

THE ROLE OF QUADRUPOLE FORCES IN
VAN DER WAALS ATTRACTIONSBY HENRY MARGENAU
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ABSTRACT

van der Waals forces between atoms without permanent poles may be described as resulting from the interactions of multipoles associated with quantum transitions of the atoms. When the atoms are far apart, the dipole interaction is the only appreciable one. But at distances of the order of the kinetic theory radius, higher poles, usually neglected, must be considered. This paper examines and evaluates three terms of the series of interactions: the dipole-dipole, the dipole-quadrupole, and the quadrupole-quadrupole term, instead of the customary first term alone. The last appears to be in general small, but the dipole-quadrupole term requires consideration. Its effect is illustrated by plotting the potential energy curve for two helium atoms (a) neglecting the term, and (b) including it. The method outlined permits an easy estimate of dipole and quadrupole forces for all substances for which the wave function of only the normal state is known.

I. INTRODUCTION

IN DEALING with the interaction between nonpolar, unexcited atoms account has to be taken of two kinds of forces: repulsive forces due to the exchange of electrons, and attractive polarization forces. The former fall off exponentially near the gas-kinetic boundary of the atom, while the latter have a much larger range and predominate in the region where the wave function of the atom is small. To calculate both types of forces by means of a coherent process of approximations is in general a difficult task which has been carried through only for hydrogen.¹ For helium the repulsive forces are known with good precision,² while for more complex substances rough approximations have to be resorted to. Polarization forces have been calculated in the following manner: The classical mutual energy of the two atoms is written down as a power series in R^{-1} , R being the distance between nuclei. Of this series only the first term (proportional to R^{-6} and corresponding to dipole-dipole interaction) is retained as the perturbing potential from which the wave mechanical energies are computed. The result is then usually added to the potential function representing the exchange forces and the sum is considered to yield the potential curve for the two atoms in question. The use of such a potential curve is certainly permissible in discussing phenomena which do not depend very critically on the exact position and depth of the potential minimum; it may well describe in a general way even the pressure-volume relations and other thermodynamical properties. But when accurate numerical agreement of theoretical and experimental data is desired, or when

¹ R. Eisenschitz and F. London, *Zeits. f. Physik* **60**, 491 (1930).

² J. C. Slater, *Phys. Rev.* **32**, 349 (1928).

dissociation potentials of polarization molecules are to be determined this procedure requires somewhat closer inspection. For the polarization forces, obtained as indicated, are definitely only asymptotically correct. Discarding those terms in the classical energy expression which arise from multipole interactions, if permissible at all, calls for justification. It is indeed to be expected that they are not all negligible in the region of the potential minimum.³ This paper has the purpose of showing that, while higher poles may be neglected, the interaction between dipoles and quadrupoles furnishes an appreciable contribution to the van der Waals forces. This will be illustrated by an application to helium.

II. THE PERTURBING FIELD

The classical perturbation function which we are seeking is the mutual potential energy of two neutral molecules with nuclei separated by a distance R , and it is desired to express this energy conveniently as a series of inverse powers of R . For simplicity, we shall first consider two H-atoms. The potential ϕ_P at a point $P(r)$ produced by a proton at 0 and an electron at r_1 is $\phi_+ + \phi_-$ and may, if we suppose $r > r_1$, be developed in a Taylor series as follows:

$$\begin{aligned} \phi_P = & \frac{e}{r} - \frac{e}{r} + e \left[x_1 \frac{\partial}{\partial x} \left(\frac{1}{r} \right) + y_1 \frac{\partial}{\partial y} \left(\frac{1}{r} \right) + z_1 \frac{\partial}{\partial z} \left(\frac{1}{r} \right) \right] \\ & - \frac{1}{2} \left[x_1^2 \frac{\partial^2}{\partial x^2} \left(\frac{1}{r} \right) + y_1^2 \frac{\partial^2}{\partial y^2} \left(\frac{1}{r} \right) + z_1^2 \frac{\partial^2}{\partial z^2} \left(\frac{1}{r} \right) + 2x_1 y_1 \frac{\partial^2}{\partial y \partial x} \left(\frac{1}{r} \right) \right. \\ & \left. + 2y_1 z_1 \frac{\partial^2}{\partial y \partial z} \left(\frac{1}{r} \right) + 2x_1 z_1 \frac{\partial^2}{\partial x \partial z} \left(\frac{1}{r} \right) \right] + \dots \end{aligned}$$

