THE TWO CENTRE PROBLEM IN WAVE MECHANICS

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This problem, in the particular case of the hydrogen molecular ion, is so well known that a detailed reference to the large number of papers dealing with it is unnecessary. The investigations to which chief reference is made will be found at the end of this paper.

With atomic units in which energy is measured in terms of that of the hydrogen atom in its lowest state, lengths are measured in terms of the radius of the innermost Bohr orbit of the hydrogen atom, and the unit charge is numerically that of the electron, Schrödinger's equation is

$$\Delta\psi + (E - 2V)\psi = 0. \tag{1}$$

If N_1, N_2 are the charges on the two fixed nuclei A and B, R is the distance AB, and r_1, r_2 are the distances of the electron from A and B respectively, the potential energy V is $(N_1N_2/R) - (N_1/r_1) - (N_2/r_2)$, whence, if we write $E' = E - (2N_1N_2/R)$, (1) becomes

$$\Delta\psi + \left[E' + 2\left(\frac{N_1}{r_1} + \frac{N_2}{r_2}\right)\right]\psi = 0. \tag{2}$$

If we introduce coordinates λ and μ, where $R\lambda = r_1 + r_2$, $R\mu = r_1 - r_2$, so that the nucleus A is given by $\lambda = 1$, $\mu = -1$ and B by $\lambda = 1$, $\mu = 1$, (2) can be written

$$\frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial\psi}{\partial\lambda}\right] + \frac{\partial}{\partial\mu}\left[(1-\mu^2)\frac{\partial\psi}{\partial\mu}\right] + \left[\frac{1}{\lambda^2-1} + \frac{1}{1-\mu^2}\right]\frac{\partial^2\psi}{\partial\phi^2}$$
$$+ \left[\frac{R^2E'}{4}(\lambda^2-\mu^2) + R(N_1+N_2)\lambda - R(N_1-N_2)\mu\right]\psi = 0, \tag{3}$$

where ϕ is the azimuthal angle.

The last equation is separable and we write

$$\psi = \Sigma(\psi_m \cos m\phi + \psi'_m \sin m\phi),$$

where m is a positive integer and ψ_m, ψ'_m are both expressible as the product of two functions $\psi(\lambda)$ and $\psi(\mu)$ which satisfy the equations

$$\frac{d}{d\lambda}\left[(\lambda^2-1)\frac{d\psi}{d\lambda}\right] + \psi\left[A - p^2\lambda^2 + R(N_1+N_2)\lambda - \frac{m^2}{\lambda^2-1}\right] = 0, \tag{4}$$

$$\frac{d}{d\mu}\left[(1-\mu^2)\frac{d\psi}{d\mu}\right] + \psi\left[-A + p^2\mu^2 - R(N_1-N_2)\mu - \frac{m^2}{1-\mu^2}\right] = 0, \tag{5}$$

respectively, where A is the separation constant, and we have written

$$p^2 = -\tfrac{1}{4}R^2E',$$

since E' is negative.

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Equations (4) and (5) are the general equations for the two centre problems, and each contains three parameters, viz. p, A and a numerical multiplier of the distance R between the nuclei. It is sometimes convenient to distinguish the values of the separation constant A as determined from these equations, and they will then be denoted by $A(\lambda)$ and $A(\mu)$ respectively.

The work of section I of this paper, dealing with the case of equal nuclei, had been completed at the time when a recent paper on this problem by G. Jaffé appeared covering almost the same ground. In order to investigate the case of different nuclei, treated in section II of this paper, it is desirable to discuss the simpler case in sufficient detail but to include only those portions of the original work in which our results differ from those of Jaffé or are extensions of his work. The new matter in section I contains (i) a method of obtaining approximate values of the separation constant $A(\mu)$ for large values of p; this is essential for a satisfactory investigation of the problem of unequal nuclei; and (ii) a proof that Hylleraas' solution of the λ-equation is convergent, contrary to Jaffé's statement that it diverges.

Section I. Equal nuclei

If we take $N_1 = N_2 (= N)$, equations (4) and (5) are simplified and we have in this case

$$\frac{d}{d\lambda}\left[(\lambda^2-1)\frac{d\psi}{d\lambda}\right]+\left[A+2RN\lambda-p^2\lambda^2-\frac{m^2}{\lambda^2-1}\right]\psi=0, \tag{6}$$

$$\frac{d}{d\mu}\left[(1-\mu^2)\frac{d\psi}{d\mu}\right]+\left[-A+p^2\mu^2-\frac{m^2}{1-\mu^2}\right]\psi=0. \tag{7}$$

A. To deal with (7) we write $\psi=(1-\mu^2)^{\frac{1}{2}m}f$, where f satisfies the differential equation

$$(1-\mu^2)\frac{d^2f}{d\mu^2}-2(m+1)\mu\frac{df}{d\mu}+[p^2\mu^2-A-m(m+1)]f=0, \tag{8}$$

and A has to be determined as a function of p so as to give a solution which is finite in the range $-1\leqslant\mu\leqslant 1$. Three types of solution have been given by Wilson, who was the first to treat this problem mathematically, viz. (1) an ascending power series for f in either even or odd powers of μ; (2) a series for ψ in terms of associated Legendre polynomials; and (3) a solution of (8) in the form $e^{\pm p\mu}$[power series in $(1\mp\mu)$]. The first two types lead to a three-term recurrence relation between the coefficients of the series, and the condition for the convergence of the series at $\mu=\pm 1$ leads to the determination of A as a function of p by means either of an infinite determinant or an infinite continued fraction. Both these solutions are suitable when p is small, but neither is suitable when p is large. The advantages of the third type of solution are not apparent in Wilson's treatment. For reasons to be given below (section I, **C**) it is the appropriate solution for large values of p and, since it can also be used for small values of p, it may be considered as the standard solution of the μ-equation in the form (8). For small values of p it is not as convenient as either of the other two solutions; e.g. for the $s\sigma$ states and

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the small value $p = 1{\cdot}8$ it required the calculations of eighteen convergents of the continued fraction (12) below to prove that $B = 1{\cdot}61$ or $A = 1{\cdot}25$, whereas from Wilson's even-power series in μ only three convergents were needed.

