

Quadrupole-Quadrupole and Dipole-Octupole Dispersion Forces Between Axially Symmetric Molecules*

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Formulas are derived that express the contributions of the electric quadrupole-quadrupole and dipole-octupole forces, respectively, to the dispersion energy of two unexcited molecules possessing axial symmetry. The formulas are valid in situations where the optical dispersion curve of each molecule is adequately characterized by a pair of resonance frequencies.

1. Introduction

Let us consider a microscopic system composed of two equal but opposite electric charges, such that the positive charge is located at a fixed origin, while the negative charge e , say, is displaced from it by the vector \mathbf{r}' . Suppose a similar system with displacement \mathbf{r}'' has its origin at a point whose position vector is \mathbf{R} relative to the first origin. The potential energy pertaining to the COULOMB interaction between the two systems is then

$$V = e^2(R^{-1} + |\mathbf{R} - \mathbf{r}' + \mathbf{r}''|^{-1} - |\mathbf{R} - \mathbf{r}'|^{-1} - |\mathbf{R} + \mathbf{r}''|^{-1}). \quad (1)$$

If both r' and r'' are taken to be less than R , this function can be expanded in a power series for the reciprocal distance R^{-1} , which commences with third-order terms. One may write this series as

$$V = V_1 + V_2 + V_3 + V_4 + \dots, \quad (2)$$

where V_1 , V_2 , etc. are identical with the potential energies of respectively two dipoles, a dipole and a quadrupole, two quadrupoles, and so on for electric multipoles of increasing order. Not every term of (2) – we should remark – is of a different order; for instance, while it is true that V_1 is of the order three and V_2 of the order four in R^{-1} , both V_3 and V_4 are fifth-order terms.

The expansion (2) has been made the point of departure by MARGENAU¹ and others^{2,3} for quantum-mechanical second-order perturbation calculations of the dispersion forces between molecules in spherically symmetric ground states. These calculations are in general based on a model according to which a molecule consists effectively of a certain

number, integral or fractional, of electrons behaving as isotropic simple harmonic oscillators of the same frequency. Now, such a model can obviously not be expected to furnish useful results for molecules, such as the diatomic ones, whose electronic wave functions are markedly lacking in spherical symmetry. At least it should be realized, as LONDON⁴ pointed out, that the stiffness constant of an electronic oscillator along a bond direction would be different from the constant perpendicular to it. This view has given rise to the so-called anisotropic oscillator model of LONDON, which, on application to unexcited axially symmetric molecules, leads in the dipole-dipole approximation, $V = V_1$, to the well-known R^{-6} formula of LONDON for the dispersion energy^{4,5} with its characteristic dependence upon the orientations of the molecule axes. In a recent study⁶, the better approximation $V = V_1 + V_2$ has been employed: its effect is to augment the LONDON formula by a certain orientation-dependent dipole-quadrupole energy term, which varies as R^{-8} .

In the present paper we shall carry the generalization of LONDON's formula a step further by including moreover the fifth-order terms V_3 and V_4 in the definition of V . Because of the mere asymptotic validity of the dispersion energy series⁷, this is probably as far as one should go for immediate physical purposes. We shall not bother, in what follows, to define all our symbols, and the method of calculation will likewise be given short shrift, leaving us mainly with a summary of results. For enlightenment on the missing details, references 5 and 6 should be consulted.

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¹ H. MARGENAU, J. Chem. Phys. **6**, 896 [1938].

² R. HELLER, J. Chem. Phys. **9**, 154 [1941].

³ P. R. FONTANA, Phys. Rev. **123**, 1865 [1961].

⁴ F. LONDON, J. Phys. Chem. **46**, 305 [1942].

⁵ A. J. VAN DER MERWE, Z. Physik **196**, 212 [1966].

⁶ A. J. VAN DER MERWE, Z. Physik **196**, 332 [1966].

⁷ A. DALGARNO and J. T. LEWIS, Proc. Phys. Soc. London A **69**, 57 [1956].



