression. This means that if m_{II} becomes very large and the reaction on particle II negligible there is no exact agreement between (6) and Dirac's equation. It is thus seen that (6) is likely to be right only to the first order in e^2. Also from the point of view of the wave field theory there is much less arbitrariness in the derivation of first order effects in e^2.

With Eq. (6) it is possible to derive an equation involving two row, two column spin matrices and showing therefore the interaction of electrons as a function of their spins. This is Eq. (48). The interaction energy contains, in addition to the ordinary spin interactions, the extra term in e^4. It is seen from the above considerations that the presence of this term is subject to doubt. In the writer's previous paper it has been supposed that the term might have a physical significance. Some rough estimates of the order of magnitude of its effect indicated that it might be reconcilable with experimental facts. It was felt however that a more accurate test is needed.

A possibility of testing the spin interaction in e^4 is offered by the fine structure of the He triplet spectrum and to some extent by that of Li^+. It has been shown by Heisenberg[4] that the inverted positions of the triplet components in these spectra can be explained by taking into account the interaction of electron spins with each other. The magnitude of the separations was also shown by him to be approximately in agreement with experiment. An attempt to refine Heisenberg's calculation has been made by Sugiura.[5]

[4] Heisenburg, Zeits. f. Physik **39,** 499 (1926).

[5] Suguira, Zeits. f. Physik **44,** 190 (1927).

He considered in an approximate way the effect of polarization of the charge distribution formed by the inner electron due to the electric field of the outer one. A somewhat better agreement with the total separation in the yellow He has been obtained by using this correction. Gaunt[6] has also attempted to improve on Heisenberg's calculation but has not reached a definite conclusion. The difficulty in the application of Gaunt's calculation lies in the insufficiently accurate unperturbed eigenfunctions used by him.

In the present paper the effect of all the spin interactions is calculated using unperturbed eigenfunctions determined by the variational equation derived in the writer's recent paper.[7] These functions are also not exact but they are more accurate than those previously used. The result of the calculation is that satisfactory agreement with the experimentally observed fine structure is obtained if the extra terms in e^4 are neglected. The agreement with experiment is spoiled if the supposed additional effect of these terms is taken into account. This conclusion follows from the fine structure of He and to some extent also from the fine structure of Li^+ if the recent interpretation of the hyperfine structure of that spectrum is adopted.[8] The conclusion is therefore that the terms in e^4 have no physical significance and that Eq. (6) is not correct to higher orders than e^2. With terms of the first order in e^2 satisfactory agreement with experiment is obtained.

The present test is not able to distinguish between Gaunt's equation or Eq. (6) with the terms in e^4 omitted. Both of these agree with the observed fine structure. It is hard to believe however that the terms in $(1/2r)\left[(\boldsymbol{p}^I\boldsymbol{p}^{II})+(\boldsymbol{p}^I r)\ (\boldsymbol{p}^{II}r)/r^2\right]$ do not exist and are replaced by $(\boldsymbol{p}^I\boldsymbol{p}^{II})/r$. For this reason Gaunt's equation is also very likely to be incorrect. Further, Eq. (36) of the writer's previous paper is equivalent to Gaunt's and is seen also to contain terms in e^4. These terms do not have any influence on the fine structure being of the form $(e^4/4mc^2r^2)\ (3-2(\sigma^I\sigma^{II}))$. They cannot have a physical significance since they do not vanish if $h\rightarrow 0$.

The calculations which follow are rather laborious and it is advisable to explain at this point the comparison of the results with the experimental fine structure. The effect of spin interactions is taken into account by the ordinary method of perturbation calculations. Both in He and Li^+ this method should give, in the first order, results much more accurate than the experimental precision. This is seen directly from the fact that the separations in the fine structure are of the order of a few cm^{-1} while the total term value is of the order of $2\times 10^4\ \mathrm{cm}^{-1}$. In the perturbation calculation the effect of the spins is first of all neglected and the eigenfunctions used are determined. Their form is that of (21) in the writer's previous paper.[7] Quite independently of the form of the function F it may be shown that the relative position of the three components of a triplet P term is given to the first order of the spin perturbations (and therefore very accurately in our case) by the following expression for the energy

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[6] Gaunt, Phil. Transactions of the Roy. Soc. **A228,** 151 (1929).

[7] Breit, Phys. Rev. **35,** 569 (1930).

[8] Schüler and Brück, Zeits. f. Physik **58,** 735 (1929).

$$E = E_0 + [-3(C+D),\ 2(D-C),\ 0] \tag{1}$$

for

$$j = 0,\quad 1,\quad 2$$

where j is the inner quantum number, and C, D are certain integrals in terms of F. The term C is due to the interaction of the electric field with the electron spins. It is this term that gives rise to the ordinary multiplet structure and commonly goes under the name of the interaction of the spin with orbital angular momentum. By itself (i.e. neglecting D) it would give rise to the Landé interval rule. Although there are at present no accurate quantitative confirmations of the correctness of C, thereappears to be no reasonfor doubting it particularly on account of the large number of cases which are in qualitative agreement and it is therefore supposed that the physical nature of C is correct. The integral D however involves the interactions of the two electronic spins with each other in the form of $f(r)\ (\sigma_1 \boldsymbol{r})\ (\sigma_2 \boldsymbol{r})$.[9] The questionable terms in e^4 give rise to a part of D which will be called D_1, while the terms in e^2 give rise to another part D_0.

