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THE NORMAL STATE OF HELIUM

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Abstract

An approximate wave function for normal helium is calculated, by using theoretically determined functions for the limiting cases of large and small r's and interpolating between them. The charge density computed from this wave function is in good agreement with that found independently by Hartree. The diamagnetism of normal helium is calculated, and agrees with observation within the experimental error. The repulsive forces between two helium atoms are calculated by the method of Heitler and London, and the attractive Van der Waals forces are roughly estimated from Wang's results with hydrogen. The potential curve so found gives a "molecular diameter" in agreement with experiment, and the minimum of the curve leads to approximately correct density and boiling point for the liquid.

THE present paper describes an attempt to find a fairly accurate wave function for the normal state of the helium atom, and to apply this to the computation of several properties of atomic helium, in particular to its diamagnetic susceptibility, and to the forces of repulsion between two normal helium atoms. The method adopted is practically that described in a previous paper:[1] when one electron is at a considerable distance, the other close up, the variables are assumed to be separable, the wave function being a product of an ionic function of the inner electron, and a hydrogen-like function of the outer one, the energy constant for the latter being taken from the experimental term value. When both electrons are close up, the function is taken to be a simple form, described in the previous paper, which the actual wave function approaches in the limit as the electrons both approach the nucleus. Between these two limits, simple interpolations are used. It is plain that the method is not one for calculating the energy of the normal state; we easily convince ourselves, however, that the experimental energy is the true characteristic number of the wave problem, by observing that the functions described above, for large and small r's, join much more smoothly than they would if a different energy value were assumed. The calculations were made before the writer saw Hartree's[2] paper, in which he obtains a charge density distribution for helium in quite a different way. The wave function found in the present paper is more complicated than Hartree's in the matter of the way in which it takes the interaction energy between electrons into account. But the charge density can be computed equally well from either method, and this permits a comparison of the present results with Hartree's. The discrepancies between the two are nowhere greater than one or two percent. This is highly satisfactory, both in that it verifies the present method and Hartree's, and also that

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[1] J. C. Slater, Phys. Rev., **31**, 333 (1928).

[2] D. R. Hartree, Proc. Camb. Phil. Soc., **24**, p. 89, 1928.

it justifies us in believing this density distribution to be correct within a narrow limit of error. The other numerical results are also gratifying: the diamagnetic susceptibility agrees with the experimental value within a percent and a half, and the results for collisions of two atoms agree with experiment within the rather wide limit caused by uncertainties in the kinetic theory treatment of the imperfect gas problem.

1. The Wave Function

We assume that, for r_2 small, r_1 large, the wave function approaches $e^{-2r_2}\times$a function of r_1, the latter being that solution of the hydrogen problem which corresponds to the term value of normal helium (1.805 Rh), and remains finite at infinity. This function is easily found in a series expansion as the confluent hypergeometric function of Sugiura[3] and others. We seek a solution of Schrödinger's equation for the hydrogen problem in descending powers of r; the solution is

$$u=e^{-r/n^*}r^{(n^*-1)}(1+a_1/r+a_2/r^2\cdots)$$

where

$$a_n=-(n^*/2n)((n^*-n)(n^*-n+1)-k(k+1))a_{n-1}$$

$n^*=1/(-E)^{1/2}$, E = term value (in terms of Rh), k = azimuthal quantum number, and r's are expressed as multiples of the radius of the first Bohr orbit.

Putting in, for normal helium, $E=-1.805$ (the experimental value), $k=0$, we have $n^*=.745$, $a_1=.0707$, $a_2=-.00421$, $a_3=.00149$, etc. Thus our assumption for the wave function with r_1 large, r_2 small, is

$$e^{-2r_2}e^{-1.344r_1}r_1^{-.255}(1+.0707/r_1-.00421/r_1^2+.00149/r_1^3\cdots) \qquad (1)$$

For the case when r_1 is small, r_2 large, we may interchange the arguments, since the function must be symmetrical in the coordinates of the two electrons.

When both r's are small, we take as the wave function

$$e^{-2(r_1+r_2)+1/2r_{12}} \qquad (2)$$

This is the function introduced in the previous paper, and can be obtained as follows: we try to satisfy the wave equation as closely as possible at small r's by a function which is e raised to a linear combination of r_1, r_2, and r_{12}. By choosing the coefficients as in (2), we satisfy the wave equation as far as terms of the zero order in the r's, while with any other choice of coefficients, the errors are of the order of $1/r$.

