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Tensor Formalism for Coulomb Interactions and Asymptotic Properties of Multipole Expansions*

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A tensor notation for electric multipole interactions between molecular charge distributions is developed and applied to the evaluation of first- and second-order interaction energies. An equivalence theorem between cylindrically symmetric and linear assemblies of charge is established. The mathematical implications of using a multipole Taylor expansion in regions of configuration space where the series has no validity is discussed for the first and second orders of perturbation theory.

I. INTRODUCTION AND SUMMARY

VALUABLE information on the properties of Coulomb potentials may be inferred from developments in series of certain types. In the literature pertaining to long-range molecular interactions it has been a practice, since the early papers of Debye[1] and Keesom,[2] to expand the electrostatic potential at a distance **R** from the center of a charge distribution as a Taylor series of inverse powers of R. This expansion may be written explicitly in terms of Legendre's functions (tesseral, sectorial, and zonal harmonics) or, more formally, as a sum of products involving tensors of increasing rank. The first general notation, given by Frenkel,[3] was in tensor form. Later this notation was abandoned in favor of the Legendre functions. In either form for the electrostatic potential, part of the coefficient of $1/R^{n+1}$ is a homogeneous polynomial of degree n in the Cartesian coordinates of the elements of charge of the distribution. This term is associated with the multipole moment of order n of the charge distribution. The (ground state) expectation value of the potential then contains the expectation values of the multipole moment operators. These quantities will be referred to as (being associated with) the "molecular" multipole moments.[4]

There is a great deal of confusion in the literature on molecular interactions regarding the general definitions of the moment operators and the molecular multipole moments. We mention that three different definitions for the molecular quadrupole moment are used in the literature.[5] It will be shown in Sec. II of this paper that the moment operators of arbitrary order may be defined in an unambiguous manner on the basis of a tensor notation for the electrostatic potential. The explicit expressions for the molecular moments then follow from the expectation value of the potential. These definitions for the molecular moments depend on the symmetry properties of the distribution; they are, however, identical for all distributions with an axis of symmetry which is at least threefold. The tensor formalism is characterized by two sets of quantities: the interaction tensors $\mathbf{T}^{(n)}$ of rank n and the multipole moments $\mathbf{N}^{(n)}$ of order n. It leads to a short notation for operators such as the electrostatic potential, electric field strength, and the perturbation Hamiltonian. Therefore, in contrast with the notation in terms of Legendre's functions, it is easy to apply in problems involving the expectation values of general operators to relatively high orders of perturbation theory. The tensor algebra may be worked out in all relevant cases on the basis of two general theorems for solid spherical harmonics: a general theorem in differentiation and an integral theorem, both of which are due to Hobson.[6] Examples are given in Sec. III and Sec. IV of this paper, in a discussion of first- and second-order interaction energies. Interactions between three-dimensional distributions with "cylindrical" symmetry are often replaced in the literature by those between linear assemblies of charges. We shall prove that the equivalence exists in a multipole-type expansion for first-order interactions between distributions which have at least a threefold axis of symmetry (Sec. IID).

Since the Taylor series involved in a multipole expansion converges uniformly only if the point of reference lies outside the charge distribution, the multipole series is applicable only in a limited region of configuration space. If Taylor's series are to be retained for the whole of space, then the above condition necessitates the use of two series for the electrostatic potential and four different series for the perturbation Hamiltonian. Instead, one often uses only the series applicable if the point of reference lies outside the distribution, but integrates over *all* space. The mathematical implications of this procedure have only recently received attention.

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[1] P. Debye, Physik. Z. **21**, 178 (1920).

[2] W. H. Keesom, Physik. Z. **22**, 129 (1921).

[3] J. Frenkel, Z. Physik **25**, 1 (1924).

[4] For a detailed discussion of multipole moments and long-range interactions we refer to the review articles by K. F. Herzfeld, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2, and by H. Margenau, Revs. Modern Phys. **11**, 1 (1939), which have become classics in this field. A recent quite complete treatment of the subject is found in Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), Chap. 12.

[5] Hirschfelder, Curtiss, and Bird, reference 4, Chap. 12.

[6] E. W. Hobson, *The Theory of Spherical and Ellipsoidal Harmonics* (Cambridge University Press, New York, 1931), Chap. IV.

Brooks[7] noted the divergent character of second-order series representing long-range interactions between a hydrogen atom and a proton and also for interactions between harmonic oscillators. He established that the divergent series are the asymptotic expansions (in inverse powers of the separation R) of the true energy of interaction. Brooks ascribed the origin of the divergence to the use of the "multipole Taylor series" in regions of configuration space where it is not valid. However, Dalgarno and Lewis[8] pointed out that the exact second-order expression for the hydrogen atom—proton interaction energy yields for large values of R, when expanded in inverse powers of R, identically the same divergent series as the multipole expression. Thus the divergence must be regarded as a characteristic property of the expansion in inverse powers of the separation. It will be shown in Sec. V of this paper that the same properties are exhibited by divergent *first*-order multipole series.

II. ELECTROSTATIC INTERACTIONS IN TENSOR NOTATION

A. Interaction Tensors $\mathbf{T}^{(n)}$

Suppose that we have a Cartesian coordinate system (x,y,z) with origin O_1. Let a point charge e_i be situated at vector distance $\mathbf{r}_i$ from O_1; then the scalar potential at a point at vector distance $\mathbf{R}$ from O_1 is

$$V(\mathbf{R})=e_i|\mathbf{R}-\mathbf{r}_i|^{-1}.$$

For $r_i<R$ this expression may be expanded as an absolutely-convergent power series in ascending powers of r_i/R; we write the series as

$$r_i<R:\quad V(\mathbf{R})=\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}e_i(\mathbf{r}_i\cdot\nabla)^n\left(\frac{1}{R}\right).\tag{1}$$

It is understood in (1) that ∇ operates on R but not on r_i. On the other hand, the appropriate series for $r_i>R$ is

$$r_i>R:\quad V(\mathbf{R})=\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}e_i(\mathbf{R}\cdot\nabla_i)^n\left(\frac{1}{r_i}\right).\tag{2}$$

For the following, it is convenient to write (1) in tensor form by introducing the nth-rank tensor[9]

$$\mathbf{T}^{(n)}=-\nabla^n(1/R);\tag{3}$$

the components of $\mathbf{T}^{(n)}$ are spherical harmonics[10] of degree $-n-1$. The expression (1) for the potential may then be written as follows

$$r_i<R:\quad V(\mathbf{R})=\sum_{n=0}^{\infty}\frac{(-1)^{n+1}}{n!}\mathbf{T}^{(n)}[n]e_i\mathbf{r}_i{}^n.\tag{4}$$

In this equation $[n]$ denotes that the product of the two nth-rank tensors $\mathbf{T}^{(n)}$ and $\mathbf{r}_i{}^n$ is contracted n times. Further, since we use only rectangular Cartesian coordinate systems, we shall not distinguish between covariant and contravariant tensors.

