background density, while originally very nearly unity, has now a far greater value, in agreement with the requirement of (11).

The limit to the excess of density in the condensations being thus set by the magnitude of the original perturbation (and not the original density), one sees that in spite of condensations occurring in the highly dense cosmic fluid early in the life of the universe, condensations of high densities, as envisaged by Hoyle,[6] cannot be met with at present.

In conclusion, we note that a particularly satisfactory feature of the present investigation is that we have not introduced any assumption regarding the pressure, the pressure gradient, or the mechanism and nature of the original perturbation. We have also not introduced any nongravitational interaction.

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Convergence of Intermolecular Force Series*

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The commonly used perturbation method of estimating the Van der Waals forces between atoms is shown to lead, when carried to the extreme, to divergent results. The method employs an expansion of the classical electrostatic interaction between the atoms in a series of inverse powers of the internuclear distance. The divergence arises because this expansion is utilized in regions of configuration space where it is not convergent. In this paper, the resulting divergent intermolecular force series are shown to be asymptotic to the true molecular interaction. The divergence is removed in an approximate way and the second-order attractive energy so obtained is added to the first-order exchange energy between the atoms. The method results in an electronic energy curve for H_2^+ in reasonable accord with the exact result of Hylleraas and in a new interaction between helium atoms in good agreement with recent low temperature experiment.

I. INTRODUCTION

THE Van der Waals force between two atoms, at an internuclear distance R, is usually estimated by the use of an expansion of the classical electrostatic interaction between the atoms in a series of inverse powers of R. This expansion is considered as a perturbation upon the combined system of the two atoms and the Schrödinger perturbation theory or the variational method is employed to evaluate the resultant shift in energy levels. The shift is identified with the potential energy of the interatomic force.[1]

The expansion of the electrostatic interaction between the atoms is convergent and meaningful only in a limited region of the configuration space of the combined system. It is, however, commonly employed throughout this configuration space. This paper reports an investigation of the uncertainties arising from this procedure and suggests a method of overcoming them.

Let H_A and H_B be the (unperturbed) Hamiltonians of atoms A and B. The corresponding state functions and energy levels will be designated by $\psi_A^{(s)}$, $E_A^{(s)}$ and $\psi_B^{(t)}$, $E_B^{(t)}$, where s and t are quantum numbers. We shall refer the Hamiltonian and wave functions of each atom to a coordinate system (rectangular or spherical) with origin at its nucleus. The coordinates of charges e_i belonging to atom A are (x_i, y_i, z_i) or (r_i, θ_i, ϕ_i). Those of charges ϵ_j belonging to atom B are (ξ_j, η_j, ζ_j) or $(\rho_j, \omega_j, \chi_j)$. The z and ζ-axes are directed along the internuclear line from A to B.

The intermolecular force results when the electrostatic interaction

$$V=\sum\nolimits_{i,j} e_i\epsilon_j/r_{ij} \tag{1}$$

between the atoms is taken as a perturbation on the compound system having the Hamiltonian H_A+H_B, state functions $\psi_A^{(s)}\psi_B^{(t)}$ and energy levels $E_A^{(s)}+E_B^{(t)}$.

In carrying out a perturbation or variational calculation (1) is usually expanded in a series of inverse powers of the internuclear distance. Margenau[2,3] has given some of the lower terms in this series:‡

$$\begin{aligned} V'=\cdots&-\frac{1}{R^3}\sum_{i,j} e_i\epsilon_j(2z_i\zeta_j-x_i\xi_j-y_i\eta_j)\\ &+\frac{3}{2R^4}\sum_{i,j} e_i\epsilon_j[r_i^2\zeta_j-z_i\rho_j^2\\ &+(2x_i\xi_j+2y_i\eta_j-3z_i\zeta_j)(z_i-\zeta_j)]\\ &+\frac{3}{4R^5}\sum_{i,j} e_i\epsilon_j[r_i^2\rho_j^2-5z_i^2\rho_j^2-5r_i^2\zeta_j^2-15z_i^2\zeta_j^2\\ &\qquad+2(4z_i\zeta_j-x_i\xi_j-y_i\eta_j)^2]+\cdots. \end{aligned} \tag{2}$$

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[1] F. London, Z. Physik **63**, 245 (1930).

