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	K, $4s$–np	Rb, $5s$–np	Cs, $6s$–np
. . . .	76	73	65
t . . .	14	22	15

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ON THE ENERGY LEVELS OF A MODEL OF THE COMPRESSED HYDROGEN ATOM

by S. R. DE GROOT and C. A. TEN SELDAM

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Van der Waals-Laboratorium, Gemeente-Universiteit, Amsterdam

Summary

In the problem of the "compressed hydrogen atom" the boundary condition that the wave function φ must be zero for infinite r, is replaced by the condition that φ must have a zero point at a finite $r = r_0$. This leads to an investigation of properties of the zeros of the confluent hypergeometric function. The shifts of the $1s$, $2s$ and $2p$ levels by compression are calculated and tables and graphs are given for corresponding values of the energy and of r_0.

§ 1. *Introduction.* In the usual treatment of the Schrödinger equation for the hydrogen atom the boundary conditions imposed on the wave function φ are: regular behaviour in the origin and a node at infinity. It will however be supposed here that the hydrogen atom is enclosed in a sphere of radius r_0 [1]) [2]). At the position r_0 is an infinitely high and steep potential wall. So the wave function must now have a zero point at $r = r_0$ instead of at $r = \infty$. The new boundary condition influences only the radial part $R(r)$ of the wave function. The equation for $R(r)$ can be written in atomic units *):

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left\{2E + \frac{2}{r} - \frac{l(l+1)}{r^2}\right\} R = 0, \qquad (1)$$

with E the energy and l zero or a positive integer.

With the relations

$$\rho = 2r/n \text{ and } E = -1/2n^2, \qquad (2)$$

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*) Fundamental units e, m, and $\hbar = h/2\pi$. The unit of length is then $a_0 \equiv \hbar^2/me^2$ and the unit of energy is e^2/a_0 (Michels, De Boer and Bijl [1]) take $e^2/2a_0$ as unit of energy).

defining n and ρ, the equation reads:

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \left\{\frac{1}{4} - \frac{n}{\rho} + \frac{l(l+1)}{\rho^2}\right\} R = 0. \tag{3}$$

Substituting

$$R = e^{-\frac{1}{2}\rho}\rho^l F(\rho), \tag{4}$$

we get the equation:

$$\rho\frac{d^2F}{d\rho^2} + (2l + 2 - \rho)\frac{dF}{d\rho} + (n - 1 - l)\,F = 0 \tag{5}$$

for the confluent hypergeometic function *)

$$F = F\,(l + 1 - n, 2l + 2, \rho). \tag{6}$$

When n is an integer the series expansion for F breaks off so as to give derivatives of Laguerre polynomials. The wave function then has a node at $r_0 = \infty$, being the normal boundary condition of the free hydrogen atom.

The purpose of this article is to calculate how the 1*s*, 2*s* and 2*p* levels of the hydrogen atom are changed when it is uniformly compressed, i.e. when a node lies at finite r_0. The energy levels are shifted to higher values through the influence of the potential wall. Corresponding values of energy E and radius r_0 of the cage will be calculated for the whole range beginning with the large values of r_0. The notation †) "1*s*, 2*s* and 2*p* level" will be maintained, although the number n is only an integer for $r_0 = \infty$. The quantum number l is of course not changed by compression.

§ 2. *The method of Michels, De Boer and Bijl.* For a radius r_0 so large, that the deviation of E from its value at $r_0 = \infty$ is still very small, Michels, De Boer and Bijl 1) have developed an approximative method. They calculated the shift

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*) $$F(\alpha, \gamma, \rho) = 1 + \frac{\alpha}{\gamma}\rho + \frac{\alpha(\alpha + 1)}{\gamma(\gamma + 1)}\frac{\rho^2}{2!} + \ldots. \tag{7}$$

The confluent hypergeometric functions have specially been investigated by Whittaker 3). The connection of his symbols k, m and z with the variables l, n, and ρ used here is: $k = n$, $m = l + {}^1/_2$ and $z = \rho$. Buchholz' 4) parameters $\nu \equiv i\tau$, p and $z \equiv i\zeta$ are $\nu = n$, $p = 2l + 1$ and $z = \rho$.

†) Indicating the first symbol of this notation by N and the second by l, the number N can be defined by saying that the wave function "Nl" has $N - l - 1$ nodes between its limiting points. This "principal quantum number" N coincides with the variable n (corresponding with E by formula (2)) for $r_0 = \infty$ only.

ion reads:

$$-\left\{\frac{1}{4}-\frac{n}{\rho}+\frac{l(l+1)}{\rho^2}\right\} R = 0. \tag{3}$$

$$e^{-\frac{1}{2}\rho}\rho^l F(\rho), \tag{4}$$

$$-\rho)\frac{dF}{d\rho}+(n-1-l)F = 0 \tag{5}$$

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of the ground state 1*s*, but their method can easily be extented to the higher levels. Here it will also be calculated for the 2*s* and 2*p* levels.