2. Classical Potential Energy

On performing the TAYLOR expansion of V , we find that V_3 and V_4 in Eq. (2) are given, with $\mathbf{R}_0 = \mathbf{R}/R$, by

$$V_3 = \frac{3}{4} \frac{e^2}{R^5} [r'^2 r''^2 + 2(\mathbf{r}' \cdot \mathbf{r}'')^2 - 20(\mathbf{R}_0 \cdot \mathbf{r}')(\mathbf{R}_0 \cdot \mathbf{r}'')(\mathbf{r}' \cdot \mathbf{r}'') - 5r'^2(\mathbf{R}_0 \cdot \mathbf{r}'')^2 - 5r''^2(\mathbf{R}_0 \cdot \mathbf{r}')^2 + 35(\mathbf{R}_0 \cdot \mathbf{r}')^2(\mathbf{R}_0 \cdot \mathbf{r}'')^2] \quad (3)$$

and

$$V_4 = \frac{1}{2} \frac{e^2}{R^5} [15r'^2(\mathbf{R}_0 \cdot \mathbf{r}')(\mathbf{R}_0 \cdot \mathbf{r}'') + 15r''^2(\mathbf{R}_0 \cdot \mathbf{r}')(\mathbf{R}_0 \cdot \mathbf{r}'') - 3r'^2(\mathbf{r}' \cdot \mathbf{r}'') - 3r''^2(\mathbf{r}' \cdot \mathbf{r}'') + 15(\mathbf{R}_0 \cdot \mathbf{r}')^2(\mathbf{r}' \cdot \mathbf{r}'') + 15(\mathbf{R}_0 \cdot \mathbf{r}'')^2(\mathbf{r}' \cdot \mathbf{r}'') - 35(\mathbf{R}_0 \cdot \mathbf{r}')(\mathbf{R}_0 \cdot \mathbf{r}'')^3 - 35(\mathbf{R}_0 \cdot \mathbf{r}'')(\mathbf{R}_0 \cdot \mathbf{r}')^3] \quad (4)$$

A resolution of \mathbf{r}' and \mathbf{r}'' into their components relative to two rectangular Cartesian sets of axes located at the centers of the first and second molecules, respectively, allows us to rewrite the foregoing equations as

$$V_3 = \frac{3}{4} \frac{e^2}{R^5} \sum_i \sum_j \sum_k \sum_m (i j k m) x'_i x'_j x''_k x''_m \quad (5)$$

and

$$V_4 = \frac{1}{2} \frac{e^2}{R^5} \sum_i \sum_j \sum_k \sum_m [(i j k m) x'_i x'_j x'_k x''_m + (m, i j k) x''_i x''_j x''_k x'_m], \quad (6)$$

with appropriately defined coefficients $(i j k m)$, $(i j k, m)$, and $(m, i j k)$.

If one's purpose is to study isotropic molecules, it will clearly be proper and advantageous to choose the singly and doubly primed sets of axes to be mutually parallel, fixed in space, and such that one of the coordinate directions coincides with \mathbf{R} ; the coefficients in (5) and (6) will then simply be some integers. But, when we are dealing with anisotropic molecules, the choice of axes is no longer solely a matter of preference, as each set of axes must be attached rigidly to the molecule it spans; relative to such axes, rotating with the molecules, the coefficients are rather complicated functions of the rotation angles. For the case under consideration, where the molecules are posited to have axial symmetry, and the axes are defined as in ref. 5, these functions turn out to be^{7a}

$$\begin{aligned} (i j k m) = & \delta_{ij} \delta_{km} + 17 \cos \Theta'_i \cos \Theta'_j \cos \Theta''_k \cos \Theta''_m \\ & - 5 \delta_{ij} \cos \Theta''_k \cos \Theta''_m - 5 \delta_{km} \cos \Theta'_i \cos \Theta'_j \\ & + 2 \sin \Theta'_i \cos \Theta'_j \sin \Theta''_k \cos \Theta''_m \cos \Phi_{ik} \\ & - 18 \cos \Theta'_i \sin \Theta'_j \cos \Theta''_k \sin \Theta''_m \cos \Phi_{jm} \\ & + 2 \sin \Theta'_i \sin \Theta'_j \sin \Theta''_k \sin \Theta''_m \cos \Phi_{ik} \cos \Phi_{jm} \\ & = \pm \text{transpose of } (k m, i j) \end{aligned} \quad (7)$$