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

[3] H. Margenau, Revs. Modern Phys. **11**, 1 (1939).

‡ The symbol V' is used to denote an expanded form of V.

The terms in the series arise from the interaction of the various electric multipole moments of the two atoms. Those appearing in (2) are, respectively, the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole terms.

Recently Carlson and Rushbrooke[4] have generalized this result by deriving the following expansion in spherical coordinates:

$$V'=\sum_{i,j} e_i\epsilon_j \sum_{\lambda_A=0}^{\infty} \sum_{\lambda_B=0}^{\infty} \frac{r_i^{\lambda_A}\rho_j^{\lambda_B}}{R^{\lambda_A+\lambda_B+1}} Q_{\lambda_A\lambda_B}$$

$$\times \sum_{\mu=-\lambda_<}^{\mu=+\lambda_<} \frac{Y_{\lambda_A}{}^{\mu}(\theta_i,\phi_i)Y_{\lambda_B}{}^{-\mu}(\omega_j,\chi_j)}{[(\lambda_A+\mu)!(\lambda_A-\mu)!(\lambda_B+\mu)!(\lambda_B-\mu)!]^{\frac{1}{2}}};$$

$$Q_{\lambda_A,\lambda_B}=\frac{(-1)^{\lambda_<}4\pi(\lambda_A+\lambda_B)!}{[(2\lambda_A+1)(2\lambda_B+1)]^{\frac{1}{2}}}. \qquad (3)$$

In Eq. (3), $\lambda_<$ is the lesser of λ_A and λ_B. $Y_\lambda{}^\mu(\theta,\phi)$ is a normalized surface spherical harmonic. A term in Eq. (3) with specified values of λ_A and λ_B gives the interaction between the 2^{λ_A}-pole moment of atom A and the 2^{λ_B}-pole moment of B. If the atoms are electrically neutral, the monopole terms vanish when the summations over i and j are performed.

Expansions (2) and (3) are convergent and meaningful only in those regions of the configuration space of the compound system where the charge distributions of the two atoms do not overlap. If the expansions are used for all points of configuration space in the perturbation calculations, the resulting expressions for the interaction energy become the first terms of an infinite series which is divergent for all values of R.

In illustrating and investigating the significance of this fact we shall employ the Schrödinger perturbation theory only as far as the second-order correction. This will falsify those terms in the resulting intermolecular force series depending on R^{-9} and higher inverse powers of R. However, only the terms in R^{-6} and R^{-8} have been found to be of practical importance in calculations of the Van der Waals force between nonpolar molecules.

II. DIVERGENCE OF THE SECOND-ORDER PERTURBATION METHOD. INTERACTING HARMONIC OSCILLATORS

The interaction of simple harmonic oscillators is an example which occurs frequently in the literature of dispersion forces. Margenau,[5] using second-order perturbation theory, has found the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interaction energies. We shall compute the complete second-order interaction energy and show that the resulting infinite series is divergent for all R.

For this purpose atoms A and B are taken to be three-dimensional isotropic oscillators of classical frequency ν. The wave functions of such an oscillator, in spherical coordinates, are of the form

$$\psi_{nlm}=S_{nl}(r)Y_l{}^m(\theta,\phi) \qquad (4)$$

where $S_{nl}(r)$ is the normalized radial function. The energy levels are given by

$$E_{nl}=(2n+l+\tfrac{3}{2})h\nu \qquad (5)$$

in which n and l are non-negative integers. The single selection rule which we shall have occasion to use is the following: The matrix element $(nlm|r^\lambda Y_\lambda{}^\mu|000)$ vanishes unless $n=0$, $l=\lambda$, and $m=\mu$.