Putting $F(\rho)=\sum\limits_{\tau=0}^{\infty}b_\tau\rho^\tau$ and inserting this in the differential equation the following recursion formula is obtained:

$$\tau(\tau+2l+1)\,b_\tau = (\tau+l-n)b_{\tau-1}. \tag{8}$$

If n is an integer the series breaks off and gives a polynomial of the degree $n-l-1$. In that case the wave function has a zero point at $r_0 = \infty$. If however r_0 is not infinite, but still large enough that n is nearly an integer, we can put

$$n = N+\beta \text{ with } N \text{ integer and } |\beta| \ll N \tag{9}$$

and

$$E = -\frac{1}{2n^2} = -\frac{1}{2(N+\beta)^2} \simeq -\frac{1}{2N^2}+\frac{\beta}{N^3}, \tag{10}$$

where the first term in the last member represents the energy value for $r_0 = \infty$.

Substituting this in the recursion formula (8) and applying $|\beta| \ll N$, approximations for the coefficients b_τ are found. With the boundary condition that, for finite r_0, reads:

$$F(\rho_0) = 0, \tag{11}$$

one can easily find the first order correction for the 1*s*-level, where $N = 1$ and $l = 0$:

$$\beta_{1s} \simeq \frac{1}{\sum\limits_{\tau=1}^{\infty}\frac{1}{\tau(\tau+1)!}\rho_0^\tau} \simeq \frac{1}{\sum\limits_{\tau=1}^{\infty}\frac{2^\tau}{\tau(\tau+1)!}r_0^\tau}, \tag{12}$$

the formula of Michels, De Boer and Bijl.

The calculations for the 2*s* and 2*p* levels, where $N = 2$ and $l = 0$ and 1, yield:

$$\beta_{2s} \simeq \frac{\frac{1}{2}\rho_0 - 1}{-\frac{1}{2}\rho_0+\sum\limits_{\tau=2}^{\infty}\frac{1}{\tau(\tau-1)\cdot(\tau+1)!}\rho_0^\tau} \simeq \frac{\frac{1}{2}r_0 - 1}{-\frac{1}{4}r_0+\sum\limits_{\tau=2}^{\infty}\frac{1}{\tau(\tau-1)\,(\tau+1)!}r_0^\tau}, \tag{13}$$

$$\beta_{2p} \simeq \frac{1}{6\sum\limits_{\tau=1}^{\infty}\frac{1}{\tau(\tau+3)!}\rho_0^\tau} \simeq \frac{1}{6\sum\limits_{\tau=1}^{\infty}\frac{1}{\tau(\tau+3)!}r_0^\tau}. \tag{14}$$

Michels, De Boer and Bijl found the energy values of the 1*s*-level for $r_0 = 5, 6, 7$ and 8 atomic units, and Sommerfeld and Welker[2]) applied the formula (12) to $r_0 = 3$ and 4 atomic units.

Numerical calculation of the sums, occurring in the expressions (12), (13) and (14) can be largely simplified, because it can be shown that they are related to the exponential integral, that has been tabulated[5]). To prove this first of all it can be stated that the sums of equations (12) and (14) are of the general type

$$f_m(x) = \sum_{\tau=1}^{\infty} \frac{x^\tau}{\tau(\tau + m)!}, \qquad (15)$$

whereas the sum in (13) is equal to

$$x f_2(x) - f_1(x) + \tfrac{1}{2}x. \qquad (16)$$

The functions $f_m(x)$ can be connected to the general "exponential integral", that will be represented here by the symbol *Fi*:

$$Fi_m(x) = \int_1^x e^x x^{-m}\, dx, \qquad (17)$$

with the following relation

$$f_m(x) = \{Fi_{m+1}(x) + g_m(x) - (m!)^{-1}.\ln x\} + f_m(1) - g_m(1), \qquad (18)$$

where g_m is a polynomial in x^{-1}:

$$g_m = \sum_{\tau=1}^{m} \frac{1}{\tau(m - \tau)!\, x^\tau}. \qquad (19)$$

The formula (18) can be derived by developing the exponential under integral sign of (17) and integrating by terms.

The sums $f_m(1)$ are constants; for instance:

$$f_1(1) = 0.59962032,\ f_2(1) = 0.19066925 \text{ and } f_3(1) = 0.04635136 \qquad (20)$$

Partial integration leads to a recursion formula for the functions *Fi* of (17)

$$m Fi_{m+1}(x) = Fi_m(x) - e^x x^{-m} + e, \qquad (21)$$

so that Fi_m can be expressed with Fi_1 and elementary transcendent functions. Lastly Fi_1 is, apart from an additive constant, equal to the tabulated[5]) exponential integral $\overline{Ei}$:

$$Fi_1(x) = \overline{Ei}(x) - \overline{Ei}(1) = \overline{Ei}(x) - 1.895168, \qquad (22)$$

where

$$\overline{Ei}(x) = \lim_{\epsilon \to 0} \left(\int_{-\infty}^{-\epsilon} e^t t^{-1}\, dt + \int_{+\epsilon}^{\infty} e^t t^{-1}\, dt\right). \qquad (23)$$

The formulae (15)–(22) enable a simple calculation of the expressions (12)–(14).