In the course of the following calculations frequent use will be made of two general theorems, in a form given by Hobson.[6] The first is a special case of a theorem in differentiation and states that if $f_n(x,y,z)$ is a rational algebraic homogeneous function of degree n in x, y, z,

$$f_n\left(\frac{\partial}{\partial x},\frac{\partial}{\partial y},\frac{\partial}{\partial z}\right)\left(\frac{1}{R}\right)=(-1)^n\frac{(2n)!}{2^n n!}\frac{1}{R^{2n+1}}\times\left\{1-\frac{R^2\nabla^2}{2(2n-1)}+\cdots\right\}f_n(x,y,z).\tag{5}$$

For example, we mention as a rather trivial application of (5) that any component of a tensor $\mathbf{T}^{(n)}$, with $n\geqslant 1$, when averaged over the orientations of the coordinate system, vanishes identically. (This result follows also from the orthogonality properties of solid spherical harmonics.) An equivalent form of the theorem (5), first given by Maxwell in his theory of poles of a spherical harmonic, will be applied in evaluating first-order interactions between cylindrically symmetric molecules. Hobson's integral theorem will be discussed in connection with first- and second-order molecular interactions (Sec. III and Sec. IV). As a further useful property of the T tensors we note[11] that summation over one repeated coordinate in any component of $\mathbf{T}^{(n)}$, with $n>1$, gives zero result. These identity relations will be used in the derivation of an expression for the (scalar) molecular multipole moments of arbitrary order for cylindrically symmetric distributions of charge.

The expansion of (1) in terms of Legendre's functions is well known and will therefore not be developed here; for details the reader is referred to the work of Hirschfelder *et al.*[5] The expressions for the electrostatic potential are not yet in a suitable form for the calculation of the interactions between two charge distributions, since in that case one normally makes use of two Cartesian coordinate systems with origins O_1 and O_2, respectively. Let the position of a point in configuration space be specified by a vector $\mathbf{r}_i$ with respect to O_1, a vector $\mathbf{r}_j$ with respect to O_2, and the vector distance $\mathbf{R}$ between O_1 and O_2. Instead of $|\mathbf{R}-\mathbf{r}_i|^{-1}$ we now have to evaluate $|\mathbf{R}-\mathbf{r}_i+\mathbf{r}_j|^{-1}$, and instead of two Taylor expansions we have four different series associated with

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[7] F. C. Brooks, Phys. Rev. **86**, 92 (1952).

[8] A. Dalgarno and J. T. Lewis, Proc. Phys. Soc. (London) **A69**, 57 (1956).

[9] L. Jansen, Physica **23**, 599 (1957).

[10] We shall use the name "spherical harmonic" as an abbreviation for "solid spherical harmonic," i.e., any function which is homogeneous in x, y, z and satisfies Laplace's equation.

[11] These relations were already applied by Frenkel, reference 3. See also the review article by K. F. Herzfeld, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2, p. 444.

the different relative magnitudes of r_i, r_j, and R.[12] The case equivalent to $r_i<R$ is that $r_i+r_j<R$; we give only some formulas pertaining thereto.[13] In the tensor formalism one has simply

$$|\mathbf{R}-\mathbf{r}_i+\mathbf{r}_j|^{-1} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(-1)^{n_1+1}}{n_1!n_2!}\mathbf{r}_i^{n_1}[n_1]\mathbf{T}^{(n_1+n_2)}[n_2]\mathbf{r}_j^{n_2}. \quad (6)$$

It is expedient to specify the sign of the differential operator ∇ by the convention that it is directed from the charge distribution on the *left* of the symbol $\mathbf{T}^{(n_1+n_2)}$ to that on the *right;* thus, in (6), ∇ is directed from distribution 1 to 2. We note that (6) does not contain the relative orientations of the two coordinate systems explicitly, in contrast with the expansion in terms of Legendre's functions. The necessity of specifying at the outset the coordinate systems used does not arise in the tensor formalism. If Legendre's functions are used, then the expansion of $|\mathbf{R}-\mathbf{r}_i+\mathbf{r}_j|^{-1}$ may be accomplished by direct application of Maxwell's theory of poles. Alternatively, this expansion can also be obtained from group theoretical considerations. The results depend on the relative orientations of the two coordinate systems with origins O_1 and O_2, respectively. Carlson and Rushbrooke[14] have derived such expressions for two special cases: (a) the two sets of coordinate axes are parallel, with coinciding z axes; (b) parallel sets of axes, the line O_1O_2 has nonzero polar angles relative to the axes at O_1. They showed that the expansions may be obtained from group theory and expressed in terms of reduction coefficients for the direct product of two irreducible representations of the rotation group (Wigner coefficients). The general expansion, valid for arbitrary relative orientations of the coordinate systems, and involving the representation coefficients of the rotation group, was given by Hirschfelder, Curtiss, and Bird.[5]

The complete procedure of employing four different Taylor series for the expansion of Coulomb interactions between two distributions of charge has, to this author's knowledge, not been applied in the literature. In the theory of molecular interactions it is often possible to avoid the series with complicated boundary conditions by using different mathematical methods for small values of the separation.[15] In the region of relatively large values for R one uses only the Taylor series for $r_i+r_j<R$, and extends the integration *over all space.* The limitation to one Taylor series leads to a simple expression of Coulomb potentials in terms of interactions between electric multipole moments of the two distributions. It is consistent with this procedure to assume that the wave functions need not be antisymmetrized with respect to interatomic exchange, so that no such exchange contributions appear in the result. We restrict ourselves in the following to large values of R, i.e., we use the tensor notation (4) or (6), or the equivalent expressions in terms of Legendre's functions.