$$D = D_0 + D_1 \text{ with terms in } e^4 \tag{2}$$

$$\text{or } D = D_0 \text{ without terms in } e^4$$

The experimentally known fine structure determines from (1) both $C+D$ and $C-D$, and therefore also C and D. These values will be called *empirical* values of C and D. The comparison with experiment is made by computing D according to the first and the second Eq. (2). It is found that the first equation is in disagreement with the empirical value of D while the second agrees well with it. This agreement does not appear to be accidental because D_0 consists mainly of terms of the same sign and also because the agreement holds in He and Li$^+$.[10]

Since the physical nature of C appears to be sound this constant has been used as a check on the accuracy of the approximate form of F. It has proved difficult to obtain absolute agreement of the empirical and theoretical values of C. The difficulty lies in the laboriousness of the determination of eigenfunctions by the variational method and particularly in the fact that C is a difference of two numbers which are of approximately the same magnitude. These two approximately equal but opposite contributions to C are due to (1) the electric field of the nucleus acting on the spin of each electron and (2) the electric field of one electron acting on the spin of the other. The latter of these two effects turns out to be the larger one numerically. It depends essentially on the average value of $1/r^3$. From the agreement of the empirical and theoretical values of C it is possible to estimate the accuracy of the second part of C. The constant D_0 also depends essentially on $1/r^3$. The estimated accuracy of the second part of C gives one therefore a guide as to the accuracy of the computation for D_0.

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[9] r is written here and later for the distance between the two electrons. The two electrons are referred to from now on as 1 and 2 rather than I and II.

[10] The numerical calculations on Li$^+$ were made jointly with Mr. L. P. Granath of this

For He the result of the calculation is

$$(C, D_0, D_1) = (R_H\alpha^2/24)(-0.91, -0.62, +0.27) \qquad (3)$$

where R_H is the Rydberg constant for hydrogen and α is the fine structure constant. In comparing this with empirical material we find somewhat different data. The results of Houston[11] and of Hansen[12] agree in giving $\Delta\nu_{02}/\Delta\nu_{12}=14$ with $\Delta\nu_{02}=-3(C+D)=1.068$ cm^{-1}; $\Delta\nu_{12}=-2(C-D)=0.077$ cm^{-1}. The results of Wei[13] are somewhat different giving $\Delta\nu_{02}/\Delta\nu_{12}=10$ or 11. With the results of Hansen and Houston the empirical value of D is $(R_H\alpha^2/24)$ (-0.65) cm^{-1} while using the results of Wei it is $(R_H\alpha^2/24)$ (-0.60) cm^{-1}. Either of these values is in good agreement with D_0 and is definitely in disagreement with D_0+D_1. From the Hansen, Houston data we obtain as the empirical value of $C=-(R_H\alpha^2/24)$ 0.81. This is not in very good agreement with the computed value listed in (3). However the agreement is as good as can be expected. This may be seen by considering the numerical part of the calculation for C. In the final step of the calculation we have $C=1.302$ $R_H(\alpha^2/24)$ $(1.020-1.719)$. The first of these numbers 1.020 is due to the action of the electric field of the nucleus and the second -1.719 is due to the field of the electrons. An error of 5% in the second number is likely to be accompanied by an approximately equal error in the opposite direction for the first number because the eigenfunction is normalized. An error of 10% in 1.719 is 0.17 and this constitutes an error of 24% in the result $-0.70=1.02-1.72$. It is therefore likely that the disagreement of 12% between the computed and the empirical value of C is an indication of an accuracy of about 2.5% in the computation of either the first or the second part of it. In other words the apparently low accuracy is due to the fact that C is the difference of two parts which are approximately equal in numerical magnitude. Using Wei's value for the separation ratio $C=-(R_H\alpha^2/24)$ (0.84). If this value is right the computation for C is correct to 8.3% and a likely accuracy of the calculation of each part is 1.7%. For Wei's value of the separation ratio the empirical values of both C and D come out lower than the calculated by consistent amounts. Using Houston and Hansen's observations the empirical D is higher than the calculated and the empirical C is lower. This is somewhat inconsistent because the error in the calculation is likely to be such as to overestimate the square of the eigenfunction for low r. It is likely however that neither the experiment nor the calculation is accurate enough to decide this point. It is only clear that the computed D_0 agrees well with either set of data and that the computed C, although different from the empirical, does not differ from it by more than can be explained by reasonable errors in the calculation. The presence of D_1 is definitely excluded since it would imply an inaccuracy of 43% in the calculation of D_0. The value of the nuclear spin is immaterial for the present application.

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laboratory and the writer is very grateful to him for his permission to quote here the results.

[11] Houston, Proc. Nat. Acad. **13**, 91 (1927).

[12] Hansen, Nature **119**, 237 (1927). Also see Grotrian Graphische Darstellung etc. vol. I, pp. 111–115, Springer, 1928.