and

$$\begin{aligned} (i j k, m) = & 12 \delta_{ij} \cos \Theta'_k \cos \Theta''_m \\ & - 20 \cos \Theta'_i \cos \Theta'_j \cos \Theta'_k \cos \Theta''_m \\ & - 3 \delta_{ij} \sin \Theta'_k \sin \Theta''_m \cos \Phi_{km} \\ & + 15 \cos \Theta'_i \cos \Theta'_j \sin \Theta'_k \sin \Theta''_m \cos \Phi_{km} \\ & = \pm \text{transpose of } (m, i j k); \end{aligned} \quad (8)$$

here "transpose" denotes the result obtained on interchanging single and double primes in the function following it. In order to express the foregoing 243 coefficients in as few variables as possible, it is furthermore necessary to notice that

$$\begin{aligned} \Theta'_1 &= \Theta' + 90^\circ, & \Theta'_2 &= 90^\circ, & \Theta'_3 &= \Theta'; \\ \Theta''_1 &= \Theta'' + 90^\circ, & \Theta''_2 &= 90^\circ, & \Theta''_3 &= \Theta''; \\ \Phi_{11} &= \Phi_{13} = \Phi_{22} = \Phi_{31} = \Phi_{33} = \Phi, \\ \Phi_{12} &= \Phi_{32} = \Phi + 90^\circ, & \Phi_{21} &= \Phi_{23} = \Phi - 90^\circ. \end{aligned} \quad (9)$$

In this table Θ' and Θ'' signify the angles made by the molecule axes with the vector \mathbf{R} , and Φ the angle included by the projections of these axes onto a plane perpendicular to \mathbf{R} .

3. Quadrupole-Quadrupole Perturbation Energy

In keeping with the anisotropic oscillator model, we assume next that the wave function of a system of two widely separated molecules is the product of six oscillator wave functions, as described in ref. 5. Our problem is then to find the perturbation energy associated with the (not too close) approach of two molecules in their ground states, when the interaction $V = V_1 + V_2 + V_3 + V_4$ is used and perturbation terms of third and higher order are neg-

^{7a} Capital Greek letters replace here the corresponding small letters in the notation of ref. 6. — Although the use of irreducible tensors would have made our computations more compact, we have chosen to express the outcome in terms of simple trigonometric functions, which permit a straightforward interpretation of our final results.

lected. Inspection reveals the fortunate fact that any of the matrix elements of V here required, receives a contribution from at most one of the four terms V_j into which V has been analyzed. Consequently, one is entitled to treat each V_j separately from the others; the corresponding energies furnish on addition the total perturbation energy.

In this section we confine ourselves to V_3 , and assume that the interacting molecules contain respectively f' and f'' oscillating electrons. The first-order perturbation energy is non-zero and found to be

$$E^{(1)} = \frac{3}{4} \frac{Q' Q''}{R^5} [1 - 5(\cos^2 \Theta' + \cos^2 \Theta'') - 15 \cos^2 \Theta' \cos^2 \Theta'' + 2(4 \cos \Theta' \cos \Theta'' - \sin \Theta' \sin \Theta'' \cos \Phi)^2], \quad (10)$$

where

$$Q' = \frac{\hbar}{2} \left(\frac{f'}{m} \right)^{1/2} (\alpha'_{\parallel 1/2} - \alpha'_{\perp 1/2}), \quad (11)$$

and Q'' is similarly defined. $E^{(1)}$ is recognized as being the classical COULOMB interaction energy of two rigid quadrupoles, of moments Q' and Q'' , whose axes coincide with those of the molecules⁸. The appearance of this term was, of course, inevitable in view of the non-vanishing quadrupole moments of non-spherical molecules.