If we are not interested in interactions due to poles of higher order than quadrupoles we need not consider more terms than those written down; this limitation will be justified later. Using for the present the convention of summing over like indices and putting x^1, x^2, x^3 for x, y, z we may write

$$\phi_P = e \left(x_1^i \frac{\partial}{\partial x^i} - \frac{1}{2} x_1^i x_1^j \frac{\partial^2}{\partial x^i \partial x^j} \right) \left(\frac{1}{r} \right) \dots \quad (1)$$

Placing now another H-atom with its proton at P and its electron at r_2 relative to P the mutual potential of the two becomes, again by a Taylor expansion in which the first three terms are retained,

$$\begin{aligned} V = & e\phi_P - e\phi_P - e \left(x_2^k \frac{\partial}{\partial x^k} + \frac{1}{2} x_2^k x_2^l \frac{\partial^2}{\partial x^k \partial x^l} \right) \phi_P \\ = & -e^2 \left\{ x_1^i x_2^k \frac{\partial^2}{\partial x^i \partial x^k} - \frac{1}{2} \left(x_1^i x_1^j x_2^k \frac{\partial^3}{\partial x^i \partial x^j \partial x^k} - x_1^i x_2^k x_2^l \frac{\partial^3}{\partial x^i \partial x^k \partial x^l} \right) \right. \\ & \left. - \frac{1}{4} x_1^i x_1^j x_2^k x_2^l \frac{\partial^4}{\partial x^i \partial x^j \partial x^k \partial x^l} \right\} \left(\frac{1}{r} \right) \dots \quad (2) \end{aligned}$$

³ The possible significance of quadrupole forces was pointed out to the writer in a discussion with Professor J. Frenkel, as a result of which the present computations were made.

on account of (1). The first term in $\{ \}$ describes the dipole-dipole action, the second dipole-quadrupole action, the third quadrupole-quadrupole action. Carrying out the differentiations, putting $r=R$ and then placing the x -axis along R we obtain

$$\frac{\partial^2}{\partial x^i \partial x^k} \left(\frac{1}{r} \right) = \begin{cases} \frac{2}{R^3} & \text{if } i = k = 1, \\ -\frac{1}{R^3} & \text{if } i = k = 2 \text{ or } 3 \\ 0 & \text{otherwise.} \end{cases}$$

$$\frac{\partial^3}{\partial x^i \partial x^j \partial x^k} \left(\frac{1}{r} \right) = \begin{cases} -\frac{6}{R^4} & \text{if } i = j = k = 1, \\ \frac{3}{R^4} & \text{if } j = k \neq 1, i = 1, \\ 0 & \text{otherwise.} \end{cases}$$

$$\frac{\partial^4}{\partial x^i \partial x^j \partial x^k \partial x^l} \left(\frac{1}{r} \right) = \begin{cases} \frac{24}{R^5} & \text{if } i = j = k = l = 1, \\ \frac{9}{R^5} & \text{if } i = j = k = l = 2 \text{ or } 3, \\ -\frac{12}{R^5} & \text{if } i = j \neq k = l = 1, \\ \frac{3}{R^5} & \text{if } i = j \neq k = l = 2, \text{ or } 3, \\ 0 & \text{otherwise.} \end{cases}$$

If we now perform the summation, the desired classical energy expression is obtained:

$$\begin{aligned} V = & -\frac{e^2}{R^3} [2x_1x_2 - y_1y_2 - z_1z_2] \\ & + \frac{3}{2} \frac{e^2}{R^4} [r_1^2x_2 - x_1r_2^2 + (2y_1y_2 + 2z_1z_2 - 3x_1x_2)(x_1 - x_2)] \\ & + \frac{3}{4} \frac{e^2}{R^5} [r_1^2r_2^2 - 5r_2^2x_1^2 - 5r_1^2x_2^2 - 15x_1^2x_2^2 + 2(4x_1x_2 + y_1y_2 + z_1z_2)^2] \end{aligned} \quad (3)$$

The first term of (3) represents the familiar dipole energy. This expression may be generalized to refer to any pair of arbitrary atoms containing n electrons, each, by attaching to every quantity in (3) carrying a subscript 1 or 2 another subscript μ or ν respectively, and summing over both μ and ν from 1 to n .

