MARCH 15, 1931 PHYSICAL REVIEW VOLUME 37

THE VAN DER WAALS FORCES IN GASES

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(Received February 5, 1931)

Abstract

A calculation of van der Waal's potential of two atoms at large separation has been carried out for hydrogen and helium. The method depends upon a representation of the perturbed wave function of the system as

$$\psi=\psi_0\ (1+vR)$$

where ψ_0 is the unperturbed wave function, v the perturbing potential and R is a function of the radial coordinates of the electrons. The method is equally well adapted to the calculation of polarizabilities. A computation of the mutual energy of two hydrogen atoms confirms the results of Eisenschitz and London. The polarizability of helium is calculated as 0.210×10^{-24} cc which agrees well with the experimental value, 0.205×10^{-24}. The mutual energy of two helium atoms is found to be $-3.18\ E_0/(R/a_0)^6$. A correlation between the mutual energy of the two molecules, ϵ, and the polarizability, α, is obtained:

$$\epsilon=\ -1.36\ \nu_0^{1/2}\ a_0^{3/2}\ \alpha^{3/2}\ E_0/R^6$$

where ν_0 is the number of electrons in the highest quantum state in the molecule, E_0 the energy of the hydrogen atom in the normal state, and R is the separation of the molecules. By means of this formula, the van der Waals cohesive pressure constant is calculated for Ne, A, N_2, H_2, O_2, and CH_4.

I. Introduction

It has been recognized for some time that the van der Waals forces in gases have their origin in a mutual polarization of the molecules. The idea was suggested by Debye,[1] but his calculation of intermolecular energies, based upon an electrostatic molecular model, did not meet with great success. This fact is not surprising in the light of recent work, which has shown that a rapidly pulsating field associated with the internal motion of the electrons in the molecule is the chief factor in determining the mutual energy of two molecules at separations sufficiently large to prevent the exchange of electrons. This fact was suggested, although not explicitly stated, in a calculation of the mutual energy of two hydrogen atoms by Wang.[2] Recently, Eisenschitz and London[3] have presented a general method of calculating the mutual energy of two molecules at large separation. Their method depends upon an expansion of the wave function of the system in terms of a selected set of the unperturbed wave functions of the two molecules. They have confirmed the form of Wang's result for two hydrogen atoms, although they have shown

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[1] Debye, Phys. Zeits. **21,** 178 (1920).

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

[3] Eisenschitz and London, Zeits. f. Physik **60,** 491 (1930); London, Zeits. f. Physik **63, 245** (1930).

it to be numerically in error. Hassé,[4] with a variational method, has calculated the polarizability of helium. The wave function obtained by Waller[5] in a treatment of the quadratic Stark effect in hydrogen, serves as a basis for the calculation. An empirical extension of the method employed in this case permits him to calculate the mutual energy of two atoms at large separation both for hydrogen and helium.

The present method resembles that of Hassé in that use is made of the variation principle. However, his choice of wave function was more or less empirical and the perturbation energy was calculated as a part of the total energy. On the other hand, we have formulated the variation problem for a direct determination of the perturbation energy by itself, and from the original wave equation have obtained a simplified Euler equation for this variation problem, which when it cannot be solved directly, serves as a guide in choosing an approximate function. The method, while lacking the generality of that of London and Eisenschitz, is applicable to most non-polar molecules in the normal state.

II. Polarizability and Interatomic Energy of Hydrogen

We shall begin by considering a system of ν electrons with an unperturbed wave function ψ_0, while the correct wave function under the influence of a perturbing potential v is ψ. The wave equations in the two cases may be written

$$\begin{aligned} \nabla^2\psi_0 + \kappa^2(E_0 - V_0)\psi_0 &= 0 \\ \nabla^2\psi + \kappa^2(E - V)\psi &= 0 \end{aligned} \tag{1}$$

$$\begin{aligned} \kappa^2 &= 8\pi^2 m/h^2 \\ E &= E_0 + \epsilon \\ V &= V_0 + v. \end{aligned}$$

Here E_0 and V_0 are the initial total and potential energies of the system and ϵ is the energy acquired by virtue of the perturbation. The operator ∇^2 is understood to be referred to the 3ν dimensional configuration of the system of ν electrons. If we let

$$\psi = \psi_0(1 + \phi) \tag{2}$$

we obtain the following equation

$$\nabla^2\phi + 2\sum_{j=1}^{3\nu} \frac{\partial \ln \psi_0}{\partial x_j}\frac{\partial\phi}{\partial x_j} + \kappa^2(\epsilon - v)(1 + \phi) = 0. \tag{3}$$

Since we shall not be interested in perturbation effects of higher order than the second, it is only necessary to retain terms of the first order in v and ϕ. Thus we can replace the factor $(1+\phi)$ by 1, since it is multiplied by a small quantity. Further, in all the cases to which our method is applicable, the mean value of the perturbing potential over the unperturbed wave function

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[4] H. R. Hassé, Proc. Camb. Phil. Soc. **26**, 542 (1930).