[13] Wei, Astrophys. J. **68**, 194 (1928)

§II DETERMINATION OF APPROXIMATE UNPERTURBED FUNCTIONS

It has been shown by the writer[7] that ${}^3P$ states of a two electron configuration involving two electronic states with unequal azimuthal quantum numbers have the following complete set of normal orthogonal eigenfunctions

$$\begin{aligned} u_1 &= (3^{1/2}/4\pi)(F \sin\theta_1 e^{i\phi_1} - \tilde{F} \sin\theta_2 e^{i\phi_2}) \\ u_0 &= (6^{1/2}/4\pi)(F \cos\theta_1 - \tilde{F} \cos\theta_2) \\ u_{-1} &= (3^{1/2}/4\pi)(F \sin\theta_1 e^{-i\phi_1} - \tilde{F} \sin\theta_2 e^{-i\phi_2}) \\ F &= F(r_1, r_2; \theta), \tilde{F} = F(r_2, r_1; \theta) \end{aligned} \tag{4}$$

where (r_1, θ_1, ϕ_1), (r_2, θ_2, ϕ_2) are polar coordinates for each electron and $\cos\theta = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_2 - \phi_1)$ so that θ is the angle between r_1, r_2. This form is exact as long as the spin interactions are not brought in. If we had the exact form of F the whole problem could be solved quite accurately because as has been explained in §1 the first order of the perturbation calculation for the effect of spins should give a result of much higher accuracy than that of the experimental determinations. Unfortunately it is very difficult to determine F precisely and it is more practical to use good approximations for its form. Again, without approximations F is determined by the following conditions

$$\begin{aligned} \delta \int \Bigg\{ & \sum_{i=1,2} \left[\left(\frac{\partial F}{\partial r_i} \right)^2 - 2\cos\theta \frac{\partial F}{\partial r_i} \frac{\partial \tilde{F}}{\partial r_i} + \left(\frac{\partial \tilde{F}}{\partial r_i} \right)^2 \right] + 2F^2/r_1^2 + 2\tilde{F}^2/r_2^2 \\ & + 2\sin\theta F \frac{\partial \tilde{F}}{r_1^2 \partial\theta} + 2\sin\theta \tilde{F} \frac{\partial F}{r_2^2 \partial\theta} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left[\left(\frac{\partial F}{\partial\theta} \right)^2 - 2\cos\theta \frac{\partial F}{\partial\theta} \frac{\partial \tilde{F}}{\partial\theta} + \left(\frac{\partial \tilde{F}}{\partial\theta} \right)^2 \right] \\ & + (8\pi^2 m/h^2)(V - E)(F^2 - 2F\tilde{F}\cos\theta + \tilde{F}^2) \Bigg\} dV = 0 \end{aligned}$$

$$dV = r_1^2 r_2^2 \sin\theta dr_1 dr_2 d\theta \tag{4}$$

with the normalization condition

$$\int (F^2 - 2F\tilde{F}\cos\theta + \tilde{F}^2) dV = 1. \tag{5}$$

The ranges of integration are here $0 < r_1 < \infty$, $0 < r_2 < \infty$, $0 < \theta < \pi$. In order to determine F precisely it would be sufficient to expand it in the form of a sum of a complete set of orthogonal functions with arbitrary coefficients and then to determine the coefficients by means of (4) and (5). Since the labor involved in this is very great and since the resultant series must subsequently be used in the perturbation calculation an approximate solution of the problem has been obtained by the current variety of the Ritz method. It has been supposed that to a sufficient approximation

$$F = r_1(1 + c\cos\theta) \exp[-ar_1/2 - br_2/2]. \tag{6}$$

This form is suggested by the usual screening considerations. The first electron (1) can be thought of approximately as moving in a screened field force subject to a potential $(Z-1)/e^2r$ while the second electron (2) is moving mainly in an unscreened field Ze^2/r. If this is supposed to be true then it is found that (1) is actually likely to be found outside of the region where there is a large probability of finding (2). Approximately therefore the radial part of (6) should give the solution. It is this kind of approximation that has been used by Gaunt with values of a, b derived directly by the screening considerations. This consideration is not exact and it can be improved by introducing the dependence on c and adjusting a, b, c so that (4), (5) are satisfied. The improvement to be expected from using (6) with adjustable constants amounts essentially to correcting the field of force acting on (1) for the incomplete screening of the nucleus by (2) and also to taking into account the fact that the two electrons cannot be considered as distributed on spherical shells and that the probability of a configuration r_1, r_2, θ depends on θ. We let

$$A_{r_i} = \left(\frac{\partial F}{\partial r_i}\right)^2 - 2\mu\frac{\partial F}{\partial r_i}\,\frac{\partial \tilde{F}}{\partial r_i} + \left(\frac{\partial \tilde{F}}{\partial r_i}\right)^2; \; \mu = \cos\theta$$

$$A_\theta = \left[\left(\frac{\partial F}{\partial \theta}\right)^2 - 2\mu\frac{\partial F}{\partial \theta}\,\frac{\partial \tilde{F}}{\partial \theta} + \left(\frac{\partial \tilde{F}}{\partial \theta}\right)^2\right](r_1^{-2} + r_2^{-2}). \tag{7}$$

$$B_\theta = 2r_1^{-2}F^2 + 2r_2^{-2}\tilde{F}^2 + 2r_1^{-2}\sin\theta F\frac{\partial F}{\partial \theta} + 2r_2^{-2}\sin\theta\tilde{F}\frac{\partial \tilde{F}}{\partial \theta}.$$