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$$_{0}$$

nable a simple calculation of the expressions

In the region of large x it is sometimes convenient, in view of the slow convergence of the series (12)–(14) and the occurance of nearly equal terms of opposite sign in (18) to use the known semi-convergent asymptotic expansions of the exponential integral.

Table 1 contains the results of the calculations. In figures 1 and 2 the energy E is plotted as function of the radius r_0 of the sphere in which the hydrogen atom lives. The dotted lines represent the asymptotic approximations of this paragraph.

TABLE I

r_0	E 1s level	E 2s level	E 2p level
∞	$-{}^1/_2$	$-{}^1/_8$	$-{}^1/_8$
20		-0.12499	-0.12500
15		-0.12451	-0.12477
10		-0.1162	-0.1194
9		-0.1118	-0.1169
8	-0.49997 1)	-0.1055	-0.1124
7	-0.49986 1)	-0.0974	-0.1058
6	-0.49927 1)		
5	-0.49655 1)		
4	-0.4852 2)		
3	-0.4475 2)		

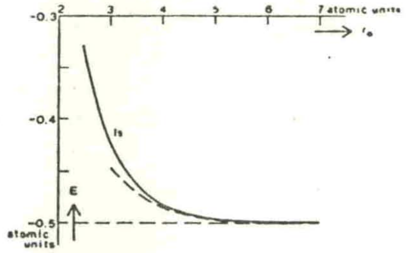

Fig. 1. Detail of the (E, r_0)-curve for the 1s level. The dotted line indicates the asymptote found by the method of Michels, De Boer and Bijl. The line $E = -0.5$ is also an asymptote.

The exact curves that will be calculated in next section are indicated by the symbols 1s, 2s and 2p. The deviations of the asymptotes calculated here from the real curve show where the approximative method is valid, when a certain accuracy is chosen. For the 2s and 2p levels the approximation is only applicable down to a value of r_0, much larger than that for the 1s level.

The second level has split up into two adjacent levels, such that the $2p$ orbit is more stable than the $2s$ orbit.

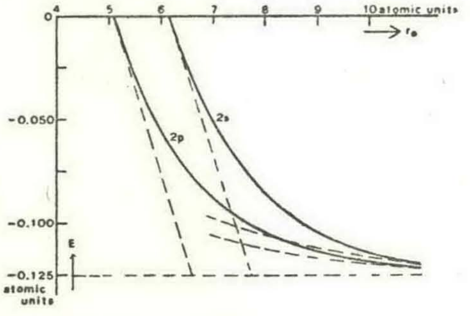

Fig. 2. Detail of the (E, r_0)-curves for the $2s$- and $2p$-levels. Dotted lines are the tangents at $E = 0$ and the asymptotes of the approximation of § 2. $E = -0.125$ is also an asymptote for both curves.

§ 3. *Nodes of the wave functions.* When certain values of the azimuthal quantum number $l = 0, 1, 2, \ldots.$ and of the energy E (corresponding with n by formula (2); n can eventually be imaginary

TABLE II

The $1s$-level $(N = 1,\ l = 0)$

n	E atomic units	r_0 atomic units	from section
1	—0.500	∞	3*a*
1.004	—0.4960	5.020	3*b*
1.017	—0.4834	4.068	3*b*
1.064	—0.4417	3.192	3*b*
1.123	—0 3965	2.807	3*b*
1.236	—0.3273	2.472	3*b*
1.467	—0.2323	2.200	3*b*
1.500	—0.2222	2.178	3*b*
2	—0.1250	2.000	3*a*
2.500	—0.0800	1.934	3*b*
3	—0.0566	1.902	3*a*
∞	0	1.835	3*c*
3 *i*	0.0566	1.778	3*d*
2 *i*	0.125	1.711	3*d*
i	0.500	1.448	3*d*
0.573 *i*	1.928	1.15^5	3*f*
0.509 *i*	2.193	1.08^5	3*f*
0.446 *i*	2.518	1.01	3*f*
0.382 *i*	3.427	0.91	3*f*
0.318 *i*	4.935	0.81	3*f*
0 *i*	∞	0	3*e*

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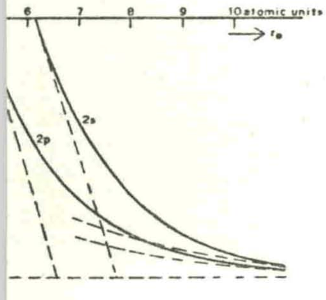

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TABLE II

1s-level ($N = 1$, $l = 0$)