We now introduce a small correction term in (2), to make it join on smoothly to (1) along the line in configuration space given by $r_2=0$. Along this line, $r_{12}=r_1$, so that (2) becomes $e^{-1.5r_1}$. The correction term which we now apply is a quadratic term in the exponent; we use the function $e^{-1.5r_1+\alpha r_1^2}$. The method of finding the value of α is shown in Fig. 1, where the quantities

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[3] Y. Sugiura, Phil. Mag., Ser. 7, 4, p. 498, 1927.

$d \log u/dr_1$ are plotted for both functions (1) and (2). The correction to (2) changes the curve from a horizontal straight line at 1.5 to a straight line with a slight slope. We naturally choose this line so that it is tangent to the curve (1), for then u'' as well as u' will join smoothly together. One sees graphically that this demands a tangent to curve (1) at about the point $r=3$. When one substitutes numerical values, this gives $\alpha=.0107$. By comparing with the curves of the function (1) for $E=1.70$ and 1.90, we see how much more easily the curve with the correct ionization potential, 1.805, joins on than any other would.

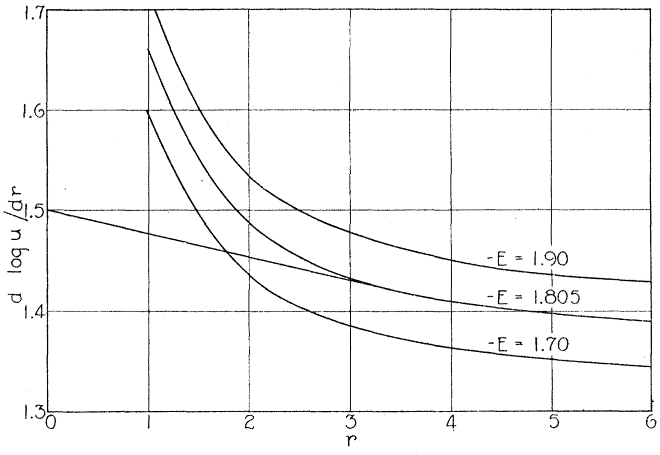

Fig. 1

Having equalized the slopes of the functions (1) and (2) at $r=3$, we must multiply one of them by a constant, so that the functions themselves will join smoothly. We find at once that we must multiply (1) by .8916. Then we have the following results: for $r_2=0$,

$$u=e^{-1.5r_1+.0107r_1^2} \quad \text{for } r_1<3$$

$$=.8916e^{-1.344r_1}r_1^{-.255}(1+.0707/r_1-.00421/r_1^2+.00149/r_1^3\cdots) \quad \text{for } r_1>3.$$

and the whole wave function can be written

$$u=e^{-2(r_1+r_2)+.5r_{12}+.0107(r_1^2+r_2^4)} \quad \text{for } r_1,\ r_2 \text{ small}$$

$$=.8916e^{-2r_2}e^{-1.344r_1}r_1^{-.255}(1+.0707/r_1-.00421/r_1^2+.00149/r_1^3\cdots)$$

$$\text{for } r_1>3,\ r_2 \text{ small}.$$

This function is not determined in detail everywhere; for we have not specified the way in which the two parts of it join, except along the lines $r_1=0$ and $r_2=0$. But this difficulty is not a serious one in most work demanding the function.

Having found a wave function, our next task is to normalize it. To do this, we require the integral of u^2 over the configuration space. The first step is to integrate u^2 over the volume element of the coordinates of one electron. The result will be the charge density in the sense of Hartree; it is a function of one electron, by which we multiply any function of the coordinates of that electron, and integrate, to get the average of the corresponding function. It is therefore what is generally needed in applying the wave function to specific problems. In two limiting cases, it can be calculated directly; these are the cases where $r_1=0$, and where r_1 is very large. In the first case, we must square the function of r_2 which we obtain by setting $r_1=0$ in u (that is, $e^{-1.5r_2+.0107r_2^2}$ for small r_2, and the other function for large r_2) and integrate over dv_2. This can be carried out without great difficulty, by expanding in series when necessary, and the result is 4π (.07630). The second case, when r_1 is very large, is simpler: there u depends on r_2 only through the term e^{-2r_2}, so that the integration over dv_2 can be immediately carried out, yielding $\int u^2 dv_2=(4\pi/32)u^2(r_1, r_2=0)$. Thus in this limit, the integral is proportional to the square of the wave function for $r_2=0$; and it is natural to write in all cases $\int u^2 dv_2=f(r_1)u^2(r_1, r_2=0)$. The function f will then approach the value $4\pi/32$ for large r_1; on the other hand, it equals 4π (.07630) for $r_1=0$, a value roughly twice as great. Our problem can be formulated as that of finding $f(r_1)$ for intermediate r_1's.