Substituting (6) and performing integrations involving only simple exponentials we find:

$$\int A_{r_i} dV = (1 + c^2/3)(8a^{-3}b^{-3} + 24a^{-5}b^{-1}) + bc(16\beta^{-7} - 24a\beta^{-8}); \; 2\beta = a + b$$

$$\int B_\theta dV = 32a^{-3}b^{-3}(1 + c^2/3) - 32c\beta^{-6}; \; \int A_\theta dV = (c^2/3)(192a^{-5}b^{-1} + 32a^{-3}b^{-3})$$

$$\int (r_1^{-1} + r_2^{-1})(F^2 - 2\mu F\tilde{F} + \tilde{F}^2)dV = (1 + c^2/3)(48a^{-4}b^{-3} + 96a^{-5}b^{-2}) - 64c\beta^{-7} \tag{8}$$

$$\int (F^2 - 2\mu F\tilde{F} + \tilde{F}^2)dV = 192[(1 + c^2/3)a^{-5}b^{-3} - (c/2)\beta^{-8}]\cdot \tag{9}$$

The integrations involving r^{-1} are somewhat more complicated. Expanding r^{-1} in zonal harmonics and powers of r_1, r_2, and then using[14]

$$\int_{-1}^{+1} \mu^n P_m(\mu)d\mu = \frac{2^{m+1}n!}{(n+m+1)!}\,\frac{\left(\frac{n}{2}+\frac{m}{2}\right)!}{\left(\frac{n}{2}-\frac{m}{2}\right)!} \quad (n \geq m) \tag{10}$$

[14] Whittaker and Watson, Modern Analysis, p. 311.

we have

$$\int_{-1}^{+1}(1+c\mu)^2r^{-1}d\mu = 2(1+c^2/3)\rho_1^{-1} + (4c/3)\rho_2\rho_1^{-2} + (4c^2/15)\rho_2^2\rho_1^{-3}$$

$$\int_{-1}^{+1}\mu(1+c\mu)^2r^{-1}d\mu = (4c/3)\rho_1^{-1} + (2/3+2c^2/5)\rho_2\rho_1^{-2} + (8c/15)\rho_2^2\rho_1^{-3} + (4c^2/35)\rho_2^3\rho_1^{-4} \qquad (11)$$

with the convention

$$r_1, r_2 = \rho_1, \rho_2 \text{ if } r_1 < r_2;\; r_1, r_2 = \rho_2, \rho_1 \text{ if } r_1 < r_2$$

Using

$$\int\int_{r_1>r_2} \exp(-ar_1 - br_2)dr_1dr_2 = a^{-1}(a+b)^{-1},$$

$$\int\int_{r_1<r_2} \exp(-ar_1 - br_2)dr_1dr_2 = b^{-1}(a+b)^{-1} \qquad (12)$$

we derive by successive differentiations with respect to a, b

$$\int_0^\infty\int_0^\infty r_1^2r_2^2\rho_1^{-1}\exp(-ar_1-br_2)dr_1dr_2 = 2\,[a^{-2}b^{-2}(a+b)^{-1}+a^{-1}b^{-1}(a+b)^{-3}] \qquad (13)$$

Again using (12)

$$\int_0^\infty\int_0^\infty r_1^2r_2^2\rho_2\rho_1^{-2}\exp(-ar_1-br_2)dr_1dr_2 = 6/[ab(a+b)^3].$$

Integrating (12) with respect to a and using

$$\int_0^\infty r^{-1}[\exp(-ar) - \exp((-a-b)r)]dr = \log(1+b/a)$$

we get

$$\int_0^\infty\int_0^\infty r_1^2r_2^2\rho_2^2\rho_1^{-3}\exp(-ar_1-br_2)dr_1dr_2 = 24a^{-5}\log(1+a/b) + 24b^{-5}\log(1+b/a) - 24(a^{-4}+b^{-4})(a+b)^{-1} - 12(a+b)^{-2}(a^{-3}+b^{-3}) - 8(a+b)^{-3}(a^{-2}+b^{-2}) - 6(a+b)^{-4}(a^{-1}+b^{-1}). \qquad (15)$$

Using (11), (13), (14), (15) one part of the integral involving r^{-1} is evaluated as

$$\int F^2r^{-1}dV = \frac{\partial^2}{\partial a^2}\int(1+c\mu)^2r^{-1}\exp(-ar_1-br_2)dV = \frac{24}{ab(a+b)^2}\left[\frac{2a+b}{a^3b} + \frac{3a+b}{a(a+b)^3}\right] + c\left[\frac{16}{a^3b(a+b)^3} + \frac{48}{a^2b(a+b)^4} + \frac{96}{ab(a+b)^5}\right] + c^2\bigg[192a^{-7}\log\frac{a+b}{b} - \frac{192}{a^6(a+b)} - \frac{96}{a^5(a+b)^2} + \frac{32}{5b^4a^2(a+b)} + \frac{32}{5b^4a(a+b)^2} \qquad (16)$$

$$-\frac{56a^{-4}+(64/5)b^{-4}}{(a+b)^3}-\frac{24a^{-3}+(96/5)b^{-3}}{(a+b)^4}+\frac{48(a^{-2}-b^{-2})}{5(a+b)^5}$$
$$\left.+\frac{48(a^{-1}+b^{-1})}{(a+b)^5}\right]$$