B. Multipole Moment Tensors $\mathbf{N}^{(n)}$

To obtain the electrostatic interaction between two distributions of charge, (6) must be summed over all charges of the assemblies. To this end we introduce[9] the multipole moment operator of order n, $\mathbf{N}^{(n)}$, as the nth-rank tensor

$$\mathbf{N}^{(n)}=\textstyle\sum_i e_i\mathbf{r}_i^{\,n}; \quad (7)$$

the summation extends over all charges. The tensors $\mathbf{N}^{(n)}$ define the multipole moments of the charge distributions: $N^{(0)}$ is the total charge, $\mathbf{N}^{(1)}$ represents the dipole operator, $\mathbf{N}^{(2)}$ stands for the quadrupole tensor, etc. The operator for the electrostatic interaction between two distributions of charge, H', is then

$$H'=\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(-1)^{n_1+1}}{n_1!n_2!}\mathbf{N}^{(n_1)}[n_1]\mathbf{T}^{(n_1+n_2)}[n_2]\mathbf{N}^{(n_2)}. \quad (8)$$

Also, the expectation value, $\langle V(\mathbf{R})\rangle$, of the electrostatic potential at vector distance $\mathbf{R}$ from O_1 is, from (3),

$$\langle V(\mathbf{R})\rangle=\sum_{n=0}^{\infty}\frac{(-1)^{n+1}}{n!}\mathbf{T}^{(n)}[n]\langle\mathbf{N}^{(n)}\rangle. \quad (9)$$

The expression for the electric field strength at $\mathbf{R}$ assumes a particularly simple form in this notation, namely

$$\langle\mathbf{F}(\mathbf{R})\rangle=-\nabla\langle V(\mathbf{R})\rangle=\sum_{n=0}^{\infty}\frac{(-1)^{n}}{n!}\mathbf{T}^{(n+1)}[n]\langle\mathbf{N}^{(n)}\rangle. \quad (10)$$

The corresponding expressions in the notation involving Legendre's functions will not be given here; they are usually considerably more complicated than (8), (9), and (10). They involve, in the general case of arbitrary relative orientations of the coordinate systems, products of complex operators Q_n^m for the separate distributions, as well as the representation coefficients of the three-dimensional rotation group.[5]

In contrast with the notation in Legendre's functions, it is relatively easy to apply the tensor formalism for the evaluation of expectation values of general operators to relatively high orders of perturbation theory.[16] The necessity of going beyond the first order usually arises, since the equations may only be applied for large

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[12] R. J. Buehler and J. O. Hirschfelder, Phys. Rev. **83**, 628 (1951); **85**, 149 (1952). The four possibilities are: $R>r_i+r_j$; $r_j>R+r_i$; $r_i>R+r_j$; and $|\mathbf{r}_i-\mathbf{r}_j|\leqslant R\leqslant r_i+r_j$.

[13] Explicit expressions for the expansion in Legendre's functions for all cases are given in Hirschfelder, Curtiss, and Bird, reference 5, Chap. 12.

[14] B. C. Carlson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. **46**, 626 (1950).

[15] See, for example, J. O. Hirschfelder and J. W. Linnett, J. Chem. Phys. **18**, 130 (1950); J. S. Dahler and J. O. Hirschfelder, *ibid.* **25**, 986 (1956); E. A. Mason and J. O. Hirschfelder, *ibid.* **26**, 173, 756 (1957).

[16] P. Mazur and L. Jansen, Physica **21**, 193, 208 (1955); L. Jansen and A. D. Solem, Phys. Rev. **104**, 1291 (1956).

separations. If the charge distributions are neutral and in their unperturbed ground states, the first order of perturbation theory often gives only trivial results. In the next section we show that the tensor notation gives a unique definition for the (scalar) molecular multipole moments of arbitrary order for cylindrically symmetric charge distributions.[17]

C. Cylindrically Symmetric Distributions of Charge

Since the Taylor series (8), or its equivalent in terms of Legendre's functions, is applicable only for relatively large values of R, its use is appropriate in problems which may be treated by perturbation methods. In that case the symmetry properties of the interacting charge distributions often cause a considerable simplification of the equations. Of particular importance in the theory of molecular interactions is the class of distributions with a symmetry axis which is at least threefold. The group includes spherically symmetric distributions, diatomic and "linear" polyatomic molecules, as well as certain nonlinear structures (such as ammonia). The following derivations pertain to this class of molecules; for our purpose we may call them "cylindrically symmetric distributions of charge." To avoid complicated subscript notation we shall use the symbols $T^{(n)}(x^a y^b z^c)$ and $N^{(n)}(x^a y^b z^c)$ to denote components of $\mathbf{T}^{(n)}$ and $\mathbf{N}^{(n)}$ which are a, b, and c fold in x, y, and z, respectively. However, components of the lowest multipole moments (dipole $\mathbf{p}$, quadrupole $\mathbf{q}$ and octupole $\mathbf{l}$) will be written, following convention, as p_z, q_{xx} or q_{x^2}, $l_{y^2z^2}$, etc. We consider the expectation value of the electrostatic potential at distance $\mathbf{R}$ from the center (of positive charge) of a cylindrically symmetric distribution; the axis of symmetry is denoted by z. For symmetry reasons, only even powers of x and y will occur in the components of $\langle \mathbf{N}^{(n)} \rangle$. From repeated application of the relations

$$T^{(n)}(z^n) = -T^{(n)}(x^2 z^{n-2}) - T^{(n)}(y^2 z^{n-2}),$$

it is easy to show[9] that

$$\mathbf{T}^{(n)}[n]\langle \mathbf{N}^{(n)} \rangle = \sum_{p \leq n/2} b_p T^{(n)}(z^n) \langle N^{(n)}(x^{2p} z^{n-2p}) \rangle, \tag{11}$$

