cm^{-1}, several medium lines lying between 98 cm^{-1} and 101.3 cm^{-1}, another group between 105 cm^{-1} and 110 cm^{-1}, as well as the following scattered strong and medium lines in the medium wave number range: 157.50 cm^{-1}, 159.10 cm^{-1}, 163.57 cm^{-1}, 173.58 cm^{-1}, and 184.69 cm^{-1}.

Neither were these lines to be explained as being due to H_2O impurities or to 2nd-order spectral impurities, as they did not coincide with the strongest H_2O lines or 2nd-order lines in the region. It was also quite improbable that they were spurious lines as they were found time and time again on different gratings and with different optical paths.

It is possible that the HDO impurities were not completely eliminated and thus were responsible for these absorptions. If so, it should be possible to eliminate them by a more complete drying out of the absorption cell. Another possibility is that certain of the allowed transitions whose intensities could not be calculated by means of the symmetric rotator matrix elements do, nevertheless, have measureable intensities and should be considered. Finally, there is the possibility that the whole assignment of theoretical transitions has been incorrect. If this be true, then it means that the effective moments of inertia calculated in the analysis are greatly in error. The assignment would have to be completely reconsidered in order to account for these lines at all. As has been previously stated, several attempts were made during the analysis to find alternative assignments which would account for the experimental data, and none were found to be nearly as satisfactory as the one developed here.

Assuming the general correctness of the analysis however, the next problem is to develop rigorous methods of computing the rotational distortion of the asymmetric rotator so that the effective moments of inertia may be recomputed with precision from the energy levels obtained from this research. The dimensions of the molecule may then be well established.

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Van der Waals Potential in Helium

H. MARGENAU
Yale University, New Haven, Connecticut

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Part I is an investigation of the fundamental question concerning the additivity of first-order exchange and second-order van der Waals potentials. The method employed is a variational one which allows both first- and second-order exchange effects to be calculated simultaneously with the second-order attractive terms. It is shown that the assumption of additivity is entirely false for atomic hydrogen, but that it is almost legitimate for He. By extrapolation one might conclude it to be quite safe for heavier structures. Part II is a redetermination of the numerical values occurring in the attractive part of the potential, based on the use of oscillator strengths (f values) which are adjusted to give the best value for the atomic polarizability of He. It appears that the value of the dipole-dipole coefficient in the Slater-Kirkwood formula has been too high. The final result for the van der Waals potential (Eq. (20)) seems on the whole to be consistent with independent determinations of this quantity from empirical data.

NUMEROUS questions arising in the study of the behavior of helium at low temperatures require for their treatment a fairly accurate knowledge of the van der Waals potential between helium atoms.

Considerable attention has therefore been devoted[1–4] to attaining an empirical answer to the

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[1] J. Lennard-Jones, Proc. Roy. Soc. **106**, 463 (1924).

[2] J. de Boer and A. Michels, Physica **5**, 945 (1938); **6**, 409 (1939).

[3] J. O. Hirschfelder, R. B. Ewell and J. R. Roebuck, J. Chem. Phys. **6**, 205 (1938).

[4] H. S. W. Massey and R. A. Buckingham, Proc. Roy. Soc. **168**, 378 (1938); **169**, 205 (1938).

problem at hand; i.e., curves for the van der Waals potential in He have been derived from thermodynamic data. The present paper is the converse to these attempts in as much as it endeavors to deduce the potential in a more *a priori* manner from the atomic structure of He.

Previous work on this problem[5, 6] stands in need of improvement principally in two respects. The first concerns the common procedure of adding exchange forces calculated by one method to the asymptotic van der Waals forces calculated by quite a different method. This, if it is legitimate at all, requires analytic justification. Secondly, the accuracy of former calculations of the coefficients of the attractive terms in the potential should be improved. In accordance with these considerations, the present paper will consist of two parts dealing with these two points.

It is perhaps unfortunate that the most interesting part of the potential in question, the minimum, arises from an interplay of two types of forces—exchange and dispersion forces—and its determination, therefore, requires about equal accuracy in our knowledge of both. This means that the calculation may not be restricted to the $1/R^6$ term in the dispersion part, and that the repulsive forces must be studied with considerable care. It is usually assumed that the potential energy in question may be written in the form

$$\Delta E = Ae^{-\mu R} - \frac{c_1}{R^6} - \frac{c_2}{R^8}; \qquad (1)$$

the higher terms of the series have been shown to be negligible for He.[6]

I. Second-Order Exchange Forces

The simple form of Eq. (1) is the result of the following procedure. One adds the *second*-order perturbation $(-c_1/R^6 - c_2/R^8)$ calculated with atomic functions *not* satisfying the Pauli principle to the *first*-order perturbation $(Ae^{-\mu R})$ calculated with functions *satisfying* the Pauli principle. This is clearly inconsistent; for if it is necessary to go to the second perturbation in connection with the attractive terms this should also be done with the others. Eisenschitz and London[7] have calculated the complete second-order perturbation for atomic hydrogen. Their method, however, is not easily applied to the Helium problem, nor does it yield results which allow a ready comparison with the terms of (1). We shall use for the same purpose a more direct variational method, the results of which are equivalent to those of Eisenschitz and London for hydrogen. The procedure will first be described in detail for hydrogen, and afterwards the complications appearing in the helium problem will be dealt with.