Another part of the integral in r^{-1} is given by the second line of (11). Using (12) we find

$$\begin{aligned}
&\tfrac{1}{2}\int_0^\infty\int_0^\infty r_1^3r_2^3\rho_2^3\rho_1^{-4}\exp\left[-\beta(r_1+r_2)\right]dr_1dr_2=(720\log 2-497.625)\beta^{-7}\\
&\tfrac{1}{2}\int_0^\infty\int_0^\infty r_1^3r_2^3\rho_2^2\rho_1^{-3}\exp\left[-\beta(r_1+r_2)\right]dr_1dr_2=(15/8)\beta^{-7}\\
&\tfrac{1}{2}\int_0^\infty\int_0^\infty r_1^3r_2^3\rho_2\rho_1^{-2}\exp\left[-\beta(r_1+r_2)\right]dr_1dr_2=(21/8)\beta^{-7}\\
&\tfrac{1}{2}\int_0^\infty\int_0^\infty r_1^3r_2^3\rho_1^{-1}\exp\left[-\beta(r_1+r_2)\right]dr_1dr_2=(33/8)\beta^{-7}.
\end{aligned}\tag{17}$$

Substituting these expressions (17) into the second line of (11) it is found that

$$\int\mu F\tilde{F}r^{-1}dV=\{3.5+13c+[2.1+(8/35)(720\log 2-497.625)]c^2\}\beta^{-7}\tag{18}$$

Combining (16) and (18) we also have $\int r^{-1}(F^2-2\mu F\tilde{F}+\tilde{F}^2)dV$. The variational Eq. (4) with the restricting condition (5) is now obtained by using (8), (9), (16), (18). On performing the substitutions it is convenient to use dimensionless variables x, y defined by

$$a=xG,\ b=yG,\ G=8\pi^2mZe^2/h^2.\tag{19}$$

The constant G is related to the Rydberg constant by

$$4R_Z=GZe^2.\tag{20}$$

The variational Eq. (4) becomes equivalent to the requirement that the fraction

$$\frac{E}{R_Z}=\frac{\alpha_0+2\alpha_1c+\alpha_2c^2}{\beta_0+2\beta_1c+\beta_2c^2}\tag{21}$$

should become a minimum. Here

$$\begin{aligned}
\alpha_0&=x^2+y^2-x-2y+\frac{x}{Z}\left[\frac{x^2y^2}{(x+y)^2}\left\{\frac{2x+y}{x^2y}+\frac{3x+y}{(x+y)^3}\right\}-\frac{56x^4y^3}{3(x+y)^7}\right]\\
2\alpha_1&=x^5y^3\left\{\frac{256y}{3(x+y)^7}-\frac{256xy}{(x+y)^8}-\frac{128}{3(x+y)^6}+\frac{512}{3(x+y)^7}\right.\\
&\qquad\left.+\frac{2}{Z}\left[\frac{1}{3x^3y(x+y)^3}+\frac{1}{x^2y(x+y)^4}+\frac{2}{xy(x+y)^5}-\frac{104}{3(x+y)^7}\right]\right\}\\
\alpha_2&=(5/3)y^2+(5/9)x^2-x/3-2y/3+\frac{2}{Z}[x^5y^3(\zeta/180)-6.48x^5y^3(x+y)^{-7}]
\end{aligned}\tag{22}$$

$$\beta_0 = 1, \; 2\beta_1 = -\, 128x^5y^3(x+y)^{-8}, \; \beta_2 = 1/3 \tag{23}$$

$$\begin{aligned}\zeta = {} & 720x^{-7}\log(1+x/y) - 720x^{-6}(x+y)^{-1} - 360x^{-5}(x+y)^{-2} \\ & + 24x^{-2}y^{-4}(x+y)^{-1} + 24x^{-1}y^{-4}(x+y)^{-2} - (210x^{-4}+48y^{-4})(x+y)^{-3} \\ & - (90x^{-3}+72y^{-3})(x+y)^{-4} + 36(x^{-2}-y^{-2})(x+y)^{-5} + 180x^{-1}(x+y)^{-6} \\ & + 180y^{-1}(x+y)^{-6}.\end{aligned}$$

The number 6.48 in the last term α_2 is the approximate value of $(32/15)[(21/8)+(2/7)(720\log 2-497.625)]$. The result of minimizing (21) is[15]

$$x = 0.273, \; y = 1.00 \;\; c = -\, 0.0089 \tag{25}$$

and the value of E/R_z corresponding to this is

$$E/R_Z = -\, 1.0654$$

while the experimental value is

$$(E/R_Z)_{exp} = -\, 1.0666.$$

Of the three constants entering the eigenfunction the constant x is the most important one for the following computations because it determines the mean radius of the outer electron and enters as a factor x^3 in most of the important terms of the formulas for fine structure separations. It should be observed here that the eigenfunction is sufficiently exact to determine the energy value to 0.1% which is a higher order of accuracy than that aimed at in the calculation of the fine structure.