with

$$b_p = (-1)^p \frac{n!}{(2p)!(n-2p)!}. \tag{12}$$

We may now define scalar molecular multipole moments $\mathfrak{N}^{(n)}$ of order n for cylindrically-symmetric charge distributions by

$$\begin{aligned} \mathfrak{N}^{(n)} &= \sum_{p \leq n/2} b_p \langle N^{(n)}(x^{2p} z^{n-2p}) \rangle \\ &= \sum_{p \leq n/2} (-1)^p \frac{n!}{(2p)!(n-2p)!} \langle N^{(n)}(x^{2p} z^{n-2p}) \rangle, \end{aligned} \tag{13}$$

in terms of a combination of components of $\langle \mathbf{N}^{(n)} \rangle$. The potential then assumes the form

$$\langle V(\mathbf{R}) \rangle = \sum_{n=0}^{\infty} \frac{(-1)^{n+1}}{n!} T^{(n)}(z^n) \mathfrak{N}^{(n)}. \tag{14}$$

The general term in the expression for $\langle H' \rangle$ is, from (8),

$$\langle \mathbf{N}^{(n_1)} \rangle [n_1] \mathbf{T}^{(n_1+n_2)} [n_2] \langle \mathbf{N}^{(n_2)} \rangle;$$

this term may be rewritten in a way similar to (14) as

$$T^{(n_1+n_2)}(z_1^{n_1} z_2^{n_2}) \mathfrak{N}^{(n_1)} \mathfrak{N}^{(n_2)},$$

where $\mathfrak{N}^{(n_1)}$ and $\mathfrak{N}^{(n_2)}$ are the molecular multipole moments of order n_1 and n_2 of charge distribution 1, 2, respectively. The axes z_1 and z_2 coincide with the two symmetry axes. Thus

$$\langle H' \rangle = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \frac{(-1)^{n_1+1}}{n_1! n_2!} T^{(n_1+n_2)}(z_1^{n_1} z_2^{n_2}) \mathfrak{N}^{(n_1)} \mathfrak{N}^{(n_2)}. \tag{15}$$

Equations (14) and (15) show that for interactions between cylindrically-symmetric charge distributions, the multipole moment tensors occur only in certain combinations of their components. In addition, the expressions contain only components of the T tensor along the axes of cylindrical symmetry.

There exists a very simple relationship between the molecular multipole moments $\mathfrak{N}^{(n)}$, defined by (13), and the scalar coefficients Q_n^m occurring in the expression for the potential in terms of Legendre's functions. With the help of the definition for the Legendre polynomial of degree n, we write (14) as

$$\langle V(\mathbf{R}) \rangle = \sum_{n=0}^{\infty} \frac{P_n(\cos\theta)}{R^{n+1}} \mathfrak{N}^{(n)}. \tag{14'}$$

On the other hand, the equivalent expression in terms of the Q_n^m reads

$$\langle V(\mathbf{R}) \rangle = \sum_{n=0}^{\infty} \frac{P_n(\cos\theta)}{R^{n+1}} \langle Q_n^0 \rangle. \tag{14''}$$

It follows then that

$$\mathfrak{N}^{(n)} = \langle Q_n^0 \rangle = \langle \textstyle\sum_i e_i r_i^n P_n(\cos\theta_i) \rangle, \tag{16}$$

for cylindrically-symmetric distributions of charge. The identity (16) may also be proven directly by expressing x_i and z_i (substituted for x and z) in (13) in polar coordinates, integrating over the azimuth angle, and making use of the alternate expression[18]

$$P_n(\cos\theta_i) = \sum_{p \leq n/2} (-1)^p \frac{n!}{2^{2p}(p!)^2(n-2p)!} \times \sin^{2p}\theta_i \cos^{n-2p}\theta_i, \tag{17}$$

for the zonal harmonic of degree n. Molecular multipole

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[17] Only the tensor $\mathbf{T}^{(2)}$ appears to have been used regularly in the literature. See also A. D. Buckingham and J. A. Pople, Trans. Faraday Soc. **51**, 1029 (1955), and R. W. Zwanzig, J. Chem. Phys. **25**, 211 (1956).

[18] E. W. Hobson, reference 6, p. 23.

moments of order $n>2$ may also readily be found on the basis of (13). If we abbreviate the octupole and hexadecapole moments by L and M, and the corresponding tensors by $\mathbf{l}$ and $\mathbf{m}$, respectively, then

$$\text{mol. octupole moment } L=\langle l_{z^3}\rangle-3\langle l_{x^2z^2}\rangle,$$

$$\text{mol. hexadecapole moment } M=\langle m_{z^4}\rangle-6\langle m_{x^2z^2}\rangle+\langle m_{x^4}\rangle,$$

where $l_{z^3}=\sum_i e_i z_i^3$; $m_{x^2z^2}=\sum_i e_i x_i^2 z_i^2$; etc. It should be noted that the choice of $\mathfrak{N}^{(n)}=\langle Q_n^0\rangle$ for the (scalar) molecular multipole moments of cylindrically-symmetric distributions is consistent with the definition $\mathbf{N}^{(n)}=\sum_i e_i \mathbf{r}_i^n$ for the moment operators. For example, the expression $Q=\langle q_{zz}\rangle-\langle q_{xx}\rangle$ for the molecular quadrupole moment follows from the definition $\mathbf{q}=\sum_i e_i\mathbf{r}_i\mathbf{r}_i$ for the quadrupole moment operator. Often used is a definition for this operator as the traceless tensor ($\mathbf{U}$ is the unit second-rank tensor)

$$\mathbf{q}'=\sum_i e_i[3\mathbf{r}_i\mathbf{r}_i-r_i^2\mathbf{U}], \tag{18}$$

which shows some similarity[19] with $\mathbf{T}^{(2)}$. For cylindrically-symmetric distributions the molecular quadrupole moment is then defined as $\langle q_{zz}'\rangle=-2\langle q_{xx}'\rangle=2Q$. A logical choice for the definition of multipole moments should, however, be based on a general expansion of the electrostatic potential. The tensor formalism and the expansion in terms of Legendre's functions lead without ambiguity to the same definition. The multipole moments associated with a given cylindrically-symmetric distribution of charge may be found by using the definition (13). However, if the charge density $\rho(r_i,\theta_i)$ is given as a series of Legendre polynomials, it is simpler to employ the identity (16). In that case we write[5]

$$\rho(r_i,\theta_i)=\sum_{n=0}^{\infty}\rho_n(r_i)P_n(\cos\theta_i), \tag{19}$$

with

$$\rho_n(r_i)=\frac{2n+1}{2}\int_0^{\pi}P_n(\cos\theta_i)\rho(r_i,\theta_i)\sin\theta_i d\theta_i.$$

