TABLE II. Mean values of $T_{\frac{1}{2}}$ for $C^{14}$ as derived from four groups of mounts.

| Group | Sample | Description | $T_{\frac{1}{2}}$ |
|---|---|---|---|
| I | 3.35% $C^{14}$ | not repurified (mean result from 5 mounts) | 5000 yrs. |
| II | 3.35% $C^{14}$ | repurified (mean result from 6 mounts) | 5100 yrs. |
| III | 3.23% $C^{14}$ | repurified (mean result from 6 mounts) | 5200 yrs. |
| IV | 3.35% $C^{14}$ | repurified, mounted by technique Hendricks (mean result from 4 mounts) | 5100 yrs |

carbon by flaming and flushing with $CO_2$-free oxygen. The $C^{14}O_2$ was eluted with 1 N HCl, reprecipitated as the $BaC^{14}O_3$, and washed, dried, mounted, and counted in the standard fashion. The specific activity of the 3.35 percent sample remained unchanged, while that of the 3.23 percent sample increased into essential agreement. The results of the groups of samples, variously treated, are given in Table II in terms of the deduced half-life of $C^{14}$.

For the twenty-one individual mounts, the highest value for $T_{\frac{1}{2}}$ was 5500 years, and the lowest 4700 years. We conclude that the half-life of $C^{14}$ is $5100 \pm 200$ years; the indicated error is the probable error of the mean as obtained from the two analyzed samples, and includes the uncertainties in the solid angle and back-scatter determinations. This value is lower by 200 years than a preliminary value reported previously by the authors.[18]

## 9. ACKNOWLEDGMENTS

[18] L. D. Norris and M. G. Inghram, Phys. Rev. 70, 772 (1946).

# The Influence of Retardation on the London-van der Waals Forces

H. B. G. CASIMIR AND D. POLDER
*Natuurkundig Laboratorium der N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands*

The influence of retardation on the energy of interaction between two neutral atoms is investigated by means of quantum electrodynamics. As a preliminary step, Part I contains a discussion of the interaction between a neutral atom and a perfectly conducting plane, and it is found that the influence of retardation leads to a reduction of the interaction energy by a correction factor which decreases monotonically with increasing distance $R$. This factor is equal to unity for $R$ small compared with the wave-lengths corresponding to the atomic frequencies, and is proportional to $R^{-1}$ for distances large compared with these wave-lengths. In the latter case the total interaction energy is given by $-3\hbar c\alpha/8\pi R^4$, where $\alpha$ is the static polarizability of the atom. Although the problem of the interaction of two atoms discussed in Part II is much more difficult to handle mathematically, the results are very similar. Again the influence of retardation can be described by a monotonically decreasing correction factor which is equal to unity for small distances and proportional to $R^{-1}$ for large distances. In the latter case the energy of interaction is found to be $-23\hbar c\alpha_1\alpha_2/4\pi R^7$.

## PART I. GENERAL FEATURES OF THE PROBLEM

### 1. Introduction

THE problem treated in this paper, though apparently a somewhat academic exercise in quantum electrodynamics, arose directly from the work of Verwey and Overbeek[1] on the stability of colloidal systems. Starting from work of Hamaker, Verwey and Overbeek have in recent years developed a theory in which the attraction between colloidal particles is exclusively ascribed to London-van der Waals forces, the repulsion being accounted for by the interaction of electric double layers. In applying this

[1] E. J. W. Verwey, J. T. G. Overbeek, and K. van Nes, *Theory of the Stability of Lyophobic Colloids* (Elsevier Publishing Company, Inc., Amsterdam, in press); E. J. W. Verwey and J. T. G. Overbeek, Trans. Faraday Soc. (In press); E. J. W. Verwey, J. Phys. and Colloid Chem. 51, 631 (1947).

theory to suspensions of comparatively large particles, they found a discrepancy between their theory and the experimental results which could be removed only by assuming that at large distances the attractive force between two atoms decreases more rapidly than $R^{-7}$. Overbeek then pointed out that on the basis of the picture customarily used for visualizing London forces, an influence of retardation on the interaction is to be expected as soon as the distance between the particles becomes comparable to the wavelength corresponding to the atomic frequencies. Although this argument is suggestive, we have not succeeded in deriving an expression for the influence of retardation based on such a simple model, and we doubt very much whether a result can be obtained in that way. In this paper hardly any reference will be made to Overbeek's original considerations. Also, the application to the problems of colloid chemistry will not be touched upon but will be left for a future publication. We want, however, to emphasize our indebtedness to Overbeek's suggestion.

So far, problems of retardation have only occasionally been treated by means of quantum electrodynamics. There is, of course, the work of Møller[2] and its justification by Bethe and Fermi.[3] Also in the work of Breit[4] on the interaction of the electrons in the He atom, retardation is taken into account. In these cases, however, we have to deal with the influence of retardation on expressions containing the square of the electronic charge, which means that we can restrict ourselves to studying the interaction between electrons and the radiation field to a second approximation. In our case, which concerns the interaction between two neutral atoms, the approximation has to be pushed to the fourth order, as the usual expression for the London energy contains the fourth power of the electronic charge. We found, however, that what seemed to us the most essential features of the final result are already clearly revealed by a problem which can be treated by means of quite simple mathematics, involving only second-order perturbation theory, i.e., the interaction of a neutral

atom with a perfectly conducting wall. According to classical ideas the energy should always be given by the interaction of the atomic dipole with its image, and retardation effects are to be expected when its distance from the wall becomes large. The result of a direct calculation by means of quantum electrodynamics, which will be given in Section 12, is not in disagreement with this notion. Yet the final result is rather unexpected. For short distances we find the usual value for the London energy between a neutral atom and a conducting wall, which is proportional to $R^{-3}$. With increasing $R$, however, the usual value must be multiplied by a monotonically decreasing factor, and for large values of $R$ the London energy is found to be proportional to $R^{-4}$ rather than to $R^{-3}$. It is remarkable that the asymptotic expression for large $R$ contains Planck's constant and, in addition, the static polarizability of the atom as the only quantity characterizing the specific properties of the atom.

The calculations in Part II, dealing with the interaction of two neutral atoms, are much more complicated, but it is of interest to remark that here also the present-day formulation of quantum electrodynamics, if properly handled, is able to give an unambiguous result. For short distances the usual expression for the London energy, in this case being proportional to $R^{-6}$, is valid again, whereas for large distances the energy of interaction is proportional to $R^{-7}$. The asymptotic expression contains Planck's constant and the product of the polarizabilities of the two atoms.