[5] Waller, Zeits. f. Physik **38**, 635 (1926).

is zero, the first order perturbation in the energy vanishes, and ϵ is small of the second order. For this reason we may replace $\epsilon - v$ by $-v$, obtaining an equation which does not contain an energy parameter at all. When we make these approximations, Eq. (3) becomes

$$\nabla^2\phi + 2\sum_{j=1}^{3\nu} \frac{\partial \ln \psi_0}{\partial x_j}\frac{\partial \phi}{\partial x_j} - \kappa^2 v = 0. \tag{4}$$

The polarization of the hydrogen atom in its normal state by an homogeneous electric field, F, affords the simplest example of the application of Eq. (4). Here

$$\begin{aligned} \psi_0 &= e^{-r} \\ v &= \sum_{j=1}^{3} g_j x_j \end{aligned} \tag{5}$$

where r is the radial distance of the electron from the nucleus expressed in units of a_0, the Bohr radius of the normal state, and

$$g_j = -eF_{x_j}.$$

The components F_{x_j} of the field, F, are referred to a rectangular system of coordinates with origin in the nucleus of the atom. If we choose as new variables, r and v, and if we let

$$\phi = \frac{vR(r)}{E_0} \tag{6}$$

where E_0 is the absolute value of the energy of the hydrogen atom in the normal state, a separation of variables in Eq. (4) is effected and there results

$$\frac{d^2R}{dr^2} + \left(\frac{4}{r} - 2\right)\frac{dR}{dr} - \frac{2R}{r} - 1 = 0 \tag{7}$$

where r is measured in units of a_0. The solution is

$$R = -\frac{1}{2}\left(1 + \frac{r}{2}\right) + C_1\left(\frac{1}{r} + \frac{1}{r^2} + \frac{1}{2r^3}\right) + C_2\frac{e^{2r}}{r}\cdot$$

In order that the integral

$$\int \psi\bar{\psi}d\tau$$

may exist, it is necessary to set C_1 and C_2 equal to zero. The new wave function takes the form

$$\psi = e^{-r}\left(1 - \frac{v}{2E_0}\left[1 + \frac{r}{2}\right]\right).$$

If the original rectangular coordinate system is chosen with z-axis parallel to the field, $v = -eFz$, and the above wave function becomes identical with that obtained by Waller.[6] The energy is given by

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[6] Waller, reference 5.

$$E = E_0 + \epsilon = -\frac{1}{\kappa^2}\frac{\int \bar{\psi} H \psi d\tau}{\int \psi\bar{\psi} d\tau}.$$

When ϕ has the form, $vR(r)$, and ψ_0 is a function of r alone, the integrals occurring in the evaluation of ϵ are of the form

$$\int v^n f(r) d\tau \quad n = 1, 2, 3.$$

If v is a harmonic function which vanishes when r is zero, the term for $n=1$ (and $n=3$) vanishes. That is, the first order perturbation energy is zero. Then the only term which we need consider is the one with $n=2$. This condition is of course fulfilled in the problem which we have just considered, and will be fulfilled in the subsequent problems to be treated. The expression for ϵ now becomes

$$\epsilon = \frac{\int v\phi\psi_0^2 d\tau}{\int \psi_0^2 d\tau} \tag{8}$$

with the neglect of perturbation terms in the normalization of ψ. These will contribute only to terms in ϵ of higher order than the second.

A computation of the polarization energy of the hydrogen atom using the wave function which we have obtained yields

$$\epsilon = -2.25 a_0^3 F^2$$

which corresponds to a polarizability

$$\alpha = 4.5 a_0^3.$$

These, values, of course, agree with those obtained by Waller.

In this simple case, the solution of Eq. (7) offers no difficulty. It is of interest, nevertheless, to see what value of the energy may be obtained, if our information is restricted to the fact that $\phi = vR(r)$. Let us try as a representation of $R(r)$ the expression, λr^ν. The energy integral becomes

$$\epsilon = \frac{\int v\phi[1 - \rho[R]]\psi_0^2 d\tau}{\int \psi_0^2 d\tau} \tag{8}$$

where

$$\rho[R] = \frac{d^2R}{dr^2} + \left(\frac{4}{r} - 2\right)\frac{dR}{dr} - \frac{2R}{r} - 1.$$

If we minimize the integral with respect to the parameters λ and ν, we obtain

$$\epsilon = -2.24 a_0^3 F^2$$
$$\lambda = -0.728/E_0; \quad \nu = 0.5.$$

This value agrees with the exact one to somewhat better than 0.50%.