The molecular multipole moment of order n is then given by

$$\mathfrak{N}^{(n)}=\frac{4\pi}{2n+1}\int_0^{\infty}\rho_n(r_i)r_i^{n+2}dr_i. \tag{20}$$

The multipole series is finite if the charge density is represented by a finite series of Legendre polynomials; the order of the highest multipole moment is the same as that of the highest polynomial occurring in $\rho(r_i,\theta_i)$. The three-dimensional anisotropic harmonic oscillator is an example of a charge density for which it is much simpler to use (13); this case will be discussed in the next section.

D. Equivalent One-Dimensional Distributions of Charge

In the previous section it was shown that the expressions for $\langle V(\mathbf{R})\rangle$ and $\langle H'\rangle$ contain the multipole moment tensors only as certain combinations of their components if the distributions of charge are cylindrically symmetric. In addition only components of $\mathbf{T}^{(n)}$ along the axes of cylindrical symmetry occur. Consequently, such assemblies of charge may be replaced by equivalent one-dimensional distributions for the determination of $\langle V(\mathbf{R})\rangle$ and $\langle H'\rangle$. The one-dimensional distribution may be obtained by solving the moment problem.[20] The axis of the linear distribution coincides with the axis of cylindrical symmetry of the three-dimensional assembly and the linear charge density $\rho(z)$ must be chosen such that the associated linear moments $\mathfrak{N}_l^{(n)}$ are the same as the molecular multipole moments $\mathfrak{N}^{(n)}$ for all n. We choose as the limits of integration $(-\infty,+\infty)$ and expand $\rho(z)$ as an infinite series of Hermite polynomials (for dimensionless βz):

$$\rho(z)=\pi^{-\frac{1}{2}}\sum_{n=0}^{\infty}a_nH_n(\beta z)\exp(-\beta^2z^2),$$

with

$$a_n=\sum_{k\leq n/2}\frac{(-1)^k\mathfrak{N}^{(n-2k)}}{k!(n-2k)!2^{2k}}\beta^{n-2k+1}. \tag{21}$$

For a chosen value of the scale parameter β, the linear distribution $\rho(z)$ can in principle be determined if the multipole moments of the three-dimensional assembly are known. A simple problem is to find the equivalent $\rho(z)$ for a three-dimensional anisotropic harmonic oscillator. The normalized charge density for the ground state is given by

$$\rho(x,y,z)=\alpha^2\gamma\pi^{-\frac{3}{2}}\exp[-\alpha^2(x^2+y^2)-\gamma^2z^2]. \tag{22}$$

The axis of cylindrical symmetry is again z; α and γ are positive and $\gamma\leqslant\alpha$. The multipole moments associated with (22) are, for even n,

$$\mathfrak{N}^{(n)}=\frac{n!}{2^n(n/2)!}\left(\frac{1}{\gamma^2}-\frac{1}{\alpha^2}\right)^{n/2}. \tag{23}$$

After inserting this expression into (21), we find

$$a_n=\frac{\beta^{n+1}}{2^n(n/2)!}\left[\left(\frac{1}{\gamma^2}-\frac{1}{\alpha^2}\right)-\frac{1}{\beta^2}\right]^{n/2}.$$

The simplest solution for $\rho(z)$ is thus given by

$$\frac{1}{\beta^2}=\frac{1}{\gamma^2}-\frac{1}{\alpha^2}, \tag{24}$$

$$a_0=\beta;\quad a_n=0,\quad\text{for}\quad n\neq 0.$$

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[19] The use of the Taylor series (2) for $r_i>R$ leads to multipole moments of negative order; the moment of order -3 has the form $\Sigma_i(e_i/r_i^5)[3\mathbf{r}_i\mathbf{r}_i-r_i^2\mathbf{U}]$, which is a traceless tensor similar to (18).

[20] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 947.

The resulting charge density is that of a linear harmonic oscillator. The multipole moments associated with $\rho(z)$ are

$$\mathfrak{N}_l^{(n)}=\frac{n!}{2^n(n/2)!\beta^n}. \tag{25}$$

When α approaches infinity the molecule reduces to a linear structure and β approaches γ. For an isotropic oscillator the equivalent charge distribution is that of a δ function, etc. The equivalence between a three-dimensional and a linear distribution for large values of R applies in general only to the unperturbed expectation values of $V(\mathbf{R})$ and H$'$. By combining (14$'$) and (25), we obtain

$$\langle V(\mathbf{R})\rangle=\sum_{n=0}^{\infty}\frac{P_n(\cos\theta)}{R^{n+1}}\frac{n!}{2^n(n/2)!\beta^n}. \tag{26}$$

It follows that the multipole series, representing the electrostatic potential at distance $\mathbf{R}$ from the center of a three-dimensional anisotropic harmonic oscillator is divergent for all values of R. It will be shown in Sec. V that the series (26) is the asymptotic expansion (in inverse powers of R) of the correct potential.