Write $f = e^{p\mu}y$ and $x = 1-\mu$; the equation for y is

$$x(2-x)\frac{d^2y}{dx^2} + 2\{px^2 - (m+1+2p)x + (m+1)\}\frac{dy}{dx} + \{2p(m+1)x - B\}y = 0, \quad (9)$$

where $B = A' + (m+2p)(m+1)$ and $A' = A - p^2$. This equation has a regular singularity at $x = 0$, where the exponents are 0 and $-m$. We therefore assume a solution of the form $y = \sum_0^\infty a_n x^n$, and obtain the three-term recurrence relation

$$2(m+n+1)(n+1)a_{n+1} - \{n(n+1+2m+4p) + B\}a_n + 2p(n+m)a_{n-1} = 0 \quad (10)$$

for $n = 0, 1, 2, 3, \ldots$, a_{-1} being taken to be zero. The usual procedure shows that $\lim_{n\to\infty} a_{n+1}/a_n$ is $\frac{1}{2}$ or 0; the former leads to divergence at $x = 2$ ($\mu = -1$), while the latter makes the series convergent if B is determined as a function of p by means of the infinite continued fraction

$$\frac{B}{2(m+1)} = \cfrac{\frac{p(m+1)}{2(m+2)}}{\frac{B+(2+2m+4p)}{4(m+2)}} - \cfrac{\frac{p(m+2)}{3(m+3)}}{\frac{B+2(3+2m+4p)}{6(m+3)}} - \cfrac{\frac{p(m+3)}{4(m+4)}}{\frac{B+3(4+2m+4p)}{8(m+4)}} - \cdots \quad (11)$$

This continued fraction can be used directly when p is small. For example, in the σ states when $m = 0$, we have

$$\frac{B}{2} = \cfrac{\frac{p}{2^2}}{\frac{B+2+4p}{2.2^2}} - \cfrac{\frac{2p}{3^2}}{\frac{B+2(3+4p)}{2.3^2}} - \cfrac{\frac{3p}{4^2}}{\frac{B+3(4+4p)}{2.4^2}} - \cdots, \quad (12)$$

where B is now equal to $A - p^2 + 2p$. For the first root of (12), giving the $s\sigma$ states, we obtain without difficulty

$$B = 2p - \tfrac{2}{3}p^2 + \frac{2p^4}{135} + \ldots, \quad \text{whence} \quad A = \tfrac{1}{3}p^2 + \frac{2p^4}{135} + \ldots,$$

in agreement with Wilson's result obtained from the solution of (8) as an even-power series in μ. Similarly for the second root of (12), giving the $p\sigma$ states, we find that $A = -2 + \frac{2}{5}p^2 + \ldots$, again in agreement with Wilson.

Thus, for any value of A determined from (11) there is a solution of (7) of the form $\psi_1 = (1-\mu^2)^{\frac{1}{2}m} e^{p\mu}\left[\sum_0^\infty a_n (1-\mu)^n\right]$, and, since (7) is unaltered by changing the sign of μ, there is also a solution $\psi_2 = (1-\mu^2)^{\frac{1}{2}m} e^{-p\mu}\left[\sum_0^\infty b_n (1+\mu)^n\right]$. Since there can only be one solution of (7) which is finite in the range $-1 \leqslant \mu \leqslant 1$, these two solutions are identical and each is effectively Wilson's solution.

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The great advantage of this type of solution is that the infinite continued fraction (11) can be used when p is large. To obtain a general formula it is inverted r times into the form

$$\frac{p(r+m+1)}{\{(r+1)(r+2+2m+4p)+B\}-\dfrac{(r+2)(r+m+2)}{2(r+2)(r+m+2)}}-\frac{p(r+m+2)}{\{(r+2)(r+3+2m+4p)+B\}-\dfrac{(r+3)(r+m+3)}{2(r+3)(r+m+3)}}-\cdots$$

$$=\frac{\{r(r+1+2m+4p)+B\}}{2(r+1)(r+m+1)}-\frac{p(r+m)}{\{(r-1)(r+2m+4p)+B\}-\dfrac{(r+1)(r+m+1)}{2r(r+m)}}-\cdots \qquad (11a)$$

in order to obtain the rth root of (11). From the right-hand side of (11a) the first approximation when p is large is $B=-4pr$. If we write $B=-4pr+B_0$ and equate the coefficients of p^0 on each side of the equation, we find that

$$r+m+1=\frac{B_0+r(r+1+2m)}{(r+m+1)(r+1)}+\frac{(r+m)^2r}{(r+m+1)(r+1)},$$

whence $B=-4pr+\{2r^2+2r(m+1)+(m+1)^2\}$. For the next approximation we write $B=-4pr+B_0+B_1p^{-1}$ and equate the coefficients of p^{-1} on each side of (11a). In this way we find that

$$B_1=\tfrac{1}{4}\{4r^3+6(m+1)r^2+2(m+1)(m+2)r+(m+1)^2\},$$

and finally, since $A=B+p^2-(m+2p)(m+1)$, we obtain the *asymptotic* formula

$$A=p^2-2p(m+1+2r)+\{2r^2+2r(m+1)+(m+1)\}$$
$$+\frac{1}{4p}\{4r^3+6(m+1)r^2+2(m+1)(m+2)r+(m+1)^2\}+\ldots. \qquad (13)$$

This result, owing to the existence of nodes in pairs with an extra node at $\mu=0$ in the odd states, is applicable to the two states in which there are $2r$ and $2r+1$ nodes in μ. For the states in which there are no nodes or one node in μ, so that $r=0$, it is found to a higher order in p^{-1} that

$$A=p^2-2p(m+1)+(m+1)+(m+1)^2\left[\frac{1}{4p}+\frac{m+2}{8p^2}+\frac{5m^2+22m+23}{64p^3}\right]+\ldots, \qquad (14)$$

giving for the $s\sigma$ and $p\sigma$ states in which $m=0$,

$$A=p^2-2p+1+\frac{1}{4p}+\frac{1}{4p^2}+\frac{23}{64p^3}+\ldots. \qquad (15)$$

As a numerical example of the use of (15) we may take (i) the relatively small value $p=4{\cdot}472$ ($p^2=20$) which gives $A=12{\cdot}13$ (Wilson's solution as a power series in μ gives $A=12{\cdot}16$), and (ii) the large value $p=10$ which gives $A=81{\cdot}028$. This latter result is proved to be correct to the figures given by using the con-

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tinued fraction (12) and working out the successive convergents directly until they agree to three decimal places.