If the oscillators are in their normal states, as we shall assume, the first-order perturbation caused by (2), or more generally (3), vanishes and the second-order perturbation energy becomes

$$\Delta E_2=-\sum_{\substack{n_A,l_A,m_A\\ n_B,l_B,m_B}}{}' \frac{|(n_Al_Am_A;n_Bl_Bm_B|V'|000;000)|^2}{E_{n_Al_A}+E_{n_Bl_B}-3h\nu}. \qquad (6)$$

Taking the perturbing energy as given by Carlson and Rushbrooke, the matrix elements involved in (6) are all of the form

$$(n_Al_Am_A;n_Bl_Bm_B|r^{\lambda_A}\rho^{\lambda_B}Y_{\lambda_A}{}^{\mu}Y_{\lambda_B}{}^{-\mu}|000;000)$$
$$=(n_Al_Am_A|r^{\lambda_A}Y_{\lambda_A}{}^{\mu}|000)(n_Bl_Bm_B|\rho^{\lambda_B}Y_{\lambda_B}{}^{-\mu}|000). \qquad (7)$$

They vanish by virtue of the selection rule stated above unless $n_A=n_B=0$; $l_A=\lambda_A$, $l_B=\lambda_B$; $m_A=-m_B=\mu$. Therefore

$$(n_Al_Am_A;n_Bl_Bm_B|V'|000;000)=\frac{e^2}{R}\frac{Q_{l_Al_B}}{R^{l_A+l_B}}$$
$$\times\frac{(0l_Am_A|r^{l_A}Y_{l_A}{}^{m_A}|000)(0l_Bm_B|\rho^{l_B}Y_{l_B}{}^{-m_A}|000)}{[(l_A+m_A)!(l_A-m_A)!(l_B+m_A)!(l_B-m_A)!]^{\frac{1}{2}}}$$
$$\times\delta_{m_B,-m_A}\cdot\delta_{n_A,0}\cdot\delta_{n_B,0}. \qquad (8)$$

Employing the selection rule and the rule for matrix multiplication:

$$|(0lm|r^lY_l{}^m|000)|^2$$
$$=\sum_{n\lambda\mu}(00|r^lY_l{}^{-m}|n\lambda\mu)(n\lambda\mu|r^lY_l{}^m|000)$$
$$=(000|r^{2l}Y_l{}^mY_l{}^{-m}|000)=(000|r^{2l}|000)/4\pi. \qquad (9)$$

The result of incorporating (8) and (9) in (6) is

$$\Delta E_2=-\frac{e^4}{h\nu R^2}\sum_{l_A,l_B,m_A}{}'\frac{(Q_{\lambda_A\lambda_B}/4\pi)^2}{R^{2\lambda_A+2\lambda_B}}$$
$$\times\frac{(000|r^{2l_A}|000)(000|\rho^{2l_B}|000)}{(l_A+l_B)(l_A+m_A)!(l_A-m_A)!(l_B+m_A)!(l_B-m_A)!}. \qquad (10)$$

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[4] B. C. Carlson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. 46, 626 (1950); see also the discussion in R. J. Buehler and J. O. Hirschfelder, Phys. Rev. 83, 628 (1951).

[5] H. Margenau, J. Chem. Phys. 6, 896 (1938).

The summation over m_A may now be performed by means of the relation,

$$\sum_{m_A=-l_<}^{m_A=+l_<}[(l_A+m_A)!(l_A-m_A)!(l_B+m_A)!(l_B-m_A)!]^{-1}=\frac{(2l_A+2l_B)!}{[(l_A+l_B)!]^2(2l_A)!(2l_B)!},\quad(11)$$

which follows simply from the "addition theorem" for binomial coefficients. Introducing the explicit form of Q_{λ_A,λ_B} in (10), we obtain

$$\Delta E_2=-\frac{e^4}{h\nu R^2}\sum_{l_A,l_B}{}'\times\frac{(2l_A+2l_B)!(000|r^{2l_A}|000)(000|r^{2l_B}|000)}{(2l_A+1)!(2l_B+1)!(l_A+l_B)R^{2l_A+2l_B}}.\quad(12)$$