Hydrogen

The variation function which yields the attractive part of the van der Waals potential may be written[8]

$$\psi = (1 + \lambda D)\psi_0,$$

where D is the operator $H - E_0$ (H being the total Hamiltonian of the system consisting of two atoms, one at a, the other at b, and E_0 twice the energy of one isolated atom), ψ_0 is the function $\varphi_a(1)\varphi_b(2)$ (φ being the atomic function for the normal state), and λ is a variation parameter. With the use of ψ we find

$$\int \psi H \psi d\tau = \int \psi (D + E_0)\psi d\tau = D_{00} + 2\lambda (D^2)_{00} + \lambda^2 (D^3)_{00} + E_0 \int \psi^2 d\tau, \qquad (2)$$

if we note the Hermitean character of D. The subscripts 0 indicate, of course, matrix elements computed with ψ_0. The order of magnitude of the different terms in (2) is important. If we denote by V the perturbation function $H - H_0$, we have $D_{00} = V_{00}$, a quantity which is of appreciable size only at distances of separation $R = |\mathbf{a} - \mathbf{b}|$ considerably smaller than that at which the van der Waals minimum occurs. Indeed when V is expanded in powers of $1/R$, as is customary, V_{00} vanishes exactly. Furthermore it may be shown that $(D^2)_{00} = (V^2)_{00}$, but we are not permitted to replace $(D^3)_{00}$ by $(V^3)_{00}$

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[5] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

[6] H. Margenau, Phys. Rev. **38**, 747 (1931).

[7] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930).

[8] The present development is essentially an application of the Hassé method, first applied to this problem in reference 5.

because of the noncommutability of the operators H_0 and V. In fact

$$(D^3)_{00}=\int D\psi_0 D^2\psi_0 d\tau=\int V\psi_0 DV\psi_0 d\tau$$

$$=(V^3)_{00}+\int V\psi_0(H_0-E_0)V\psi_0 d\tau,$$

and the last integral may be transformed by partial integrations[9] into

$$\frac{\hbar^2}{2m}\sum_i\left[\left(\frac{\partial V}{\partial x_i}\right)^2\right]_{00}.$$

But this quantity may be written as $-(1/2m)\Sigma_i \times[(P_iV)^2]_{00}$ where P_i is the momentum operator, which indicates at once that the order of magnitude of the term is not the same as that of $(V^3)_{00}$, but of $E_0(V^2)_{00}$. We see, therefore, that even if λ is small (it will be seen to be $\approx 1/E_0$), the term $\lambda^2(D^3)_{00}$ in (2) must be retained as comparable in size with $\lambda(D^2)_{00}$.

On the other hand, the integral

$$\int\psi^2 d\tau=1+2\lambda D_{00}+\lambda^2(D^2)_{00}$$

contains terms of descending orders of magnitude and may safely be approximated by 1 because $D_{00}=0$. Hence we find

$$\int\psi H\psi d\tau\Big/\int\psi^2 d\tau=2\lambda(D^2)_{00}+\lambda^2(D^3)_{00}+E_0 \quad (3)$$

and this becomes

$$\lambda'(D^2)_{00}+E_0=\lambda'(V^2)_{00}+E_0,$$

when it is minimized with respect to λ. The value of λ at the minimum, here denoted by λ' and given by $-(D^2)_{00}/(D^3)_{00}$, may be found from other considerations. The attractive part of the van der Waals potential, which will henceforth be denoted by E_2, is seen to be

$$E_2=\lambda'(D^2)_{00}. \quad (4)$$

The approximation thus obtained is equivalent to that of second-order perturbation theory.