The problem of calculating the characteristic values of A for large values of p may therefore be considered to be solved by using a solution of the type

$$\psi = (1-\mu^2)^{\frac{1}{2}m} e^{p\mu} \left[\sum_0^\infty a_n (1-\mu)^n \right],$$

leading to the infinite continued fraction (11) for the determination of these values. Wilson's discussion of the μ-equation for large values of p is unsatisfactory. It has been amended by Jaffé, but even then it is a more difficult matter to obtain higher approximations of the type given by (14), and Jaffé does not give the term of $O(p^{-1})$ in the general formula (13).

B. The differential equation (6) in λ has been discussed by several investigators. McCrea and Newing* have considered the question of the existence of solutions of a general type of differential equations of which this is a particular case, and Teller has provided a proof for this special equation that a solution exists which is finite in the range $1 \leqslant \lambda \leqslant \infty$. The value of A having been determined as a function of p by means of any of the analytical solutions of (7), a solution of (6) will then give the additional parameter $2RN$ as a function of p.

Writing $\psi = (\lambda^2-1)^{\frac{1}{2}m} f$, (6) becomes

$$(\lambda^2-1)\frac{d^2f}{d\lambda^2} + 2(m+1)\lambda\frac{df}{d\lambda} + \{A + m(m+1) - p^2\lambda^2 + 2RN\lambda\} f = 0, \quad (16)$$

of which analytical solutions have been given by Hylleraas and Jaffé. The latter's solution is, in our notation,

$$f = e^{-p\lambda}(\lambda+1)^\sigma \sum_0^\infty c_n \left(\frac{\lambda-1}{\lambda+1}\right)^n,$$

where, writing $\xi = (\lambda-1)/(\lambda+1)$ and $y = \sum_0^\infty c_n \xi^n$, the equation for y is

$$\xi(1-\xi)^2\frac{d^2y}{d\xi^2} + \frac{dy}{d\xi}[-(m+2\sigma-1)\xi^2 + 2(\sigma-2p-1)\xi + m + 1] + y[\sigma(\sigma+m)\xi + \sigma(1+2p) + m(m+1+\sigma) + A'] = 0, \quad (17)$$

where $\sigma = \frac{NR}{p} - m - 1$ and $A' = A - p^2$. A three-term recurrence relation in the coefficients c_n is obtained from the solution of (17), viz.

$$(n+1)(n+m+1)c_{n+1} - c_n[2n^2 + (4p-2\sigma)n - A' - 2p\sigma - (m+1)(m+\sigma)] + (n-1-\sigma)(n-1-\sigma-m)c_{n-1} = 0, \quad (18)$$

and it follows that, as $n \to \infty$, $c_{n+1}/c_n \to 1 \pm 2p^{\frac{1}{2}}n^{-\frac{1}{2}}$.

* McCrea and Newing, *Proc. London Math. Soc.* (2), 37 (1933), 520.

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In order to study this difference equation in more detail, we assume that

$$\frac{c_{n+1}}{c_n} \sim 1 + \frac{a}{\sqrt{n}} + \frac{b}{n} + \frac{c}{n^{\frac{3}{2}}} + \ldots,$$

whence, on substituting in (18), we find that $a^2 = 4p$ and $b = 2p - \frac{3}{4} - \frac{RN}{p}$. Hence it follows that

$$\frac{c_{n+1}}{c_n} \sim 1 \pm \frac{2\sqrt{p}}{\sqrt{n}} + \left(2p - \frac{3}{4} - \frac{RN}{p}\right) n^{-1},$$

from which we deduce that $c_n \sim n^{-\left(\frac{3}{4} + \frac{RN}{p}\right)} e^{\pm 4\sqrt{(pn)}}$. This last result is in agreement with a rigorous investigation by H. Galbrun* of the asymptotic behaviour of solutions of difference equations of which (18) is a particular case. Thus we see that, provided that we take that solution of (18) which behaves asymptotically like $e^{-4\sqrt{(pn)}}\, n^{-\left(\frac{3}{4} + \frac{RN}{p}\right)}$, the solution $y = \sum_0^\infty c_n \xi^n$ of (17) will converge for $0 \leqslant \xi \leqslant 1$.

It remains to show that in fact the solution of (18) by writing it as an infinite continued fraction will be the required solution. This can be proved by an appeal to the work of Nörlund†, in which it is shown that, if the difference equation

$$a_{n+2} + p(n)\, a_{n+1} + q(n)\, a_n = 0, \tag{18a}$$

where $p(n)$ and $q(n)$ are any functions of n, has the solutions $c(n)$ and $d(n)$, then

$$\frac{c(n+1)\, d(n+m) - d(n+1)\, c(n+m)}{c(n)\, d(n+m) - d(n)\, c(n+m)} \tag{19}$$

is equal to the finite continued fraction

$$-\frac{q(n)}{p(n)} - \frac{q(n+1)}{p(n+1)} - \cdots - \frac{q(n+m-2)}{p(n+m-2)}. \tag{20}$$

If $c(n)$ and $d(n)$ are the solutions of (18) which behave like $e^{\mp 4\sqrt{(pn)}}\, n^{-\left(\frac{3}{4} + \frac{RN}{p}\right)}$ respectively as $n \to \infty$, then as $m \to \infty$ it follows from (19) and (20) that

$$\frac{c(n+1)}{c(n)} = -\frac{q(n)}{p(n)} - \frac{q(n+1)}{p(n+1)} - \frac{q(n+2)}{p(n+2)} - \cdots,$$

which is the result of writing (18), in the notation of (18a), as an infinite continued fraction in the ordinary way, starting from any positive integer n.

It will be seen that Nörlund's method provides the most satisfactory way of dealing with all differential equations whose solution in the form of an infinite series involves a three-term difference equation connecting the coefficients in the series. It can thus be used to complete in a rigorous manner the treatment of the μ-equation by means of any of the solutions given above in **A**, provided that the asymptotic behaviour of the solutions of the corresponding difference equations is known.

* Galbrun, *Bull. Soc. Math. de France*, 49 (1921), 206.

† Nörlund, *Differenzenrechnung*, p. 440, equation 52.