## 2. Interaction of a Neutral Atom with a Perfectly Conducting Plane

Consider a region of space, defined by $0 < x < L$, $0 < y < L$, $0 < z < L$, enclosed in a box with perfectly conducting walls. The eigenstates of the electromagnetic field in this box are described by solutions of Maxwell's equations satisfying the boundary condition that the tangential components of $\mathbf{E}$, the electric field, vanish at the walls. These solutions are easily found to be

$$E_x(\mathbf{k}, \lambda) = e_x(\mathbf{k}, \lambda) \cos k_1 x \sin k_2 y \sin k_3 z \cdot C_e,$$

$$E_y(\mathbf{k}, \lambda) = e_y(\mathbf{k}, \lambda) \sin k_1 x \cos k_2 y \sin k_3 z \cdot C_e, \quad (1)$$

$$E_z(\mathbf{k}, \lambda) = e_z(\mathbf{k}, \lambda) \sin k_1 x \sin k_2 y \cos k_3 z \cdot C_e,$$

[2] C. Møller, Zeits. f. Physik **70**, 786 (1931).
[3] H. Bethe und E. Fermi, Zeits. f. Physik **77**, 296 (1932).
[4] G. Breit, Phys. Rev. **34**, 353 (1929); Phys. Rev. **36**, 383 (1930); Phys. Rev. **39**, 616 (1932).

where $\mathbf{k}$ is a wave vector with components $k_i = n_i\pi/L$, with $n_i = 0, 1, 2, 3\cdots$, and $\mathbf{e}$ is a unit vector perpendicular to $\mathbf{k}$. To each vector $\mathbf{k}$ belong two vectors $\mathbf{e}$, corresponding to the two directions of polarization; they are indicated by the symbol $\lambda$ ($\lambda = 1, 2$). The normalization factor $C_e$ is given by

$$C_e{}^2 = 16\pi\hbar c/kL^3. \qquad (2)$$

In order to verify that this is the correct normalization we write for the vector potential of the electromagnetic field in the box:

$$\mathbf{A} = \sum_{k,\lambda} (A_{k\lambda}e^{-i\omega t} + A_{k\lambda}{}^\dagger e^{i\omega t})\mathbf{E}(\mathbf{k},\lambda), \qquad (3)$$

and determine the energy $\epsilon$ of the field:

$$\epsilon = \frac{1}{8\pi}\int(E^2+H^2)dv = \frac{1}{4\pi}\int E^2 dv$$

$$= \frac{1}{4\pi}\frac{L^3}{8}\sum_{k,\lambda}\frac{16\pi\hbar c}{kL^3}k^2(A_{k\lambda}{}^\dagger A_{k\lambda}+A_{k\lambda}A_{k\lambda}{}^\dagger)$$

$$= \sum_{k,\lambda}\tfrac{1}{2}\hbar\omega(A_{k\lambda}{}^\dagger A_{k\lambda}+A_{k\lambda}A_{k\lambda}{}^\dagger). \qquad (4)$$

In quantum electrodynamics $A$ and $A^\dagger$ are operators satisfying:

$$A_{k\lambda}A_{l\mu}{}^\dagger - A_{l\mu}{}^\dagger A_{k\lambda} = \delta_{kl}\delta_{\mu\lambda}, \qquad (5)$$

and the eigenvalues of $A_{k\lambda}{}^\dagger A_{k\lambda}$ are $0, 1, 2\cdots$. In this way we have obtained the usual formulation of the quantization of the radiation field in an empty box.

We now consider the operator $G$ of the interaction between a neutral atom and the radiation field:

$$G = \sum_j \left\{ -\frac{e}{mc}(\mathbf{p}_j\mathbf{A}) + \frac{e^2}{2mc^2}A^2 \right\}, \qquad (6)$$

where the summation is over all electrons in the atom and $\mathbf{p}_j$ is the operator of the momentum of an electron. We determine the energy perturbation of the lowest level of the system consisting of the atom and the radiation field. Since $A$ has no diagonal elements, there is no first-order perturbation proportional to $e$. Therefore we use second-order perturbation theory for the terms with $e$ in $G$ and first-order perturbation theory for the terms with $e^2$. In the course of the following calculation we shall determine the

perturbation energies for the case in which the atom is situated at a very large distance from the walls of the box and for the case in which it is at a short distance from one of the walls. In both cases the result is given by a divergent series over the excited states of the atom, each term of which is a convergent sum over the excited states of the radiation field. The difference between the perturbation energies in both cases can be found without ambiguity and is finite; this difference will be interpreted as the energy of interaction between the atom and the wall so far as it is due to the interaction of the atom with the radiation field.

The second-order perturbation energy of the lowest level due to an operator $H$ is given by

$$\Delta_2 E = -\sum_g \frac{|H_{0g}|^2}{E_g - E_0}. \qquad (7)$$

In our system the excited states $g$ are labeled by the index $n$ for the states of the atom and by the indices $k$, $\lambda$ for the states of the radiation field in which one light quantum is present. The energy difference between the level $n$, $k$, $\lambda$ of our system and the lowest level is given by $\hbar c(k_n + k)$ and, therefore, the perturbation energy is

$$\Delta_2 E = -\frac{e^2}{m^2 c^2}\sum_{n,k,\lambda}\frac{|(\mathbf{A}_{0;k\lambda}\mathbf{p}_{0;n})|^2}{\hbar c(k_n+k)} \qquad (8)$$

(where $\mathbf{p} = \sum_j \mathbf{p}_j$), to which must be added the first-order perturbation due to terms with $e^2$, which according to the laws of matrix multiplication can be written as:

$$\Delta_1 E = \sum_j \frac{e^2}{2mc^2}\sum_{k,\lambda}\sum_{x,y,z}|A_{0;k\lambda}{}^x|^2. \qquad (9)$$

In writing these formulae we have made one approximation: we have neglected the variation of the electromagnetic field inside the atom. It is well known that due to this approximation the contribution to the second-order perturbation energy from one excited level of the atom already becomes infinite since the integral over $\mathbf{k}$ does not converge for $|k|\to\infty$. Instead of taking these effects into account rigorously we shall introduce a factor $e^{-\gamma k}$, which makes the integral convergent, and put $\gamma = 0$ in the final result. In reality it should be of the order of the radius of

the atom, but this does not appreciably affect the results.

In order to obtain a simple expression for $\Delta_r E = \Delta_2 E + \Delta_1 E$, we make use of the sum rule

$$\delta_{xy} \sum_j \frac{e^2}{2mc^2}$$

$$= \frac{e^2}{m^2 c^2} \sum_n \frac{\frac{1}{2}(p_0; {}_{n^x}p_n; {}_{0^y} + p_0; {}_{n^y}p_n; {}_{0^x})}{\hbar c k_n}, \quad (10)$$

and the relation $e p_{0; n} = -i m c k_n q_{0; n}$, where $q$ is the operator of the total dipole moment. We find for the total perturbation energy

$$\Delta_r E = \frac{1}{\hbar c} \sum_{n, k, \lambda} \frac{k k_n}{k + k_n} |(\mathbf{A}_{0; k\lambda}\mathbf{q}_{0; n})|^2. \quad (11)$$