Let us now turn to the repulsive exchange energy. In the Heitler-London method, which was used by Slater[10] in calculating the term $Ae^{-\mu R}$ for He, it is given simply by

$$E_1=\int\psi D\psi d\tau\Big/\int\psi^2 d\tau, \quad (5)$$

when ψ is taken to be $(1-P)\psi_0$, ψ_0 being defined as before. P is understood to be the operator which permutes electrons 1 and 2. In expanded form, Eq. (5) reads

$$E_1=\frac{D_{00}-(DP)_{00}}{1-P_{00}}. \quad (6)$$

On comparing the two variation functions which yield, respectively, E_1 and E_2, it is clear that the two separate procedures may be combined and a better approximation to the van der Waals forces obtained by using the variation function

$$\Psi=(1+\lambda D)(1-P)\psi_0. \quad (7)$$

It leads to the following integrals:

$$\int\Psi^2 d\tau=2\{1-P_{00}+2\lambda[D_{00}-(DP)_{00}]$$

$$+\lambda^2[(D^2)_{00}-(D^2P)_{00}]\}.$$

Here again, terms in different powers of λ form a rapidly descending sequence, and restriction to the terms linear in λ is proper.

$$\int\Psi D\Psi d\tau=2\{D_{00}-(DP)_{00}$$

$$+2\lambda[(D^2)_{00}-(D^2P)_{00}]+\lambda^2(\ \ )\}. \quad (8)$$

The term in λ^2 is comparable in size with the one preceding it. In minimizing $\int\Psi D\Psi d\tau/\int\Psi^2 d\tau$ with respect to λ, which is the next step to be taken, one can easily convince himself that the term proportional to λ in the denominator has very little effect upon the value of the minimum. Beyond this we shall assume in order to simplify the analysis, that the value of λ which minimizes (8) is nearly the same as the one which minimizes (3). As before, we get for this value of λ an expression identical with (8), but with the term in λ^2 missing and the numerical coefficient of the preceding one reduced to unity. Con-

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[9] Cf. for instance H. Margenau, Rev. Mod. Phys. **11**, 1, 25 (1939).

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

sequently

$$\int \Psi D\Psi d\tau \Big/ \int \Psi^2 d\tau = \frac{D_{00}-(DP)_{00}+\lambda'[(D^2)_{00}-(D^2P)_{00}]}{1-P_{00}+2\lambda'[D_{00}-(DP)_{00}]}.$$

This expression represents the van der Waals energy we are seeking. When it is compared with (6) and (4) it is at once seen to reduce to

$$\Delta E=\frac{E_1+(1-P_{00})^{-1}[E_2-\lambda'(D^2P)_{00}]}{1+2\lambda' E_1}. \tag{9}$$

Of course our result shows clearly that one may not, in general, add E_1 and E_2 and expect to get a good approximation to the van der Waals energy. Let us look at the magnitude of the various quantities in (9). For atomic hydrogen the minimum comes at $R\approx 7a_0$, a_0 being the first Bohr radius. (Cf. Eisenschitz and London or reference 9.) At this distance, E_1 and $-E_2$ are about 2 millivolts. $\lambda'\approx 1/E_0$ (cf. below). Therefore the quantity $2\lambda' E_1$ is less than 0.001 and may be neglected against 1 for our purposes. A further simplification arises on decomposing P_{00}. We have

$$P_{00}=\int \psi_0 P\psi_0 d\tau=\int \varphi_a(1)\varphi_b(2)\varphi_a(2)\varphi_b(1)d\tau=\delta^2,$$

where

$$\delta=\int \varphi_a\varphi_b d\tau_1=e^{-\rho}(1+\rho+\rho^2/3)$$

and

$$\rho\equiv R/a_0.$$

At $\rho=7$, $\delta=0.022$ so that $1-P_{00}$ may be safely replaced by 1. At larger distances the error is even smaller, and smaller distances are not of interest in connection with the present problem. We may say, therefore, that as long as the overlap integral δ^2 is small compared to unity, the van der Waals energy is composed additively of 3 terms:

$$\Delta E=E_1+E_2-\lambda'(D^2P)_{00}, \tag{10}$$

the last of which will now be calculated.

As to notation, we specify that r_{12} shall be the distance between electrons 1 and 2, and that a_2, for instance, shall be the distance between nucleus a and electron 2. On writing down the Hamiltonian operator H and also recalling that ψ_0 and $P\psi_0$ satisfy the equations

$$[E_{\text{kin}}-e^2(a_1^{-1}+b_2^{-1})\psi_0=E_0\psi_0,$$
$$[E_{\text{kin}}-e^2(b_1^{-1}+a_2^{-1})P\psi_0=E_0P\psi_0,$$

one sees immediately that

$$D\psi_0=e^2(r_{12}^{-1}+R^{-1}-b_1^{-1}-a_2^{-1})\psi_0$$

and

$$DP\psi_0=e^2(r_{12}^{-1}+R^{-1}-a_1^{-1}-b_2^{-1})P\psi_0.$$

Consequently

$$(D^2P)_{00}=\int D\psi_0 DP\psi_0 d\tau=e^4\int (r_{12}^{-1}+R^{-1}-b_1^{-1}-a_2^{-1})(r_{12}^{-1}+R^{-1}-a_1^{-1}-b_2^{-1})\psi_0P\psi_0 d\tau.$$