E omic units	r_0 atomic units	from section
—0.500	∞	3*a*
—0.4960	5.020	3*b*
—0.4834	4.068	3*b*
—0.4417	3.192	3*b*
—0 3965	2.807	3*b*
—0.3273	2.472	3*b*
—0.2323	2.200	3*b*
—0.2222	2.178	3*b*
—0.1250	2.000	3*a*
—0.0800	1.934	3*b*
—0.0566	1.902	3*a*
0	1.835	3*c*
0.0566	1.778	3*d*
0.125	1.711	3*d*
0.500	1.448	3*d*
1.928	1.15^5	3*f*
2.193	1.08^5	3*f*
2.518	1.01	3*f*
3.427	0.91	3*f*
4.935	0.81	3*f*
∞	0	3*e*

and non-integer) are chosen, the wave function (4), (6) is known as function of r or ρ.

Each time when a zero point of this wave function is found this node can be considered as the radius r_0 of the cage in which the hydrogen atom is compressed. This gives sets of corresponding values of E and r_0. For $l = 0$ and no nodes between $r = 0$ and $r = r_0$ a point of the $1s$-level energy curve is found.

When for $l = 0$ there lies one node between the limiting points of the coordinate r, this is a wave function of a $2s$-state. For $l = 1$ and when no zero point occurs, one finds points of the $2p$-curve, etcetera. The various regions of energy will now be considered and methods described of finding nodes.

a) $E < 0$. When n is an integer, the wave function degenerates into a derivative of a Laguerre polynomial, with a number of

TABLE III

The 2s-level ($N = 2$, $l = 0$)

n	E atomic units	r_0 atomic units	from section
2	—0.1250	∞	3*a*
2.072	− 0.1165	10.36	3*b*
2.213	—0.1021	8.852	3*b*
2.5	—0.0800	7.815	3*b*
2.559	—0.0764	7.677	3*b*
2.885	—0.0601	7.212	3*b*
3	—0.0566	7.096	3*a*
3.412	—0.0429	6.824	3*b*
3.5	—0.0408	6.785	3*b*
4	—0.0312	6.611	3*a*
5	—0.0200	6.429	3*a*
∞	0	6.153	3*c*
4 i	0.0312	5.808	3*d*
3 i	0.0556	5.589	3*d*
2 i	0.1250	5.111	3*d*
i	0.5000	3.823	3*d*
0.902 i	0.6143	3.609	3*d*
0.637 i	1.234	2.91^5	3*f*
0.557 i	1.611	2.67	3*f*
0.477 i	2.193	2.39	3*f*
0.446 i	2.518	2.26^5	3*f*
0.414 i	2.920	2.15	3*f*
0.382 i	3.427	2.03	3*f*
0.350 i	4.078	1.92	3*f*
0.318 i	4.935	1.76	3*f*
0 i	∞	0	3*e*

TABLE IV

The $2p$-level ($N = 2,\ l = 1$)

n	E atomic units	r_0 atomic units	from section
2	—0.1250	∞	3*a*
2.047	—0.1193	10.235	3*b*
2.135	—0.1097	8.540	3*b*
2.363	—0.0895	7.089	3*b*
2.5	—0.0800	6.701	3*b*
2.599	—0.0740	6.497	3*b*
3	—0.0566	6.000	3*a*
3.5	—0.0408	5.696	3*b*
4	—0.0312	5.528	3*a*
5	—0.0200	5.355	3*a*
∞	0	5.086	3*c*
4 *i*	0.0312	4.770	3*d*
3 *i*	0.0556	4.554	3*d*
2 *i*	0.1250	4.110	3*d*
i	0.5000	2.698	3*d*
0.778 *i*	0.8261	2.528	3*d*
0.445 *i*	2.524	1.68	3*f*
0.401 *i*	3.116	1.55	3*f*
0.356 *i*	3.943	1.41	3*f*
0 *i*	∞	0	3*e*

$n - l - 1$ nodes between the points $r = 0$ and $r = \infty$. For several values of n and for $l = 0$ and 1 zero points have been calculated and given in tables II–IV (indication § 3*a*) and represented in the figures 1–3. Here again the splitting up of the second level into 2*s* and 2*p* curves is evident. It is obvious that by using only integer values of n a large gap in the curves is left between $n = l + 1$ and $n = l + 2$ i.e. between $r_0 = \infty$ and a comparatively small value of r_0. On the side of large radii r_0 this gap could be filled by the method of § 2, but this gives only approximative values.

b) For the rest of the gap in the curve it is necessary to find zero points of the confluent hypergeometric function with real arguments. These can be interpolated from tables [6]) [7]) with the help of well-known interpolation procedures (v. tables II–IV and figures).

c) $E = 0$. The limiting case of $n \to \infty$ has been studied by Sommerfeld and Welker [2]), especially for the 1*s* level. The confluent hypergeometric function (6) for $n \to \infty$ is proportional to a Bessel function:

$$\lim_{n \to \infty} F(l + 1 - n, 2l + 2, \rho) \sim J_{2l+1}(2\sqrt{\rho n}) = J_{2l+1}(2\sqrt{2r}). \quad (24)$$