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Hylleraas' analytical solution of (16) is of a different type. Putting $\lambda = 1 + x/2p$, this equation becomes

$$x(x+4p)\frac{d^2f}{dx^2} + 2(m+1)(x+2p)\frac{df}{dx} + \left[A' + m(m+1) + 2RN + x\left(\frac{RN}{p} - p\right) - \frac{x^2}{4}\right]f = 0,$$

and this is satisfied by the solution

$$f = \sum_m^\infty c_n \frac{e^{-\frac{1}{2}x}}{n!} L_n^m(x),$$

where $L_n^m(x)$ is the associated Laguerre polynomial. If we put $n = m + s$, so that the solution is

$$f = \sum_0^\infty c_s \frac{e^{-\frac{1}{2}x}}{(m+s)!} L_{m+s}^s(x), \tag{21}$$

the three-term recurrence relation to which this solution leads is

$$(s+m+1)(s-m-\sigma)c_{s+1} + s(s-1-\sigma)c_{s-1} = c_s[2s^2 + 2s(2p-\sigma) - \{A' + 2p\sigma + (m+1)(m+\sigma)\}], \tag{22}$$

where $A' = A - p^2$, and $\sigma = \dfrac{RN}{p} - m - 1$. The difference equation (22) is of the same type as (18), and a similar treatment shows that, for large values of s,

$$\frac{c_{s+1}}{c_s} \sim 1 \pm 2\sqrt{(p/s)} + (2p - \tfrac{3}{4})s^{-1},$$

whence $c_s \sim e^{\pm 4\sqrt{(ps)}} s^{-\frac{3}{4}}$. Again Nörlund's work proves that the method of infinite continued fractions can be applied to find the characteristic values of A for that solution of (22) in which $c_s \sim e^{-4\sqrt{(ps)}} s^{-\frac{3}{4}}$.

Finally, in order to prove that Hylleraas' solution is convergent, we use the inequality*

$$\frac{e^{-\frac{1}{2}x}\,|\,L_n^m(x)\,|}{n!} \leqslant \frac{(n+m+1)!}{n!\,(m+1)!} \quad \text{for } x \geqslant 0,$$

which shows that the series in (21) is absolutely convergent for $x \geqslant 0$, since $c_s \sim e^{-4\sqrt{(ps)}} s^{-\frac{3}{4}}$†. Jaffé states that Hylleraas' solution is divergent, but in view of the above argument this cannot be the case. It is well known that a function satisfying the conditions imposed on the wave function $\psi(\lambda)$ can be expanded in a series of associated Laguerre polynomials‡, and we shall show later that the infinite continued fraction obtained from (22) does give characteristic values of A which are in agreement with the physical results.

* G. Szegö, *Math. Zeit.* 25 (1926), 87.

† McCrea and Newing (*loc. cit.* p. 534) have discussed in a somewhat similar manner the convergence of Hylleraas' solution when $m = 0$.

‡ W. Myller-Lebedeff, *Math. Ann.* 64 (1910), 388.

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C. The reason why the solution of (7) in the form

$$\psi(\mu) = (1-\mu^2)^{\frac{1}{2}m} e^{p\mu} \Sigma c_n (1-\mu)^n \qquad (22a)$$

is so suitable for large values of p is evident from the following considerations, which in fact suggested this type of solution. Take the case of the $1s\sigma$ state and suppose that R is large; this is effectively a hydrogen atom in a small uniform field $F\,(=1/R^2)$, the electron being near the nucleus $B\,(\lambda=1, \mu=1)$. It is known in this case that the approximate wave function is

$$\psi = e^{-r_2}(1 + Fx_2 + \tfrac{1}{2}Fx_2 r_2),$$

where x_2 is measured in the direction AB from B. In terms of the coordinates λ and μ this becomes

$$e^{-\frac{1}{2}R\lambda} e^{-\frac{1}{2}R\mu}\left[1 + \frac{FR}{2}(1-\lambda\mu) + \frac{FR^2}{8}(1-\lambda\mu)(\lambda+\mu)\right].$$

Since the electron is near B, we write $\lambda = 1+\lambda'$, $\mu = 1-\mu'$, where λ' and μ' are small and of the same order, and ψ is then, correct to the second order, equal to

$$e^{-\frac{1}{2}R\lambda}(1 - \epsilon\lambda' - \tfrac{1}{8}\lambda'^2)\, e^{\frac{1}{2}R\mu}(1 + \epsilon\mu' + \tfrac{1}{8}\mu'^2), \qquad (23)$$

where $\epsilon \equiv \frac{1}{2}R^{-1}$ and is of the same order as λ' and μ', and is the product of functions of λ and μ, as we should expect. Replacing μ' by $1-\mu$, the approximate solution of the μ-equation for large R is in this case

$$\psi_1 = e^{\frac{1}{2}R\mu}\left[1 + \frac{1-\mu}{2R} + \tfrac{1}{8}(1-\mu)^2\right]. \qquad (24)$$

Similarly if, for large R, the electron is near the nucleus $A\,(\lambda=1, \mu=-1)$ the approximate solution is

$$\psi_2 = e^{-\frac{1}{2}R\mu}\left[1 + \frac{1+\mu}{2R} + \tfrac{1}{8}(1+\mu)^2\right], \qquad (25)$$

and the complete solutions which are even and odd in μ are then $\psi_1 \pm \psi_2$ respectively.

Further it follows from (23) that the approximate solution of the λ-equation for large R is

$$\psi = e^{-\frac{1}{2}R\lambda}\left[1 - \frac{\lambda-1}{2R} - \tfrac{1}{8}(\lambda-1)^2\right]. \qquad (26)$$

Since in the case under consideration $R = 2p$ when R is large, the solution (22a) may be considered as the generalization of (24) with a solution similar to (22a) with a change of sign of μ as the generalization of (25), while Hylleraas' solution may be looked upon from this point of view as the generalization of (26).

D. We can now proceed to obtain approximate results for $A\,(\lambda)$ and $A\,(\mu)$ when p is either large or small, and to deduce the corresponding values of E'. These are of course known, having been obtained by other methods, but their derivation from the analysis given above serves as a verification of the results of this section.