The integrals here encountered are all listed in the appendix to the paper by Eisenschitz and London.[11] When the results are collected, the expression reads

$$\begin{aligned}(D^2P)_{00}=\frac{e^4}{a^2}\Big\{&e^{-2\rho}\Big(\frac{5}{4\rho}-\frac{13}{10}+\frac{24}{5}\rho+\frac{53}{15}\rho^2+\frac{2}{3}\rho^3-\frac{4}{81}\rho^4-\frac{4}{27}\rho^5\Big)\\&+2e^{-\rho}\delta\Big[\Big(1-\frac{1}{\rho}\Big)(1-C-\log\rho)\Big]\\&+\frac{\delta^2}{\rho^2}\Big[1+\frac{12}{5}(C+\log\rho)\Big]\\&+\frac{4}{3}e^{-\rho}Ei(-\rho)\Big(\rho^2+\rho^3+\frac{2}{9}\rho^4-\frac{1}{9}\rho^5-\frac{1}{27}\rho^6\Big)\\&-E_i(-2\rho)\Big(\frac{24\delta\delta'}{5\rho^2}-\frac{4}{\rho}+\frac{8}{3}\rho+\frac{4}{3}\rho^2-\frac{20}{27}\rho^4+\frac{16}{81}\rho^6\Big)\\&+Ei(-4\rho)\Big[\frac{12\delta'^2}{5\rho^2}+e^{\rho}\delta'\Big(2-\frac{2}{\rho}\Big)\Big]\Big\};\end{aligned} \tag{11}$$

$$\delta'=e^{\rho}(1-\rho+\rho^2/3); \quad C=0.577.$$

It now becomes necessary to evaluate λ. It is well known from the work of London that

$$E_2=-(V^2)_{00}/p|E_0|$$

where p is a number, usually not far from unity,

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[11] The last integral in their list contains an error (presumably typographical). It should read: $2e^{-\rho}\sqrt{S}$. Their S is our δ^2.

which depends on the position of the "centroid" of excited energy states. For hydrogen, $p=0.92$. But according to Eq. (4),

$$E_2=\lambda'(D^2)_{00}=\lambda'(V^2)_{00}.$$

Hence

$$\lambda'=-1/p|E_0|.$$

To illustrate the significance of the correction term we assemble the constituents of ϵ for $\rho=7$, i.e., near the v.d.W.-minimum in hydrogen:

E_1	E_2	$-\lambda(D^2P)_{00}$	ΔE
2.2	-1.95	-0.98	-0.73 millivolts

E_2 here includes, as it should, the dipole-quadrupole and quadrupole-quadrupole contributions. The result agrees with that of reference 7, which was obtained by second-order perturbation theory. The second-order exchange term is indeed larger than the depth of the minimum itself, and its omission would falsify the total result completely.

For purposes of rough calculations it is convenient to have a simpler function by means of which $(D^2P)_{00}$ can be approximated. It was found that

$$(D^2P)_{00}\doteq-(e^4/a_0{}^2)4.20e^{-1.675\rho} \tag{12}$$

within an accuracy of 5 percent for values of ρ between 6 and 10.

Helium

The energy E_1 has been calculated by Slater[10] with the use of a nonanalytic wave function which describes the atomic properties of He very well, a function which is undoubtedly superior by far to the one we shall employ in the calculation of the second-order exchange effect. To carry through the integrations conveniently hydrogenic wave functions with suitable screening constants will be chosen in this work. This has the further advantage that the calculations yield expressions similar to those which have already been evaluated for hydrogen.

Let φ_a stand for the wave function of a single electron. Screening may be taken account of by a change in the "equivalent Bohr radius" a: the exponent in the wave function is $(Z-s)(r/a_0)=r/a$; this makes $a=a_0/1.688$ for He. Thus all integrals will be the same as for H except for this change in a. The usual v.d.W.-energy E_2 corresponds to the function

$$\psi=(1+\lambda D)\psi_0$$

with

$$\psi_0=\varphi_a(1)\varphi_a(2)\varphi_b(3)\varphi_b(4).$$

On the other hand, E_1 corresponds to

$$\psi=(1+P_{13}P_{24}-P_{24}-P_{13})\psi_0,$$

where P_{ij} is the operator interchanging the arguments of the ith and jth electrons in the function on which it acts. Explicitly,

$$E_2=\lambda'(D^2)_{00}\text{ as before, and}$$

$$E_1=(1-\delta^2)^{-2}[D_{00}-(DP_{13})_{00}-(DP_{24})_{00}+(DP_{13}P_{24})_{00}].$$