§III SECULAR EQUATION FOR FINE STRUCTURE

Denoting, as is customary, the electronic spin functions by S_α, S_β with $S_\alpha = \binom{1}{0}$, $S_\beta = \binom{0}{1}$ we have a system of three normal orthogonal linearly independent functions

$$S_1 = S_\alpha{}^1 S_\alpha{}^2, \;\; S_0 = 2^{-1/2}(S_\alpha{}^1 S_\beta{}^2 + S_\alpha{}^2 S_\beta{}^1), \;\; S_{-1} = S_\beta{}^1 S_\beta{}^2 \tag{26}$$

the upper indices referring to the two electrons. These three functions when combined with the three coordinate functions (4) form a complete set of normal orthogonal functions of an unperturbed ^3P state. The system may be arranged in a table as follows

$$\begin{array}{cccc} m & & & \\ 2 & u_1S_1 & & \\ 1 & u_1S_0 & u_0S_1 & \\ 0 & u_1S_{-1} & u_0S_0 & u_{-1}S_1 \\ -1 & & u_0S_{-1} & u_{-1}S_0 \\ -2 & & & u_{-1}S_{-1} \end{array} \tag{27}$$

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[15] Dr. R. W. G. Wyckoff of the Rockefeller Institute has performed most of the numerical calculations on a calculating machine. The writer is very grateful to him for this assistance.

each row corresponding to a fixed magnetic quantum number m. The perturbation energy[16] is

$$\Delta H = \boldsymbol{A}\boldsymbol{\sigma}_1 + \boldsymbol{B}\boldsymbol{\sigma}_2 + \mathcal{D}_0 + \mathcal{D}_1 \tag{28}$$

with

$$\begin{aligned} \boldsymbol{A} &= \frac{he^2}{8\pi m^2c^2}\{Zr_1^{-3}\boldsymbol{M}_1 + r^{-3}[(\boldsymbol{r}_1 - \boldsymbol{r}_2) \times (2\boldsymbol{p}_2 - \boldsymbol{p}_1)]\} \\ \boldsymbol{B} &= \frac{he^2}{8\pi m^2c^2}\{Zr_2^{-3}\boldsymbol{M}_2 + r^{-3}[(\boldsymbol{r}_2 - \boldsymbol{r}_1) \times (2\boldsymbol{p}_1 - \boldsymbol{p}_2)]\} \end{aligned} \tag{28'}$$

$$\mathcal{D}_0 = R_0(r)(\boldsymbol{\sigma}_1\boldsymbol{r})(\boldsymbol{\sigma}_2\boldsymbol{r}), \quad R_0(r) = -(eh/4\pi mc)^2 3r^{-5} \tag{28''}$$

$$\mathcal{D}_1 = R_1(r)(\boldsymbol{\sigma}_1\boldsymbol{r})(\boldsymbol{\sigma}_2\boldsymbol{r}), \quad R_1(r) = (e^4/8mc^2)r^{-4} \tag{28'''}$$

The $\boldsymbol{M}$ are the orbital angular momentum operators $[\boldsymbol{r}\times\boldsymbol{p}]$. We have included here only those terms of the perturbation energy which have an influence on the fine structure and we have omitted therefore terms in $(\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)$. The first three terms of (28) i.e. (28′), (28″) are of the second degree in the electronic charge e and the last is of the fourth degree. We have written this last term separately so as to be able to see the result with it and without it. Letting

$$\boldsymbol{C} = \boldsymbol{A} + \boldsymbol{B} \tag{29}$$

we have

$$\begin{aligned} (\boldsymbol{A}\boldsymbol{\sigma}_1 + \boldsymbol{B}\boldsymbol{\sigma}_2)uS_1 &= C_z uS_1 + 2^{-1/2}(C_x + iC_y)uS_0 \\ (\boldsymbol{A}\boldsymbol{\sigma}_1 + \boldsymbol{B}\boldsymbol{\sigma}_2)uS_0 &= 2^{-1/2}(C_x - iC_y)uS_1 + 2^{-1/2}(C_x + iC_y)uS_{-1} \\ (\boldsymbol{A}\boldsymbol{\sigma}_1 + \boldsymbol{B}\boldsymbol{\sigma}_2)uS_{-1} &= 2^{-1/2}(C_x - iC_y)uS_0 - C_z uS_{-1} \end{aligned} \tag{30}$$

On the right side of these formulas all terms in the antisymmetric combinations $2^{-1/2}\,(S_\alpha{}^1S_\beta{}^2 - S_\alpha{}^2S_\beta{}^1)$ have been omitted since they do not belong to the triplet state. We are justified in doing this in the present calculation because the formulas (30) are to be used in the calculation of matrix elements for the secular equation and only matrix elements between eigenfunctions belonging to the unperturbed ^3P state are of interest to us. Similarly we find[17]

$$\begin{aligned} (\boldsymbol{\sigma}_1\boldsymbol{r})(\boldsymbol{\sigma}_2\boldsymbol{r})S_1 &= z^2S_1 + (2)^{1/2}z(x + iy)S_0 + (x + iy)^2S_{-1} \\ (\boldsymbol{\sigma}_1\boldsymbol{r})(\boldsymbol{\sigma}_2\boldsymbol{r})S_0 &= (2)^{1/2}z(x - iy)S_1 + (x^2 + y^2 - z^2)S_0 - (2)^{1/2}z(x + iy)S_{-1} \\ (\boldsymbol{\sigma}_1\boldsymbol{r})(\boldsymbol{\sigma}_2\boldsymbol{r})S_1 &= (x - iy)^2S_1 - (2)^{1/2}z(x - iy)S_0 + z^2S_{-1} \end{aligned} \tag{31}$$

Formulas (30), (31) give the effect of all the operations due to the spins. Other angular momentum operations are involved in the operator C itself.

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[16] See (1). The σ's are here Pauli's matrices with unchanged signs i.e. with signs opposite to those used in the above reference.