The method may be applied with almost equal simplicity to the interaction of two hydrogen atoms. If the separation, R_0, of the two atoms is sufficiently large to prevent electron interchange, the wave function of the system is

$$\psi_0 = \psi_{01}\psi_{02} = e^{-(r_1+r_2)}$$

where r_1 and r_2 are the respective radial distances of each electron from its own nucleus. When referred to two rectangular coordinate systems with their respective origins in the two nuclei and with z-axes directed along R_0, the dipole term in the perturbing potential is given by

$$\frac{e^2}{R_0^3}[x_1x_2 + y_1y_2 - 2z_1z_2].$$

Terms due to multipoles of higher order will be neglected. If we let

$$\phi = \frac{vR(r_1, r_2)}{E_0}$$

and change the variables in Eq. (4) to v, r_1 and r_2, a separation is again effected and we have

$$\frac{\partial^2 R}{\partial r_1^2} + \frac{\partial^2 R}{\partial r_2^2} + \left(\frac{4}{r_1} - 2\right)\frac{\partial R}{\partial r_1} + \left(\frac{4}{r_2} - 2\right)\frac{\partial R}{\partial r_2} - 2R\left(\frac{1}{r_1} + \frac{1}{r_2}\right) - 1 = 0 \quad (9)$$

The existence of a solution of this equation is assured by the negative value of the coefficient of R.[7] A solution by successive approximation may be obtained in the following manner. Let us write Eq. (9) as

$$R = -\frac{1}{2}\frac{r_1r_2}{r_1 + r_2}\left\{1 - \left[\frac{\partial^2 R}{\partial r_1^2} + \frac{\partial^2 R}{\partial r_2^2} + \left(\frac{4}{r_1} - 2\right)\frac{\partial R}{\partial r_1} + \left(\frac{4}{r_2} - 2\right)\frac{\partial R}{\partial r_2}\right]\right\}.$$

If the differential function is neglected

$$R = -\frac{1}{2}\frac{r_1r_2}{r_1 + r_2}. \quad (10)$$

Substitution of this expression in the differential function will yield a second approximation. Repetition of this process will yield a still closer approximation. If we use merely the first approximation (10), we calculate a value of the energy,

$$\epsilon = -6.14\frac{e^2a_0^5}{R_0^6}.$$

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[7] Goursat, Cours d'Analyse Mathematique, vol. III, 249.

This is about 5 percent higher than the value

$$-6.47\frac{e^2a_0^5}{R_0^6}$$

obtained by Eisenschitz and London.[8] The use of higher terms in the expansion of R would permit us to approach the true value as closely as we pleased. Although no difficulty is encountered in the evaluation of the integrals occurring in the energy expression, the tedium of the calculation is reduced by using the variation method. Eq. (10) suggests as a representation of R, the expression

$$\lambda r_1^\nu r_2^\nu.$$

If the function is inserted in the energy integral and the latter is minimized with respect to the parameters λ and ν one obtains

$$\epsilon = -6.49\frac{e^2a_0^5}{R_0^6}$$

$$\nu = 0.325.$$

This is in excellent agreement with the result of London and Eisenschitz. The fact that their value lies slightly higher instead of slightly lower than the one which has just been obtained is doubtless attributable to an error in estimating the contribution of the continuous spectrum in their expansion of ψ, since the variation method cannot give too low a value of the energy.

The fact that the wave function in the two cases which have been considered may be expressed as

$$\psi_0(1 + vR)$$

where R is a function of the radial distances of the electrons from their nuclei, is indeed logical from a physical point of view. In the absence of degeneracy, one would expect the distortion of the wave function to depend in some simple way upon the perturbing potential. Moreover, for a given value of the perturbing potential it is evident that the distortion will be greater, as the distance of the electron from the nucleus becomes greater, since the restoring force exerted by the nucleus will be smaller. The function R provides for this effect. The separation of the differential Eq. (4) in terms of v and the r's appears to depend upon the linear properties of v in the rectangular coordinates of the electrons, and the spherical symmetry of the unperturbed wave function.