The ground-state wave function for the oscillator is

$$(000|=(\beta/\pi)^{\frac{3}{4}}\exp(-\tfrac{1}{2}\beta r^2);\quad\beta=e^2/\alpha h\nu\quad(13)$$

where α is the polarizability (classical as well as quantum) of the system. Hence,

$$(000|r^{2l}|000)=\beta^{-l}(2l+1)!/2^{2l}\,l!.\quad(14)$$

Substituting this result in (12) we find

$$\Delta E_2=-\frac{e^4}{h\nu R^2}\sum_{l_A,l_B}\frac{[2l_A+2l_B]!}{2^{2l_A+2l_B}l_A!l_B!(l_A+l_B)}\times\frac{1}{(\sqrt{\beta}R)^{2l_A+2l_B}},\quad(15)$$

or, in terms of $L=l_A+l_B$,

$$\Delta E_2=-\frac{e^4}{h\nu R^2}\sum_{L=2}^{\infty}\frac{C_L}{(\sqrt{\beta}R)^{2L}};\quad C_L=\frac{(2L)!(2^L-2)}{2^{2L}\cdot L!\cdot L}.\quad(16)$$

When (16) is written out explicitly we obtain

$$\Delta E_2=-\frac{3}{2}\frac{e^4}{R^6}\frac{1}{2h\nu\cdot\beta^2}-\frac{45}{4}\frac{e^4}{R^8}\frac{1}{3h\nu\cdot\beta^3}-\frac{315}{8}\frac{e^4}{R^{10}}\frac{1}{4h\nu\cdot\beta^4}-\frac{4725}{16}\frac{e^4}{R^{12}}\frac{1}{5h\nu\cdot\beta^5}-\frac{322245}{32}\frac{e^4}{R^{14}}\frac{1}{6h\nu\cdot\beta^6}\cdots.\quad(17)$$

The first three terms of this expansion are identical with those calculated by Margenau who employed them to estimate the magnitude of quadrupole contributions to the dispersion forces between real molecules.

The general term of (16), however, reveals the fact that the infinite series is divergent for all values of R. The behavior is not caused by any inherent divergence in the perturbation theory (because, after all, we have used only the second-order correction formula). Rather, it is caused by the use, in evaluating the matrix elements involved in (6), of the series expansions (2) or (3) in regions of configuration space where they are divergent and meaningless.

We have shown that the divergence occurs in the case of interacting oscillators where the wave function is comparatively "tightly bound," i.e., falls off as $\exp(-r^2)$. It will therefore occur *a fortiori* in a calculation of the interaction of real molecules where the wave functions fall off only as e^{-r}.

Since the divergence is associated with the limited region of validity of expansions (2) and (3), it will also effect a variational calculation which employs these expansions.

III. THE ASYMPTOTIC NATURE OF THE DISPERSION FORCE SERIES

The considerations of Sec. II suggest the following question: What is the relation of a divergent intermolecular force series $\sum C_j/R^j$ to the true atomic interaction $E(R)$? If the coefficients C_j are determined accurately, the series is asymptotic to $E(R)$ in the sense of Poincaré. This will now be proved in a simple manner.

An expansion of the form $\sum C_j/R^j$ is said to be asymptotic to a function $E(R)$ in the sense of Poincaré if, for every positive integral N,

$$\lim_{R\to\infty}R^N\left[E(R)-\sum_{j=0}^{N}C_j/R^j\right]=0,\quad(18)$$

or, equivalently

$$\left[E(R)-\sum_{j=0}^{N}C_j/R^j\right]=O(R^{-N-1}).\quad(19)$$

Such expansions are unique in the sense that a given function $E(R)$ has at most one.[6] They are useful for estimating values of $E(R)$ for large R.