TABLE IV

p-level ($N = 2$, $l = 1$)		
E mic units	r_0 atomic units	from section
—0.1250	∞	3*a*
-0.1193	10.235	3*b*
—0.1097	8.540	3*b*
—0.0895	7.089	3*b*
—0.0800	6.701	3*b*
—0.0740	6.497	3*b*
—0.0566	6.000	3*a*
—0.0408	5.696	3*b*
—0.0312	5.528	3*a*
—0.0200	5.355	3*a*
0	5.086	3*c*
0.0312	4.770	3*d*
0.0556	4.554	3*d*
0.1250	4.110	3*d*
0.5000	2.698	3*d*
0.8261	2.528	3*d*
2.524	1.68	3*f*
3.116	1.55	3*f*
3.943	1.41	3*f*
∞	0	3*e*

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function (6) for $n \rightarrow \infty$ is proportional

$$,\rho) \backsim J_{2l+1}(2\sqrt{\rho n}) = J_{2l+1}(2\sqrt{2r}). \qquad (24)$$

The first and second node of J_1 give the values for the 1*s* and 2*s* level. The first zero point of J_3 gives the intersection of the 2*p* level with the r_0-axis. (v. tables II–IV and figures).

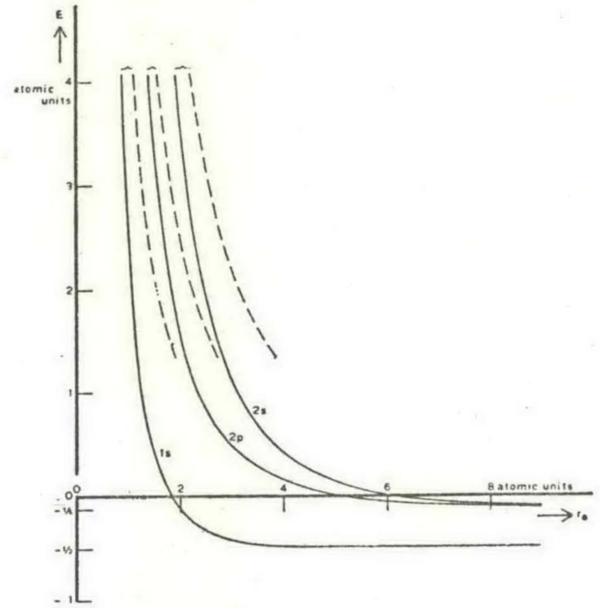

Fig. 3. The (E, r_0)-curves for the 1*s*, 2*s* and 2*p*-levels. Asymptotes are the dotted lines and $r_0 = 0$, $E = -0.5$ (for the 1*s* surve) and $E = -0.125$ (for the 2*s* and 2*p* curves).

Sommerfeld and Welker stressed the importance of a more general investigation of the behaviour of confluent hypergeometric functions F in the neighbourhood of $n = \infty$ or $E = 0$. For that purpose function F of equation (6) must be expanded as a power-series in n^{-1}. By the definition of F (7) and with (6) and (2) the wave function can be written:

$$F(l+1-n,\, 2l+2,\, 2rn^{-1}) = \sum_{k=0}^{\infty} \frac{(-1)^k\,(2r)^k\,(2l+1)!}{k!\,(2l+k+1)!} \prod_{\nu=1}^{k} \{1-(l+\nu)n^{-1}\}. \qquad (25)$$

The product can be written as the sum $\sum_{\nu=0}^{k} (-1)^{\nu}\, a_{\nu}^{k,l}\, n^{-\nu}$ where $a_{\nu}^{k,l}$ is the sum of the $\binom{k}{\nu}$ products of ν different numbers of the series $l + 1, l + 2, \ldots, l + k$ (without repetitions). The first three *) are

$$a_0^{k,l} = 1, \qquad (26)$$

$$a_1^{k,l} = \tfrac{1}{2}k(k + 2l + 1), \qquad (27)$$

$$a_2^{k,l} = k(k-1)\{\tfrac{1}{2}l^2 + \tfrac{1}{2}(k+1)\,l + {}^{1}\!/_{24}\,(k+1)(3k+2)\}. \qquad (28)$$

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*) The Newton relations [2]) that can eventually be used to calculate these coefficients are of course also valid here.