We propose to use the function

$$\Psi=(1+\lambda D)(1+P_{13}P_{24}-P_{24}-P_{13})\psi_0,$$

assuming again that the minimizing value of λ for this function is not affected by the addition of the exchange operators. The minimum value of the expression $\int\Psi D\Psi d\tau/\int\Psi^2 d\tau$ with this function is

$$\Delta E=\frac{(1-\delta^2)^{-2}\{[D_{00}-(DP_{13})_{00}-(DP_{24})_{00}+(DP_{13}P_{24})_{00}]+\lambda'[(D^2)_{00}-(D^2P_{13})_{00}-(D^2P_{24})_{00}+(D^2P_{13}P_{24})_{00}]\}}{1+2\lambda'(1-\delta^2)^{-2}[D_{00}-(DP_{13})_{00}-(DP_{24})_{00}+(DP_{13}P_{24})_{00}]}$$
$$\doteq E_1+E_2-\lambda'[(D^2P_{13})_{00}+(D^2P_{24})_{00}-(D^2P_{13}P_{24})_{00}].$$

In the last step we have again neglected δ^2 and $2\lambda'E_1$ against unity, an approximation which is entirely safe in the neighborhood of the v.d.W.-minimum and beyond. It is now necessary to compute three correction terms.

We have

$$H=E_{\text{kin}}+e^2(-2a_1{}^{-1}-2a_2{}^{-1}+r_{12}{}^{-1}-2b_3{}^{-1}-2b_4{}^{-1}+r_{34}{}^{-1}-2b_1{}^{-1}-2b_2{}^{-1}-2a_3{}^{-1}-2a_4{}^{-1}+r_{13}{}^{-1}+r_{14}{}^{-1}+r_{23}{}^{-1}+r_{24}{}^{-1}+4R^{-1}),$$

whereas ψ_0 satisfies the equation

$$[E_{\text{kin}}+e^2(-2a_1^{-1}-2a_2^{-1}+r_{12}^{-1}-2b_3^{-1}-2b_4^{-1}+r_{34}^{-1})]\psi_0=E_0\psi_0.$$

Therefore $D\psi_0=(H-E_0)\psi_0=U\psi_0$

where

$$U=e^2(-2b_1^{-1}-2b_2^{-1}-2a_3^{-1}-2a_4^{-1}+r_{13}^{-1}+r_{14}^{-1}+r_{23}^{-1}+r_{24}^{-1}+4R^{-1}).$$

(U is not symmetrical with respect to an interchange of electrons, as is D.) The integral

$$(D^2P_{13})_{00}=\int D\psi_0 DP_{13}\psi_0 d\tau=\int U\psi_0 P_{13}(U\psi_0)d\tau$$
$$=\int (UP_{13}U)(\psi_0 P_{13}\psi_0)d\tau.$$

The next integral is equal to this; for ψ_0 is symmetrical with respect to the transpositions (1, 2) and (3, 4), so that

$$(D^2P_{24})_{00}=\int \psi_0 D^2P_{24}\psi_0 d\tau$$
$$=\int P_{12}P_{24}\{\psi_0 D^2P_{24}\psi_0\}d\tau=\int \psi_0 D^2P_{13}\psi_0 d\tau.$$

Finally, in the approximation in which δ^2 is neglected against unity, the integral $(D^2P_{13}P_{24})_{00}$ may be disregarded. This can be seen roughly as follows.

The factor $(\psi_0 P_{13}P_{24}\psi_0)$ appearing in the integrand would, if integrated alone, yield δ^4, while the (00)-element of the single permutation P_{13} is δ^2. Though this does not prove the smallness of all integrals appearing in $(D^2P_{13}P_{24})_{00}$, it is a hint which is verified on calculating this quantity in detail.

We may say, then, that

$$\Delta E \doteq E_1+E_2-2\lambda'(D^2P_{13})_{00} \tag{13}$$

and we shall now show that the integral of the correction term is reasonably well approximated by the quantity $(D^2P)_{00}$ already computed for hydrogen.

This can be seen on physical grounds. When the helium atom is in its normal state, the chance that both of its electrons be far away from the nucleus is very much smaller than that one shall be far away and one near it. Thus, when two helium atoms interact, at distances several times the atomic diameter, exchange will effectively take place only between two electrons at one time. The other two will be near their nuclei, so that the interaction is essentially hydrogenic. When one is interested in the forces at smaller distances of separation, this argument may not be used.