If $\phi(R)$ is the true normalized ground-state function for the compound system of the two atoms and $\mathcal{H}=H_A+H_B+V$, then

$$E(R)=\int\phi^*\mathcal{H}\phi d\tau.\quad(20)$$

Let V_N' represent the series (3) up to and including the terms in R^{-N}. If we use V_N' instead of the true interaction V, we obtain

$$E_N'(R)=\int\phi^*\mathcal{H}_N'\phi d\tau\quad(21)$$

where $\mathcal{H}_N'=H_A+H_B+V_N'$. It is now easy to show that

$$E(R)-E_N'(R)=\int\phi^*[V-V_N']\phi d\tau\quad(22)$$

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[6] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, London, 1948), p. 153.

is $O(R^{-N-1})$. Within the region Ω of configuration space where the series (2) and (3) are convergent, $V-V_N'$ is $O(R^{-N-1})$ and therefore

$$\int_\Omega \phi^*[V-V_N']\phi d\tau = O(R^{-N-1}). \tag{23}$$

Since the wave function goes to zero exponentially at large distances, the integral over the remainder of configuration space is of the order of $\exp(-pR)$, $p>0$. Moreover,

$$E_N'(R) = T(R) + \sum_{j=0}^{N} C_j/R^j \tag{24}$$

where T is a term of order $\exp(-pR)$. Hence

$$\left[E(R) - \sum_{j=0}^{N} C_j/R^j\right] = O(R^{-N-1}).$$

We conclude that the dispersion force series, although divergent, are asymptotic to $E(R)$, and thus are the best possible representation of the atomic interaction in a series of inverse powers of R.

IV. REMOVAL OF THE DIVERGENCES. RECALCULATION OF THE POLARIZATION ENERGY COMPONENT OF THE PROTON-HYDROGEN ATOM BOND

The divergent, but asymptotic intermolecular force series may legitimately be used to estimate the force at sufficiently large values of R, providing not too many terms of the divergent series are employed. However, at small values of R even the first term in the series greatly overestimates the attractive force. Since the series are the best possible representation of $E(R)$ in a series of inverse powers of R, we must resort to a new form of expression for the interaction energy if the overestimate is to be eliminated.

The significance of these statements can be illustrated simply with reference to the hydrogen-molecule ion. We propose to study the polarization energy which accounts for a part of the strength of the bond in this molecule and which can be estimated mathematically in the same manner as intermolecular force.

Consider a hydrogen atom (A) and a proton (B). The electrostatic interaction V' between these systems may be written

$$V' = -\frac{1}{R}\sum_{\lambda=1}^{\infty}\left(\frac{r}{R}\right)^{\lambda} P_\lambda(\cos\theta), \quad r<R. \tag{25}$$

Atomic units are employed here. [Unit distance $=a$, the Bohr radius; unit energy $=e^2/a=27$ ev.] Expansion (25), to which (3) reduces in this case, is uniformly convergent for $r<R$.

The second-order perturbation caused by (25) is

$$\Delta E_2 = -\sum_j{}' \frac{|(j|V'|0)|^2}{E_j - E_0}. \tag{26}$$

Employing an approximation first used by Unsöld,[7] we replace each denominator in (26) by the constant ϵ, $\frac{3}{8}\leq\epsilon\leq\frac{1}{2}$. Then (26) becomes

$$\Delta E_2 = -(0|V'^2|0)/\epsilon. \tag{27}$$

With the use of the ground-state wave function for hydrogen, $e^{-r}/\sqrt{\pi}$, and the orthogonality property of the Legendre polynomials, the matrix element is found to be

$$(0|V'^2|0) = \frac{1}{R^2}\sum_{\lambda=1}^{\infty}\frac{(0|r^{2\lambda}|0)}{2\lambda+1}R^{-2\lambda}. \tag{28}$$