III. Generalization of the Method: Polarizability and Interatomic Energy of Helium

For the helium atom, or in general for an atom with ν electrons each having a spherically symmetrical distribution, the wave function may be approximately represented by

$$\psi_0 = \prod_{j=1}^{\nu}\psi_j(r_j) \tag{11}$$

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[8] Eisenschitz and London, reference 3.

where the function ψ_j depends only upon the radial coordinate of the electron j. Such a function may be approximated by an expression

$$r^{n-1}e^{-(Z-s)r/n}$$

where n is an effective quantum number, s a screening constant, Z the total nuclear charge. If we wish to represent the wave function accurately in the region of its maximum, we may choose n and s by minimizing the total energy, as Zener has done. If, however, we are more interested in the value of the function for large values of r, we may choose s to be equal to the total number of electrons except for the one being considered, and use an effective quantum number which is non-integral. Thus for He, in the neighborhood of the maximum, we choose $Z-s=1.6875$ (or, for some purposes, 1.70), $n=1$; while for large r's, we take $Z-s=1$, $n=0.745$.[9] We use these formulas for approximate computation of polarizability and interatomic force.

A better representation of the wave function can be obtained by more complicated methods, as that of Hartree,[10] or the method used by one of the authors on He.[11] These give almost identical results for He, as far as the purposes of this paper go, and for quantitative work we make use of the latter in one calculation of the polarizability and interatomic energy of helium.

We shall first consider the polarization of the molecule by an homogeneous field F. The perturbing potential is

$$v = \sum_{j=1}^{\nu} v_j$$

where

$$v = -e\sum_{k=1}^{3} F_{x_{jk}} x_{jk}$$

If we let

$$\phi = \frac{1}{E_0}\sum_{j=1}^{\nu} v_j R(r_j) \tag{12}$$

and make use of the facts that $\partial \ln \psi_0/\partial r_j$ depends only upon r_j, the distance of electron j from the nucleus and that

$$\sum_{k=1}^{3} x_{jk}\frac{\partial v}{\partial x_{jk}} = v_j$$

we find that Eq. (4) splits into ν equations of the form

$$\frac{d^2R}{dr^2} + \left(\frac{4}{r} + 2\frac{d \ln \psi_0}{dr}\right)\frac{dR}{dr} + \frac{d \ln \psi_0}{dr}\frac{R}{r} - 1 = 0. \tag{13}$$

If we use a wave function of the simpler type discussed above this equation becomes

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[9] C. Zener, Phys. Rev. **36,** 51 (1930); J. C. Slater, Phys. Rev. **32,** 349 (1928); J. C. Slater, Phys. Rev. **36,** 57 (1930).

[10] D. R. Hartree, Proc. Camb. Phil. Soc. **24,** 89 (1928).

[11] J. C. Slater, Phys. Rev. **32,** 349 (1928).

$$\frac{d^2R}{dr^2}+2\left(\frac{n+1}{r}-\frac{Z-s}{n}\right)\frac{dR}{dr}+2\left(\frac{n-1}{r^2}-\frac{Z-s}{nr}\right)R-1=0. \quad (14)$$

The energy given by Eq. (8) is

$$\epsilon=\frac{\int\sum_{j=1}^{\nu}\sum_{k=1}^{\nu}v_j\phi_k\psi_0^2d\tau}{\int\psi_0^2d\tau}\cdot$$

Since upon integration all terms involving $v_j\phi_k$ with $j\neq k$ vanish

$$\epsilon=\sum_{j=1}^{\nu}\epsilon_j$$

and

$$\epsilon_j=\frac{\int v_j\phi_j\psi_0^2d\tau}{\int\psi_0^2d\tau}\cdot$$

In the computation of ϵ_j it will be convenient to use the variation method rather than to solve Eq. (14) explicitly. The expression becomes

$$\epsilon_j=\frac{\int v_j\phi_j[1-\rho[R_j]]\psi_0^2d\tau}{\int\psi_0^2d\tau}$$

where

$$\rho[R_j]=\frac{d^2R_j}{dr_j^2}+2\left(\frac{n_j+1}{r_j}-\frac{Z-s_j}{n_j}\right)\frac{dR_j}{dr_j}+2\left(\frac{n_j-1}{r_j^2}-\frac{Z-s_j}{n_jr_j}\right)R_j-1.$$

We shall try

$$R=\lambda e^{\beta(z-s)r/n}$$

which is analytically somewhat more convenient than the representation λr^{ν} employed in the case of hydrogen. When the energy integral is minimized with respect to the parameter λ there results

$$\epsilon=\frac{1}{E_0}\frac{J_1^2}{J_2}e^2F^2$$

where

$$J_1=\frac{\int r^{2n}\cos^2\theta e^{\beta(z-s)r/n}\psi_0^2d\tau}{\int\psi_0^2d\tau}$$

$$=\frac{(n+1)(n+\frac{1}{2})}{3}\left(\frac{n}{Z-s}\right)^2a_0^2\frac{1}{(1-\beta/2)}2n+3$$

$$J_2 = \frac{\int \left\{ \left(\frac{n}{Z-s} \right)^2 (\beta^2 - 2\beta) r^{2n} + \frac{n}{Z-s} [(n+1)\beta - 1] r^{2n-1} + 2(n-1) r^{2n-2} \right\}}{\int \psi_0{}^2 d\tau}$$

$$e^{2\beta(z-s)r/n} \cos^2 \theta \psi_0{}^2 d\tau \doteq - a_0 \frac{1 + (2n-5)\beta/3 + (2n^2 - n + 5)\beta^2/6}{(1-\beta)^{2n+3}} .$$