III. FIRST-ORDER INTERACTIONS

The electrostatic energy of interaction in the first order of perturbation theory is given by the unperturbed expectation value of H'. According to (8), the general expression is

$$E_1=\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(-1)^{n_1+1}}{n_1!n_2!}\times\langle\mathbf{N}^{(n_1)}\rangle[n_1]\mathbf{T}^{(n_1+n_2)}[n_2]\langle\mathbf{N}^{(n_2)}\rangle. \tag{27}$$

If the molecules are cylindrically symmetric, we may write instead

$$E_1=\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(-1)^{n_1+1}}{n_1!n_2!}T^{(n_1+n_2)}(z_1{}^{n_1}z_2{}^{n_2})\mathfrak{N}^{(n_1)}\mathfrak{N}^{(n_2)}, \tag{28}$$

where

$$T^{(n_1+n_2)}(z_1{}^{n_1}z_2{}^{n_2})=-\frac{\partial^{n_1+n_2}}{\partial z_1{}^{n_1}\partial z_2{}^{n_2}}\left(\frac{1}{R}\right), \tag{29}$$

and where $\mathfrak{N}^{(n_1)}$ and $\mathfrak{N}^{(n_2)}$ are the molecular multipole moments of order n_1 and n_2, respectively. The axes of cylindrical symmetry are denoted by z_1 and z_2. The "mixed" tensor components (29) may be evaluated directly by applying Maxwell's theory of poles.[21] Suppose that in three-dimensional space the directions of n axes $h_1, h_2, \cdots, h_n$ are given with respect to a fixed Cartesian coordinate system. Let λ_i denote the cosine of the angle between the radius vector $\mathbf{R}$ and the direction of h_i, and let μ_{ij} denote the cosine of the angle between h_i and h_j. Then we have

$$\frac{\partial^n}{\partial h_1\partial h_2\cdots\partial h_n}\left(\frac{1}{R}\right)=\frac{(-1)^n}{R^{n+1}}\sum_{m\leq n/2}(-1)^m\frac{(2n-2m)!}{2^{n-m}(n-m)!}\sum(\lambda^{n-2m}\mu^m), \tag{30}$$

where the summation extends over a range of integral values for m from $m=0$ to $m=n/2$ or $(n-1)/2$ according as n is even or odd. The symbol $\sum(\lambda^{n-2m}\mu^m)$ stands for the sum of the products of m of the quantities μ and $(n-2m)$ of the quantities λ, each suffix occurring only once. The T components in (29) represent therefore only a special case of (30), namely with n_1 coinciding axes z_1 and n_2 coinciding axes z_2.

If the charge distributions deviate from cylindrical symmetry, the first-order interactions are no longer given by (28). In such cases one may still derive expressions similar to (28) by making use of the specific symmetry elements involved (for example for "planar" molecules). The scalar molecular quantities at which one arrives in this manner may again be defined as molecular multipole moments, although their definition will differ from that for the quantities $\mathfrak{N}^{(n)}$. In the most general case we may compute $\langle H'\rangle$ and obtain a multipole series which consists either of a finite or an infinite number of terms, depending on the analytic form for the charge density. The expansion (19) of $\rho(\mathbf{r}_i)$ now contains also the Legendre associated functions. The order of the last term of the series is the same as that of the highest Legendre function occurring in $\rho(\mathbf{r}_i)$. This property follows also readily from the tensor formalism. Note that in (27),

$$\langle\mathbf{N}^{(n_1)}\rangle[n_1]\mathbf{T}^{(n_1+n_2)},$$

is a spherical harmonic of degree n_1 in x_1, y_1, z_1, since it is proportional to

$$\langle\mathbf{r}_1{}^{n_1}\rangle[n_1]\nabla^{n_1}\nabla^{n_2}(1/R)=\langle(\mathbf{r}_1\cdot\nabla)^{n_1}\rangle\nabla^{n_2}(1/R); \tag{31}$$

we abbreviate this harmonic by $Y_{n_1}(x_1,y_1,z_1)$. We suppose that the charge density of distribution 1, $\rho(x_1,y_1,z_1)$, may be represented by an absolutely convergent power series, each term being of the form

$$x_1{}^{p_1}y_1{}^{p_2}z_1{}^{p_3}g(r_1), \tag{32}$$

with $p_1+p_2+p_3\leqslant s$. It is assumed that the radius of convergence is infinite and that the power series is uniformly convergent on the surface of a sphere with arbitrary radius. We multiply (32) by (31) and integrate over the surface of a sphere with radius r_1. The result is given in Hobson's integral theorem[22] (we omit subscripts 1):

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[21] E. W. Hobson, reference 6, pp. 129 ff.; T. M. MacRobert, *Spherical Harmonics* (Dover Publications, New York, 1947), p. 231 ff.

[22] E. W. Hobson, reference 6, p. 154 ff.

$$\iint x^{p_1}y^{p_2}z^{p_3}Y_n(x,y,z)dS$$
$$=4\pi r^{s+n+2}\frac{2^n[\frac{1}{2}(s+n)]!}{[\frac{1}{2}(s-n)]!(s+n+1)!}$$
$$\times\nabla^{s-n}Y_n\left(\frac{\partial}{\partial x},\frac{\partial}{\partial y},\frac{\partial}{\partial z}\right)x^{p_1}y^{p_2}z^{p_3}, \quad (33)$$

where x, y, and z are put equal to zero after the operation is performed. The result is zero if $s<n$ (and also if $s-n$ is odd). Thus the multipole series (27,28) terminate with the term $n_1=s$; this result holds, under the above conditions for the charge density, even as s approaches infinity. A characteristic property of first-order interactions between permanent multipole moments is that, if E_1 is averaged over the orientations of either one of the two charge distributions, the result is zero, except for the term $n_1=n_2=0$. This follows, as was established before (Sec. IIA), from the properties of the T tensors.