But

$$(0|r^{2\lambda}|0) = (2\lambda+2)!/2^{2\lambda+1}$$

and, hence,

$$\Delta E_2 = -\frac{1}{\epsilon R^2}\sum_{\lambda=1}^{\infty}\frac{(2\lambda+2)!}{2^{2\lambda+1}(2\lambda+1)}R^{-2\lambda}. \tag{29}$$

We now choose $\epsilon=4/9$ in order to bring the first term of (29) into accord with the known polarizability of the hydrogen atom. The first few terms of this expression then become

$$\Delta E_2 = -9/4R^4 - 81/8R^6 - 405/4R^8 \cdots. \tag{30}$$

They are the monopole-dipole, monopole-quadrupole, and monopole-octopole terms. Series (29–30) are divergent, as a Cauchy ratio test shows. [This is to be expected since in evaluating the matrix element $(0|V'^2|0)$ we have integrated over all configuration space including regions for which $r>R$ and where V' is divergent and meaningless.]

Coulson[8] has calculated the interaction for this case without resort to Unsöld's approximation or specialization to second-order perturbation theory, but still employing (25) even outside its region of convergence. His ingenious, but laborious, method yields the again apparently divergent expression

$$-9/4R^4 - 15/2R^6 - 213/4R^7 - 7755/64R^8 \cdots. \tag{31}$$

The H_2^+ case has been selected for consideration here because of the availability of an exact solution of the problem, as well as a reliable calculation of the first-order energy, against which to check the validity of the approximate methods widely in use for estimating Van der Waals forces. The exact interaction curve for the ground state has been computed by Hylleraas.[9] The first-order energy, to which ΔE_2 must be added to obtain an approximate total interaction curve, has been calculated by Pauling.[10] This energy which results from the simplest of molecular structure calculations is

$$\begin{aligned} \Delta E_1 &= (1/R) - (J+K)/(1+\Delta); \\ J &= 1/R - e^{-2R}(1+1/R); \\ K &= e^{-R}(1+R); \\ \Delta &= e^{-R}(1+R+\tfrac{1}{3}R^2). \end{aligned} \tag{32}$$

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[7] A. Unsöld, Z. Physik 43, 563 (1927).

[8] C. A. Coulson, Proc. Roy. Soc. Edinburgh 61, 20 (1941).

[9] E. A. Hylleraas, Z. Physik 71, 739 (1931).

[10] L. Pauling, Chem. Rev. 5, 173 (1928).

TABLE I. H_2^+ electronic energy curve. The exact result of Hylleraas and various approximations. Energy is measured in units of $e^2/a=27$ ev, where a = Bohr radius.

$R(a)$	Hylleraas	$\Delta E_1+\Delta E_2$ (2 terms)	$\Delta E_1+\Delta E_{2,\Omega}$ (2 terms)	$\Delta E_1+\Delta E_{2,\Omega}$ (1 term)
1	+0.0477	−12.237	−0.028	+0.019
2	−0.1026	− 0.353	−0.123	−0.106
3	−0.0776	− 0.101	−0.084	−0.079
4	−0.041	− 0.051	−0.047	−0.045
5	···	− 0.023	−0.023	−0.023

The Pauling first-order energy ΔE_1 plus the first two terms of Eq. (30), i.e.,

$$\Delta E_1-9/4R^4-81/8R^8, \tag{33}$$

is compared with the Hylleraas energy in Table I. The tremendous overestimate of the polarization energy at small values of R is apparent. If more terms of (30) had been included the results would have been even worse.

The origin of the overestimate has been explained. We now propose to eliminate it in the following simple manner. In evaluating matrix element of V'^2 we shall limit the integration to the region $\Omega(r<R)$ of configuration space in which V' is convergent and entirely neglect contributions to the interaction energy arising from regions outside Ω. This procedure cannot be rigorously justified, although it is certainly more reasonable than the use of V' where it is divergent. (It should be noted that the whole concept of multipole interaction is only meaningful within the region of convergence of V'.)