Mathematically, the result comes about in this way. When

$$(D^2P_{13})_{00}=\int U(P_{13}U)\varphi_a(1)\varphi_b(1)\varphi_a^2(2)\times\varphi_a(3)\varphi_b(3)\varphi_b^2(4)d\tau$$

is expanded, it contains, besides the integrals occurring in the foregoing section, a considerable number which do not represent pure exchange but involve direct parts as well. Examples are:

$$\int \frac{\varphi_a^2(1)\varphi_a(2)\varphi_b(2)}{b_1 r_{12}}d\tau$$

and

$$\int \frac{\varphi_a^2(1)\varphi_a(2)\varphi_b(2)\varphi_a(3)\varphi_a(3)}{r_{13}r_{23}}d\tau.$$

The leading term in these integrals is obtained by treating φ_a^2 as strongly concentrated about the nucleus a (δ-function). In the complete integral this term is multiplied by an expression of the form $[1+e^{-\rho}$ (polynomial)$]$. This will here be taken as 1; the error thus introduced is hardly greater than 5 percent at values of ρ in which we are interested here ($e^{-\rho}\approx 10^{-4}$). If this procedure is adopted, these two integrals reduce to

$$\frac{1}{R}\int \frac{\varphi_a(1)\varphi_b(1)}{b_1}d\tau_1$$

and

$$\int \frac{\varphi_a(1)\varphi_b(1)\varphi_a(2)\varphi_a(2)}{a_2 r_{12}}d\tau.$$

When similar approximations are carried out on all integrals of this type, $(D^2P_{13})_{00}$ for helium collapses to $(D^2P)_{00}$ for hydrogen (though D^2 contains many more and quite different terms in the former case than in the latter).

λ' will be determined as before; p is very nearly 1, so that $\lambda'=-1/2E_i$, where E_i is the first ionizing potential of He. For $(D^2P)_{00}$ we may take the approximate expression (12). Now the minimum of the v.d.W. potential in helium occurs at about $R=5.5a_0=9.3a$, that is, the equivalent $\rho(=R/a)$ for He is much greater than that for $H(=R/a_0)$, although the minimum actually occurs at a smaller distance of separation in He.

On inserting these values, we have

$$-2\lambda'(D^2P)_{00}\doteq-(e^4/E_ia^2)\cdot 4.20e^{-1.675\rho}$$
$$=-350e^{-1.675\rho}\text{ volts,}$$

which, for $\rho=9.3$, has the value -5.9×10^{-5} ev. Again we list the constituent parts of ΔE at the minimum ($R=2.9$A). The conclusion is that the

E_1	E_2	$-2\lambda(D^2P)_{00}$	ΔE
0.72	−1.75	−0.06	−1.09 e. millivolts

second-order exchange effect for He is almost negligible, a fact which is perhaps surprising in view of the large rôle it plays in H. It explains why the simpler theories have had some measure of success in connection with the helium problem.

It is probably safe to add a remark about the magnitude of this effect in the heavier rare gases without further calculation. A detailed investigation would be complicated by the fact that the electrons involved are no longer 1*s*-electrons. Nevertheless, if the exponential part of the wave function is the decisive feature, the effect is determined by the magnitude of $(D^2P)_{00}$ for the equivalent value of ρ at the v.d.W. minimum, and this equivalent value of ρ depends on the screening constant for the outer electrons through a. If we take Slater's screening constants and identify the distance of the v.d.W. minimum with the kinetic theory diameter, the values of ρ turn out quite large; for Ne and Ar, e.g., they are about 18. At these distances the exponential (12) is entirely insignificant even after multiplication by the factor 8, the number of electrons in the outer shell. We conclude, therefore, that for heavier atoms the second-order exchange effect is negligible.

Slater's expression for the first-order exchange potential in He is not likely to be much in error; at any rate it would be very difficult to improve it. Hence we turn our attention now to the attractive terms in Eq. (1).

II. Attractive Forces

Several calculations of these terms, using widely different methods, have been made;[12] the results are not as consistent, however, as might be desired. The most important quantity is c_1, the coefficient of the dipole term; the main part of the subsequent considerations will deal with its evaluation.

Survey of previous results for the coefficient c_1

There are two general methods for calculating c_1. The first is based upon the use of London's formula

$$c_1=\frac{3}{2}\left(\frac{e^2\hbar^2}{m}\right)^2\times\sum_{ij}\frac{f_{0i}f_{0j}}{(E_0-E_i)(E_0-E_j)(2E_0-E_i-E_j)},\qquad(14)$$

wherein the f_{0i} are the spectroscopic oscillator strengths pertaining to transitions to the ground state. They may be taken from empirical dispersion formulas. Now it happens that the refractive index of He is given with very good approximation by a formula in which only one f appears,[13] at least in the relatively small range to which observations are confined. In that case (2) is equivalent to

$$c_1=-\tfrac{3}{4}\Delta\cdot\alpha^2,\qquad(15)$$

where Δ is the energy difference between ground state and mean excited state, and α the static polarizability.[9] Using Cuthbertson's Δ, Eq. (3) gives