For the energy we have

$$\epsilon_j = - 2 \frac{(n_j+1)^2 (n_j + \frac{1}{2})^2 n_j{}^4}{9(Z-s_j)^4} a_0{}^3 F^2 (1 + \theta_j) \tag{13a}$$

where

$$\theta_j = \frac{(1-\beta)^{2n_j+3}}{(1-\beta/2)^{4n_j+6}[1 + (2n_j - 5)\beta/3 + (2n_j{}^2 - n_j + 5)\beta^2/6]} - 1$$

Minimizing with respect to β shows that for $n=1$, $\theta_j = 0.124$. In general $0.124 \leqq \theta_j \leqq 0$; $n_j \geqq 1$. For the total polarization energy we may write

$$\epsilon = - 2a_0{}^3 F^2 \sum_{j=1}^{\nu} \frac{n_j{}^4 (n_j+1)^2 (n_j + \frac{1}{2})^2 (1+\theta_j)}{9(Z-s_j)^4}$$

and for the polarizability

$$\alpha = 4a_0{}^3 \sum_{j=1}^{\nu} \frac{n_j{}^4 (n_j+1)^2 (n_j + \frac{1}{2})^2 (1+\theta_j)}{9(Z-s_j)^4} .$$

We shall first compute the polarizability of helium taking n as 1 and $Z-s$ as 1.6875, the values obtained by minimizing the total energy of the atom. We obtain

$$\alpha = 1.11 a_0{}^3 = 0.164 \times 10^{-24} \text{cc}.$$

If on the other hand we use the limiting values at large distances for n and $Z-s$ we have $n = 0.745$; $Z-s=1$, and we obtain

$$\alpha = 1.51 a_0{}^3 = 0.222 \times 10^{-24} \text{cc}.$$

The value of α corresponding to measurements of the refractive index is 0.205×10^{-24}. As we should have anticipated it lies between the two values which we have calculated. The first wave function which emphasizes the smaller r's at the expense of the larger gives a value of α about 20 percent below the experimental one, while the second wave function which emphasizes the larger r's gives a value about 8 percent higher than the experimental one. The second wave function which is accurate only for large values of r gives a surprisingly good result.

A more exact determination of the polarizability of helium may be obtained with the use of the more accurate wave function mentioned above. After normalization and integration over the configuration space of one electron, the square of the wave function for each electron may be represented by

$$0.7604(1 + 1.440e^{-1.692r})e^{-3r+0.0214r^2};\ r < 3$$

$$0.6048(1 + 1.440e^{-1.692r})e^{-2.688r}r^{-0.510}\left(1 + \frac{0.1414}{r} + \cdots\right);\ r > 3.$$

We shall use as a representation of R the function λr^{ν}. Minimizing the energy integral with respect to the parameter λ gives

$$\epsilon = \frac{1}{E_0}\frac{J_1^2}{J_2 J_0}e^2 a_0^2 F^2$$

where

$$J_0 = \int \psi_0^2 d\tau$$

$$J_1 = \int r^{\nu+2}\psi_0^2 d\tau$$

$$J_2 = \int \left\{ \nu(\nu + 2)r^{2\nu} + 2(\nu + 1)\frac{d \ln \psi_0}{dr} r^{2\nu+1} \right\} \psi_0^2 d\tau.$$

Properly, this expression should be computed for different ν's and the minimum chosen. On account of the labor of the integration, however, we have arbitrarily chosen the value $\nu = 0.5$. This was the value found for the simple wave functions used above, and moreover it was found that the result was so insensitive to ν that a variation of ± 0.1 in ν did not affect the final result by more than one percent. The above integrals have been computed graphically for $\nu = 0.5$ and the polarizability of helium was found to be

$$\alpha = 1.43 a_0^3 = 0.210 \times 10^{-24}\text{cc}.$$

This yields a value of the dielectric constant at 0° and 1 atm. of 1.0000715 which is slightly lower than the experimental value, 1.000074. It is however, somewhat higher than the square of the measured refractive index extrapolated to infinite wave-length, 1.000070. The agreement among the various values is not unsatisfactory when one remembers that the accuracy in the measured refractive index, and dielectric constant cannot be very great, in view of the experimental difficulties in such measurements.