The second-order perturbation energy corresponding to V_3 provides the quadrupole-quadrupole dispersion energy; we obtain

$$\begin{aligned} -\frac{\hbar E^{(2)}}{(3/4 e^2/R^5)^2 f' f''} = & (32 \nu'_{\perp} \beta'_{\perp})^{-1} (1/\beta'_{\perp} - 1/\beta'_{\parallel})^2 (T^2, -) \\ & + [16(\nu'_{\perp} + \nu') \beta'_{\perp} \beta'_{\parallel}]^{-1} (1/\beta'_{\perp} - 1/\beta'_{\parallel})^2 (TA, -) + (16 \nu'_{\parallel} \beta'_{\parallel})^{-1} (1/\beta'_{\perp} - 1/\beta'_{\parallel})^2 (A^2, -) \\ & + [64(\nu'_{\perp} + \nu'_{\parallel}) (\beta'_{\perp} \beta'_{\parallel})^2]^{-1} (T^2, T^2) + [8(\nu'_{\perp} + \nu'_{\parallel}) (\beta'_{\perp} \beta'_{\parallel})^2]^{-1} (T^2, A^2) \\ & + [16(\nu'_{\parallel} + \nu'') (\beta'_{\parallel} \beta'_{\parallel})^2]^{-1} (A^2, A^2) + [16(2\nu'_{\perp} + \nu'_{\parallel} + \nu'') \beta'_{\perp} \beta'_{\parallel} \beta'_{\parallel}]^{-1} (T^2, TA) \\ & + [32(\nu'_{\perp} + \nu'_{\parallel} + \nu'_{\perp} + \nu'_{\parallel}) \beta'_{\perp} \beta'_{\parallel} \beta'_{\perp} \beta'_{\parallel}]^{-1} (TA, TA) + [8(\nu'_{\perp} + \nu' + 2\nu'_{\perp}) \beta'_{\perp} \beta'_{\parallel} \beta'_{\perp}]^{-1} (TA, T^2) \\ & + [16(\nu'_{\parallel} + \nu'_{\perp}) (\beta'_{\parallel} \beta'_{\perp})^2]^{-1} (A^2, T^2) + [8(2\nu' + \nu'_{\perp} + \nu'_{\parallel}) \beta'_{\parallel} \beta'_{\perp} \beta'_{\parallel}]^{-1} (A^2, TA) + \text{transpose}; \end{aligned} \quad (12)$$

herein the coefficients $(T^2, -)$, $(TA, -)$, etc. (T =transverse, A =axial) are the following rather complicated functions of the orientation angles:

$$\begin{aligned} (T^2, -) &= [(21, 33) + (12, 33)]^2 + 2(11, 33)^2 + 2(22, 33)^2, \\ (TA, -) &= [(31, 33) + (13, 33)]^2 + [(23, 33) + (32, 33)]^2, \\ (A^2, -) &= (33, 33)^2, \\ (T^2, T^2) &= 4(11, 11)^2 + 8(22, 11)^2 + 4(22, 22)^2 \\ &\quad + [(21, 21) + (12, 21) + (21, 12) + (12, 12)]^2 \\ &\quad + 4[(21, 11) + (12, 11)]^2 + 4[(22, 21) + (22, 12)]^2, \\ (T^2, A^2) &= (11, 33)^2 + (22, 33)^2, \\ (A^2, A^2) &= (33, 33)^2, \\ (T^2, TA) &= [(21, 31) + (12, 31) + (21, 13) + (12, 13)]^2 \\ &\quad + [(21, 23) + (12, 23) + (12, 32) + (21, 32)]^2 \\ &\quad + 2[(22, 31) + (22, 13)]^2 + 2[(22, 23) + (22, 32)]^2, \\ (TA, TA) &= [(31, 31) + (13, 31) + (31, 13) + (13, 13)]^2 \\ &\quad + 2[(23, 31) + (32, 31) + (23, 13) + (32, 13)]^2 \\ &\quad + [(23, 23) + (23, 32) + (32, 23) + (32, 32)]^2, \\ (TA, T^2) &= [(31, 11) + (13, 11)]^2 + [(23, 11) + (32, 11)]^2, \\ (A^2, T^2) &= [(33, 21) + (33, 12)]^2, \\ (A^2, TA) &= [(33, 31) + (33, 13)]^2 + [(33, 23) + (33, 32)]^2. \end{aligned} \quad (13)$$

In the special case of spherical molecules, it is evident from Eq. (11) that $Q' = Q'' = 0$ and thus $E^{(1)} = 0$; calculation reveals furthermore that the formula (12) reduces to

$$E^{(2)} = -\frac{315 e^4 f' f''}{16 \hbar (\beta' \beta'')^2 (\nu' + \nu'')} \frac{1}{R^{10}} = -\frac{315 \hbar^3}{16 e m^{3/2}} \frac{(\alpha' \alpha'')^{3/2}}{(f' \alpha'')^{1/2} + (f'' \alpha')^{1/2}} \frac{1}{R^{10}}, \quad (14)$$

all of which agrees with the results of HELLER² and FONTANA³.