The confluent hypergeometric function can now be expressed as:

$$F(l + 1 - n,\ 2l + 2,\ 2rn^{-1}) = \sum_{\nu=0}^{\infty} n^{-\nu}\, \Phi_{l,\nu}\,(r), \tag{29}$$

with

$$\Phi_{l,\nu} = (-1)^{\nu}\,(2l + 1)!\sum_{k=\nu}^{\infty} \frac{(-1)^k\, a_{\nu}^{k,l}\,(2r)^k}{k!\,(2l + 1 + k)!}. \tag{30}$$

The functions $\Phi_{l,\nu}$, can be transformed to sums of Bessel functions, when the coefficients $a_{\nu}^{k,l}$ are written in a convenient form. It follows then that the first functions $\Phi_{l,\nu}$ are, when the abbreviation $z = 2\sqrt{2r}$ is used:

$$\Phi_{l,0}(z) = (2l + 1)!\ (\tfrac{1}{2}z)^{-2l-1} J_{2l+1}(z), \tag{31}$$

$$\Phi_{l,1}(z) = \tfrac{1}{2}(2l + 1)!\ (\tfrac{1}{2}z)^{-2l+1} J_{2l+1}(z), \tag{32}$$

$$\Phi_{l,2}(z) = \tfrac{1}{24}(2l + 1)!\ [\{ (\tfrac{1}{2}x)^{-2l-1}\,(8l^3 + 12l^2 + 4l) + (\tfrac{1}{2}z)^{-2l+1}(2l+2) + \\ + 3(\tfrac{1}{2}z)^{-2l+3}\}\, J_{2l+1}(z) + \{- (\tfrac{1}{2}z)^{-2l}\,(4l^2 + 4l) - 2(\tfrac{1}{2}z)^{-2l+2}\}\, J_{2l}(z)]. \tag{33}$$

To obtain these expressions, $a_{\nu}^{k,l}/k!$ should be written down as a sum of reciprocal factorials; so is e.g. the form

$$\frac{a_2^{k,l}}{k!} = \frac{{}^1\!/_2 l^2 + {}^3\!/_2 l + 1}{(k-2)!} + \frac{{}^1\!/_2 l + {}^5\!/_6}{(k-3)!} + \frac{{}^1\!/_8}{(k-4)!} \tag{34}$$

appropriate. After that, recurrence formulae for the Bessel functions should be applied.

Of special interest for the electronic levels, studied is this note, are the cases $l = 0$:

$$\Phi_{0,0}(z) = ({}^1\!/_2 z)^{-1} J_1(z), \tag{35}$$

$$\Phi_{0,1}(z) = {}^1\!/_4 z\, J_1(z), \tag{36}$$

$$\Phi_{0,2}(z) = \{{}^1\!/_{12}({}^1\!/_2 z) + {}^1\!/_8({}^1\!/_2 z)^3\}\, J_1(z) - {}^1\!/_{12}({}^1\!/_2 z)^2\, J_0(z), \tag{37}$$

and $l = 1$:

$$\Phi_{1,0}(z) = 6({}^1\!/_2 z)^{-3}\, J_3(z), \tag{38}$$

$$\Phi_{1,1}(z) = 3({}^1\!/_2 z)^{-1}\, J_3(z), \tag{39}$$

$$\Phi_{1,2}(z) = \{6({}^1\!/_2 z)^{-3} + ({}^1\!/_2 z)^{-1} + {}^3\!/_4({}^1\!/_2 z)\}\, J_3(z) + \{-2({}^1\!/_2 z)^{-2} - {}^1\!/_2\}\, J_2(z). \tag{40}$$

To find the character of the $(E,\ r_0)$-curve in the neighbourhood of $E = 0$ or $n^{-1} = 0$ it is necessary to consider the nodes r_0 of F or, by way of approximation, of a certain number of terms of the development (29) When we take:

$$\Phi_{l,0} + n^{-1}\,\Phi_{l,1} + n^{-2}\,\Phi_{l,2} = 0, \tag{41}$$

and put

$$r_0 = r_{00} + r_{01} + r_{02}, \tag{42}$$

where r_{00} is of zeroth order and r_{01} and r_{02} of first and second order in n^{-1}, it is found after expanding the function Φ in Taylor series and equating terms of equal order [2]):

etric function can now be expressed as:

$$+ 2,\ 2rn^{-1}) = \sum_{\nu=0}^{\infty} n^{-\nu}\, \Phi_{l,\nu}(r), \tag{29}$$

$$+ 1)! \sum_{k=\nu}^{\infty} \frac{(-1)^k\, a_\nu^{k,l}\, (2r)^k}{k!\,(2l+1+k)!}. \tag{30}$$

e transformed to sums of Bessel func-
s $a_\nu^{k,l}$ are written in a convenient form. It
functions $\Phi_{l,\nu}$ are, when the abbreviation

$$(2l+1)!\ (\tfrac{1}{2}z)^{-2l-1} J_{2l+1}(z), \tag{31}$$

$$\tfrac{1}{2}(2l+1)!\ (\tfrac{1}{2}z)^{-2l+1} J_{2l+1}(z), \tag{32}$$

$$^{-2l-1}\,(8l^3+12l^2+4l)+(\tfrac{1}{2}z)^{-2l+1}(2l+2)+$$

$$-(\tfrac{1}{2}z)^{-2l}\,(4l^2+4l)-2(\tfrac{1}{2}z)^{-2l+2}\}\ J_{2l}(z)]. \tag{33}$$