To a certain degree of accuracy, we can approximate to $f(r_1)$ by assuming u to have the value (2), and actually carrying out the integration over the coordinates of the second electron. This can be done by using elliptic coordinates, and one finds

$$f(r_1)=2\pi\left[(4/15)^2(1-1/4e^{-5r_1})+(4/15)^3(1-e^{-5r_1})/r_1\right]$$

This function approaches 4π $(2/27)=4\pi$ (.07407) rather than 4π (.07360) as the correct function does; this is because, in the integration, the term $e^{.0107r^2}$ in u was neglected. But more serious than this, it approaches quite a wrong value at infinity, 2π $((4/15)^2+(4/15)^3)=4\pi$ (.0355) rather than 4π (.03215). This is because the function (2) fails decidedly at large distances in the matter of the interaction energy of the electrons. Thus the function f found above can do no more than serve as a general guide in forming a function to approach the proper values at the limits of small and large r_1. It possesses one feature, however, which seems to be of importance: if we expand it about $r_1=0$, the expansion commences with the terms $4\pi(2/27)$ $(1-r_1 \cdots)$. That is, the slope at the origin is numerically equal to the function; f (r_1) starts off, in other words, as e^{-r_1}. Since $u^2(r_1, r_2=0)$ starts as e^{-3r_1} the integral, or $\int u^2 dv_2$ acts as e^{-4r_1}, which is the behavior of the solution of a central-field problem with a nuclear charge of 2 units. This of course is what Hartree's function does; it is of great interest that our solution does the same, and it seems as if this property were one to be retained in the final function f.

We wish, then, an interpolation formula for $f(r_1)$, reducing to 4π (.07630) for $r_1=0$, having a negative slope numerically equal to this at the origin, decreasing asymptotically to 4π (.03125), and having the general form of the function f found above. A function which satisfies all these demands is the simple exponential interpolation formula $f=4\pi\,(.03125+.04504\,e^{-1.692r_1})$, where there are just enough conditions to determine the constants. Examination of the function shows that it reaches substantially its asymptotic value soon after r_1 passes outside the range of the second electron, a condition which the function should satisfy. Since it seems satisfactory in every way, we are justified in using it.

Taking the value of f just found, we may multiply it by $u^2(r_1,\ r_2=0)$ and obtain an approximation for $\int u^2dv_2$. Then it is a simple matter to integrate over r_1; and the result is $\pi^2\ (.05233)=\int u^2dv_1dv_2$. To normalize our wave function, we must then divide by the square root of this, and the result is

$$\left.\begin{aligned}
u&=1.392e^{-2(r_1+r_2)+.5r_{12}+.0107(r_1^2+r_2^2)} \quad \text{for } r_1,\ r_2<3\\
u&=1.241e^{-2r_2}e^{-1.344r_1}r_1^{-.255}(1+.0707/r_1\cdots) \text{ for } r_1>3,\ r_2 \text{ small}\\
u&=1.241e^{-2r_1}e^{-1.344r_2}r_2^{-.255}(1+.0707/r_2\cdots) \text{ for } r_2>3,\ r_1 \text{ small}
\end{aligned}\right\}\tag{3}$$

These represent our estimate of the normalized wave function of normal helium. Similarly we have

$$\left.\begin{aligned}
\int u^2dv_2&=.7604(1+1.440e^{-1.692r_1})e^{-3r_1+.0214r_1^2} \text{ for } r_1<3\\
&=.6048(1+1.440e^{-1.692r_1})e^{-2.688r_1}r_1^{-.510}(1+.1414/r_1-.0034/r_1^2\cdots)\\
&\qquad\qquad\qquad\qquad\qquad\qquad \text{for } r_1>3
\end{aligned}\right\}\tag{4}$$

The function $\int u^2dv_2$, given in (4), should be the density distribution of charge, in Hartree's sense; multiplied by 2 (on account of the two electrons of helium), it should give just his dZ/dr. In Table 1 we show a comparison of the values given by both methods; the resemblance is striking. The only difference is a slight tendency of the present function to emphasize the smaller r's at the expense of the larger. It is hard to say which function is to be preferred.