⁸ W. H. KEESOM, Physik. Z. **22**, 129 [1921].

4. Dipole-Octupole Dispersion Energy

As was to be expected, no contribution to the energy arises from V_4 in first-order perturbation theory. The second-order energy is the dipole-octupole dispersion energy and turns out to be given by

$$\begin{aligned}
 -\frac{\hbar E^{(2)}}{(\frac{1}{2} e^2/R^5)^2 f' f''} = & [16(\nu'_{\perp} + \nu''_{\perp}) \beta'_{\perp} \beta''_{\perp}]^{-1} (T, T) + [16(\nu'_{\parallel} + \nu''_{\parallel}) \beta'_{\parallel} \beta''_{\parallel}]^{-1} (A, T) \\
 & + [16(\nu'_{\parallel} + \nu''_{\parallel}) \beta'_{\parallel} \beta''_{\parallel}]^{-1} (A, A) + [8(2\nu'_{\perp} + \nu'_{\parallel} + \nu''_{\perp}) \beta'^2_{\perp} \beta''_{\perp}]^{-1} (T^2 A, T) \\
 & + [8(2\nu'_{\perp} + \nu'_{\parallel} + \nu''_{\parallel}) \beta'^2_{\perp} \beta''_{\parallel}]^{-1} (T^2 A, A) + [8(3\nu'_{\perp} + \nu''_{\perp}) \beta'^3_{\perp} \beta''_{\perp}]^{-1} (T^3, T) \\
 & + [8(\nu'_{\perp} + 2\nu'_{\parallel} + \nu''_{\perp}) \beta'_{\perp} \beta'^2_{\parallel} \beta''_{\perp}]^{-1} (TA^2, T) + [8(3\nu'_{\perp} + \nu''_{\parallel}) \beta'^3_{\perp} \beta''_{\parallel}]^{-1} (T^3, A) \\
 & + [8(\nu'_{\perp} + 2\nu'_{\parallel} + \nu''_{\parallel}) \beta'_{\perp} \beta'^2_{\parallel} \beta''_{\parallel}]^{-1} (TA^2, A) + [8(3\nu'_{\parallel} + \nu''_{\perp}) \beta'^3_{\parallel} \beta''_{\perp}]^{-1} (A^3, T) \\
 & + [8(3\nu'_{\parallel} + \nu''_{\parallel}) \beta'^3_{\parallel} \beta''_{\parallel}]^{-1} (A^3, A) + \text{transpose};
 \end{aligned} \quad (15)$$

the angle-dependent coefficients appearing in this formula are defined as follows:

$$\begin{aligned}
 (T, T) &= (1/\beta'_{\perp} - 1/\beta'_{\parallel})^2 \{ [3(111, 1) + (221, 1)]^2 + (332, 1)^2 + (332, 2)^2 \} \\
 &\quad + (1/\beta'_{\perp} - 1/\beta'_{\parallel})(1/\beta''_{\perp} - 1/\beta''_{\parallel}) \{ [3(111, 1) + (221, 1)] [3(1, 111) + (221, 1)] \\
 &\quad - 2(332, 1) [3(2, 111) + (2, 221)] + (332, 2)(2, 332) \} \\
 &\quad + (1/\beta''_{\perp} - 1/\beta''_{\parallel})^2 [3(2, 111) + (2, 221)]^2, \\
 (A, T) &= 9(1/\beta'_{\perp} - 1/\beta'_{\parallel})^2 [(333, 1)^2 + (333, 2)^2] \\
 &\quad + 6(1/\beta'_{\perp} - 1/\beta'_{\parallel})(1/\beta''_{\perp} - 1/\beta''_{\parallel}) \{ (333, 2)(3, 332) - (333, 1) [3(3, 111) + (3, 221)] \} \\
 &\quad + (1/\beta''_{\perp} - 1/\beta''_{\parallel})^2 \{ [3(3, 111) + (3, 221)]^2 + (3, 332)^2 \}, \\
 (A, A) &= 9(1/\beta'_{\perp} - 1/\beta'_{\parallel})^2 (333, 3)^2 + 3(1/\beta'_{\perp} - 1/\beta'_{\parallel})(1/\beta''_{\perp} - 1/\beta''_{\parallel}) (333, 3)(3, 333), \\
 (T^2 A, T) &= [(113, 1) + (131, 1) + (311, 1)]^2 + [(113, 2) + (131, 2) + (311, 2)]^2 \\
 &\quad + (223, 1)^2 + (223, 2)^2 + 2[(312, 1)^2 + (312, 2)^2], \\
 (T^2 A, A) &= [(113, 3) + (131, 3) + (311, 3)]^2 + (223, 3)^2 + 2(312, 3)^2, \\
 (T^3, T) &= (112, 1)^2 + (112, 2)^2 + (221, 1)^2 + (221, 2)^2 \\
 &\quad + 3[(111, 1)^2 + (111, 2)^2 + (222, 1)^2 + (222, 2)^2], \\
 (TA^2, T) &= [(133, 1) + (313, 1) + (331, 1)]^2 \\
 &\quad + [(133, 2) + (313, 2) + (331, 2)]^2 + (332, 1)^2 + (332, 2)^2, \\
 (T^3, A) &= (112, 3)^2 + (221, 3)^2 + 3[(111, 3)^2 + (222, 3)^2], \\
 (TA^2, A) &= [(133, 3) + (313, 3) + (331, 3)]^2 + (332, 3)^2, \\
 (A^3, T) &= 3[(333, 1)^2 + (333, 2)^2], \\
 (A^3, A) &= 3(333, 3)^2.
 \end{aligned} \quad (16)$$

For spherical molecules, Eq. (15) reduces to

$$E^{(2)} = -\frac{105 e^4 f' f''}{4 \hbar \beta' \beta'' R^{10}} \left[\frac{1}{\beta''^2 (\nu' + 3 \nu'')} + \frac{1}{\beta'^2 (\nu'' + 3 \nu')} \right] = -\frac{105 \hbar^3 \alpha' \alpha''}{4 e m^{3/2} R^{10}} \left[\frac{(f'/f')^{1/2} \alpha''}{(f'' \alpha'')^{1/2} + 3(f'' \alpha')^{1/2}} + \frac{(f''/f')^{1/2} \alpha'}{(f'' \alpha')^{1/2} + 3(f' \alpha'')^{1/2}} \right], \quad (17)$$

again as required by the work of other authors^{2,3}.

5. Formulas for Some Special Orientations

In view of the unwieldiness of the general formulas (12) and (15), it will be useful, for calculations and other purposes, to display here their simplified forms for the special orientations (a) to (d) defined in ref. 5. We have, for similar molecules,

$$\begin{aligned}
 \text{a) } E_{\text{qq}}^{(2)} = & - (3/4 R^5)^2 (\hbar^3/16 e m^{3/2} f^{1/2}) \\
 & \times [2(17 \alpha_{\perp}^{3/2} + 9 \alpha_{\parallel}^{3/2})(\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2 + 169 \alpha_{\perp}^{5/2} + 204(\alpha_{\perp} \alpha_{\parallel})^{3/2}(\alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} + 9 \alpha_{\parallel}^{5/2}],
 \end{aligned} \quad (18)$$

$$\begin{aligned} \text{b) } E_{\text{qq}}^{(2)} = & - (3/4 R^5)^2 (\hbar^3/8 e m^{3/2} f^{1/2}) \\ & \times [(45 \alpha_{\perp}^{3/2} + 16 \alpha_{\parallel}^{3/2}) (\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2 + 21 \alpha_{\perp}^{5/2} \\ & + 154 (\alpha_{\perp} \alpha_{\parallel})^{3/2} (\alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} + 8 \alpha_{\parallel}^{5/2} + 136 \alpha_{\perp}^2 \alpha_{\parallel} (\alpha_{\perp}^{1/2} + 3 \alpha_{\parallel}^{1/2})^{-1}] , \end{aligned} \quad (19)$$