IV. SECOND-ORDER INTERACTIONS

In conventional perturbation theory, the second-order interaction energy is given by the matrix sum

$$E_2=\sum_{\kappa}{}'\frac{H_{0\kappa}'H_{\kappa 0}'}{E_0-E_\kappa}, \quad (34)$$

where κ labels the energy eigenstates of the system. E_κ is the energy eigenvalue of the state κ, and the summation extends over all excited states. To simplify the evaluation of (34), it is assumed that the ground state is nondegenerate and that the excited levels lie in a relatively narrow band on the energy scale (narrow compared with the average distance to the ground level). In that case the energy denominators may be replaced by a single "average excitation energy" of the system,[23,24] and the problem reduces to the computation of the first and second powers of the perturbation Hamiltonian in the ground state. We need here only be concerned with $\langle H'^2\rangle$. For "nonoverlapping" charge distributions the general term in $\langle H'^2\rangle$ may be written as

$$\frac{(-1)^{k_1+l_1}}{k_1!k_2!l_1!l_2!}\langle\mathbf{N}^{(l_1)}\mathbf{N}^{(k_1)}\rangle[k_1]\mathbf{T}^{(k_1+k_2)}[k_2]$$
$$\times\langle\mathbf{N}^{(k_2)}\mathbf{N}^{(l_2)}\rangle[l_2+l_1]\mathbf{T}^{(l_1+l_2)}. \quad (35)$$

We consider first *spherical* distributions. It follows from (35) that in this case $k_1=l_1$ and $k_2=l_2$. This may be seen by noting that

$$\mathbf{N}^{(l_1)}[l_1]\mathbf{T}^{(l_1+l_2)}, \quad (36)$$

is a spherical harmonic of degree l_1 in x_1, y_1, z_1; on the other hand,

$$\mathbf{N}^{(k_1)}[k_1]\mathbf{T}^{(k_1+k_2)},$$

is a spherical harmonic of degree k_1 in x_1, y_1, z_1. However, the surface integral of the product of two spherical harmonics of unequal degree is zero. [The same result follows directly when we apply the integral theorem (33) twice to (35).] Accordingly, there are no "mixed" second-order multipole interactions between spherically symmetric distributions of charge. Next we choose an arbitrary component of $\mathbf{N}^{(l_1)}$, say $x_1{}^py_1{}^qz_1{}^r$, multiply by the spherical harmonic (36), and integrate over the surface S of a sphere with radius r_1. If we abbreviate (36) by $Y_{l_1}(x_1,y_1,z_1)$, we obtain for the surface integral, according to Hobson's theorem (33),

$$\iint x_1{}^py_1{}^qz_1{}^rY_{l_1}(x_1,y_1,z_1)dS$$
$$=4\pi r_1{}^{2l_1+2}\frac{2^{l_1}l_1!}{(2l_1+1)!}Y_{l_1}\left(\frac{\partial}{\partial x_1},\frac{\partial}{\partial y_1},\frac{\partial}{\partial z_1}\right)x_1{}^py_1{}^qz_1{}^r, \quad (37)$$

evaluated at the origin $x_1=y_1=z_1=0$. After inserting (37) and (36) into (34), one obtains

$$\langle H'^2\rangle=\sum_{l_1=0}^{\infty}\sum_{l_2=0}^{\infty}\frac{2^{l_1+l_2}\langle r_1{}^{2l_1}\rangle\langle r_2{}^{2l_2}\rangle}{(2l_1+1)!(2l_2+1)!}$$
$$\times\mathbf{T}^{(l_1+l_2)}[l_1+l_2]\mathbf{T}^{(l_1+l_2)}. \quad (38)$$

Thus the scalar product of two T tensors occurs in the expression for the second-order energy between two spherically symmetric charge distributions. There are several methods for deriving a more explicit expression for the tensor product; the simplest one is the following. Consider the identity

$$(\boldsymbol{\nabla}\cdot\boldsymbol{\nabla})^n(1/R^2)=(2n)!/R^{2n+2}.$$

The left-hand member of this equation gives upon evaluation, remembering that

$$\nabla^2(1/R)=0,$$
$$(\boldsymbol{\nabla}\cdot\boldsymbol{\nabla})^n(1/R^2)=2^n\boldsymbol{\nabla}^n(1/R)[n]\boldsymbol{\nabla}^n(1/R)$$
$$=2^n\mathbf{T}^{(n)}[n]\mathbf{T}^{(n)}.$$

Thus we find that

$$\mathbf{T}^{(n)}[n]\mathbf{T}^{(n)}=(2n)!/2^nR^{2n+2}. \quad (39)$$

Substitution of (39) into (38) gives

$$\langle H'^2\rangle=\sum_{l_1=0}^{\infty}\sum_{l_2=0}^{\infty}\frac{(2l_1+2l_2)!\langle r_1{}^{2l_1}\rangle\langle r_2{}^{2l_2}\rangle}{(2l_1+1)!(2l_2+1)!R^{2l_1+2l_2+2}}. \quad (40)$$

If the distribution 2 consists of a point charge (a proton, for example), then $l_2=0$ and (40) goes over into

$$\sum_{l_1=0}^{\infty}\frac{\langle r_1{}^{2l_1}\rangle}{(2l_1+1)R^{2l_1+2}}; \quad (41)$$

this expression was first given by Brooks,[7] using Legendre's polynomials. In case of a harmonic oscillator

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

[24] J. P. Vinti, Phys. Rev. **41**, 813 (1932); A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) **A240**, 284 (1957).

it is found[7] that the second-order energy is still proportional to (41), except that each term in the summation is divided by (l_1+l_2). For a Gaussian distribution, $\rho(r)\sim\exp(-\beta^2r^2)$, we have

$$\langle r^{2l}\rangle\sim(2l+1)!/2^{2l}l!\beta^{2l}; \tag{42}$$

whereas, for a charge density proportional to $\exp(-\beta r)$,

$$\langle r^{2l}\rangle\sim(2l+2)!/2\beta^{2l}. \tag{43}$$

When (42) and (43) are inserted into (40) and (41), or into the expression representing second-order interactions between harmonic oscillators, it is found that the series *diverge* as l for a Gaussian distribution, and as l^2 for a charge density $\sim\exp(-\beta r)$, for all values of R. The divergent character of second-order multipole series was first pointed out by Brooks.[7]