$$c_1=1.20\times 10^{-60}\text{ erg cm}^6.\qquad\text{(a)}$$

Herzfeld and Wolf[14] suggest a slightly different one-term dispersion formula, and also one containing two f's. Both, if used in calculating (2), lead to

$$c_1=1.28\times 10^{-60}\text{ erg cm}^6.\qquad\text{(b)}$$

The inaccuracy of results (a) and (b) arises

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[12] See references 5, 6, 9; prior to these F. London's well-known papers; more recently R. A. Buckingham, Proc. Roy. Soc. **160**, 94 (1937); C. H. Page, Phys. Rev. **53**, 426 (1938).

[13] C. and M. Cuthbertson, Proc. Roy. Soc. **84**, 13 (1910).

[14] K. F. Herzfeld and K. L. Wolf, Ann. d. Physik [4] **76**, 567 (1925).

principally from the circumstance that the mean f value to be inserted in the dispersion formula is not identical with the proper mean for Eq. (14). These results can only be improved by taking detailed account of the variation of f with frequency, both in the discrete and in the continuous spectrum.

The second method for determining c_1 is the variational one, in which ψ_0 is approximated in a suitable manner and the perturbing van der Waals energy is computed. In the hands of Slater and Kirkwood[5] it has yielded

$$c_1 = 1.49\times 10^{-60} \text{ erg cm}^6, \tag{c}$$

whereas Buckingham[12] computes

$$c_1 = 1.62\times 10^{-60} \text{ erg cm}^6. \tag{d}$$

The error in these results is difficult to estimate; but it is to be noted that they may not be interpreted as upper limits to the true value of c_1. This simply follows from the fact that the perturbation energy is calculated as the difference between the perturbed energy E and E_{00}, the latter being only approximate because ψ_0 is not exact. A survey of cases other than helium indicates that the variational method generally gives values of c_1 considerably greater than would be obtained from any empirical dispersion formula. One is therefore inclined to believe that its tendency is to overshoot the mark.

Recalculation of c_1

It is possible to make a calculation which is based upon Eq. (14), taking adequate account of the variation of the f values with frequency. The method to be employed has already been used for this purpose,[15] but with a rather uncertain choice of f's. (It yielded $c_1 = 1.44\times 10^{-60}$.) Meanwhile, f values for He have been calculated by Wheeler.[16] They will here be used as basis for computation, later to be corrected for empirical reasons.

We denote the f values relating to the discrete spectrum by f_{0i}; for the continuous spectrum they are available as df_{0E}/dE. In accordance with this division of the frequency range Eq. (14) may be written

$$c_1 = A\left\{\sum_{ij}\frac{f_{0i}f_{0j}}{v_iv_j(v_i+v_j)} + 2\sum_i\int_0^\infty \frac{f_{0i}(df_{0\epsilon}/d\epsilon)d\epsilon}{v_i(1+\epsilon)(1+v_i+\epsilon)} + \int\int_0^\infty \frac{(df_1/d\epsilon_1)(df_2/d\epsilon_2)d\epsilon_1 d\epsilon_2}{(1+\epsilon_1)(1+\epsilon_2)(2+\epsilon_1+\epsilon_2)}\right\}, \tag{16}$$

use being made of the following abbreviations:

$$A = -\frac{3}{2}\left(\frac{e^2\hbar^2}{m}\right)^2 \frac{1}{|E_0|^3}, \quad v_i = 1 - \frac{E_i}{E_0}, \quad \epsilon = \frac{E}{-E_0}.$$

E without subscript refers to the continuous spectrum. In evaluating (16) it is convenient to introduce the auxiliary function

$$G(\alpha) \equiv \int_0^\infty \frac{(df/d\epsilon)d\epsilon}{(1+\epsilon)(\alpha+\epsilon)}, \tag{17}$$

which can be computed for a sufficient range of α's by numerical integrations. In terms of it, we now have

$$c_1 = A\left\{\sum_{ij}\frac{f_{0i}f_{0j}}{v_iv_j(v_i+v_j)} + 2\sum_i \frac{f_{0i}G(1+v_i)}{v_i} + \int_0^\infty \frac{(df/d\epsilon)G(2+\epsilon)d\epsilon}{1+\epsilon}\right\}.$$

In calculating the first sum, only the v's corresponding to the first four lines of the principal series need be considered; the remainder may be treated as a single transition near the series limit ($v_5 = 0.99$). The integration has been carried out numerically, since it seems difficult to approximate G by simple functions. The three terms in brackets yield, respectively, 0.126, 0.358, and 0.271. The coefficient A has the value -1.97×10^{-60}; hence

$$c_1 = 1.49\times 10^{-60} \text{ erg cm}^6$$

in exact agreement with the result of Slater and Kirkwood (Eq. (c)).