TABLE I.

r	dZ/dr present theory	dZ/dr Hartree	r	dZ/dr present method	dZ/dr Hartree
0	.000	.00	1.6	.468	.48
.1	.314	.30	1.8	.319	.33
.2	.851	.83	2.0	.216	.22
.3	1.307	1.28	2.2	.145	.15
.4	1.605	1.57	2.4	.095	.10
.6	1.745	1.73	2.6	.063	.06
.8	1.544	1.55	2.8	.041	.04
1.0	1.231	1.25	3.0	.026	.026
1.2	.924	.94			
1.4	.664	.68			

2. DIAMAGNETIC SUSCEPTIBILITY

Van Vleck[4] has shown the diamagnetic susceptibility of a monatomic gas to be given by $\chi=-(e^2L/6mc^2)\Sigma\overline{r^2}$ where the summation is the sum of all

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[4] J. H. Van Vleck, Proc. Nat. Acad. Sci., **12**, 662 (1926); Phys. Rev. **31**, 598 (1928).

the r^2's of the various electrons, averaged over the orbit. We have $\overline{r_1^2} = \int u^2 r_1^2 dv_1\, dv_2 = \int dv_1 r_1^2 \int u^2 dv_2$. This shows that we are to use the function (4) in computing such an average. Carrying out the integration, we find $\overline{r_1^2} = 1.1569$ (in terms of a_0^2). Since this also equals $\overline{r_2^2}$, we have $\Sigma \overline{r^2} = 2.3138$. Then $\chi = 1.853 \times 10^{-6}$. The experimental value of Wills and Hector[5] is 1.88×10^{-6}. The discrepancy is but $1\frac{1}{2}$ percent. Whether it is on account of experimental error, or from inaccuracy in the calculations, one cannot see. The uncertainty in the wave function indicated by the difference between the two functions of Table I would account for an error of about this magnitude. For comparison, we note that Wang's[6] calculation of χ, using Kellner's wave function, is 1.53×10^{-6}, with an error of 20%. The great advantage of the present function, in point of accuracy, is obvious.

3. Forces Between Atoms

Heitler and London[7] have discussed the repulsive forces between atoms, indicating that the electronic wave functions for two atoms near to each other must be taken as linear combinations of the wave functions of the individual atoms, and showing that the average of H over this combined wave function (giving the first order perturbation energy) results in a repulsive energy increasing rapidly as the atoms approach, in case each atom contains electrons only in closed shells. This is an interference effect of the waves of the two, becoming appreciable only to the extent to which the wave functions actually overlap, so that it decreases exponentially with the distance. In addition, Wang[8] has treated the second order perturbation energy between two hydrogen atoms, showing that it contains an inverse sixth power attractive energy. (The writer is indebted to Dr. H. A. Kramers for the information that this effect was discussed some time ago in lectures by Dr. Pauli). This term is, in a certain way, a Debye attraction of the variable electric moment of one atom (the variable terms are not zero, even in the normal state, although the diagonal term is) for the dipole which it induces in the other atom. The first of these terms gives the repulsion of atoms at close distances, resulting in their impenetrability; the second results in the Van der Waals attraction at large distances. The former can be calculated from the knowledge of the normal state alone; and this calculation is given in the present paper. It is unsatisfactory in some details, on account of the mathematical difficulty, but is probably a fairly accurate deduction from the assumed wave function. The other term, being a second order one, demands a knowledge of the other wave functions as well, so that no exact calculation is possible. We content ourselves with a rough estimate from Wang's value for hydrogen, taking account of the differing size and polarisibility (as determined experimentally) of helium. The results are in rough agreement with the values found from kinetic theory;

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[5] Wills and Hector, Phys. Rev., **23**, 209 (1924); **24**, 418 (1924).