[17] A systematic way of obtaining the matrices involved in (30) and (31) is to observe that $\boldsymbol{A}\boldsymbol{\sigma}_1 + \boldsymbol{B}\boldsymbol{\sigma}_2$ with symmetrical $\boldsymbol{A}, \boldsymbol{B}$ is equivalent to an angular momentum matrix so far as operations on symmetric spin functions are concerned. From this point of view (30) is obvious and is easily generalized to any number of electrons. For (31) we can use (30) if it is remembered that $(\boldsymbol{\sigma}_1\boldsymbol{r} + \boldsymbol{\sigma}_2\boldsymbol{r})^2 = 2r^2 + 2(\boldsymbol{\sigma}_1\boldsymbol{r})(\boldsymbol{\sigma}_2\boldsymbol{r})$.

We see that

$$\mathbf{C} = \frac{he^2}{8\pi m^2c^2}\{Z(r_1^{-3}\boldsymbol{M}_1 + r_2^{-3}\boldsymbol{M}_2) - 3^{-3}[(\boldsymbol{r}_1 - \boldsymbol{r}_2) \times (\boldsymbol{p}_1 - \boldsymbol{p}_2)]\}. \qquad (30')$$

Applying C to the eigenfunctions u_1, u_0, u_{-1} it is found that

$$\begin{aligned} C_z(u_1, u_0, u_{-1}) &= C(u_1, u_0, u_{-1}) \\ (C_x + iC_y)(u_1, u_0, u_{-1}) &= C(0, -(2)^{1/2}u_1, (2)^{1/2}u_0) \\ (C_x - iC_y)(u_1, u_0, u_{-1}) &= C(-(2)^{1/2}u_0, (2)^{1/2}u_{-1}, 0) \end{aligned} \qquad (32)$$

where

$$\begin{aligned} \mathbf{C} = \left(\frac{eh}{4\pi mc}\right)^2 \Bigg\{ Z \int\Bigg[&\frac{F^2}{r_1{}^3} + \frac{\tilde{F}^2}{r_2{}^3} - \left(\frac{1}{r_1{}^3} + \frac{1}{r_2{}^3}\right)F\tilde{F}\cos\theta + \frac{1}{2}\left(\frac{1}{r_2{}^3}\right. \\ &\left.- \frac{1}{r_1{}^3}\right)\left(\tilde{F}\frac{\partial F}{\partial\theta} - F\frac{\partial\tilde{F}}{\partial\theta}\right)\sin\theta\Bigg]dV - 3\int\frac{1}{r^3}\Bigg[F^2 + \tilde{F}^2 - 2F\tilde{F}\cos\theta \\ &+ \frac{r_1}{r_2}\tilde{F}(F - \tilde{F}\cos\theta) + \frac{r_2}{r_1}F(\tilde{F} - F\cos\theta) + \frac{1}{2}\sin^2\theta\Bigg\{r_2\left(\tilde{F}\frac{\partial F}{\partial r_1}\right. \\ &\left. - F\frac{\partial\tilde{F}}{\partial r_1}\right) - r_1\left(\tilde{F}\frac{\partial F}{\partial r_2} - F\frac{\partial\tilde{F}}{\partial r_2}\right) + \left(\frac{r_2}{r_1} - \frac{r_1}{r_2}\right)\left(\tilde{F}\frac{\partial F}{\partial\theta} - F\frac{\partial\tilde{F}}{\partial\theta}\right)\cot\theta \\ &- \left(\frac{r_2}{r_1} + \frac{r_1}{r_2}\right)F\tilde{F}\Bigg\}\Bigg]dV\Bigg\}. \end{aligned} \qquad (33)$$

It is also found that:

$$\begin{aligned} (2)^{1/2}z(x + iy)R(r)(u_1, u_0, u_{-1}) &= (0, Du_1, Du_0) \\ (2)^{1/2}z(x - iy)R(r)(u_1, u_0, u_{-1}) &= (Du_0, Du_{-1}, 0) \\ (x + iy)^2R(r)(u_1, u_0, u_{-1}) &= (2Du_{-1}, 0, 0) \\ (x - iy)^2R(r)(u_1, u_0, u_{-1}) &= (0, 0, 2Du_1) \\ (r^2 - 3z^2)R(r)(u_1, u_0, u_{-1}) &= (Du_1, -2Du_0, Du_{-1}) \\ z^2R(r)(u_1, u_0, u_{-1}) &= (D'u_1, (D + D')u_0, D'u_{-1}) \end{aligned} \qquad (34)$$

with

$$\begin{aligned} D &= \int \tfrac{1}{5}\{2(a\alpha + b\beta)^2 - (a\beta - \alpha b)^2\}R(r)dV \\ D' &= \int \tfrac{1}{5}\{(a\alpha + b\beta)^2 + 2(a\beta - \alpha b)^2\}R(r)dV \end{aligned} \qquad (35)$$

where

$$a = F - \tilde{F}\cos\theta,\ b = \tilde{F}\sin\theta,\ \alpha = r_1 - r_2\cos\theta,\ \beta = r_2\sin\theta. \qquad (35\ )$$

In formulas (32), (34) we omit everywhere terms involving other functions than u_1, u_0, u_{-1}. The reason for this is the same as that for the omission of terms in $2^{-1/2}\,(S_\alpha^1 S_\beta^2 - S_\alpha^2 S_\beta^1)$ in (30), (31). These formulas (30), (31), (32), (34) can be used to form the secular determinant for the whole problem.