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Taking the case of p large, the value of $A(\mu)$ is given in (13) and (14) to different orders of p^{-1}. In the case of the λ-equation, approximations for p large can be obtained without any difficulty from either Jaffé's or Hylleraas' solution, i.e. from the continued fractions corresponding to (18) or (22). For example, when there are only nodes, m in number, in the azimuthal angle ϕ, we write the equation arising from (22) in the form

$$\frac{Y}{(m+1)(m+\sigma)} = -\cfrac{\sigma/(m+2)(1-m-\sigma)}{2+2(2p-\sigma)-Y} - \cfrac{2(1-\sigma)/(m+3)(2-m-\sigma)}{2.2^2+4(2p-\sigma)-Y} - \ldots, \quad (27)$$

where $Y = A' + 2p\sigma + (m+1)(m+\sigma)$, and we find by successive approximation that

$$\frac{Y}{(m+1)(m+\sigma)} = -\frac{\sigma}{4p} + \frac{\sigma(1-\sigma)}{8p^2} - \frac{\sigma}{64p^3}[5\sigma^2 - \sigma(m+12) - (m^2+m-6)],$$

and therefore that $A(\lambda)$ is equal to

$$p^2 - 2p\sigma - (m+1)(m+\sigma) - \frac{\sigma(m+1)(m+\sigma)}{4p} + \frac{\sigma(1-\sigma)(m+1)(m+\sigma)}{8p^2} - \frac{\sigma(m+1)(m+\sigma)}{64p^3}[5\sigma^2 - \sigma(m+12) - (m^2+m-6)]. \quad (28)$$

Equating this expression for $A(\lambda)$ to that given in (14) for $A(\mu)$ and solving for σ by successive approximation, we find, writing $m+1=k$, that

$$\sigma = k - \frac{k^2}{p} + \frac{k^3}{4p^2} + \frac{k(k^2-1)}{8p^3} - \frac{k^3(k^2+9k+9)}{64p^4} + \ldots.$$

Since $NR/p = k+\sigma$, the value of p for large R is given by

$$2pk = NR + k^2 - \frac{k^4}{2RN} + \frac{k^4}{2R^2N^2} + \frac{k^6}{8R^3N^3}(3k^2+9k+1) + \ldots,$$

and we have finally, since $E' = -4p^2/R^2$,

$$E = E' + \frac{2N}{R} = -N^2\left[\frac{1}{k^2} + \frac{k^2-k^4}{R^3N^3} + \frac{k^4}{4R^4N^4}(4k^2+9k+5)\right].$$

This result is in agreement with the expression for the Stark effect in this case with the addition of the term $(k^4-k^2)/NR^3$, which arises from the fact that the force N/R^2 due to the nucleus at a large distance R is only equivalent to a uniform field to a first approximation. To a second approximation the potential due to this force is $-\frac{N}{R}\left(1+\frac{rx}{R^2}\right)$, and a simple perturbation calculation confirms the value given above for the additional energy due to it.

The general case, in which there are s nodes in λ, r nodes in μ and m nodes in ϕ, could be dealt with in a similar manner, but the algebra becomes rather long and we only give here the derivation of the formula to $O(p^{-1})$. An approximation

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to the sth root of (27) for p large is obtained by inverting it s times, and then we find that $A(\lambda)$ is equal to

$$p^2-2p\sigma+4ps+2s^2-2s\sigma-(m+1)(m+\sigma)-\frac{1}{4p}\{\sigma^2(2s+m+1)$$
$$-\sigma[6s^2+2s(m+1)-m(m+1)]+s[4s^2-2m(m+1)]\}+O(p^{-2}). \quad (29)$$

Equating this expression for $A(\lambda)$ to that given in (13) for $A(\mu)$ and solving for σ by successive approximation we find that, putting $n=m+r+s+1$,

$$\sigma=(n+r+s)-\frac{n^2}{p}+\frac{n^2}{4p^2}[(m+1)^2+(5s-r)(m+1)-2(r^2-rs-2s^2)].$$

Since $NR/p=m+\sigma+1$, the value of p for large R is given by

$$2p=\frac{NR}{n}+n-\frac{n}{2RN}[(m+1)^2+(5s-r)(m+1)-2(r^2-rs-2s^2)],$$

so that $$E=-\frac{4p^2}{R^2}+\frac{2N}{R}=\frac{-N^2}{(m+r+s+1)^2}-\frac{3(r-s)(m+r+s+1)}{R^2},$$

which is the general formula for the first-order Stark effect.

The case of p small is best dealt with in the general case of unequal nuclei from which that of equal nuclei can be deduced, so that its consideration is postponed to section II, **C**.

II. Unequal nuclei

A. Starting from equations (4) and (5), we write $R_1=R(N_1-N_2)/2$ and $R_2=R(N_1+N_2)/2$, and the first problem is to find approximations to the value of A from these equations when p and R, and therefore R_1 and R_2, are either both small or both large.

Considering first of all equation (5), a solution in the form of a product of $(1-\mu^2)^{\frac{1}{2}m}$ and an ascending power series in μ must contain both even and odd powers of μ. This solution leads to a four-term recurrence relation in the coefficients to which the theory of ordinary continued fractions cannot be applied, and the same is true of a solution in the form of a series of associated Legendre polynomials. Attempts to find a solution which would lead to a three-term recurrence relation resulted in the discovery of the solution

$$\psi=e^{p\mu}\sum_{n=m}^{\infty}c_n P_n^m(\mu). \quad (30)$$

This is, so far, the only solution which has been found to be applicable to the case of unequal nuclei, and is at the same time suitable for calculation when p and R_1 are both small. Writing $\psi(\mu)=e^{p\mu}y$, the equation for y is

$$(1-\mu^2)\frac{d^2y}{d\mu^2}+2\frac{dy}{d\mu}[p(1-\mu^2)-\mu]+y\left[p^2-A-2\mu(R_1+p)-\frac{m^2}{1-\mu^2}\right]=0.$$

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If we assume that $y=\sum_m^\infty c_n P_n^m(\mu)$, and use the formulae

$$(2n+1)\,\mu P_n^m=(n-m+1)\,P_{n+1}^m+(n+m)\,P_{n-1}^m,$$

$$(2n+1)\,(1-\mu^2)\,\frac{d}{d\mu}P_n^m=(n+1)\,(n+m)\,P_{n-1}^m-n\,(n-m+1)\,P_{n+1}^m,$$

we find the recurrence relation

$$\frac{2c_{n+1}}{2n+3}(n+m+1)(pn+p-R_1)-c_n[n(n+1)+A']-\frac{2c_{n-1}}{2n-1}(n-m)(pn+R_1)=0, \tag{31}$$

in which $n=m,\ m+1,\ m+2,\ \ldots$. The usual procedure shows that c_{n+1}/c_n behaves for large values of n either like $-p/n$ or like n/p; whence, to a higher degree of approximation, c_{n+1} behaves either like $(-p)^n n^a/n!$ or like $n!\,n^b/p^n$, where

$$a=\frac{R_1}{p}-m-\tfrac{3}{2} \quad \text{and} \quad b=\frac{R_1}{p}-m+\tfrac{1}{2}.$$