[6] S. C. Wang, Proc. Nat. Acad. Sci., **13**, 798 (1927).

[7] Heitler and London, Zeits. f. Physik, **44**, 455 (1927).

[8] S. C. Wang, Phys. Zeits., **28**, 663 (1927).

from the equilibrium position of two atoms under the attractive and repulsive forces, we can estimate the density and boiling point of the liquid; and from the distance to which atoms with the average temperature energy would approach, we compute a molecular diameter. These results are in as close agreement with experiment as would be expected, when we consider the various errors in the calculations.

We shall now consider the first order term in the interaction energy. The first step is to set up the correct unperturbed wave function. Let us suppose that the wave function for the atom a by itself, with the electrons 1 and 2 in it, is $u_a(1, 2)$. This is to be taken, say, as the function of r_1 and r_2 described in (3), where r_1 is the distance of the 1st electron from the nucleus a, etc. It is symmetric in the coordinates 1 and 2, so that $u_a(1, 2)=u_a(2, 1)$. Similarly for an atom b with electrons 3 and 4, the wave function is $u_b(3, 4)$. A conceivable unperturbed wave function for the problem of four electrons would be $u_a(1, 2)u_b(3, 4)$. But this is not the proper wave function. We have instead, if we assume the function in which the electrons 1 and 3 have their spin in one direction, 2 and 4 in the opposite direction, the combination which is anti-symmetric in the electron coordinates 1 and 3, and also in 2 and 4:

$$u_a(1,2)u_b(3,4)-u_a(1,4)u_b(2,3)-u_a(2,3)u_b(1,4)+u_a(3,4)u_b(1,2).$$

Now when we square the wave function, to use either for normalization or for integrating H, terms of three kinds arise: diagonal terms, as $u_a^2(1, 2)$ $u_b^2(3, 4)$; terms corresponding to the interchange of two electrons, one in each atom, as $u_a(1, 2)u_b(3, 4)u_a(1, 4)u_b(2, 3)$; and terms corresponding to the interchange of all four electrons, as $u_a(1, 2)u_b(3, 4)u_a(3, 4)u_b(1, 2)$. There are four terms of the first type, eight of the second (each with negative sign), and four of the third (with positive sign). The second type of term is large only in that part of configuration space in which an electron of each atom (here the 2d and 4th) have both considerable probability of being found; the third is large only where all four electrons are likely to be found at once. Thus, for a moderate separation of the nuclei, the second term varies, so to speak, directly as the amount of penetration of one atom by the other; the third as the square of this. For this reason, the latter is small, and we may neglect it in our approximate calculations. We thus have, if

$$I_1=\int u_a^2(i,j)u_b^2(k,l)dv=1 \text{ (by normalization of separate } u\text{'s)}$$

$$I_2=\int u_a(i,j)u_b(k,l)u_a(i,l)u_b(k,j)dv$$

that the normalization integral is $4\ I_1-8\ I_2$. Similarly if H is the perturbation energy, and

$$H_1=\int Hu_a^2(i,j)u_b^2(k,l)dv$$

$$H_2=\int Hu_a(i,j)u_b(k,l)u_a(i,l)u_b(k,j)dv$$

the integral of H is 4 H_1-8H_2. Thus the first order perturbation energy is $(H_1-2H_2)/(I_1-2I_2)$.

We first evaluate I_2. In carrying this out, we meet certain approximations which we must make in each such integral. The integrand is large only at points corresponding to arrangements of electrons in which two electrons, the jth and lth, have considerable probability of belonging to either atom. Since the atoms are assumed to be some little distance apart, this means that these two electrons must be in the region between the two nuclei, at a considerable distance from either nucleus. For the integrand to be large, then, the other two electrons, the ith and kth, must be fairly close to the ath and bth nucleus respectively. Thus in the essential region, $u_a(i, j)$ or $u_a(i, l)$ correspond to the case where electron i is close, electron j or l far away, with a corresponding situation for the u_b's. Then we can approximately use the forms, from (3),

$$u_a(i,j)=1.241e^{-2r_{ai}}e^{-1.344r_{aj}}r_{aj}^{-.255}(1+.0707/r_{aj}\cdots)$$
$$u_a(i,l)=1.241e^{-2r_{ai}}e^{-1.344r_{al}}r_{al}^{-.255}(1+.0707/r_{al}\cdots)$$