A calculation of the mutual energy of two atoms may be carried out in a similar manner. The dipole term in the perturbation potential may be written

$$v = \sum_{j=1}^{\nu}{}' \sum_{k=1}^{\nu}{}' v_{jk}$$

where the sum is understood to be taken over all possible electron pairs between the two atoms. Each v_{jk} has the form

$$\frac{e^2}{R_0^3}[x_k x_j + y_k y_j - 2 z_k z_j].$$

If we let

$$\phi = \frac{1}{E_0} \sum_{j=1}^{\nu}{}' \sum_{k=1}^{\nu}{}' v_{jk} R(r_j, r_k).$$

Eq. (4) separates into ν^2 equations of the form

$$\begin{aligned} \frac{\partial^2 R}{\partial r_j^2} + \frac{\partial^2 R}{\partial r_k^2} + \left(\frac{4}{r_j} + \frac{2\partial \ln \psi_0}{\partial r_j}\right)\frac{\partial R}{\partial r_j} + \left(\frac{4}{r_k} + \frac{2\partial \ln \psi_0}{\partial r_k}\right)\frac{\partial R}{\partial r_k} \\ + 2R\left(\frac{1}{r_j} \frac{\partial \ln \psi_0}{\partial r_j} + \frac{1}{r_k} \frac{\partial \ln \psi_0}{\partial r_k}\right) - 1 = 0. \end{aligned} \tag{17}$$

Moreover the energy may be written

$$\epsilon = \sum_{j=1}^{\nu}{}' \sum_{k=1}^{\nu}{}' \epsilon_{jk}$$

where

$$\epsilon_{jk} = \frac{\int v_{jk}\phi_{jk}(1 - \rho_{jk})\psi_0^2 d\tau}{\int \psi_0^2 d\tau}.$$

If an exact solution of Eq. (17) is used, ρ_{jk} which is the differential expression on the left hand side of Eq. (17) vanishes. We shall use the two representations

$$R_{jk} = \lambda r_j^{\nu} r_k^{\nu}; \quad R_{jk} = \lambda e^{\beta(r_j + r_k)}$$

which proved effective in the case of hydrogen, according to their analytical convenience in conjunction with the unperturbed wave function which is chosen. The parameters are determined by minimizing the energy integral. The details of the calculation are quite similar to those in the calculation of polarizabilities. With the simple wave function

$$\psi_0 = \prod_{j=1}^{\nu} r_j^{n_j - 1} e^{-\gamma_j r_j / n_j}; \quad \gamma_j = Z - s_j$$

we obtain the following result

$$\epsilon = -\frac{13}{27} \frac{e^2 a_0^5}{R_0^6} \sum_{j=1}^{\nu} \sum_{k=1}^{\nu} \frac{n_j^4 n_k^4 (n_j+1)^2 (n_j+\frac{1}{2})^2 (n_k+1)^2 (n_k+\frac{1}{2})^2}{\gamma_j^2 \gamma_k^2 \{\gamma_k^2 n_j^2 (n_j+1)(n_j+\frac{1}{2}) + \gamma_j^2 n_k^2 (n_k+1)(n_k+\frac{1}{2})\}} \tag{18}$$

For convenience in representation certain factors $1+\theta_{jk}$ occurring in each term have all been assigned the value which they assume for 1-quantum electrons. Since

$$0 \leqq \theta_{jk} \leqq 0.07$$

the above formula will approximate the true one to within a few percent in every case. We shall calculate the mutual energy of two helium atoms first taking $Z - s = 1.6875$ and $n = 1$. We obtain

$$\epsilon = -1.13\frac{e^2a_0^5}{R_0^6}\cdot$$

If we now take the values $n=0.745$, $Z-s=1$, which occur in the asymptotic form of the wave function we obtain as in the case of the polarizability a somewhat larger value:

$$\epsilon = -1.78\frac{e^2a_0^5}{R_0^6}\cdot$$

The same calculation has been made with the use of the more accurate wave function for He. As a representation of the function R, $\lambda r_j^\nu r_k^\nu$ was selected. The integrals, similar to those encountered in the calculation of the polarizability, were evaluated graphically. The energy of two helium atoms was computed as

$$\epsilon = -1.59\frac{e^2a_0^5}{R_0^6} = -3.18\frac{E_0}{(R_0/a_0)^6}\cdot$$

This value lies between the two values obtained with the hydrogenic wave function. It is about 30 percent higher than that obtained with values of Z and n determined to give the best energy for the atom and about 13 percent below the value obtained with the asymptotic values of n and Z. Since the wave function which gave the above value also gives a good value of the polarizability, it is likely that the above value is correct within one or two percent. Hassé obtains a value