In order to simplify the problem we assume the zero state of the atom to be a state with angular momentum $J = 0$, which means that matrix elements of $\mathbf{p}$ exist only between this state and the threefold degenerate states with $J = 1$. The three wave functions belonging to a state with $J = 1$ may be chosen without loss of generality in such a way that they have the same transformation properties under a rotation as $x$, $y$, and $z$. Then all cross products of the type $q_{0; n^x}q_{0; n^y}$ vanish and (11) can be written as:

$$\Delta_r E = \frac{1}{\hbar c} \sum_{n, k, \lambda} \frac{k k_n}{k + k_n} \sum_{x, y, z} |A_{0; k\lambda^x}|^2 |q_{0; n^x}|^2, \quad (12)$$

where $n$ denotes the states with $J = 1$. Substituting (3) and (1) in (12) we have

$$\Delta_r E = \frac{16\pi}{L^3} \sum_{n, k, \lambda} \frac{k_n}{k + k_n} \{ |q_{0; n^x}|^2 e_x^2(\mathbf{k}, \lambda) \cos^2 k_1 x \sin^2 k_2 y \sin^2 k_3 z$$

$$+ |q_{0; n^y}|^2 e_y^2(\mathbf{k}, \lambda) \sin^2 k_1 x \cos^2 k_2 y \sin^2 k_3 z + |q_{0; n^z}|^2 e_z^2(\mathbf{k}, \lambda) \sin^2 k_1 x \sin^2 k_2 y \cos^2 k_3 z \}. \quad (13)$$

In order to carry out the summation over $\lambda$ we use the relation

$$\sum_\lambda e_i^2(\mathbf{k}, \lambda) = 1 - k_i^2/k^2. \quad (14)$$

We assume that the box is very large and therefore the summation over all values of $\mathbf{k}$ can be replaced by an integral. Since the integrand is an even function of $k_i$, the summation is equal to $L^3/8\pi^3$ times a threefold integral from $-\infty$ to $+\infty$ over $k_1$, $k_2$ and $k_3$. At the same time we introduce the convergence factor $e^{-\gamma k}$. We obtain

$$\Delta_z E = \frac{2}{\pi^2} \int\int\int_{-\infty}^{+\infty} dk_1 dk_2 dk_3 \sum_n \frac{k_n e^{-\gamma k}}{k + k_n} \left\{ |q_{0; n^x}|^2 \left(1 - \frac{k_1^2}{k^2}\right) \cos^2 k_1 x \sin^2 k_2 y \sin^2 k_3 z \right.$$

$$\left. + |q_{0; n^y}|^2 \left(1 - \frac{k_2^2}{k^2}\right) \sin^2 k_1 x \cos^2 k_2 y \sin^2 k_3 z + |q_{0; n^z}|^2 \left(1 - \frac{k_3^2}{k^2}\right) \sin^2 k_1 x \sin^2 k_2 y \cos^2 k_3 z \right\}. \quad (15)$$

We assume that the distance of the atom from the walls $y = 0$ and $z = 0$ is very large so that the value of the integral does not change if we put $\sin^2 k_2 y$, $\cos^2 k_2 y$, $\sin^2 k_3 z$, and $\cos^2 k_3 z$ equal to $\frac{1}{2}$. When the distance from the wall $x = 0$ is also very large, the same may be done with $\sin^2 k_1 x$ and $\cos^2 k_1 x$. For the difference between the perturbation energies in the case in which the atom is situated at a distance $R$ from the wall $x = 0$ and in the case in which the atom is at a large distance, we find, therefore:

$$\Delta_d E = \frac{1}{4\pi^2} \sum_n \int\int\int_{-\infty}^{+\infty} dk_1 dk_2 dk_3 \frac{k_n e^{-\gamma k}}{k + k_n} \left\{ |q_{0; n^x}|^2 \left(1 - \frac{k_1^2}{k^2}\right)(2 \cos^2 k_1 R - 1) \right.$$

$$\left. + |q_{0; n^y}|^2 \left(1 - \frac{k_2^2}{k^2}\right)(2 \sin^2 k_1 R - 1) + |q_{0; n^z}|^2 \left(1 - \frac{k_3^2}{k^2}\right)(2 \sin^2 k_1 R - 1) \right\}. \quad (16)$$

Introducing polar coordinates in the **k** space we obtain:

$$\Delta_d E = \sum_n \int_0^\infty -dk \left[ \frac{e^{-\gamma k}}{2\pi i} \frac{k^2 k_n}{(k+k_n)} \left\{ |q_{0;\,n^x}|^2 \frac{e^{2ikR}}{2kR} \left( \frac{2i}{2kR} - \frac{2}{4k^2R^2} \right) \right.\right.$$

$$\left.\left. + (|q_{0;\,n^y}|^2 + |q_{0;\,n^z}|^2) \frac{e^{2ikR}}{2kR} \left( 1 + \frac{i}{2kR} - \frac{1}{4k^2R^2} \right) \right\} + \text{complex conjugate} \right]. \quad (17)$$

It is interesting to remark that the expression in { } suggests the existence of an interpretation of formula (17) on the basis of the correspondence principle. If multiplied by a factor $k^3$, the first term in the expression equals the energy of a complex dipole $q^x e^{-ikct}$ in the retarded electric field of a dipole $q^x e^{ikct}$ at a distance $2R$, and this second dipole might be interpreted as the "electrical image" of the complex conjugate of the first dipole, with regard to a perfectly conducting plane at a distance $R$ from the first dipole. A similar interpretation can be given to the second term in { }, but we have not been able to find a general consideration, based on the correspondence idea, by means of which at least the form of Eq. (17) could be foretold. In this connection we should like to point out that in dealing with the behavior of an atom in an excited state we usually meet with a factor $1/(k-k_n)$ instead of the factor $1/(k+k_n)$ occurring here, and the result is mainly determined by the residue at $k=k_n$ so that one definite frequency is singled out and an interpretation in terms of oscillators with well-determined frequencies becomes possible.

We now proceed with the calculation of the energy of interaction between an atom and a conducting wall by taking into consideration the electrostatic interaction. The electrostatic energy between a dipole $q^x$ at $x=R$ and a conducting wall at $x=0$ is

$$\epsilon_x^e = -(q^x)^2/8R^3. \quad (18)$$

For a dipole $q^y$ or $q^z$ the energy is:

$$\epsilon_{y,z}^e = -(q^{y,z})^2/16R^3. \quad (19)$$

The first-order perturbation energy of the lowest level of our system due to the electrostatic terms is:

$$\Delta_e E = -\left[ \frac{2((q^x)^2)_{00} + ((q^y)^2 + (q^z)^2)_{00}}{16R^3} \right]$$

$$= -\frac{\sum_n (2|q_{0;\,n^x}|^2 + |q_{0;\,n^y}|^2 + |q_{0;\,n^z}|^2)}{16R^3}. \quad (20)$$