The effect of this procedure is to replace the matrix elements $(0|r^{2\lambda}|0)$ in (28) by

$$(0|r^{2\lambda}|0)_\Omega=(0|r^{2\lambda}|0)\cdot\Gamma_{2R}(2\lambda+3)/\Gamma_\infty(2\lambda+3), \tag{34}$$

where

$$\Gamma_x(p+1)=\int_0^x e^{-\xi}\xi^p d\xi \tag{35}$$

is the incomplete Γ-function. The quotient $\Gamma_x(p+1)/\Gamma_\infty(p+1)=I(x,p)$ has been tabulated by Pearson.[11] It is always between zero and one and approaches unity as x increases, more slowly the larger the value of p. The higher multipole interactions are therefore reduced more by this correction. This is reasonable since these interactions received proportionately larger contributions from the region of configuration space where V' is divergent.

The new polarization force series resulting from the above steps is

$$\Delta E_{2,\Omega}=-\frac{1}{\epsilon R^2}\sum_{\lambda=1}^{\infty}\frac{(2\lambda+2)!}{2^{2\lambda+1}(2\lambda+1)}\frac{I(2R,2\lambda+2)}{R^{2\lambda}}. \tag{36}$$

This series is convergent for $R>0$. The Pauling energy plus the first two terms of $\Delta E_{2,\Omega}$ is tabulated in Table I. A marked improvement in the position of the minimum ($R\cong 2a$) and the depth of the minimum will be noticed, although the curve is still somewhat below that of Hylleraas. If only the first term of (36) is used in conjunction with the Pauling energy (Table I), a surprisingly accurate result is obtained, agreeing with the Hylleraas curve to within 5 percent everywhere around the minimum.

The conclusion to be drawn from these results is that the suggested procedure for removing the divergent behavior of the intermolecular force series greatly improves the quantitative accuracy of the perturbation method of estimating these forces. The uncorrected procedure makes increasingly larger errors in the higher multipole terms.

V. THE INTERACTION BETWEEN HELIUM ATOMS

The helium atom is structurally the simplest chemically saturated atom. The theory of Van der Waals forces thus meets its first important quantitative test in the case of the interaction between two helium atoms.[12]

A number of estimates of the dispersion force in the helium case have been made. Slater and Kirkwood[13] were the first to calculate the dipole-dipole component. They used a variational method. Margenau[2] subsequently recognized the importance of the higher multipole terms and employed second-order perturbation theory to compute the dipole-quadrupole and quadrupole-quadrupole interactions. A later re-examination of the problem by Margenau[14] resulted in the expression

$$E(R)=\{770e^{-4.60R}-560e^{-5.33R}-1.39R^{-6}-3.0R^{-8}\}\times 10^{-12}\text{ erg}. \tag{37}$$

(R in A.) The first term in (37) is the first-order exchange energy computed by Slater.[12] The second term is a small second-order exchange energy. The remaining terms are the dipole-dipole and dipole-quadrupole Van der Waals energies.

We propose to apply a correction of the type described in the preceding section to the Van der Waals force terms in (37).

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[11] K. Pearson, ed., *Tables of the Incomplete* Γ*-function* (H. M. Stationery Office, London, 1922). Pearson actually tabulates $I(u,p)$, where $u=x/(p+1)^{\frac{1}{2}}$.

[12] The problem is complicated by uncertainties affecting the repulsive exchange force. Slater's calculation [Phys. Rev. **32**, 349 (1928)], which uses very accurate state functions, has been regarded as the most satisfactory. N. Rosen [Phys. Rev. **38**, 255 (1931)] in a recomputation has found a weaker repulsive force. Recently, P. Rosen [J. Chem. Phys. **18**, 1182 (1950)] has arrived at a much stronger force than either of the above. The value of this latter work is in its retention of higher exchange integrals which Slater neglects. This advantage may, however, be offset by his use of poorer wave functions. The results of the present paper seem to show that Slater's potential, when modified in accordance with Eq. (37), is essentially correct.