We require now an inequality for $P_n^m(\mu)$ corresponding to $|P_n(\mu)|\leqslant 1$. It can be proved that*

$$\frac{d^m}{d\mu^m}P_n(\mu)=\sum_0 A_r P_{n-m-2r}(\mu),$$

where the coefficients A_r are all positive. It follows that $\frac{d^m}{d\mu^m}P_n(\mu)$ has its greatest numerical value when $\mu=1$. Since $P_n(\mu)=\frac{1}{2^n n!}\frac{d^n}{d\mu^n}(\mu^2-1)^n$, it can easily be shown that

$$|P_n^m(\mu)|\leqslant\frac{(1-\mu^2)^{\frac{1}{2}m}}{2^m m!}\frac{(n+m)!}{(n-m)!}.$$

Choosing that solution c_n of the recurrence relation (31) which behaves like $(-p)^n n^a/(n!)$, it follows immediately that the series $\sum_m c_n P_n^m(\mu)$ is absolutely convergent for $-1\leqslant\mu\leqslant 1$ and all finite values of p, and an appeal to Nörlund's work proves that the infinite continued fraction occurring in the equation from which the characteristic values of A are determined is convergent.

Taking for simplicity the case of $m=0$, the equation for the characteristic values of A' from (31) can be written as an infinite continued fraction in the form

$$\frac{-3A'}{2(p-R_1)}=\cfrac{\frac{5}{1}\cdot\frac{1}{2}\cdot\frac{p+R_1}{2p-R_1}}{\frac{5}{4}\cdot\frac{A'+2}{2p-R_1}+\cfrac{\frac{7}{3}\cdot\frac{2}{3}\cdot\frac{2p+R_1}{3p-R_1}}{\frac{7}{6}\cdot\frac{A'+6}{3p-R_1}+\ldots}} \tag{32}$$

In the case of equal nuclei $R_1=0$, and then (32) gives in one equation the values of A' for both the even- and odd-power series solutions as given by Wilson.

* Hobson, *Spherical and Ellipsoidal Harmonics*, p. 35, Ex. 4.

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Since (5) is unaltered by changing the sign of both μ and R_1, it is clear that there is a solution

$$\psi(\mu) = e^{-p\mu} \sum_m a_n P_n^m(\mu), \tag{33}$$

leading to a recurrence relation, and the corresponding equation for A' in terms of an infinite continued fraction, which can be obtained from (31) and (32) by changing the sign of R_1. Since there is only one solution which is finite in the range $-1 \leqslant \mu \leqslant 1$, it follows that the solutions (30) and (33) are identical, and that the characteristic values of A' are the same. This is confirmed by the expression for the approximate value of A' when p and R_1 are small, viz. for the ground state,

$$A' = -\tfrac{2}{3}(p^2 - R_1^2)\left\{1 - \frac{p^2 + 11R_1^2}{45} - \frac{2(p^2 - 4R_1^2)(p^2 + 47R_1^2)}{45 \cdot 63} + \ldots\right\},$$

which contains only even powers of p and R_1. This solution is, both for equal and unequal nuclei, very suitable for small values of p and R_1, but the infinite continued fraction in (32) converges more slowly for moderate values of p and R_1.

A solution of (5) which is more convenient for large values of p and R_1 is obtained, as in section I, **A**, by writing

$$\psi = (1-\mu^2)^{\frac{1}{2}m} e^{p\mu} \sum_0 c_n (1-\mu)^n, \tag{34}$$

for which we find the recurrence relation

$$2(n+1)(n+m+1)c_{n+1} - c_n[n(n+1) + n(4p+2m) + B] + 2c_{n-1}(R_1 + pm + pn) = 0, \tag{35}$$

where $B \equiv A - p^2 + 2(R_1 + mp + p) + m(m+1)$. This solution corresponds to the case where, at a large distance R, the electron is near the nucleus of charge N_2 at B, i.e. near $\mu = 1$, $\lambda = 1$.

A similar solution

$$\psi = (1-\mu^2)^{\frac{1}{2}m} e^{-p\mu} \sum_0 c_n (1+\mu)^n, \tag{36}$$

in which the electron is near the nucleus of charge N_1 at A, i.e. near $\mu = -1$, $\lambda = 1$, when R is large, is obtained by changing the sign of μ, and therefore of R_1, in the recurrence relation (35).

These two solutions provide an approximation to the value of B when p and R_1 are large, for the case when $m = 0$ and there are no nodes in μ in the neighbourhood of the electron, in the *asymptotic* form

$$B = \left(1 \pm \frac{R_1}{p}\right)\left[1 + \frac{1}{4p}\left(1 \pm \frac{R_1}{p}\right) + \frac{1}{8p^2}\left(1 \pm \frac{R_1}{p}\right)\left(2 \pm \frac{R_1}{p}\right) + \frac{1}{64p^3}\left(1 \pm \frac{R_1}{p}\right)\left(23 \pm 22\frac{R_1}{p} + 5\frac{R_1^2}{p^2}\right)\right], \tag{37}$$

in which the upper or lower sign is to be taken according as, for large R, the electron is near the nucleus of charge N_2 or N_1 respectively, and

$$B \equiv A - p^2 + 2(p \pm R_1).$$

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When $R_1 = 0$, the two values of B coincide, which means that the two states in which there is (i) no node in μ, and (ii) a node at $\mu = 0$, give the same value of B, and therefore of A, for large R, as mentioned above in section I, **A**.

As a numerical example of the convergence of the infinite continued fraction in the equation from which the characteristic values of A in (5) are obtained, a calculation for the small values $p = 1{\cdot}5$, $R_1 = 0{\cdot}5$, used in section II, **B** below, required six convergents when using the solution (30) and fourteen when using the solution (34) which is known to be less suitable for small values of p and R_1. The four solutions given by (30), (33), (34) and (36) must be identical, since there is only one solution valid in the range $-1 \leqslant \mu \leqslant 1$, and the corresponding equations giving the values of A' must have the same roots, but the two *asymptotic* results of the type (37) for large R must then refer to different states.

The λ-equation (4) presents no difficulties, since it is of the same form both for equal and unequal nuclei, and either Hylleraas' or Jaffé's solution may be used.