It is known that the matrix elements of ΔH between any two eigenfunctions belonging to different rows in (27) must vanish and that, therefore, the secular determinant can be broken up into five independent subdeterminants. With the aid of the results just described it is found that the subdeterminant $m=0$ is

$$\begin{vmatrix} -C-\lambda', & C+D, & 2D \\ C+D & -D-\lambda' & -C-D \\ 2D, & -C-D, & -C-\lambda' \end{vmatrix} = 0, \quad \lambda' = \lambda - D' \tag{36}$$

having roots $\lambda' = (-2C-3D,\ 2D-C,\ C)$. The other subdeterminants are similarly found and give some of the same roots the first occurring on the whole 1, the second 3, and the third 5 times. The result is that the energy is to within a common additive constant

$$E = E_0 + [-\ 3(C+D),\ 2(D-C),\ 0] \qquad (1)^{18}$$

for $j=0,\ 1,\ 2$.

§IV COMPUTATION OF C AND D[19]

Formula (6) is substituted into (33) and the integrations are performed. It is found that

$$\int (F^2 r_1^{-3} + \tilde{F}^2 r_2^{-3} - F\tilde{F} r_1^{-3}\cos\theta - F\tilde{F} r_2^{-3}\cos\theta)\,dV$$
$$= 8a^{-2}b^{-3}(1 + c^2/3) + 16c(a/2 + b/2)^{-5}. \tag{37}$$

In the remainder of the calculation terms in c^2 are dropped, this being justified by the small numerical value of c.

$$\int r^{-3}\Bigg\{ 2F^2 - 2F\tilde{F}\cos\theta + 2(r_1/r_2)(F\tilde{F} - \tilde{F}^2\cos\theta) + (1/2)\sin^2\theta\Bigg[2r_2\Bigg(\tilde{F}\frac{\partial F}{\partial r_1}$$
$$- F\frac{\partial \tilde{F}}{\partial r_1}\Bigg) - 2(r_2/r_1)F\tilde{F}\Bigg]\Bigg\}dV = 8\left[\frac{1}{a^2b(a+b)^2} + \frac{2b-a}{ab(a+b)^4} + \frac{20b}{(a+b)^6}\right] \tag{38}$$
$$+ 16c\left[\frac{2b-a}{ab(a+b)^4} + \frac{2}{(a+b)^5} + 4.168\frac{b-a}{(a+b)^6}\right].$$

Here $4.168 = (16/5)\ (120 \log 2 - 81.875)$. Substituting these expressions into (33), remembering the normalization condition (5) and (9), then substituting

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[18] The same result can be checked by using the theorem emphasized by Slater: the sum of the roots of a secular determinant is equal to the sum of the diagonal elements. The first row in (27) gives the last root ($j=2$), the second gives the sum of the last two, the third the sum of the three roots.

[19] The writer is very grateful to Dr. F. W. Doermann for checking some of these formulas.

the dimensionless constants x, y by means of (19) and noting that $G^3\mu^2 = 4Z^3R_H\alpha^2$ we have

$$\left(1 - 128\frac{x^5y^3}{(x+y)^8}c\right)C = R_HZ^3\alpha^2x^3\left\{\frac{Z}{6}\left[1 - \frac{64x^2y^3}{(x+y)^5}c\right] - \frac{1}{2}\left[\frac{y^2}{(x+y)^2} + \frac{xy^2(2y-x)}{(x+y)^4} + 20\frac{x^2y^4}{(x+y)^6}\right] - c\left[\frac{xy^2(2y-x)}{(x+y)^4} + \frac{2x^2y^3}{(x+y)^5} + 4.168\frac{y-x}{(x+y)^6}\right]\right\}.$$

The first term involving Z is due to the action of the electric field of the nucleus and the remaining part of C is due to the interaction of the two electrons. It is seen that the two parts of C have opposite signs. For large Z the first part predominates and gives the usual effect for high atomic numbers. For small Z the second part may be numerically the larger one and C may be negative.

The part of D arising from $\mathcal{D}_0$, given by (28″), is similarly found to be D_0 given by

$$\left(1 - 128\frac{x^5y^3}{(x+y)^8}c\right)D_0 = -(R_HZ^3\alpha^2x^3/5)\left\{\frac{y^2}{(x+y)^2} + \frac{xy^2(2y-x)}{(x+y)^4} + 2c\left[\frac{xy^2(2y-x)}{(x+y)^4} + \frac{xy^2}{(x+y)^3} - \frac{4x^2y^3}{(x+y)^5}\right]\right\}. \tag{40}$$

The part of D arising from $\mathcal{D}_1$, given by (28‴), is, neglecting c altogether

$$D_1 = (R_HZ^2\alpha^2x^2/120)\left[3 + \frac{256x^3y^3}{(x+y)^6} + 48\frac{x^4y^4(x^2+3y^2)}{(x^2-y^2)^5}\log\frac{x}{y} + 2x^2y^2\frac{x^4 - 11y^4 - 38x^2y^2}{(x^2-y^2)^4} + \frac{2x^2y^2}{(x^2-y^2)^2} + \frac{y^2+3x^2}{y^2-x^2}\right] \tag{41}$$

Substituting the numerical values of x, y, c of §2 the values of C, D_0, D_1 listed in § 1 are obtained.