ns, $a_\nu^{k,l}/k!$ should be written down as a sum of
. the form

$$\frac{/_2 l+1}{2)!} + \frac{{}^1/_2 l + {}^5/_6}{(k-3)!} + \frac{{}^1/_8}{(k-4)!} \tag{34}$$

currence formulae for the Bessel func-

electronic levels, studied is this note, are the

$$(z), \tag{35}$$

$$\tag{36}$$

$$+ {}^1/_8({}^1/_2 z)^3\}\ J_1(z) - {}^1/_{12}({}^1/_2 z)^2\ J_0(z), \tag{37}$$

$$J_3(z), \tag{38}$$

$$J_3(z), \tag{39}$$

$$+{}^3/_4({}^1/_2 z)\}\ J_3(z) + \{-2({}^1/_2 z)^{-2} - {}^1/_2\}\ J_2(z). \tag{40}$$

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he function Φ in Taylor series and equa-

$$\Phi_{l,0}(r_{00}) = 0 \quad \text{or} \quad J_{l+1}(2\sqrt{2r_{00}}) = 0 \text{ gives } r_{00}, \tag{43}$$

$$r_{01} = 0, \tag{44}$$

$$\Phi'_{l,0}(r_{00})\, r_{02} + n^{-2}\, \Phi_{l,2}(r_{00}) = 0 \quad \text{gives } r_{02}. \tag{45}$$

It follows by using some relations between Bessel functions and their derivatives, that for s-levels ($l = 0$):

$$r_{02} = \tfrac{1}{6} n^{-2}\, r_{00}^2, \tag{46}$$

so that, in total:

$$r_0 = r_{00} + \tfrac{1}{6} n^{-2}\, r_{00}^2 = r_{00} - \tfrac{1}{3} E\, r_{00}^2; \tag{47}$$

this being the equation of the tangent in $E = 0$ at the (E, r_0) curve for a s-level, with r_{00} following from the nodes of the Bessel function J_1.

The first node gives the tangent of the $1s$-level:

$$r_0 = 1.835 - 1.123\, E, \tag{48}$$

whereas the second node gives the tangent of the $2s$-level:

$$r_0 = 6.153 - 12.620\, E. \tag{49}$$

For the p-levels ($l = 1$) it is found after a simple calculus that

$$r_{02} = n^{-2}\, (\tfrac{1}{3} r_{00} + \tfrac{1}{6} r_{00}^2), \tag{50}$$

and so for the tangent

$$r_0 = r_{00} + n^{-2}\, (\tfrac{1}{3} r_{00} + \tfrac{1}{6} r_{00}^2), \tag{51}$$

$$r_0 = r_{00} - E(\tfrac{2}{3} r_{00} + \tfrac{1}{3} r_{00}^2), \tag{52}$$

with r_{00} from $J_3(2\sqrt{2r_{00}}) = 0$.

For the $2p$-level we need the first node of J_3, so that the tangent is

$$r_0 = 5.086 - 12.015\, E. \tag{53}$$

The tangents (49) and (53) are indicated in figure 2.

d) $E > 0$. In the region of positive energies *), the confluent hypergeometric function (6) has imaginary parameters n and ρ (v.(2)). No tables for this region being available for $l = 0$ and $l = 1$, zero points have been calculated by using for the confluent hypergeometric function the series expansion of Buchholz[4]). The results are given in tables II–IV and plotted in figure 3.

e) $E \to \infty$. For the asymptotic case of small radii r_0 and thus large positive energies in the problem of the encaged hydrogen atom the influence of the proton on the electron can be neglected in

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*) The curve of reference 2 is only roughly sketched in that region and numerically not reliable.

comparison with the action of the potential wall. To show this let n approach zero in the equation (3), giving:

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \left\{\frac{1}{4} + \frac{l(l+1)}{\rho^2}\right\} R = 0 \qquad (54)$$

or modified by writing $\rho = 2rn^{-1} = 2ir\sqrt{2E}$ (2)

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left\{2E - \frac{l(l+1)}{r^2}\right\} R = 0. \qquad (55)$$

This is indeed the equation of the particle in a spherical box. The solutions of (55) are the Bessel-functions

$$J_{l+\frac{1}{2}}(r\sqrt{2E}), \qquad (56)$$

that can also readily be found as an asymptotic case of (4) for $E \rightarrow \infty$ as a series expansion shows.