III. WAVE MECHANICAL MUTUAL ENERGY

We return to the consideration of 2 H-atoms and assume both of them to be in the ground state, which will be characterized by a subscript 0. Neglecting exchange degeneracy and spins the wave function for the unperturbed system may be written $\psi_0(1)\psi_0(2)$ where each ψ_0 is the H-wave function for the lowest state and the arguments are electron coordinates referred to the separate nuclei as origins. The first order perturbation energy is the average of V over the space of the two electrons, taken with the weighting function $\psi_0^2(1)\psi_0^2(2)$. This clearly vanishes on account of the spherical symmetry of the latter. (Terms in (3) which do not vanish on integration add up to zero.)

The unperturbed wave function for any state of our combined system is $\psi_\alpha(1)\psi_\beta(2)$, where α and β stand for triples of quantum numbers n, l, m . The second order perturbation energy here required is

$$\Delta_2 E = \sum'_{\alpha\beta} \frac{|V_{00,\alpha\beta}|^2}{2E_0 - E_\alpha - E_\beta} \quad (4)$$

where E_α is the energy of one H-atom in the state α . Terms with vanishing denominators are excluded from the summation ($'$), and $V_{00,\alpha\beta}$ is defined by

$$\int \psi_0(1)\psi_0(2)V(1,2)\psi_\alpha(1)\psi_\beta(2)d\tau_1d\tau_2. \quad (5)$$

The products $\psi_\alpha\psi_\beta$ satisfy the conditions of completeness and orthogonality, as do the ψ -functions singly. Moreover, one can convince himself that V is of such character as to make the $V_{\alpha\beta,\alpha'\beta'}$'s obey the ordinary matrix rules. Hence, if it were not for the dependence of the denominator on α and β , (4) could easily be evaluated by the relation

$$\sum_{\alpha\beta} |V_{00,\alpha\beta}|^2 = (V^2)_{00,00} \quad (6)$$

the being omitted because $V_{00,00} = 0$. For our purposes it is permissible to omit E_α and E_β in (4). This simplification seems violent at present, since from the form of (4) no direct estimate of the magnitude of the error committed may be derived. The justification arises only from a more detailed consideration which we relegate to the appendix.

Eq. (4) now reduces to

$$\Delta_2 E = \frac{(V^2)_{00,00}}{2E_0} \quad (7)$$

and the right hand side can be computed very simply if we remember that all odd powers of the coordinates in the square of (3) vanish on integration and no cross terms between the brackets appear. The result is

$$\Delta_2 E = \frac{1}{3} \frac{e^4}{E_0 R^6} \left[(r^2)_{00}^2 + \frac{3}{R^2} (r^4)_{00} (r^2)_{00} + \frac{21}{5R^4} (r^4)_{00}^2 \right]. \quad (8)$$

For hydrogen, $\psi_0 = e^{-r/a}$, where a is the smallest Bohr radius $= 0.528 \times 10^{-8}$ cm, and $(r^2)_{00} = 3a^2$, $(r^4)_{00} = 22.5 a^4$. Hence, putting

$$\frac{R}{a} = \rho,$$

$$\Delta_2 E = \frac{12E_0}{\rho^6} \left[1 + \frac{22.5}{\rho^2} + \frac{236}{\rho^4} \right] \quad (9)$$

where use has been made of the relation $E_0 = -e^2/2a$.