$$-2.93\frac{E_0}{(R/a_0)^6}$$

which differs from our result by about 8 percent. Both of these values are slightly above the upper limit for the mutual energy of two helium atoms calculated by London:

$$\epsilon = -3/4\alpha^2V_i/R^6$$

where α is the polarizability and V_i the ionization potential. This has the value

$$-2.65\frac{E_0}{(R/a_0)^6}\cdot$$

The fact that both Hassé's and our values lie above London's upper limit is not to be considered as alarming. For London, in using the second order perturbation method, neglected a factor which has been rather consistently overlooked in such calculations: transitions in which two electrons are excited may contribute appreciably to the dispersion and similar terms, and they are connected with larger energy differences than the ionization potential, so that in the upper limit of such an expression as London's we should really have the highest potential connected with a double jump, much larger than V_i. The relation of our results to London's limit suggests that these double jumps are strong enough to shift the center of gravity of the term system beyond the ionization potential.

A result of considerable interest may be obtained from formulas (16) and (18). While neither of them gives particularly accurate representations of α or ϵ, it is possible to reach through them a correlation between these two quantities. First, it is to be noted that in both formulas only terms arising from electrons in the outer shell of the atoms contribute appreciably to the sums. Terms arising from inner shells (if any), are virtually nullified both through a decrease in the effective quantum number and by an increase in the effective nuclear charge. We may therefore write

$$\alpha = \frac{4.5\nu_0 a_0^3}{(Z-S_0)^4}\,\frac{n_0^4(n_0+1)^2(n_0+\frac{1}{2})^2}{9}$$

$$\epsilon = -\frac{6.5\nu_0^2}{(Z-S_0)^6}\,\frac{e^2a_0^5}{R_0^6}\,\frac{n_0^6(n_0+1)^3(n_0+\frac{1}{2})^3}{27}$$

where ν_0 is the number of electrons in the outer shell of the atom; n_0 and S_0 are the effective quantum number and screening constant of these electrons. Elimination of n_0 and $(Z-S_0)$ gives

$$\epsilon = -\beta/R_0^6$$

where

$$\beta = 1.36\nu_0^{1/2}a_0^{3/2}\alpha^{3/2}E_0. \tag{19}$$

Corresponding to the empirically determined polarizability for He, this gives a value $\beta = 3.16a_0^6E_0$. This is in excellent agreement with the value 3.18, calculated with the aid of the accurate wave function above.

IV. CORRELATION WITH THE EQUATION OF STATE

Although the computation of the last section applied only to atoms for which each electron had a spherically symmetrical distribution, still it is interesting provisionally to compute van der Waals forces in other cases from the polarizability. In cases where the whole atom is spherically symmetrical, though individual electrons are not, this seems fairly reasonable. Thus we obtain values of $\beta/a_0^6E_0$ for the noble gases as listed in Table I:

TABLE I.

He	Ne	A	Kr	Xe
3.16	17.0	148	275	582

These values can be tested by calculating the equation of state. Of course, the attractive force is not the only interatomic force; there is also a repulsive force, increasing very rapidly as the atoms approach. This is often represented by assuming the atoms to be rigid, and if the van der Waals attraction is fairly large this is justified. For He, however, large errors are committed by this assumption. The repulsive potential has been computed for atomic hydrogen[12] and for helium.[13] It appears possible to represent it in the range of importance in thermal interaction between gas molecules by the approximation formula

$$\epsilon_r = \lambda e^{-cR_0}.$$

It should therefore be possible to write approximately

$$\epsilon = \lambda e^{-cR_0} - \beta/R_0{}^6$$

for the total interaction energy of two molecules. If the equation of state of a gas is written in the familiar virial form

$$\frac{pV}{RT} = 1 + \frac{B}{V} +$$

where p is the pressure, V the volume, R the ideal gas constant, and T the absolute temperature, it is possible to show that at high temperatures

$$B = 2\pi N \int_0^\infty (1 - e^{-\epsilon/kT}) R^2 dR$$

under the assumption the molecules are spherically symmetrical. Here ϵ is the mutual potential energy of two molecules. If, further the molecules are treated as rigid spheres of diameter σ, and the exponential function in the above integral is expanded, it is found that approximately