and similarly for the other u's. We can immediately integrate over dv_i (and similarly over dv_k), obtaining

$$\begin{aligned}\int u_a(i,j)u_a(i,l)u_b(k,j)u_b(k,l)dv_idv_k\\ = (.6048)^2e^{-1.344r_{aj}}r_{aj}^{-.225}(1+.0707/r_{aj}+\cdots)e^{-1.344r_{al}}r_{al}^{-.255}\\ (1+.0707/r_{al}\cdots)e^{-1.344r_{bj}}r_{bj}^{-.255}(1+.0707/r_{bj}\cdots)\\ e^{-1.344r_{bl}}r_{bl}^{-.255}(1+.0707/r_{bl}\cdots).\end{aligned}$$

Thus we have

$$I_2=\left[.6048\int e^{-1.344(r_{aj}+r_{bj})}(r_{aj}r_{bj})^{-.255}(1+.0707/r_{aj}\cdots)(1+.0707/r_{bj}\cdots)dv_j\right]^2$$

$$=\left[\int u_au_b\right]^2 \text{ (for abbreviation)}$$

We make a further approximation, by neglecting all except the constant term, in the summations at the end. The remaining integral can be evaluated by using elliptical coordinates. If $R=r_{ab}$, $\lambda=(r_{aj}+r_{bj})/R$, $\mu=(r_{aj}-r_{bj})/R$, $\rho=1.344$ R, we have, since $dv=\pi/4$ $R^3(\lambda^2-\mu^2)d\lambda d\mu$ in these coordinates,

$$\int u_au_b=.6048\pi/4R^3\int\int e^{-\rho\lambda}(R/2)^{-.510}(\lambda^2-\mu^2)^{.745}d\lambda d\mu$$

$$=.6765R^{2.49}\int\int e^{-\rho\lambda}(\lambda^2-\mu^2)^{.745}d\lambda d\mu,$$

where λ goes from 1 to ∞, μ from -1 to $+1$. The integration cannot be carried out directly. We therefore adopt an approximate method. We may write the integrand $e^{-\rho\lambda}(\lambda^2-\mu^2)^k$ with $k=.745$. Now the integration can be carried out exactly for integral values of k, and the result is a uniformly varying function of ρ and k. We find this for a number of values of k, and interpolate for $k=.745$. We have

$$\int u_a u_b = .6765R^{2.49}2e^{-\rho}/\rho[1] \quad \text{for } k=0$$

$$= .6765R^{2.49}2e^{-\rho}/\rho[2/3+2/\rho+2/\rho^2] \quad \text{for } k=1$$

$$= .6765R^{2.49}2e^{-\rho}/\rho[8/15+8/3\rho+32/3\rho^2+24/\rho^3+24/\rho^4] \text{ for } k=2, \text{etc.}$$

By plotting the coefficients of the powers of $1/\rho$ against k, we can interpolate for the coefficients for $k=.745$, and the result is

$$\int u_a u_b = .6765R^{2.49}2e^{-\rho}/\rho[.725+1.675/\rho+.20/\rho^2]$$

From this result, I_2 can be immediately found.

Next it is convenient to find H_2, since it involves the same sort of integrals as I_2. For this, we have, where H is the perturbation energy,

$$Hu_a(i,j)u_b(k,l) = [8/r_{ab}-4/r_{bi}-4/r_{bj}-4/r_{ak}-4/r_{al} +2/r_{ik}+2/r_{il}+2/r_{jk}+2/r_{jl}]u_a(i,j)u_b(k,l).$$