Eq. (9), while not exact, shows clearly the relative magnitudes of the different types of interaction. At the minimum of the potential energy curve, where $\rho = 6.5$, the dipole-quadrupole term (2nd in brackets) contributes about $\frac{1}{2}$, the quadrupole-quadrupole term (3rd in brackets) less than $\frac{1}{7}$ as much as the dipole-dipole term. Comparison with the work of Eisenschitz and London¹ shows this term in (9) to be in error by 8 percent as a consequence of replacing the excited energy states appearing in (4) by the ionization energy; the uncertainty in the other terms is smaller (see appendix).⁴

A main advantage of Eq. (8) lies in its applicability to other atoms or molecules for which the wave functions for the normal state are known. It may be shown to be valid, except for the inclusion of a constant factor not much different from one and determinable from an exact knowledge of the dipole energy, if $e(r^2)_{00}$ and $e(r^4)_{00}$ are interpreted as the sum of similar quantities formed for the individual electrons. E_0 then refers, of course, to the ionization energy of the atom or molecule.

Let us apply the equation to helium, for which the dipole energy has recently been calculated.⁵ Since we are primarily interested in the relative magnitudes of the three terms in brackets, we shall use a simple wave function of the type

$$\psi_0 = \rho^{n-1} e^{-(\frac{Z-s}{n})\rho}.$$

Then the normalizing factor becomes

$$\int \psi_0^2 \rho^2 d\rho = \frac{\Gamma(2n+1)}{\left(\frac{2(Z-s)}{n}\right)^{2n+1}},$$

and

$$(r^2)_{00} = \frac{(2n+2)(2n+1)}{\left(\frac{2(Z-s)}{n}\right)^2} \quad (10)$$

$$(r^4)_{00} = \frac{(2n+4)(2n+3)(2n+2)(2n+1)}{\left(\frac{2(Z-s)}{n}\right)^4}. \quad (11)$$

⁴ The coefficient of the dipole-dipole term in (8) agrees, as it should, with that of $1/\rho^8$ in Eisenschitz and London's expression (54) for the second order perturbation energy, if this is expanded in powers of $1/\rho$.

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

Letting now⁵ $n = 1$, $Z - s = 1.688$, (10) and (11) become

$$(r^2)_{00} = 1.05a^2; \quad (r^4)_{00} = 2.79a^4.$$

The presence of two electrons introduces a factor 4 (appendix) into Eq. (8), which may now be written

$$\begin{aligned} \Delta_2 E &= 4 \frac{e^4}{2a^2 V \rho^6} \left[0.739 + \frac{5.86}{\rho^2} + \frac{21.8}{\rho^4} \right] \\ &= - \frac{0.70}{\rho^6} \left[1 + \frac{7.9}{\rho^2} + \frac{30}{\rho^4} \right] \cdot 10^{-10} \text{ ergs} \end{aligned} \quad (12)$$

where V is the ionization potential of helium. It is known that the correct

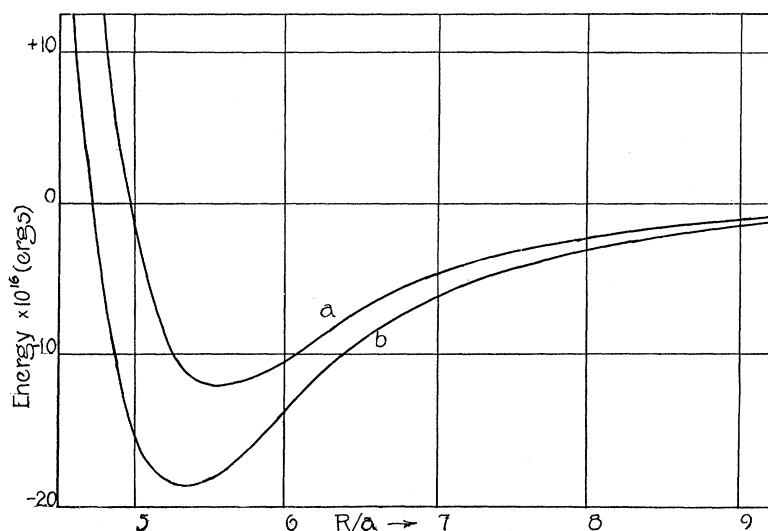


Fig. 1. Mutual energy of two helium atoms against distance of separation. (a) is the curve calculated by Slater and Kirkwood, (b) is the result of including the dipole-quadrupole energy

mean value of the energy to be inserted instead of V is larger than the ionization potential, so that we should expect the coefficient 0.70 in (12) to be too large. As a matter of fact, its true value is known to be 0.68.