The values of the separation constant A obtained from the solutions of the λ- and μ-equations must be the same in any physical problem, and the choice of the appropriate solutions is for the present purpose most easily determined by means of an energy diagram of the kind given by Hund*. Any numerical example will only verify in detail the correctness of such a diagram which connects the approximate solutions for large and small values of the internuclear distance R. We have not succeeded in deriving from the analysis of this paper a relation between the solutions of the λ- and μ-equations in a form from which it would be evident at once which solution near $R = 0$ connects up with a particular solution near $R = \infty$. We can only suggest that, considered merely in relation to the analysis of this section, if we attempt to connect up the energy curves for two given states near $R = 0$ and $R = \infty$ respectively by a continuous curve, it will be found that, for such connections as are physically impossible, there will be, for intermediate values of R, no point of intersection of the A (λ) and A (μ) curves as functions of p. The reasons for this difficulty, which is a purely mathematical one, are discussed further in section II, **B** below. It cannot arise in the case of equal nuclei where A is determined directly from the μ-equation as a function of p and then the remaining parameter $2RN$ is found directly from the λ-equation as a function of p, so that every solution has a physical interpretation.

B. One particular case when $N_1 = 2$, $N_2 = 3$ has been worked out numerically as an example. The energy in the ground state for the combined nuclei is -25 and, on separating the nuclei, this corresponds to an energy -9 at an infinite distance apart when the electron goes into the ground state of the nucleus of charge 3. A higher state for the combined nuclei is that in which there is a node in μ, the energy being $-\frac{25}{4}$, and this corresponds to the state at an infinite distance in

* Hund, *Zeit. für Physik*, 40 (1927), 755.

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which the electron is in the ground state of the nucleus of charge 2, the energy being -4. This case is of more interest than the preceding one in view of the variation of the position of the node with R. The calculation is necessarily much longer than any similar calculation for equal nuclei and is carried out as follows: a value of R is chosen, and the separation constant A is calculated as a function of p from the λ- and μ-equations, and the value of p found for which $A(\lambda) = A(\mu)$. So far as the λ-equation is concerned, the calculation proceeds as in section I above and presents no difficulties, since the continued fractions associated with both Hylleraas' and Jaffé's solutions are fairly rapidly convergent and not more than five or six convergents are necessary, at any rate in the particular case considered.

The μ-equation is more difficult to deal with. On account of the node, it is necessary to invert (32) into the form

$$-\frac{5}{3}\frac{p^2-R_1^2}{A'(2p-R_1)}-\frac{5}{4}\frac{A'+2}{2p-R_1}=\frac{7.2}{3.3}\frac{2p+R_1}{3p-R_1}\Bigg/\frac{7}{6}\frac{A'+6}{3p-R_1}+\frac{9.3}{5.4}\frac{3p+R_1}{4p-R_1}\Bigg/\frac{9}{8}\frac{A'+12}{4p-R_1}+\ldots, \qquad (38)$$

and obtain an approximation for small values of p and R_1. This leads to the result

$$A'+2=-\frac{2}{5}(p^2+R_1^2)+\frac{2}{5^3.7}(3p^4-74p^2R_1^2+73R_1^4)$$

$$-\frac{4}{3^3.5^5.7}(p^2-4R_1^2)(9p^4+3278p^2R_1^2-3281R_1^4)+\ldots.$$

With this approximation as a guide, a trial value of A' is found and this has to be revised by a direct calculation from (38), in which the number of convergents required for $R=1$, 2, 3 was 6, 8, 10 respectively. For example, the case of $R=1$ gave the following results:

p	$A(\mu)$	$A(\lambda)$
1·3	−1·130	−1·788
1·4	−0·973	−1·127
1·5	−0·808	−0·483

whence $A(\lambda) = A(\mu)$ when $p = 1{\cdot}432$ and then $A = -0{\cdot}920$.

For $R=4$ (37) with the lower sign was a good guide to a trial value of B, to be revised by a direct calculation from the equation arising from (35) inverted into the form

$$\frac{2+4p+B}{2.2^2}-\frac{p-R_1}{2B}=\frac{(2p-R_1)/3^2}{(6+8p+B)/2.3^2-(12+12p+B)/2.4^2-\cdots}$$

because of the presence of the node, ten convergents being required.

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The position of the node was then calculated approximately from the solution (30) and the following table gives the final results:

R	p	$E' = -4p^2/R^2$	Value of μ for the node
1	1·432	−8·202	0·291
2	2·653	−7·038	0·562
3	3·686	−6·038	0·785
4	4·695	−5·511	0·943

These results suggest that, as R increases, the node in μ approaches the "unoccupied" nucleus, i.e. the nucleus of charge 3 at $\mu = 1$, the electron itself approaching the nucleus of charge 2 at $\mu = -1$. The numerical values in the last column must, however, be regarded as becoming less accurate as R increases, since the convergence of the series $\Sigma c_n P_n(\mu)$ is not very rapid for large values of p, and the same is true of the series $\Sigma c_n (1-\mu)^n$ in (34).

This brings us back to the difficulty mentioned in section II, **B**, which is now seen to be due to the fact that the solutions (30) and (34), though suitable for a determination of the values of A for finite values of R, are not suitable for an accurate determination of the wave function, and therefore of the position of the node, as $R \to \infty$. The problem is that of finding what happens to the additional node (when it exists) which arises as the nuclei are brought together from an infinite distance apart. Its solution, which should provide a direct verification of Hund's energy diagram in all cases, must be left over for further consideration.

C. It is possible, as in section I, **D**, to obtain approximate results for large and small values of R. For large R, and considering only the lowest state, we have to equate the value of $A(\lambda)$ given in (28) to that of $A(\mu)$ given by $p^2 - 2(p + R_1) + B$, where B is given by (37) with the upper sign. Solving by successive approximation, we find finally that

$$\frac{2p}{R} = N_2 + \frac{N_1}{N_2 R} - \frac{N_1^2}{2N_2^3 R^2} + \frac{N_1^3}{2N_2^5 R^3} + \frac{N_1^2}{8N_2^5 R^4}\left(18 - 5\frac{N_1^2}{N_2^2}\right),$$

whence

$$E' \equiv -\frac{4p^2}{R^2} = -\left\{N_2^2 + \frac{2N_1}{R} + \frac{9}{2}\frac{N_1^2}{N_2^4 R^4}\right\},$$

and

$$E = E' + \frac{2N_1 N_2}{R} = -N_2^2 + \frac{2N_1}{R}(N_2 - 1) - \frac{9}{2}\frac{N_1^2}{N_2^4 R^4}, \tag{39}$$

for the case when the electron is near the nucleus of charge N_2. A similar equation, corresponding to the lower sign in (37), with N_1 and N_2 interchanged gives the energy when the electron is near the nucleus of charge N_1. The second term in

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(39) arises from the potential energy of the nucleus N_1 and the charge $N_2 - 1$ at a distance R, and the last term is the polarization energy of the electron near the nucleus N_2 due to the field of the nucleus N_1. Equation (39) is of course a particular case of the Stark effect and is given here merely as a verification of the formulae of this section.