The total interaction energy between the atom and the wall is

$$\Delta_t E = \Delta_d E + \Delta_e E. \quad (21)$$

A closer examination of $\Delta_d E$ shows that the integrand in (17) remains finite at $k=0$, but that both the term within [ ] that is completely written out and its complex conjugate have a simple pole. We shall integrate each of these terms separately from $\epsilon$ to $\infty$ and let $\epsilon$ tend to zero afterwards. We now want to replace the integration along the real axis by the integration along path 1 in Fig. 1 for the first integral and along path 2 for the second. In the limit $\epsilon \to 0$, we easily find for the integration on the semicircle:

$$\frac{1}{16R^3} \sum_n (2|q_{0,\,n^x}|^2 + |q_{0;\,n^y}|^2 + |q_{0;\,n^x}|^2),$$

which exactly cancels the term $\Delta_e E$ in $\Delta_t E$. Introducing the variable $u=-ik$ for the integration from $i\epsilon$ to $i\infty$ and $u=ik$ for the integration from $-i\epsilon$ to $-i\infty$, we find

$$\Delta_t E = -\frac{1}{\pi} \sum_n \int_0^\infty \frac{k_n u^2 du}{u^2 + k_n^2} \frac{e^{-2uR}}{2R}$$

$$\times \left\{ 2|q_{0;\,n^x}|^2 \left( \frac{1}{2uR} + \frac{1}{4u^2R^2} \right) \right.$$

$$\left. + (|q_{0;\,n^y}|^2 + |q_{0;\,n^x}|^2) \left( 1 + \frac{1}{2uR} + \frac{1}{4u^2R^2} \right) \right\}. \quad (22)$$

In the limit of very small distances $R$, it is

easily found that the formula reduces to

$$\Delta_t E(R \to 0)$$

$$= -\frac{1}{16R^3} \sum_n (2|q_{0;\,n^x}|^2 + |q_{0;\,n^y}|^2 + |q_{0;\,n^z}|^2), \quad (23)$$

being equal to the value of the London energy, derived by the elementary theory which takes into account the electrostatic interaction only. For very large $R$ ($R$ larger than all $\lambda_n = 2\pi/k_n$) it is immediately seen that (22) reduces to

$$\Delta_t E(R \to \infty)$$

$$= -\sum_n \frac{(|q_{0;\,n^x}|^2 + |q_{0;\,n^y}|^2 + |q_{0;\,n^z}|^2)}{4\pi k_n R^4}, \quad (24)$$

which can be written in terms of the static polarizability $\alpha$ of the atom:

$$\Delta_t E(R \to \infty) = -\frac{\hbar c}{8\pi R^4}(\alpha_x + \alpha_y + \alpha_z). \quad (25)$$

Because we wanted to see more clearly the role of the $x$, $y$, and $z$ dipoles individually, we have not yet used the relation

$$\sum |q_{0;\,n^x}|^2 = \sum |q_{0;\,n^y}|^2 = \sum |q_{0;\,n^z}|^2 = |q_{0;\,n}|^2, \quad (26)$$

where the summation extends over the three states with $J = 1$, belonging to one degenerate level, which will be indicated from now by one symbol $n$. With the aid of this relation, Eq. (22) may be written as

$$\Delta_t E = -\frac{2}{\pi} \sum_n \int_0^\infty \frac{k_n u^3 du}{u^2 + k_n^2} \frac{e^{-2uR}}{2R}$$

$$\times |q_{0;\,n}|^2 \left(1 + \frac{2}{2uR} + \frac{2}{4u^2R^2}\right), \quad (27)$$

where each term of the sum over $n$ represents the contribution of all three states with $J = 1$ belonging to one degenerate level. In Fig. 2 we have given the result of a numerical calculation of the factor $\Delta_t E/\Delta_e E$ for the case in which only one excited level $n$ (with $E_n = hc/\lambda_n$) gives a contribution to the London energy. It is seen that the value of the factor decreases monotonically with increasing $R$. It starts with the value 1 (for $R \to 0$), while for large $R$ it is approximately equal to $3\lambda_n/2\pi^2 R$.

## PART II. THE INTERACTION BETWEEN TWO ATOMS

### 1. Outline of Method

The energy of interaction between two neutral atoms will be determined by solving the following perturbation problem. The unperturbed states of the system, consisting of two atoms and the radiation field, will be assumed to be the states which are completely defined by the indication of the states of the two atoms and the state of the radiation field in empty space.

The perturbation operator, which is responsible for the interaction of the two atoms, contains the electrostatic interaction $Q$ between the charged particles of the first atom with those of the second atom, the interaction $G_A$ between the first atom and the radiation field, and the interaction $G_B$ between the second atom and the radiation field.

With the aid of the perturbation operator $G_A + G_B + Q$ we shall determine the energy perturbation; we have already remarked in Part I that the approximation has to be pushed to the fourth power of the electronic charge $e$. For this purpose we shall apply first-, second-, third-, and fourth-order perturbation theory. By the order of the perturbation theory we mean the degree in which the perturbation operator occurs in the expression for the energy perturbation. It does not indicate the power of the electronic charge occurring in this expression, as the perturbation operator contains terms with $e$ as well as with $e^2$. The total result of the calculation will be divergent, but, as in Part I, we shall find a finite value for those terms that depend on the distance $R$ between the two atoms; this value will be interpreted again as the total energy of interaction between the atoms.

In order to carry out the perturbation procedure we shall have to examine carefully the matrix elements occurring in the expression for the first-, second-, third-, and fourth-order perturbation in the energy. The examination does not give rise to special difficulties and, therefore, we shall only mention the results. Restricting outselves to those terms in the energy perturbation which depend on $R$ and which are proportional to $e^m$, with $m \leqslant 4$, we find that in our problem there is no first-order perturbation in

the energy. Further, matrix elements of $Q$ occur only in the expression for the second-order perturbation in the energy, namely, as the products of two matrix elements of $Q$, and in the third-order perturbation in the energy, namely, as the products of one matrix element of $Q$, one matrix element of $G_A$, and one matrix element of $G_B$. All the other terms in the energy perturbations do not involve $Q$.

We have thus to deal with the following terms:

(a) Terms obtained by applying second-order perturbation theory with the electrostatic interaction, which itself is proportional to $e^2$. The result is proportional to $e^4$ and is equal to the usual expression for the London energy.

(b) Terms obtained by applying third-order perturbation theory, restricting ourselves to the terms involving $Q$. We shall carry out the perturbation procedure in a somewhat unconventional way by successively applying first-order perturbation theory for the electrostatic interaction and second-order perturbation theory for the interaction with the radiation field: We calculate to the first order of the perturbation (which is an approximation proportional to $e^2$) the wave functions of the two atoms coupled by electrostatic interaction, and we then proceed to calculate, in exactly the same way as in the first part of this paper, the second-order interaction energy of this compound system with the radiation field. Again the result is proportional to $e^4$.

(c) Terms obtained by determining the energy perturbation with the aid of the operator $G_A + G_B$, the electrostatic interaction now being omitted. Again we shall solve this perturbation problem in a somewhat unconventional way: We first calculate in the usual way the second-order



Fig. 1. Path of integration for the integral in (17).

interaction energy of the atom $A$ with a radiation field. In this way we obtain also the interaction between the two atoms if for the vector-potential we do not use the matrix representations corresponding to the electromagnetic field in empty space, but the matrices corresponding to a regular solution for the system, consisting of atom $B$ and the radiation field. It is obviously sufficient to know these matrix elements of the vector potential correctly to the order of approximation $e^2$. The vector potential satisfies Maxwell's equations also in quantum electrodynamics and the terms with $e^2$ in the vector potential can be derived, therefore, by means of classical formulae from the expression for the current involving first powers of $e$. This method is often referred to as Heisenberg's method.[5] The resulting energy perturbation is again proportional to $e^4$.