We multiply by $u_a(i, l)u_b(k, j)$ and integrate over the ith and kth electrons. In this integration, the term $4/r_{bi}$ (or $4/r_{ak}$), multiplied by $e^{-4r_{ai}}$ (or $e^{-4r_{bk}}$) represents the potential of the spherical charge distribution $e^{-4r_{ai}}$ at the point b. Now we may reasonably say that b is entirely outside this distribution; for the distribution e^{-4r} decreases so much faster than that of the other electron, $e^{-2.688r}$, that although the latter distributions overlap appreciably in the region between nuclei, the former will not appreciably extend to the other nucleus. Thus in these terms, by the fundamental properties of the potential of spherical distributions, we may replace $4/r_{bi}$ (or $4/r_{ak}$) by $4/r_{ab}$. Similarly in the term $2/r_{ik}$, one electron is definitely attached to the one nucleus, the other to the other, without overlapping, so that we may replace this by $2/r_{ab}$. In the terms $2/r_{il}$, $2/r_{jk}$, one electron (the ith or kth) is definitely attached to one nucleus, the other wanders with greater freedom. By the same arguments used above, we may replace them to a good approximation by $2/r_{al}$, $2/r_{bj}$. Then we have approximately

$$H_2 = \int u_a(i,l)u_b(k,j)Hu_a(i,j)u_b(k,l)dv$$

$$= \int u_a(i,l)u_b(k,j)u_a(i,j)u_b(k,l)dv[2/r_{ab}-2/r_{al}-2/r_{bj}+2/r_{jl}]$$

The result is just as if we considered the interaction energy only of the pair of electrons in resonant interaction, concentrating the other electron of each atom at its nucleus.

In carrying out the integrations, we may now integrate over the ith and kth electrons as before. The first term gives $2\ I_2/r_{ab}$. The second and third unite to give $-4\int u_a u_b \int (u_a u_b/r_{al})$ where $\int (u_a u_b/r_{al})$ is an abbreviation for

$$.6048 \int e^{-1.344(r_{al}+r_{bl})}(r_{al}r_{bl})^{-.255}/r_{al}(1+.0707/r_{al}\cdots)(1+.0707/r_{bl}\cdots)dv_l.$$

The latter integral we evaluate much as we did $\int u_a u_b$. The result is approximately

$$\int (u_a u_b/r_{al}) = .6765R^{2.49}(2/R)(2e^{-\rho}/\rho)[1.15+.22/\rho].$$

The last term of H_2 is, after carrying out the integration over the ith and kth electrons,

$$2(.6048)^2 \int (e^{-1.344(r_{aj}+r_{bj}+r_{al}+r_{bl})}/r_{jl})(r_{aj}r_{bj}r_{al}r_{bl})^{-.255}(1+\text{etc.})dv_j\,dv_l.$$

If it were not for the term raised to the power $-.255$, this would be essentially the same integral as that evaluated by Sugiura.[9] The presence of this term can be allowed for as with the other integrals, by letting $k=1-.255$, integrating for integral values of k, and interpolating. On account of the difficulty of this integration, even for integral k's, we content ourselves with a linear interpolation between $k=0$ and $k=1$. For $k=1$, the result is essentially the same as Sugiura's; we have the term

$$\begin{aligned}=(16/5)(.6765)^2R^{3.98}\rho^{-5}[&-e^{-2\rho}(-25/8+23\rho/4+3\rho^2+\rho^3/3)\\&+(6/\rho)\{S(C+\log\rho)+S'E_i(-4\rho)-2(SS')^{1/2}E_i(-2\rho)\}]\end{aligned}$$

where

$$S=(1+\rho+\rho^2/3)^2e^{-2\rho},\ S'=(1-\rho+\rho^2/3)^2e^{2\rho},\ C=.5772.$$

For $k=0$, by methods essentially similar to Sugiura's, we find

$$\begin{aligned}(16/5)(.6775)^2R^{3.98}\rho^{-5}[(5/2)\rho^3\{&e^{-2\rho}/2(C+\log\rho)\\&-E_i(-2\rho)+e^{2\rho}/2E_i(-4\rho)\}].\end{aligned}$$

We take as the result the linear interpolation between these two functions (which, when worked out, are not very different, so that the interpolation is not a doubtful one). By putting all these terms together properly, we find H_2.

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[9] Y. Sugiura, Zeits. f. Phys., **45**, 484 (1927).

Finally we must evaluate H_1, the diagonal term. Since this is not a particularly large term, and since its calculation involves no particular difficulties, we merely state the result, which is

$$H_1 = e^{-2\rho}[2.10R^{-.510}(1+1/2\rho\cdots)-1.458R(.81+2.13/\rho\cdots)].$$

The second term preponderates, giving a negative energy. This term, however, is never of a size at all comparable numerically with H_2, which is positive, and results in a repulsion.