For $l = 0$ the Bessel function (56) has nodes at $r_0\sqrt{2E} = q\pi$ where q is an integer. So for the energy curve of the 1s level the cubic hyperbole

$$E = \pi^2/2r_0^2 \qquad (57)$$

is found to be an asymptote. For the 2s level it is:

$$E = 2\pi^2/r_0^2, \qquad (58)$$

whereas for $l = 1$ the first node of (56) lies at $r_0\sqrt{2E} = 4.4934$ so as to give

$$E = 10.0953/r_0^2 \qquad (59)$$

for the asymptote of the 2p level. All three asymptotes are indicated in figure 3 as dotted lines. The $r_0 = 0$ axis is evidently also an asymptote of the energy curves calculated.

f) By plotting $E^{-\frac{1}{2}}$ as a function of r_0, the asymptotes (57), (58) and (59) become straight lines through the origin, being there tangent to the corresponding $(E^{-\frac{1}{2}}, r_0)$ curves. It is easy to find now graphically points of the (E, r_0) curve.

The results are listed in tables II–IV with the indication § 3*f* and represented in figure 3.

g) Although it follows from section *c* of this paragraph that the energy values E for $\lim r_0 \rightarrow 0$ are the same as for a spherical box, it is not allowed to conclude that the quantum mechanical average potential energy $\overline{V}$ is zero, as with the box.

In fact, it is only true that $\lim\limits_{r_0 \rightarrow 0} \overline{V}/E = 0$. Taking the value of

of the potential wall. To show this let n
ion (3), giving:

$$-\left\{\frac{1}{4}+\frac{l(l+1)}{\rho^2}\right\}R=0 \qquad (54)$$

$$= 2rn^{-1} = 2ir\sqrt{2E}\ (2)$$

$$+\left\{2E-\frac{l(l+1)}{r^2}\right\}R=0. \qquad (55)$$

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re the Bessel-functions

$${}_{+\frac{1}{2}}(r\sqrt{2E}), \qquad (56)$$

nd as an asymptotic case of (4) for $E \rightarrow \infty$
s.

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$$E = 2\pi^2/r_0^2, \qquad (58)$$

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3.

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$\rightarrow 0$ are the same as for a spherical box,
le that the quantum mechanical average
, as with the box.
that $\lim\limits_{r_0\rightarrow 0} \overline{V}/E = 0$. Taking the value of

$\lim\limits_{r_0\rightarrow 0} \overline{V}$ for the $1s$ level as an example we have by (56):

$$\overline{V} = -\int_0^{r_0} J_{\frac{1}{2}}^2\,(\pi r/r_0)r^{-1}r^2dr \Big/ \int_0^{r_0} J_{\frac{1}{2}}\,(\pi r/r_0)r^2dr. \qquad (60)$$

Integration gives:

$$\overline{V} = -\{C + \ln\pi - Ci(2\pi)\}r_0^{-1} = -2.4422r_0^{-1}. \qquad (61)$$

with $C = 0.5577$, the constant of Euler–Mascheroni, and $Ci(2\pi)$ the cosine integral for the argument 2π equalling —0.0271.

For $r_0 \rightarrow 0$ the potential energy $\overline{V} \rightarrow -\infty$, but because E is proportional to r_0^{-2} it is really so that $\lim \overline{V}/E = 0$.

h) The concordance between the set of levels at $r_0 \rightarrow 0$ and at $r_0 = \infty$ is very simple. The n-fold degeneracy of the levels at $r_0 = \infty$, where $N = n$, is removed when r_0 is finite, until at $r_0 \rightarrow 0$ the wave function is asymptotically $J_{l+\frac{1}{2}}$ with $l = 0, 1, \ldots\ n-1$ and with $N - l - 1$ nodes between its limiting points. On the other hand the wave functions $J_{1/2}$ correspond to the $1s$, $2s$, $3s$, etc. levels with increasing number of zero-points, whereas $J_{3/2}$ belongs to the p levels etc.

§ 4. *Possible physical importance of the problem.* Michels, De Boer and Bijl have investigated the ground level of the encaged hydrogen atom for fairly large values of r_0 in order to get an idea of the influence of pressure on the wave function and by consequence on the polarizibility. The study of higher levels might give some information about the shift of spectral lines under pressure. It must however be taken in mind that the procedure followed is a very rough one. In the first place replacing of the influence of pressure by the action of an infinitely high and steep potential wall neglects the effect of Van der Waals attraction forces between molecules, and gives only an idea of the effect of repulsion forces, that act at very high density. Also the resonance broadening of levels when atoms of the same kind come close together is not taken into account, so that we must think that the cage around the hydrogen atom considered, does not consist of hydrogen atoms.

It may however all the same be concluded that the shift of spectral wave lengths can be a considerable one under a pression of some hundreds or thousands of atmospheres. This is visible in figure 3, because $r_0 = 7$ corresponds with 111 atmospheres and $r_0 = 5$ with

4860 atmospheres (pressure $= -(dE/dr_0)/4\pi r_0^2$). The shifts of spectral lines could also have an influence on the Lorentz–Lorenz function. In fact the behaviour of the Lorentz–Lorenz expression 8) as function of density could be partially explained by assuming that the wave lengths of spectral lines diminish by an amount of some percents or some tens of percents (cf. also 9) and 10)).

Our thans are due to Mr A. Botzen for valuable help with numerical calculations.

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