The case of R small, and therefore p small, is much more difficult, and we have not succeeded in obtaining a general formula from the analysis of this paper. Particular cases for small values of s, r and m, the number of nodes in λ, μ and ϕ respectively, can easily be dealt with, but the general formula will involve certain finite continued fractions which we have not been able to sum. If there are only nodes in the azimuthal angle ϕ, we can obtain the general formula as follows. It is first of all necessary to find an approximate formula for A (μ) when p and R_1 are small; this is obtained from the recurrence relation (31) and is

$$A'(\mu) = -m(m+1) - \frac{2[p^2(m+1)^2 - R_1^2]}{(m+1)(2m+3)} + \ldots.$$

If we write $\sigma = \sigma_0 + \sigma_1 p + \sigma_2 p^2 + \ldots$, a consideration of the case when $R = 0$ proves that $\sigma_0 = 0$ and then the value of Y in (27) is to $O(p^2)$

$$2p^2\sigma_1 + (m+1)(\sigma_1 p + \sigma_2 p^2) - \frac{2[p^2(m+1)^2 - R_1^2]}{(m+1)(2m+3)}.$$

If C denotes the finite continued fraction

$$\frac{1}{\frac{(m-1)(m+2)}{2.1^2} + \frac{1.2}{\frac{(m-2)(m+3)}{2.2^2} + \frac{2.3}{\frac{(m-3)(m+4)}{2.3^2} + \ldots,}}},$$

where the last term is $\dfrac{(m-1)m}{\dfrac{2m+1}{2m^2}}$, and whose sum is $1/(m+1)$, it will be found on

substituting for Y in (27) that $\sigma_1 = 0$, and that σ_2 is given by

$$(m+1)\sigma_2 p^2 - \frac{2[p^2(m+1)^2 - R_1^2]}{(m+1)(2m+3)} = -m(m+1)C\sigma_2 p^2 = -m\sigma_2 p^2,$$

whence

$$(2m+1)\sigma_2 p^2 = \frac{2[p^2(m+1)^2 - R_1^2]}{(m+1)(2m+3)}.$$

Since σ is in the general case equal to $(R_2/p) - m - 1$, and $R_2 = (N_1 + N_2)R/2$, $R_1 = (N_1 - N_2)R/2$, it follows that

$$\frac{(N_1+N_2)R}{2p} = (m+1) + \frac{2[p^2(m+1)^2 - R_1^2]}{(m+1)(2m+1)(2m+3)},$$

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whence $$\frac{2p(m+1)}{(N_1+N_2)R} = 1 - \frac{2R^2N_1N_2}{(m+1)^2(2m+1)(2m+3)},$$

and finally $$E' = -\frac{4p^2}{R^2} = -\frac{(N_1+N_2)^2}{(m+1)^2}\left\{1 - \frac{4R^2N_1N_2}{(m+1)^2(2m+1)(2m+3)}\right\}. \qquad (40)$$

The following table gives the results for those states in which there are also nodes in λ and μ and the total quantum number is not greater than 3, excluding those to which the formula given in (40) would apply.

State	$-E'$
$2s\sigma$	$\frac{\alpha^2}{4}(1-\frac{2}{3}\beta R^2)$
$3s\sigma$	$\frac{\alpha^2}{9}(1-\frac{1}{9}\beta R^2)$
$2p\sigma$	$\frac{\alpha^2}{4}(1+\frac{2}{15}\beta R^2)$
$3p\sigma$	$\frac{\alpha^2}{9}(1+\frac{1}{45}\beta R^2)$
$3d\sigma$	$\frac{\alpha^2}{9}(1+\frac{1}{315}\beta R^2)$
$3d\pi$	$\frac{\alpha^2}{9}(1+\frac{2}{315}\beta R^2)$
$3p\pi$	$\frac{\alpha^2}{9}(1-\frac{2}{45}\beta R^2)$

These results, in which α and β have been written for N_1+N_2 and N_1N_2 respectively, are in agreement with the known results for $N_1=N_2$.

A general formula for the case of equal nuclei has been obtained by Bethe* by a perturbation method. The table given above and the formula given in (40) suggest that Bethe's result can be extended to cover the case of unequal nuclei in the form

$$E' = -\frac{(N_1+N_2)^2}{n^2} - \frac{4[l(l+1)-3m^2]N_1N_2(N_1+N_2)^2R^2}{n^3l(l+1)(2l-1)(2l+1)(2l+3)}, \qquad (41)$$

where n is the total quantum number and is equal to $m+r+s+1$, and $l=m+r$.

Following a suggestion made to us by Dr Heitler, (41) can be deduced very simply from Bethe's work. If we take as the origin O of polar coordinates r, θ, ϕ the point which divides the line AB joining the nuclei in the ratio N_2 to N_1, the disturbing potential, due to a separation of the nuclei from O to a distance R apart, is $-(N_1/r_1)-(N_2/r_2)+(N_1+N_2)/r$ and can be expanded in series involving terms of the type $r^nP_n(\cos\theta)$ and $r^{-(n+1)}P_n(\cos\theta)$. With this particular choice of origin the term in $r^{-2}P_1(\cos\theta)$ is absent and then the important term for the perturbation calculation is the same as that in Bethe's work and a simple calculation leads to (41) above. When $l=0$, and therefore $m=0$, the required result

* H. Bethe, *Handbuch der Physik*, 24, 1, 527.

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follows either by taking the limiting value as $l \to 0$ of the second term in (41) or by a direct proof, the important term in the expansion of the disturbing potential being in this case the term independent of θ.

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Complete references will be found in (3) and (4).

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