When we compute the first order energy of interaction, from the complicated formulas found above, it appears that it is a simple function of the distance, always repulsive, increasing very rapidly as the distance decreases. It is in fact possible to approximate very accurately to the complicated result by a simple exponential expression, without theoretical significance, but nevertheless very useful. This is the following: Potential of two helium atoms at distance $r=$

$$7.70\times 10^{-10}e^{(-r\,(\mathrm{cm})/.218\times 10^{-8})}\ \text{ergs},$$

where now we have expressed distances in centimeters, energy in ergs. This formula expresses the results of our calculations, with errors no greater than the other errors introduced in the method, for values of r between 1 $A°$ and large distances.

Now that we have derived the first order repulsive energy, we shall try to make a rough estimate of the second order attractive energy. Wang finds that, for two hydrogen atoms, this energy has a leading term of $-(243/28)(2/R^6)$ (where energy is in terms of Rh, distances in terms of a_0). He further interprets the constant as being of the nature of the polarizibility multiplied by the square of an electric moment (this moment representing the variable electric moment of the atom). We may then expect that very roughly the corresponding term of helium will be to the hydrogen term as the ratio of polarizibility, multiplied by the square of electric moment. Now the polarizibility of atomic hydrogen, as computed from the second order Stark effect by Waller,[10] is $.66\times 10^{-24}$; for helium, as one can find it simply from measured dielectric constants and refractive indices, it is about $.213\times 10^{-24}$. For the ratio of moments, we may roughly take the ratio of the linear dimensions of the atoms. Since the square of the linear dimensions of a shell is inversely proportional to the ionization potential, this means that the square of the moment for helium can be taken roughly 1/1.8 times as great as for hydrogen. Thus our rough estimate for this term is

$$-(243/28)(2/R^6)\times(.213/.66)\times(1/1.8) = -3.11/R^6.$$

Expressing energy in ergs, distances in centimeters, this is $-.67\times 10^{-10}/(R/a_0)^6$. This figure is to be regarded as highly uncertain. One could with right say that, since helium has two electrons, hydrogen but one, it should

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[10] I. Waller, Zeits. f. Phys., **38**, 635, (1926).

be doubled. On the other hand, one could argue that the square of the moment, which appears in the formula, should be proportional to the polarizibility, so that instead of 1/1.8 as a ratio we should have had another factor .213/.66, resulting in a term about half as great. Thus a factor of 2 either way is not impossible.

We have found the forces between two neutral helium atoms to consist of two terms, one repulsive, the other attractive:

$$\text{Energy}=7.7\times 10^{-10}e^{-2.43/(R/a_0)}-.67\times 10^{-10}/(R/a_0)^6.$$

This function has a minimum at $R/a_0=5.6$, $R=3.0\times 10^{-8}$ cm. Its value at that point is -1.21×10^{-15} ergs. These figures may be brought into rough connection with the properties of liquid helium. This has a density of about .14, so that each atom of the liquid occupies a volume of $(3.62\times 10^{-8})^3$ cubic centimeters. The distance apart in the liquid is then obviously of the order of the distance of equilibrium found above. The critical temperature is 5.2° Abs; the mean kinetic energy of a molecule at this temperature is 1.07×10^{-15} ergs, a quantity of the same order of magnitude as the energy of separation found above. Thus the equilibrium position which we have found seems to correspond with fair accuracy to that which must actually occur in the liquid. It must not be forgotten, however, that our results are subject to great error, particularly in the attractive term.

It is also possible to draw parallels between the potential which we have found and the "radius" of helium atoms as determined from kinetic theory. Various estimates of this quantity, given in Jeans' "Dynamical Theory of Gases," range from $.99\times 10^{-8}$ cm, to 1.10×10^{-8} cm. The corresponding values of our energy function are 6.35×10^{-14} ergs and 1.84×10^{-14} ergs. These are the average kinetic energies of atoms at 309° Abs (or 36°C) and 90° Abs respectively. Thus the various distances represent the distances of closest approach of average atoms in the temperature range usually used; this is surely the only thing one could mean by a diameter of such a structure. This agreement is then satisfactory; it is also more sure than those for the liquid, for at the smaller distances used here, the attractive term in the energy is relatively less important.

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