Had we chosen a wave function of the simple type used here, but with $n = 0.745$, $Z - s = 1$, which is more accurate for large ρ 's, the coefficient in (12) would have been somewhat larger, and the effect of the dipole-quadrupole and the quadrupole terms would have been 25 percent greater than the corresponding ones in (12).

It is seen that at the minimum of the potential energy curve for two helium atoms, which occurs near $\rho = 5.5$, the second term in (12) amounts to 26/100, the third to 3/100 of the first. Hence the quadrupole-quadrupole interaction is negligible indeed, but the dipole-quadrupole energy must be considered. The result of including it in the potential energy, using Slater's expression for the repulsive energy: $\epsilon = 7.7 \times 10^{-10} e^{-2.43\rho}$ is plotted in Fig. 1.

The effect on the minimum is seen to be rather appreciable. Moreover, the use of the simple wave function here chosen places the lower curve almost certainly too high. We estimate the error in the absolute depth of the minimum of curve b which is due to the uncertainty of the polarization forces to be less than 2×10^{-16} ergs.⁶

APPENDIX

1. Hydrogen. It appears desirable to go through the calculation of (4) in greater detail and to justify some previous statements. The summation may be carried out over the three quantum numbers m , l , n , successively, and difficulties are not encountered until the sums over n , i.e. the radial part of the matrices, are to be evaluated.

Recalling the definition of $V_{00, \alpha\beta}$ in (5) we observe that the integrations involved can be performed over the coordinates of electrons 1 and 2 separately, so that $V_{00, \alpha\beta}$ decomposes into a sum of products of coordinate matrices $q_{0\alpha} q_{0\beta}$, each referring to the wave function of only one atom, e.g.

$$q_{0\alpha} = \int \psi_0 q \psi_\alpha d\tau.$$

Hence using (3)

$$V_{00, \alpha\beta} = -\frac{e^2}{R^3} \left[A_{\alpha\beta} + \frac{3}{2R} (B_{\alpha\beta} - B_{\beta\alpha}) + \frac{3}{4R^2} C_{\alpha\beta} \right], \quad (13)$$

where

$$\begin{aligned} A_{\alpha\beta} &= 2x_{0\alpha}x_{0\beta} - y_{0\alpha}y_{0\beta} - z_{0\alpha}z_{0\beta} \\ B_{\alpha\beta} &= (r^2)_{0\alpha}x_{0\beta} + 2(xy)_{0\alpha}y_{0\beta} + 2(xz)_{0\alpha}z_{0\beta} - 3(x^2)_{0\alpha}x_{0\beta} \\ C_{\alpha\beta} &= (r^2)_{0\alpha}(r^2)_{0\beta} - 5(x^2)_{0\alpha}(r^2)_{0\beta} - 5(r^2)_{0\alpha}(x^2)_{0\beta} + 17(x^2)_{0\alpha}(x^2)_{0\beta} \\ &\quad + 2(y^2)_{0\alpha}(y^2)_{0\beta} + 2(z^2)_{0\alpha}(z^2)_{0\beta} + 16(xy)_{0\alpha}(xy)_{0\beta} \\ &\quad + 16(xz)_{0\alpha}(xz)_{0\beta} + 4(yz)_{0\alpha}(yz)_{0\beta}. \end{aligned}$$

In forming the square of $V_{00, \alpha\beta}$ we see at once that the sum over differences like $A_{\alpha\beta}B_{\alpha\beta} - A_{\alpha\beta}B_{\beta\alpha}$ and $B_{\alpha\beta}C_{\alpha\beta} - B_{\beta\alpha}C_{\alpha\beta}$ is zero, since $A_{\alpha\beta} = A_{\beta\alpha}$, $C_{\alpha\beta} = C_{\beta\alpha}$, and we may interchange at liberty indices of summation in each term. The calculation is further simplified by another consideration. The energies appearing in the denominator of (4) do not depend on the magnetic quantum number m , and the summation over m_α and m_β , which amounts to averaging