It may be remarked that the terms (b) and (c) can also be calculated by systematically writing down all the products of matrix elements occurring in the expressions for the second-, third-, and fourth-order perturbation in the energy. We have carried out this systematic calculation and found the result to be in agreement with the results derived in this paper.

In the following sections we shall first restate briefly the field theory and verify Heisenberg's method for the case of a single atom. This will also teach us in which way the singularities in the solution of the perturbation equations are to be avoided. In a subsequent section (Section 4) we calculate the terms mentioned under (a) and (b). The terms under (c) will be determined in Section 5, and the final result is discussed in Section 6.

Since the perturbation procedure involves a number of rather lengthy calculations, we do not want to go into the details but shall only mention the most important steps and give the results.

## 2. The Radiation Field

We want to carry out the quantization of the radiation field by means of traveling waves, from which we demand periodicity in the $x$, $y$, and $z$ directions with a period $L$. Using the
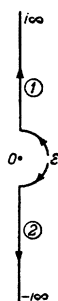
[5] W. Heisenberg, Ann. d. Physik (5) 9, 338 (1931).

notation of Section 12, we write for the vector potential

$$\mathbf{A} = \sum_{k, \lambda} cC_k \mathbf{e}(\mathbf{k}, \lambda)$$

$$\times \{A_{k, \lambda} e^{-i(\omega t - \mathbf{k} \mathbf{r})} + A_{k, \lambda}^{\dagger} e^{i(\omega t - \mathbf{k} \mathbf{r})}\}, \quad (28)$$

where the values of the components of the wave vector $\mathbf{k}$ are restricted to $k_i = 2\pi n_i / L$; with $n_i = 0$, $\pm 1$, $\pm 2$, $\cdots$. For some details of the calculations of the following sections it is suitable to assume $\mathbf{e}(\mathbf{k}, \lambda) = \mathbf{e}(-\mathbf{k}, \lambda)$. The value of the normalization factor $C_k$,

$$C_k = (2\pi\hbar/\omega L^3)^{\frac{1}{2}}, \quad (29)$$

can easily be verified by determining the energy of the field. In the following work we only need the matrix element of $A$ or $A\dagger$ between the zero state of the field, $\psi(0, 0\cdots)$, and the state in which one light quantum is present, $\psi(0, 0\cdots 1_{k\lambda} \cdots)$:

$$\int \psi^*(0, 0\cdots)A_{k\lambda}\psi(0, 0\cdot 1_{k\lambda}\cdot) = 1. \quad (30)$$

We shall always assume that $L$ is very large so that a summation over all values of $\mathbf{k}$ can be replaced by $L^3/8\pi^3$ times an integration over all values of $\mathbf{k}$.

We want to remark that the vector potential $\mathbf{A}$ satisfies $\mathrm{div}\mathbf{A} = 0$. For the interest of the next section we now write down the classical expression for the retarded vector potential satisfying the same condition and belonging to a periodic current $I = I_0 \exp(ikct)$ inside an atom. Neglecting the dimensions of the atom as being small in comparison with $R$, it is easy to derive from Maxwell's equations that

$$A_z^{(\mathrm{ret})} = \frac{I_z}{c}\left[\frac{e^{-ikR}}{R}\left(-\frac{2}{ikR} + \frac{2}{k^2R^2}\right) - \frac{2}{k^2R^3}\right],$$

$$(31)$$

$$A_{x,y}^{(\mathrm{ret})} = \frac{I_{x,y}}{c}\left[\frac{e^{-ikR}}{R}\left(1 + \frac{1}{ikR} - \frac{1}{k^2R^2}\right) + \frac{1}{k^2R^3}\right],$$

where for the sake of simplicity, we assumed $\mathbf{R}$ to point in the direction of the positive $z$ axis. We shall use this formula also in Section 5.

## 3. Heisenberg's Method

The fundamental idea of Heisenberg's method is that even when the quantities of the electromagnetic field are considered as matrices, they satisfy Maxwell's equations. When we regard the elementary charge, $e$, as the perturbation parameter in the perturbation problem arising from the interaction, $G$, of the charged particles with the radiation field, it follows that, in order to determine the matrix elements of a field quantity to the order of approximation $e^a$, it is sufficient to know the matrix elements of the electric current to the order $e^{a-1}$.* In this section we shall give an illustration of Heisenberg's method by discussing the matrix element of the vector potential $(m; 00\cdots |A| 0; 000\cdots)$ when one neutral atom is present in the radiation field. In the notation of the two states the first number indicates the level of the atom and the following numbers denote the number of quanta with different $(\mathbf{k}\lambda)$ in the radiation field. We shall first give a direct calculation of the matrix element in first approximation, and afterwards we shall verify that the result can be obtained with the aid of Maxwell's equations from the matrix element of the current in the zero approximation.

In the following calculation we assume that the atom is situated at $x = y = z = 0$. The dimensions of the atom are assumed to be very small in comparison with the distance $R$ at which we want to know the vector potential. We also neglect the variation of the electromagnetic field within the atom. The last approximation gives rise to divergencies of the type discussed in Section 12, but they can always be removed by introducing a factor $\exp(-\gamma|k|)$.

With the use of $G$ as perturbation operator, we find for the first approximation of the zero state $\psi(0; 00\cdots)$ of our system, consisting of the atom and the radiation field:

$$\psi'(0; 0\cdots) = \psi(0; 0\cdots)$$

$$+ \sum_{n, k, \lambda} \frac{eC_k}{m\hbar c} \frac{(\mathbf{e}(\mathbf{k}, \lambda)\mathbf{p}_{n; 0})}{k_n + k}\psi(n; 0\cdots 1_{k\lambda}\cdots), \quad (32)$$

---

* *Note added in proof.* This statement may be misleading. What is meant is, that since the current operator always contains one factor $e$ explicitly, the matrix element multiplying this factor has only to be known to the order $e^{a-1}$.

and for the excited states we are interested in:

$$\psi'(n; 00\cdots) = \psi(n; 00\cdots)$$

$$+\sum_{k,\lambda} \frac{eC_k}{m\hbar c} \frac{(\mathbf{e}(k,\lambda)\mathbf{p}_{0;\,n})}{k-k_n}\psi(0;0\cdots 1_{k\lambda})+\cdots, \quad (33)$$

$$\psi'(0; 0\cdots 1_{k\lambda}\cdots) = \psi(0; 0\cdots 1_{k\lambda}\cdots)$$

$$+\sum_{n} \frac{eC_k}{m\hbar c} \frac{(\mathbf{e}(\mathbf{k},\lambda)\mathbf{p}_{n;\,0})}{k_n-k}\psi(n; 00\cdots)+\cdots. \quad (34)$$

In the last two formulae we have omitted a number of terms which we shall not need in the following calculations. The matrix element of the vector potential $\mathbf{A}$ in first approximation is now easily found with the aid of (32) and (33).

$$(m; 0\cdots|\mathbf{A}|0; 0\cdots) = \sum_{k,\lambda} \frac{eC_k^2}{m\hbar}\mathbf{e}(\mathbf{k},\lambda)(\mathbf{e}(\mathbf{k},\lambda)\mathbf{p}_{m;\,0})$$

$$\times\left\{\frac{e^{i\mathbf{k}\mathbf{r}}}{k_m+k}-\frac{e^{-i\mathbf{k}\mathbf{r}}}{k_m-k}\right\}. \quad (35)$$