The present method is of course exact as far as the coefficient c_1 is concerned; errors are due only to the use of inaccurate f values, and these may be estimated and corrected. We subject the f's to two requirements: they shall satisfy the sum rule

$$\sum_i f_{0i} = 2, \tag{18}$$

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[15] H. Margenau, Phys. Rev. **37**, 1425 (1931).

[16] J. E. Wheeler, Phys. Rev. **43**, 258 (1933).

and they shall yield the correct polarizability

$$\alpha=\frac{e^2\hbar^2}{m}\sum_i\frac{f_{0i}}{(E_0-E_i)^2}.$$

In terms of our present convention, and with the use of the function (17), this reads

$$\alpha=\frac{e^2\hbar^2}{m}\left\{\sum_i\frac{f_{0i}}{v_i^2}+G(1)\right\}. \qquad (19)$$

Wheeler's f values already satisfy Eq. (18). They give for the bracketed expression in (19) the value $\{0.532+0.621\}$, and thus for α: 2.11×10^{-25} cm³. Experimentally, α may be obtained from measurements of the dielectric constant of He at radiofrequencies[17] and from extrapolation on the refractive index.[13] The former lead to the value 2.1×10^{-25} cm³. However, the experimental difficulties attending these measurements are such as to make this value less certain than that deduced from Cuthbertson's observations on the refraction of visible light. From these, Born and Heisenberg[18] have found $\alpha=2.02\times10^{-25}$ cm³.

Assuming this to be correct, we conclude that Wheeler's f values are slightly in error. In correcting them, we assume the trend of $df/d\epsilon$ to be unaltered, but redistribute the relative weights of the discrete and the continuous spectrum in such a way that both Eq. (18) and Eq. (19) are satisfied for $\alpha=2.02\times10^{-25}$ cm³. Thus if f' denotes the corrected oscillator strength, we put

$$f_{0i}'=(1-a)f_{0i} \quad\text{and}\quad df'/d\epsilon=(1+b)(df/d\epsilon).$$

It is found that $a=0.134$, $b=0.036$. This correction seems quite compatible with the accuracy of Wheeler's calculation. If now we use the corrected f's in Eq. (14), the result is

$$c_1=1.39\times10^{-60}\ \text{erg cm}^6.$$

A change in the value of α produces about twice as great a relative change in c_1 in the same direction.

CONCLUSION

As to the coefficient c_2 of Eq. (1), there are several detailed calculations which agree quite well. In particular, they lead to almost the same ratio c_2/c_1, and this turns out to be 2.2×10^{16} cm². Thus we take c_2 to be 3.0×10^{-76} erg cm⁸.

Summarizing the present results we obtain:

$$\Delta E=\left\{770e^{-4.60R}-560e^{-5.33R}-\frac{1.39}{R^6}-\frac{3.0}{R^8}\right\}10^{-12}\ \text{erg} \qquad (20)$$

as the formula which appears best in the face of present evidence. Here R is measured in A.U. The repulsive term is taken from Slater without recalculation. As already pointed out, the second term is a small correction; its form is valid in the region of the minimum and down to about 2A. For purposes of using the formula in calculations it may well be taken care of by increasing the dipole-quadrupole coefficient from 3.0 to 3.7. The minimum of ΔE comes at $R\approx2.8$A and has a value of -1.8×10^{-16} erg.

The formula most frequently used in applications is Slater and Kirkwood's, which neglects the quadrupole term but has -1.49 for the coefficient of the dipole term. It seems that the reason for its approximate validity lies in the compensating effect of these two features. Recent calculations of Gropper[19] on the second virial coefficient of He indicate that the correct potential must lie between the Slater-Kirkwood potential and that obtained by the present author on adding the quadrupole term to the latter. The same result is reached by de Boer and Michels[2] who actually deduce a potential which best fits experimental data. The potential given here (Eq. (20)) does have the property of being intermediate between the two. Dr. de Boer has kindly pointed out,[20] however, that this expression does not give quite as good a fit with the experimental data of Keesom and Kraak[21] as the one derived by him from an analysis of thermodynamic data.

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[17] H. E. Watson, G. Gundo Rao and K. L. Ramaswamy, Proc. Roy. Soc. **A132**, 569 (1931).

[18] M. Born and W. Heisenberg, Zeits. f. Physik **23**, 388 (1924).

[19] L. Gropper, Phys. Rev. **55**, 1095 (1939).

[20] Private communication, for which the author wishes to express his gratitude.

[21] W. H. Keesom and H. H. Kraak, Physica **2**, 37 (1935).