⁶ In a recent paper, J. G. Kirkwood and F. G. Keyes, [Phys. Rev. **37**, 832 (1931)], calculated the second virial coefficient for He and found good agreement with experience despite their neglect of quadrupole forces. This agreement can have been only accidental and resulted from a second approximative feature in their calculation. As was pointed out by London, [Zeits. f. Physik **63**, 245 (1930)] in connection with He, the second virial coefficient can not be obtained accurately by an evaluation of its classical representative on account of the existence of an excluded region of phase space. A later approximate calculation of virial coefficients for a number of gases, made by the present author, [Phys. Rev. **36**, 1782 (1930)] has again shown the necessity of modifying the classical procedure for He and H₂. This modification involves the determination of vibrational states of structures of the type (He)₂ and (H₂)₂. As was also discussed previously, these two inaccuracies introduce errors of opposite signs, which may account for the agreement obtained by Kirkwood and Keyes.

over the angular orientations of the two atoms, may therefore be carried out treating the denominator as constant. Now every wave function occurring here may be written

$$\psi_\alpha = R_{n,l} P_l^m e^{im\phi},$$

and a matrix such as for instance $(x^2)_{0\alpha}$ has the form

$$(x^2)_{0\alpha} = \int R_{1,0}(r) r^2 \cos^2 \theta R_{n,l} P_l^m e^{im\phi} r^2 \sin \theta dr d\theta d\phi,$$

where the normalization is, of course, to be properly carried out. It is well known that, if such expressions are summed over all possible m -values, they reduce to simple terms. We write down the significant results of this procedure.

$$\begin{aligned} \sum_{m_\alpha} x_{0\alpha}^2 &= \sum_{m_\alpha} y_{0\alpha}^2 = \sum_{m_\alpha} z_{0\alpha}^2 = Q_\alpha r_{0\alpha}^2 \\ \sum_{m_\alpha} (x^2)_{0\alpha} &= \sum_{m_\alpha} (y^2)_{0\alpha} = \sum_{m_\alpha} (z^2)_{0\alpha} = G_\alpha (r^2)_{0\alpha} \\ \sum_{m_\alpha} (x^2)_{0\alpha} (y^2)_{0\alpha} &= \sum_{m_\alpha} (x^2)_{0\alpha} (z^2)_{0\alpha} = \sum_{m_\alpha} (y^2)_{0\alpha} (z^2)_{0\alpha} = L_\alpha (r^2)_{0\alpha}^2 \\ \sum_{m_\alpha} (xy)_{0\alpha} &= \sum_{m_\alpha} (xz)_{0\alpha} = \sum_{m_\alpha} (yz)_{0\alpha} = M_\alpha (r^2)_{0\alpha}^2 \\ \sum_{m_\alpha} (r^2)_{0\alpha} (x^2)_{0\alpha} &= \sum_{m_\alpha} (r^2)_{0\alpha} (y^2)_{0\alpha} = \sum_{m_\alpha} (r^2)_{0\alpha} (z^2)_{0\alpha} = N_\alpha (r^2)_{0\alpha}^2. \end{aligned} \quad (14)$$

All other terms which appear on squaring $V_{00,\alpha\beta}$, if summed over m_α and m_β , reduce to zero. The symbols used here are defined as follows:

$$\begin{aligned} G_\alpha &= \frac{1}{9} \delta_0^{l_\alpha} + \frac{4}{45} \delta_2^{l_\alpha}; & L_\alpha &= \frac{1}{9} \delta_0^{l_\alpha} - \frac{2}{45} \delta_2^{l_\alpha} \\ M_\alpha &= \frac{1}{15} \delta_2^{l_\alpha}; & N_\alpha &= \frac{1}{3} \delta_0^{l_\alpha}; & Q_\alpha &= \frac{1}{3} \delta_1^{l_\alpha}. \end{aligned} \quad (15)$$

The δ 's are the usual Kronecker symbols.