$$B = B_0 - A/RT$$

where

$$B_0 = \frac{2\pi N\sigma^3}{3}$$

$$A = -\ 2\pi N^2 \int_\sigma^\infty \epsilon R^2 dR$$

and the equation of state may be written in the van der Waals form

$$p = \frac{RT}{V - B_0} - \frac{A}{V^2}\cdot$$

Moreover, if the repulsive potential is ignored when $R > \sigma$, we may replace ϵ by ϵ_a calculated from Eq. (19). The expression for A then becomes

$$A = 4.76 \times 10^{11} \beta/B_0 \text{ ergs cc/mol} \tag{20}$$

where B_0 is expressed in cc/mol. It is to be remembered that this is a very rough approximation, for in reality the repulsive potential cannot be adequately represented by a potential wall which rises to infinity when $R = \sigma$. This model is indeed entirely inadequate when the attractive field is very

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[12] Heitler and London, Zeits. f. Physik **44**, 455 (1927); Suguira, Zeits. f. Physik **45**, 484 (1927).

[13] J. C. Slater, reference 11.

weak as in the case of helium and hydrogen. This is illustrated in Fig. 1. The interatomic potential

$$\epsilon = \left\{ 7.7e^{-2.43R/a_0} - \frac{0.68}{(R/a_0)^6} \right\} \cdot 10^{-10} \text{ ergs}$$

which we have obtained for helium has been plotted as a function of the separation of the two atoms. The dotted line represents the attractive component alone and the distance marked σ on the R-axis represents the effective atomic diameter calculated from the van der Waals B_0 constant. In a later paper a calculation of the second virial coefficient B of helium, based upon the above expression for the interatomic potential, will be presented. It leads to an equation of state and to a description of the thermodynamic properties of helium which are in striking agreement with experiment.

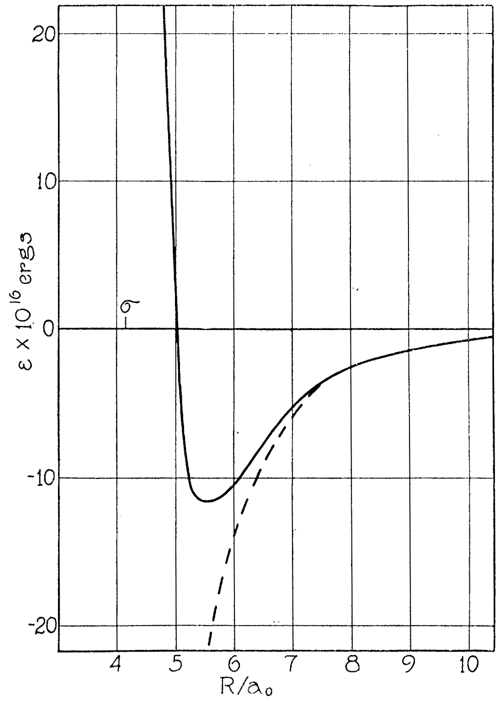

Fig. 1. The mutual energy of two helium atoms plotted as a function of the interatomic distance.

In the present paper, however, we shall content ourselves with the approximation of rigid molecules. We have calculated values of A for several gases by means of Eqs. (19) and (20), from the experimental values of the refractive index and the constant B_0. We have not restricted ourselves to the noble gases, but have included several gases with poly-atomic molecules. The electron configuration in most non-polar molecules resembles that of the noble gases except in the particular case of spherical symmetry. It was thought that Eq. (19) might still be approximately valid in these cases, since most of the characteristics of the wave function employed in the calculation of α and ϵ were eliminated in the formulation of this relation. The computed values of A are compared with the empirical values of Beattie and Bridgeman[14] in Table II. The A constants for Kr and Xe were computed from viscosity measurements. The agreement appears to be quite satisfactory. The computed values of A are of course somewhat larger than the empirical ones due to the neglect of the repulsive potential outside the sphere $R=\sigma$. However, as A becomes large, the error introduced by this approximation becomes less important just as we should expect. It is to be hoped that a method of calculating the repulsive potential may soon be developed, in order that a more adequate comparison with experiment may be made.

TABLE II.

	$\alpha . 10^{24}$ (cc)	B_0 (cc/mol)	A(calc)$.10^{-12}$ (ergs cc)	A(exp)$.10^{-12}$ (ergs cc)
Ne	0.39	20.6	0.37	0.21
A	1.65	39.3	1.67	1.29
Kr	2.50	52.8	2.33	2.07
Xe	4.12	70.4	3.70	3.86
N_2	1.74	50.5	1.58	1.34
H_2	0.82	21.0	.55	0.20
O_2	1.59	46.2	1.64	1.49
CH_4	2.59	55.9	2.32	2.28

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[14] Beattie and Bridgeman, Proc. Nat. Acad. **63,** 229 (1928).