After a small calculation we find for the $z$ component of $\mathbf{A}$ at the point $\mathbf{r}$, given by $x=y=0$, $z=R$:

$$(m; 0\cdots|A_z|0; 0\cdots) = -\frac{ep_{m;\,0}^{(z)}}{2\pi mc}$$

$$\times\int_{-\infty}^{+\infty} \frac{dk}{k_m-k}\left\{\frac{e^{ikR}}{iR}\left(-\frac{2i}{kR}+\frac{2}{k^2R^2}\right)\right.$$

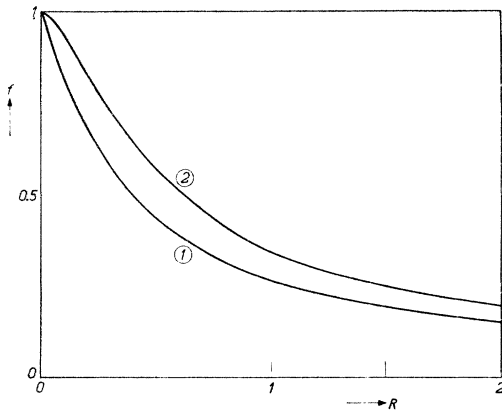$$+\text{complex conjugate}\left.\right\}\exp(-\gamma|k|), \quad (36)$$

Fig. 2. Correction factor due to retardation for the contribution of one excited state to the usual London energy. (1) For the interaction between a neutral atom and a metallic wall. $R$ is measured in units $\frac{1}{2}\lambda_n$. (2) For the interaction between two neutral atoms. $R$ is measured in units $\lambda_l$.



Fig. 3. Path of integration for the integral in (36).

in which formula we have introduced again the factor $\exp(-\gamma|k|)$.

The integrand is regular at $k=0$, but has a simple pole at $k=k_m$. In order to see in which way this singularity must be avoided, we remark that finally we want to obtain a retarded expression for the vector potential, i.e., an expression in which the terms with $\exp(ikR)$ do not occur. (The time factor of our matrix element is $\exp(ik_mct)$, thus retarded expressions will contain a factor $\exp(-ik_mR)$.) For this purpose we write $k_m-i\zeta-k$ instead of $k_m-k$ in the denominator, by means of which the singularity is now fixed at a small distance $\zeta$ below the real axis of the complex $k$ plane. It will turn out that this procedure gives the desired retarded expression in the final result. For the integration from $-\infty$ to $+\infty$ we take the path illustrated in Fig. 3. We carry out the integration of the terms with $\exp(ikR)$ and $\exp(-ikR)$ separately. The integral of the terms first mentioned can be replaced by an integral over a closed contour with the aid of a large semicircle above the real axis, and since there are no singularities within this contour, the value of the integral is zero. The integral with the other terms can be replaced by an integral over a closed contour with the aid of a large semicircle below the real axis. Within this contour there are two singularities for the terms with $\exp(-ikR)$, one at $k=k_m-i\zeta$ and one at $k=0$. The residues at these points determine the value of the integral, which is now easily found to be

$$(m; 0\cdots|A_z|0; 0\cdots) =$$

$$\frac{ep_{m;\,0}^z}{mc}\left[\frac{e^{-ik_mR}}{R}\left(-\frac{2}{ik_mR}+\frac{2}{k_m^2R^2}\right)-\frac{2}{k_m^2R^3}\right]. \quad (37)$$

With the foregoing calculation we have obtained the matrix elements of the vector potential in first approximation. The operation of the current is given by

$$I=\sum_i \frac{e}{m}\left(\mathbf{p}_j-\frac{e}{c}\mathbf{A}\right),$$

and, therefore, $e p_{m;0}{}^i/m$ are the corresponding matrix elements of the current in the zero approximation. It is seen, by comparing (37) with (31), that the matrix elements of the vector potential in first approximation could have been obtained immediately from the matrix elements of the current in the zero approximation.

In Section II2 we have explicitly restricted ourselves to retarded solutions of Maxwell's equations. The restriction to retarded solutions is also implied in the calculation of this section, namely, by the way in which the singularity at $k = k_m$ is avoided. It was found to be adequate to write $k_m - i\zeta$ instead of $k_m$ in the denominator of (36), and as the complex conjugate of the function $\psi(m; 00\cdots)$ occurred in the matrix element of the vector potential, we have to write $k_n + i\zeta$ instead of $k_n$ in the denominator of (33) in order to stay in the domain of retarded expressions.

In the course of the following sections we shall also use Eq. (34), and we shall have to determine in which way singularities arising form the denominator in (34) must be avoided. Remarking that the perturbed eigenfunctions can be obtained from the unperturbed functions by means of a unitary transformation, we conclude that in (34) $k_n$ must be replaced by $k_n - i\zeta$.

## 4. Perturbation Terms Involving Electrostatic Interaction

The electrostatic interaction between two neutral atoms $A$ and $B$ is given by

$$Q = \frac{q_A q_B}{R^3} - \frac{3(q_A R)(q_B R)}{R^5}, \tag{38}$$

when we neglect higher powers of the ratio between the atomic dimensions and **R**. We shall assume at once that the vector **R**, pointing

from atom $B$ to atom $A$, is in the direction of the positive $z$ axis and that atom $B$ is situated at $x = y = z = 0$. Further, we shall assume, as in Section 12, that each of the two atoms has a state with $J = 0$ as zero state. The second-order perturbation energy is now easily found to be

$$\Delta_q E =$$
$$- \frac{1}{R^6} \sum_{l,m} \frac{(q_l{}^x q_m{}^x)^2 + (q_l{}^y q_m{}^y)^2 + 4(q_l{}^z q_m{}^z)^2}{\hbar c(k_l + k_m)}. \tag{39}$$

In this notation the indices $l$ and $m$ denote the states with $J = 1$ of the atoms $A$ and $B$, respectively; $q_l{}^i$ is the matrix element of the total dipole moment between the zero state of atom $A$ and the state $l$ of this atom. The matrix elements are assumed to be real, which can be done without loss of generality. It is obvious that the symbols $A$ and $B$ can be omitted in this notation without giving rise to confusion. As in Section 12, we do not yet use relation (26). The expression (39), being the usual London energy between two neutral atoms, gives the terms mentioned under (a) in Section II1.

The calculation of the terms mentioned under (b) proceeds along the lines indicated in the outline of method. In the calculation we restrict ourselves to the terms which give a contribution proportional to the fourth power, or to a smaller power, of the electronic charge to the final result. The result will be divergent, but we determine the difference between the energy perturbation in the case of a distance $R$ between the two atoms and the case of a very large distance; this difference will be finite.