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

[14] H. Margenau, Phys. Rev. **56**, 1000 (1939).

If orbitals of the Slater type

$$\psi_0=(Z/\pi a^3)^{\frac{1}{2}}e^{-Zr/a}, \quad Z=27/16=1.688, \tag{38}$$

are employed for each electron in the two helium atoms, a straightforward application of second-order perturbation theory in conjunction with (2) or (3) yields for the dipole-dipole and dipole-quadrupole energies, the expression:

$$\Delta E_2=-A(0|r^2|0)^2R^{-6}-B(0|r^2|0)(0|r^4|0)R^{-8}. \tag{39}$$

A and B are constants, as are

$$(0|r^2|0)=\int_0^\infty \psi_0{}^2 4\pi r^4 dr=1.05a^2 \tag{40}$$

and

$$(0|r^4|0)=\int_0^\infty \psi_0{}^2 4\pi r^6 dr=2.79a^2. \tag{41}$$

We choose this form for ΔE_2 because it expresses the approximate dependence of the Van der Waals energy on the matrix elements $(0|r^2|0)$ and $(0|r^4|0)$. The integrations involved in these matrix elements extend over all configuration space, and therefore necessarily involve regions in which the dipole-dipole and dipole-quadrupole terms of V' as given by (2) or (3) are incorrect. A minimum region Ω of this space in which V' is convergent and in which these terms are accurate is that where the r for each electron is allowed to range only from 0 to $R/2$.

Therefore in Eq. (39) we replace $(0|r^2|0)$ and $(0|r^4|0)$ by

$$(0|r^2|0)_\Omega=\int_0^{R/2} \psi_0{}^2 4\pi r^4 dr \tag{42}$$

and

$$(0|r^4|0)_\Omega=\int_0^{R/2} \psi_0{}^2 4\pi r^6 dr. \tag{43}$$

We then adjust the constants A and B so that as R approaches infinity, the resulting expression agrees with the Van der Waals terms in (37), which is presumed to be accurate for sufficiently large R.

TABLE II. Interaction between helium atoms. Equations (37) and (44). Energy in ergs, R in A.

R(A)	Equation (37) $\Delta E_2\times 10^{16}$	Equation (44) $\Delta E_{2,\Omega}\times 10^{16}$
2.5	$+7.74$	$+10.76$
2.6	-15.49	-3.37
2.7	-18.57	-10.60
2.8	-19.01	-13.76
2.9	-18.06	-14.57
3.0	-16.46	-14.13
3.2	...	-11.74
3.4	...	-9.07

The effect of this procedure is, as before, the introduction of incomplete Γ-functions and (39) becomes

$$\Delta E_{2,\Omega}=\{770e^{-4.60R}-560e^{-5.33R}-1.39R^{-6}[I(x,4)]^2 \\ -3.0R^{-8}[I(x,4)I(x,6)]\}\times 10^{-12}\text{ erg} \tag{44}$$

with $x=ZR/a=3.191R$(A).

Equation (44) is tabulated in Table II along with Eq. (37). The new curve has a minimum at $R=2.9$A and an energy of -14.6×10^{-16} erg or -9.11×10^{-4} ev. It is in close agreement with low temperature experimental data. Buckingham, Hamilton, and Massey,[15] working with low temperature data, find for the position of the minimum $R_0=2.93$A and for the depth $E_0=-14.2\times 10^{-16}$ erg. Kistemaker and Keesom[16] studying the isotherms of helium from 2.7 to 1.7°K find $-E_0R_0{}^2=120\times 10^{-32}$ erg-cm². Equation (44) yields $-E_0R_0{}^2=123\times 10^{-32}$ erg-cm².

On the other hand, Schneider and Yntema,[17] on the basis of high temperature second virial coefficient measurements (0–1200°C), have recently reported a very much weaker helium atom interaction energy. They find that the values $E_0\cong -11\times 10^{-16}$ erg and $R_0\cong 3$A best fit their experimental data.

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