$$\begin{aligned} \text{c) } E_{\text{qq}}^{(2)} = & - (3/4 R^5)^2 (\hbar^3/16 e m^{3/2} f^{1/2}) \\ & \times [2 (25 \alpha_{\perp}^{3/2} + \alpha_{\parallel}^{3/2}) (\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2 + 97 \alpha_{\perp}^{5/2} \\ & + 108 (\alpha_{\perp} \alpha_{\parallel})^{3/2} (\alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} + \alpha_{\parallel}^{5/2} + 512 \alpha_{\perp}^2 \alpha_{\parallel} (\alpha_{\perp}^{1/2} + 3 \alpha_{\parallel}^{1/2})^{-1}] , \end{aligned} \quad (20)$$

$$\begin{aligned} \text{d) } E_{\text{qq}}^{(2)} = & - (3/4 R^5)^2 (\hbar^3/2 e m^{3/2} f^{1/2}) \\ & \times [8 (\alpha_{\perp}^{3/2} + 8 \alpha_{\parallel}^{3/2}) (\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2 + 3 \alpha_{\perp}^{5/2} + 48 (\alpha_{\perp} \alpha_{\parallel})^{3/2} (\alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} + 8 \alpha_{\parallel}^{5/2}] ; \end{aligned} \quad (21)$$

$$\begin{aligned} \text{a) } E_{\text{do}}^{(2)} = & - (1/2 R^5)^2 (\hbar^3/16 e m^{3/2} f^{1/2}) \\ & \times [2 (153 \alpha_{\perp}^{3/2} + 54 \alpha_{\parallel}^{3/2}) (\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2 + 612 (\alpha_{\perp} \alpha_{\parallel})^{3/2} (\alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} + 507 \alpha_{\perp}^{5/2} + 27 \alpha_{\parallel}^{5/2}] , \end{aligned} \quad (22)$$

$$\begin{aligned} \text{b) } E_{\text{do}}^{(2)} = & - (1/2 R^5)^2 (\hbar^3/32 e m^{3/2} f^{1/2}) \\ & \times [81 \alpha_{\perp}^{3/2} (\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2 + 2346 (\alpha_{\perp} \alpha_{\parallel})^{3/2} (\alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} (\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2 \\ & + 2376 \alpha_{\perp}^2 \alpha_{\parallel} (\alpha_{\perp}^{1/2} + 3 \alpha_{\parallel}^{1/2})^{-1} + 306 (\alpha_{\perp} \alpha_{\parallel})^{3/2} (\alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} \\ & + 2028 \alpha_{\perp} \alpha_{\parallel}^2 (3 \alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} + 207 \alpha_{\perp}^{5/2} + 219 \alpha_{\parallel}^{5/2}] , \end{aligned} \quad (23)$$

$$\begin{aligned} \text{c) } E_{\text{do}}^{(2)} = & - (1/2 R^5)^2 (3 \hbar^3/e m^{3/2} f^{1/2}) \\ & \times [6 \alpha_{\perp}^{3/2} (\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2 + 6 \alpha_{\perp} \alpha_{\parallel} (\alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} (\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2 \\ & - 27 \alpha_{\perp}^2 \alpha_{\parallel} (\alpha_{\perp}^{1/2} + 3 \alpha_{\parallel}^{1/2})^{-1} + 7 \alpha_{\perp}^{5/2} + 6 (\alpha_{\perp} \alpha_{\parallel})^{3/2} (\alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} + 3 \alpha_{\perp} \alpha_{\parallel}^2 (3 \alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1}] , \end{aligned} \quad (24)$$

$$\begin{aligned} \text{d) } E_{\text{do}}^{(2)} = & - (1/2 R^5)^2 (\hbar^3/2 e m^{3/2} f^{1/2}) \\ & \times [24 (3 \alpha_{\perp}^{3/2} + 4 \alpha_{\parallel}^{3/2}) (\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2 + 144 (\alpha_{\perp} \alpha_{\parallel})^{3/2} (\alpha_{\perp}^{1/2} + \alpha_{\parallel}^{1/2})^{-1} + 9 \alpha_{\perp}^{5/2} + 24 \alpha_{\parallel}^{5/2}] . \end{aligned} \quad (25)$$

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