The calculations are rather elaborate but do not give rise to special difficulties. Taking into consideration that for the zero states of the atoms $I = 0$, we find finally:

$$\Delta_3 E = + \frac{2}{R^6} \frac{(q_l{}^x q_m{}^x)^2 + (q_l{}^y q_m{}^y)^2 + 4(q_l{}^z q_m{}^z)^2}{\hbar c(k_l + k_m)} - \frac{4}{\pi \hbar c R^4} \sum_{l,m} \int_0^\infty \frac{k_l k_m u^2 du}{(k_l{}^2 + u^2)(k_m{}^2 + u^2)}$$

$$\times \left\{ ((q_l{}^x q_m{}^x)^2 + (q_l{}^y q_m{}^y)^2) e^{-uR} \left( 1 + \frac{1}{uR} + \frac{1}{u^2 R^2} \right) + 4(q_l{}^z q_m{}^z)^2 e^{-uR} \left( \frac{1}{uR} + \frac{1}{u^2 R^2} \right) \right\}. \tag{40}$$

In the course of the calculations the two terms in (40) were obtained by means of the same procedure of complex integration as was applied to Eq. (17) in Section 12.

## 5. The Terms Not Involving the Electrostatic Interaction

So far we have carried out our perturbation procedures in an entirely symmetrical way with respect to the atoms $A$ and $B$. In this section it is our aim to determine the terms mentioned under (c) in the outline of method. We have to solve a perturbation problem in which $G_A + G_B = G$ is the perturbation operator:

$$G = \sum_{i_A} \left\{ -\frac{e}{mc}(\mathbf{p}_{iA}\mathbf{A}_A) + \frac{e^2}{2mc^2}A_A{}^2 \right\}$$
$$+ \sum_{i_B} \left\{ -\frac{e}{mc}(\mathbf{p}_{jB}\mathbf{A}_B) + \frac{e^2}{2mc^2}A_B{}^2 \right\}. \quad (41)$$

Now we have to take recourse to an unsymmetrical attack on the situation. The reason is the following. We have already remarked several times that, in consequence of the form of the operator of the interaction between the charged particles and the radiation field, there is no first-order perturbation between an atom and the electromagnetic field that is proportional to $e$. The terms in $G$ that are proportional to $e$ only give rise to a second-order perturbation, while the terms with $e^2$ are responsible for the first-order perturbation. As we are interested only in terms with $e^4$ in the final expression for the energy perturbation, we now have the opportunity to solve our perturbation problem in two steps. First, we calculate the vector potential to the order of approximation $e^2$ in the system consisting of atom $B$+radiation field, and then proceed to determine the first- and second-order perturbation energy of the atom $A$ in this perturbed electromagnetic field. This procedure is necessarily unsymmetric in the atoms $A$ and $B$, but in the final stage of the calculation the asymmetry vanishes, as must be the case for any consistent treatment of our problem.

We label the states of the system ($B$+radiation field) with the index $N$. The energy perturbation of the atom $A$ in the electromagnetic field of this system is now given by

$$\Delta_4 E = \frac{1}{\hbar c} \sum_{l, N} \frac{k_N k_l}{k_N + k_l} \sum_{x, y, z} |A_{0; N}{}^x(A)|^2 |q_{0; i}{}^x|^2. \quad (42)$$

Here we have at once combined the first-order

and the second-order perturbation in the same way as was done in Section 12. The index $l$ denotes the states with $J = 1$ of the atom $A$.

We want to know $|A_{0; N}{}^x|^2$ to the order of approximation $e^2$. There are two possibilities: either the matrix element $A_{N; 0}{}^i$ vanishes in zeroth approximation, i.e., terms not containing the factor $e$ do not occur in the matrix element, or the matrix element does not vanish in zeroth approximation. In the first case, we only need to know the matrix element to the order of approximation $e$. Matrix elements of this type that do not vanish in this approximation, are found only if the state $N$ is one of the states with wave functions $\psi'(m; 0, 0 \cdots)$. This statement immediately follows from Heisenberg's method, discussed in Section 3. In that section the matrix element $(m; 00 | A_i | 0; 00 \cdots)$ has already been calculated, so that we can at once write down the contribution to (42) from this special series of states $N$:

$$\Delta_a E = \frac{1}{\hbar c R^2} \sum_{l, m} \frac{k_m{}^3 k_l}{k_m + k_l}(q_l{}^x q_m{}^x)^2$$

$$\times \left\{ \left(1 - \frac{1}{k_m{}^2 R^2} + \frac{2}{k_m{}^4 R^4}\right) \right.$$

$$+ \left[\frac{e^{ik_m R}}{k_m{}^2 R^2}\left(1 + \frac{i}{k_m R} - \frac{1}{k_m{}^2 R^2}\right)\right.$$

$$\left.\left. + \text{complex conjugate}\right]\right\}. \quad (43)$$

In order to simplify the formula we have not written down terms proportional to $(q_l{}^y q_m{}^y)^2$ and $(q_l{}^z q_m{}^z)^2$. We shall omit these terms in all formulas of this section. In the second case, where the matrix element of the vector potential contains terms independent of $e$, we must know the vector potential to the order of approximation $e^2$. This case is realized only if the state $N$ is of the type $\psi'(0; 00 \cdots 1_{k\lambda} \cdots)$. By Heisenberg's method it is easily seen that the corresponding matrix element of the vector potential contains no terms proportional to $e$, so that we can write

$$(0; 0 \cdots 1_{k\lambda} \cdots | A_i | 0; 0 \cdots 0 \cdots)$$

$$= A_{k\lambda; 0}{}^{(0) i} + A_{k\lambda; 0}{}^{(2) i}. \quad (44)$$

When we insert these matrix elements in (42), we shall have to deal only with the cross products:

$$A_{0;\,k\lambda}{}^{(0)i}A_{k\lambda;\,0}{}^{(2)i}+A_{0;\,k\lambda}{}^{(2)i}A_{k\lambda;\,0}{}^{(0)i},$$

the other products being either independent of $R$ or proportional to a too high power of $e$.

The vector potential in second approximation is calculated by means of Heisenberg's method with the aid of the current in first approximation:

$$I_{k\lambda;\,0}{}^i = \int \psi'^*(0;0\cdots1_{k\lambda}\cdots)$$

$$\times\left\{\sum_{jB}\frac{e}{m}\left(p_{jB}{}^i-\frac{e}{c}A_B{}^i\right)\right\}\psi'(0;0\cdots).\quad(45)$$

Here we use the wave functions given by (32) and (34), introducing at once the term $i\zeta$ in the denominator of (34). Collecting the terms with $e^2$ in (45) we find

$$I_{k\lambda;\,0}{}^i = \sum_m \frac{e^2 C_k}{m^2\hbar c}|p_{m;\,0}{}^i|^2 e_i(k\lambda)$$

$$\times\left(\frac{1}{k_m-k+i\zeta}+\frac{1}{k_m+k}\right)-\sum_{jB}\frac{e^2 C_k}{m}e_i(k\lambda),\quad(46)$$

and with the aid of (31) we find the matrix element $A_{k\lambda;\,0}{}^{(2)i}(A)$. The matrix element $A_{k\lambda;\,0}{}^{0i}$ is simply

$$A_{k\lambda;\,0}{}^{0i}(A) = cC_k e_i(k\lambda)e^{-ik_z R}.\quad(47)$$

Applying the sum rule (10) to the last term in (46), we can now calculate the contribution to (42) arising from the states $\psi'(0;0\cdots1_{k\lambda}\cdots)$.