Eq. (4) now becomes

$$\Delta_2 E = \frac{e^4}{R^6} \sum_{\alpha\beta} \frac{1}{2E_0 - E_\alpha - E_\beta} \sum_{m_\alpha, m_\beta} \left\{ A_{\alpha\beta}^2 + \frac{9}{2R^2} (B_{\alpha\beta}^2 - B_{\alpha\beta} B_{\beta\alpha}) + \frac{9}{16R^4} C_{\alpha\beta}^2 \right\},$$

α and β now include only n_α, l_α , and n_β, l_β . Moreover, because of (14),

$$\begin{aligned} \sum_{m_\alpha, m_\beta} A_{\alpha\beta}^2 &= 6Q_\alpha Q_\beta r_{0\alpha}^2 r_{0\beta}^2 \\ \sum_{m_\alpha, m_\beta} (B_{\alpha\beta}^2 - B_{\alpha\beta} B_{\beta\alpha}) &= (\delta_0^{l_\alpha} + 8M_\alpha + 9G_\alpha - 6N_\alpha) Q_\beta (r^2)_{0\alpha}^2 r_{0\beta}^2 \\ \sum_{m_\alpha, m_\beta} C_{\alpha\beta}^2 &= [\delta_0^{l_\alpha} \delta_0^{l_\beta} + 25G_\alpha \delta_0^{l_\beta} + 25G_\beta \delta_0^{l_\alpha} + 297G_\alpha G_\beta \\ &\quad + 528M_\alpha M_\beta - 10N_\alpha \delta_0^{l_\beta} - 10N_\beta \delta_0^{l_\alpha} + 92N_\alpha N_\beta \\ &\quad - 170G_\alpha N_\beta - 170N_\alpha G_\beta - 40L_\alpha N_\beta - 40N_\alpha L_\beta + 144L_\alpha L_\beta]. \end{aligned}$$

The first of these expressions becomes, on substitution of (15), $(1/9)\delta_1^{l\alpha}\delta_1^{l\beta}$, the second $(4/9)\delta_2^{l\alpha}\delta_1^{l\beta}$ and the third reduces to $0\cdot\delta_0^{l\alpha}\delta_0^{l\beta} - 0\cdot\delta_0^{l\alpha}\delta_2^{l\beta} - 0\cdot\delta_2^{l\alpha}\delta_0^{l\beta} + (224/45)\delta_2^{l\alpha}\delta_2^{l\beta}$. The dipole-dipole energy arises from transitions in which the l for each atom changes from 0 to 1. The dipole-quadrupole part is due to transitions in which one l changes from 0 to 2 and the other from 0 to 1, while the quadrupole-quadrupole interaction is caused only by jumps of both atoms from $l=0$ to $l=2$, as might have been expected.

Writing now for convenience $n_\alpha = n$, $n_\beta = \nu$, the expression for the second order perturbation energy may be put in the form

$$\Delta_2 E = \frac{e^4}{R^6} \left\{ \frac{2}{3} \sum_{n,\nu} \frac{r_{10,n1}^2 \cdot r_{10,\nu1}^2}{2E_0 - E_n - E_\nu} \right. \quad (a)$$

(dipole-dipole) (a)

$$+ \frac{2}{R^2} \sum_{n,\nu} \frac{(r^2)_{10,n2}^2 \cdot r_{10,\nu1}^2}{2E_0 - E_n - E_\nu} \quad (b) \quad (16)$$

(dipole-quadrupole) (b)

$$+ \frac{14}{5R^4} \sum_{n,\nu} \frac{(r^2)_{10,n2}^2 \cdot (r^2)_{10,\nu2}^2}{2E_0 - E_n - E_\nu} \quad (c)$$

(quadrupole-quadrupole) (c)