The calculation leads to a rather complicated integral over $k$, and the integrand requires a careful examination at the points $k=0$ and $k=k_m$ before the integral can be evaluated by means of complex integration. The way in which the singularity at $k=k_m$ must be avoided is prescribed unambiguously, however, by a term $i\zeta$ occurring in a denominator which originates from the corresponding denominator with the term $i\zeta$ in Eq. (46). Therefore, a straightforward evaluation of the integral is possible. We find finally:

$$\Delta_\beta E = \sum(q_l{}^x q_m{}^x)^2(B_1+B_2+B_3),\quad(48)$$

where

$$B_1 = -\frac{1}{\hbar cR^2}\left[\frac{1}{k_m R^4}+\frac{k_m{}^3 k_l}{k_m+k_l}\left(1-\frac{1}{k_m{}^2 R^2}+\frac{1}{k_m{}^4 R^4}\right)\right],$$

$$B_2 = -\frac{1}{\hbar cR^4}e^{ik_m R}\left(1+\frac{i}{k_m R}-\frac{1}{k_m{}^2 R^2}\right)\frac{k_m k_l}{k_m+k_l}$$

$$+\text{complex conjugate},$$

$$B_3 = \frac{4}{\pi\hbar c}\int_0^\infty \frac{k_l k_m u^2 du}{(k_l{}^2+u^2)(k_m{}^2+u^2)}$$

$$\times\frac{e^{-uR}}{R^4}\left(1+\frac{1}{uR}+\frac{1}{u^2 R^2}\right)$$

$$-\frac{2}{\pi\hbar c}\int_0^\infty \frac{k_l k_m u^4 du}{(k_l{}^2+u^2)(k_m{}^2+u^2)}$$

$$\times\frac{e^{-2uR}}{R^2}\left(1+\frac{1}{uR}+\frac{1}{u^2 R^2}\right)^2.$$

## 6. Result and Discussion

We have now calculated all the terms that contribute to the energy of interaction $\Delta_L E$ of two neutral atoms in $S$ states:

$$\Delta_L E = \Delta_q E+\Delta_3 E+\Delta_\alpha E+\Delta_\beta E.\quad(49)$$

Fortunately a number of terms cancel, and the final result is comparatively simple. It may be remarked that this result has regained symmetry with respect to the atoms $A$ and $B$. Adding at once the terms proportional to $(q_l{}^y q_m{}^y)^2$ and $(q_l{}^z q_m{}^z)^2$ we find:

$$\Delta_L E = -\frac{2}{\pi\hbar c}\sum_{l,m}\int_0^\infty \frac{k_l k_m u^4 du}{(k_l{}^2+u^2)(k_m{}^2+u^2)}\frac{e^{-2uR}}{R^2}$$

$$\times\left\{((q_l{}^x q_m{}^x)^2+(q_l{}^y q_m{}^y)^2)\left(1+\frac{1}{uR}+\frac{1}{u^2 R^2}\right)^2\right.$$

$$\left.+4(q_l{}^z q_m{}^z)^2\left(\frac{1}{uR}+\frac{1}{u^2 R^2}\right)^2\right\}.\quad(50)$$

In the limit of a very small distance $R$, $R\ll\lambda_l = 2\pi/k_l$, $R\ll\lambda_m$ it is easily found that the formula reduces to:

$$\Delta_L E(R\to 0)$$

$$= -\frac{1}{R^6}\sum_{l,m}\frac{(q_l{}^x q_m{}^x)^2+(q_l{}^y q_m{}^y)^2+4(q_l{}^z q_m{}^z)^2}{\hbar c(k_l+k_m)},\quad(51)$$

being equal to the value of the London energy as derived by the elementary theory, which takes into account the electrostatic interaction only. For very large $R$ ($R$ larger than all $\lambda_l$ and $\lambda_m$) it is found, after a short calculation, that (50) reduces to:

$$\Delta_L E(R \to \infty) = -\frac{1}{2\pi \hbar c R^7}$$

$$\times \sum_{l,m} \frac{13[(q_l{}^x q_m{}^x)^2 + (q_l{}^y q_m{}^y)^2] + 20(q_l{}^z q_m{}^z)^2}{k_l k_m}, \quad (52)$$

which can be written in terms of the static polarizability of the atoms:

$$\Delta_L E(R \to \infty) = -\frac{\hbar c}{8\pi R^7}\{13(\alpha_x(A)\alpha_x(B)$$

$$+ \alpha_y(A)\alpha_y(B)) + 20\alpha_z(A)\alpha_z(B)\}. \quad (53)$$

So far we have not yet used the relations

$$\sum |q_l{}^x|^2 = \sum |q_l{}^y|^2 = \sum |q_l{}^z|^2 = q_l{}^2,$$
$$\sum |q_m{}^x|^2 = \sum |q_m{}^y|^2 = \sum |q_m{}^z|^2 = q_m{}^2, \quad (54)$$

where the summation extends over the three states with $J=1$ belonging to one degenerate level, which will be indicated hereafter by one symbol $l$ or $m$, respectively. With the aid of (54), Eq. (50) can now be written as:

$$\Delta_L E = -\frac{4}{\pi \hbar c} \sum_{l,m} \int_0^\infty \frac{k_l k_m u^4 du}{(k_l{}^2 + u^2)(k_m{}^2 + u^2)}(q_l q_m)^2$$

$$\times \frac{e^{-2uR}}{R^2}\left(1 + \frac{2}{uR} + \frac{5}{u^2 R^2} + \frac{6}{u^3 R^3} + \frac{3}{u^4 R^4}\right), \quad (55)$$

where each term of the sum over $l$, $m$ represents the contribution from all three states with $J=1$ belonging to one degenerate level $l$ together with all three states belonging to the level $m$.

Equation (53) may now be written

$$\Delta_L E(R \to \infty) = -\frac{23\hbar c}{4\pi R^7}\alpha(A)\alpha(B), \quad (56)$$

which is equal to

$$\Delta_L E(R \to \infty) = -\frac{23}{4\pi}\frac{\hbar c}{e^2} \cdot \frac{e^2}{R^7}\alpha(A)\alpha(B)$$

$$\approx 251\frac{e^2}{R}\frac{\alpha(A)\alpha(B)}{R^6}. \quad (57)$$

In Fig. 2 we have given the result of a numerical calculation of the factor $\Delta_L E/\Delta_q E$ for the case in which the two atoms are identical and in which for both atoms only one excited state $l$ (with $E_l = \hbar c/\lambda_l$) gives a contribution to the London energy. The factor decreases monotonically with increasing $R$. It starts with the value 1 (for $R \to 0$) while for large $R$ it is approximately equal to $23\lambda_l/6\pi^2 R$.

The very simple form of Eq. (56) and the analogous formula (25) suggest that it might be possible to derive these expressions, perhaps apart from the numerical factors, by more elementary considerations. This would be desirable since it would also give a more physical background to our result, a result which in our opinion is rather remarkable. So far we have not been able to find such a simple argument.