The second subscript of the radial matrices denotes the value of l , upon which the energies do not depend. The $r_{10,n1}$ are known, and the $(r^2)_{10,n2}$ may be computed. It must be considered, however, that the sum includes an integration over the continuous spectrum which is not easily performed for the second and third term of (16). Our knowledge of the result of the first summation, together with a computation of a limited succession of the $(r^2)_{10,n2}$ from which their manner of convergence is ascertained, may guide us in estimating the sums. It is found that the r^2 -matrices converge less rapidly than the r -matrices, which shifts the weight of (16b) and (16c) to higher n 's and ν 's. The absolute value of the denominator in all three sums is $< 2|E_0|$ for the discrete spectrum and $> 2|E_0|$ for the continuous. The "mean" denominator of (16a) is $0.93 \times 2E_0$. While in (16a) the denominator of the first term is $0.75 \times 2E_0$, (b) and (c) start with terms having denominators $0.82 \times 2E_0$ and $0.89 \times 2E_0$. All the circumstances mentioned combine to make the "mean" denominators of (16b) and (c) more nearly equal to $2E_0$.

Taking then this quantity in front of the summation and using the relation⁷

$$\sum_n (r^p)_{10,nl}^2 = (r^{2p})_{10,10}$$

there results Eq. (8).

⁷ That this is true for any value of l may be shown as follows: Let S_{nl} be the radial part of the wave function. Then $\int S_{nl} S_{n'l} r^2 dr = \delta_{nn'}$. Expanding $r^p S_{10} = \sum_n c_n S_{nl}$, we must have $c_n = (r^p)_{10,n1}$. But $\sum_n (r^p)_{10,n1}^2 = \sum_n c_n \int S_{10} r^p S_n r^2 dr = \int S_{10} r^p \sum_n c_n S_n r^2 dr = \int S_{10} r^p r^p S_{10} r^2 dr = (r^{2p})_{10,10}$.

2. Helium. Instead of carrying through the calculation for helium it will suffice here to illustrate the procedure with reference to the dipole-dipole interaction only. The other terms introduce nothing new, and it would absorb too much space to write them down. The classical interaction energy is

$$V = -\frac{e^2}{R^3} \sum_{ij} (2x_{1i}x_{2j} - y_{1i}y_{2j} - z_{1i}z_{2j}) \text{ where } i, j = 1, 2.$$

Neglecting again spins and exchanges of particles, and denoting by $\psi(12)$ the wave function of electron 2 belonging to nucleus 1, the wave function of the two atoms in states α and β respectively becomes

$$\psi_{\alpha_1}(11)\psi_{\alpha_2}(12)\psi_{\beta_1}(21)\psi_{\beta_2}(22).$$

The normal state, designated by $\alpha_1 = \alpha_2 = \beta_1 = \beta_2 = 0$, is again spherically symmetrical, and we find

$$V_{00,\alpha\beta} = -\frac{e^2}{R^3} [(2x_{0\alpha_1}x_{0\beta_1} - y_{0\alpha_1}y_{0\beta_1} - z_{0\alpha_1}z_{0\beta_1})\delta_0^{\alpha_2}\delta_0^{\beta_2}] \quad (17)$$

+ three similar nonidentical terms formed by permuting $\alpha_1\alpha_2\beta_1\beta_2$.

The summation in (4) is now to be carried over $\alpha_1\alpha_2\beta_1\beta_2$ independently. Forming the square of (17) and summing over all m by means of (14), many terms drop out and we are left with

$$\sum_{\text{all } m} |V_{00,\alpha\beta}|^2 = \frac{2}{3} \frac{e^4}{R^6} [r_{0\alpha_1}^2 r_{0\beta_1}^2 \delta_0^{\alpha_2}\delta_0^{\beta_2} + \text{three similar terms}]$$

if all l_α, l_β appearing as matrix subscripts are 1, = 0 otherwise. Consequently, if the electrons are equivalent,

$$\Delta_2 E = \frac{2e^4}{3R^6} \cdot 4 \sum_{\alpha,\beta} \frac{r_{0\alpha}^2 r_{0\beta}^2}{2E_0 - E_{\alpha_1} - E_{\beta_1}},$$

where the summation extends only over such α 's and β 's as have $l=1$.