The second-order interactions between *non*spherical distributions of charge do not exhibit any new characteristics as far as the asymptotic properties of the multipole series is concerned; we shall not discuss them in detail. To illustrate the use of the tensor formalism in this case, let z_1 and z_2 denote the axes of cylindrical symmetry of two molecules. We suppose that these molecules are identical and do not possess permanent electric dipole moments. Further, let κ denote the anisotropy factor of the polarizability; we indicate by $\langle p^2\rangle_{\mathrm{Av}}$ one-third of the sum $\langle p_z^2\rangle+2\langle p_x^2\rangle$. For $k_1=l_1=k_2=l_2=1$ (second-order dipole interactions) the expression (35) reads, if we replace the symbol $[n]$ for $n=1$, 2 by the more conventional notation $(\cdot)$ and $(:)$,

$$\begin{aligned}\langle\mathbf{p}_1\mathbf{p}_1\rangle\cdot\mathbf{T}^{(2)}\cdot\langle\mathbf{p}_2\mathbf{p}_2\rangle:\mathbf{T}^{(2)}\\ =\langle p^2\rangle_{\mathrm{Av}}{}^2\{(1-\kappa)^2\mathbf{T}^{(2)}:\mathbf{T}^{(2)}+3\kappa(1-\kappa)[(\mathbf{T}^{(2)}\cdot\mathbf{T}^{(2)})(z_1z_1)\\ +(\mathbf{T}^{(2)}\cdot\mathbf{T}^{(2)})(z_2z_2)]+9\kappa^2[T^{(2)}(z_1z_2)]^2\}.\end{aligned} \tag{44}$$

If it is assumed that the fundamental frequencies parallel and perpendicular to the length axis of the molecule may be taken as equal, then (44), divided by -2 times the average excitation energy, represents the second-order London dipole interaction. The equivalent form of (44) in terms of the orientations of the molecular symmetry axes was first derived by de Boer and Heller.[25] Anisotropic components of higher-multipole interactions may be evaluated in a similar manner. Note that the first-order expressions contain z components of one T tensor, whereas in second order the z components of the product of two T tensors occur.

V. ASYMPTOTIC PROPERTIES OF THE MULTIPOLE SERIES

It was established before that the first-order multipole series (26), representing the electrostatic potential at distance $\mathbf{R}$ from the center of an anisotropic Gaussian charge distribution, is divergent for all values of R. In addition, the second-order multipole series (40) was found to be divergent both for a Gaussian charge distribution $\sim\exp(-\beta^2r^2)$ and for a simple exponential $\exp(-\beta r)$. It is therefore important to analyze the relation between the multipole representations and the (correct) finite energy of interaction between distributions of charge.

Brooks[7] asserted that the second-order series diverges because of the use of Taylor's expansion for $r_i<R$ in regions of space where this condition is not satisfied. He removed the divergence by limiting the integration to the region $(r_i<R)$ of configuration space, neglecting contributions to the energy of interaction outside that region. The new series is then convergent for $R>0$. However, it was pointed out by Dalgarno and Lewis[8] that Brooks' assumption concerning the origin of the divergence is incorrect. The second-order energy between a ground-state hydrogen atom and a proton had been evaluated by Roe[26] without the use of Taylor's expansions: the result, expressed in atomic units, is

$$\begin{aligned}\langle H'^2\rangle-\langle H'\rangle^2=(2/R)\{(2R+1)\exp(-2R)\,\overline{\mathrm{Ei}}(2R)\\ +(2R-1)\exp(+2R)\,\mathrm{Ei}(-2R)\\ -2/R+4(1+1/R)\exp(-2R)\\ -2R(1+1/R)^2\exp(-4R)\}.\end{aligned} \tag{45}$$

In this expression $\overline{\mathrm{Ei}}(x)$, $\mathrm{Ei}(-x)$ are the exponential integrals

$$\overline{\mathrm{Ei}}(x)=\int_{-\infty}^{x}t^{-1}\exp(+t)dt;$$

$$\mathrm{Ei}(-x)=\int_{x}^{+\infty}t^{-1}\exp(-t)dt.$$

When (45) is expanded as a series of inverse powers of R and exponentially decreasing terms are neglected in the result, then it reduces to the same divergent series (41). Thus, *if the point of reference lies inside the charge distribution, the second-order series diverges, whether or not a Taylor expansion is employed for H'.* Apparently the divergence is inherent in the type of expansion used (power series in R^{-1}). It can now readily be shown that the series (41) is the asymptotic expansion in inverse powers of R of the true energy of interaction; this was already concluded by Brooks. If a real function $f(R)$ of a real variable R can be formally expanded as

$$f(R)=\sum_{n=0}^{\infty}a_n/R^n, \tag{46}$$

and if f_N represents the sum of the first N terms of this series, then (46) is said to be the asymptotic expansion of $f(R)$ if

$$\lim_{R\to\infty}R^N(f-f_N)=0,$$

for all positive N (Poincaré). It follows that the series (41) is the asymptotic expansion of (45) and, since

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[25] J. H. de Boer and G. Heller, Physica 4, 1045 (1937).

[26] G. M. Roe, Phys. Rev. 88, 659 (1952).

asymptotic expansions are unique,[27] (41) is the appropriate representation of (45) even though the series diverges. For each value of the distance R there is an optimal number of terms of the series to be used to represent $f(R)$. The error involved is of the order of the last term retained; the smaller R, the larger the error and the smaller the optimal number of terms. To minimize the error it is usual practice to include for a given R all terms up to the smallest one and to add half of the smallest term.[28] If this proves too lengthy a procedure then other approximate methods are available.[29]

It will now be shown that similar properties are exhibited by the divergent *first-order* multipole series (26). Let x, y, z denote the Cartesian coordinates of an element of charge of an anisotropic Gaussian distribution; the normalized charge density is given by (22) and the z axis coincides with the axis of cylindrical symmetry of the distribution. We evaluate the electrostatic potential $\langle V(\mathbf{R})\rangle$ for convenience along the z axis, and we restrict ourselves to such large values of R that terms decreasing exponentially with increasing R may be ignored. In terms of the coordinates $u=|\mathbf{R}-\mathbf{r}|$ and z, the expression for the potential is

$$\langle V(R)\rangle = 2\alpha^2\gamma\pi^{-\frac{1}{2}}\exp(+\alpha^2R^2) \times\int_{-\infty}^{+\infty}\exp[(\alpha^2-\gamma^2)z^2-2\alpha^2Rz]dz \times\int_{|R-z|}^{\infty}\exp[-\alpha^2u^2]du. \quad (47)$$

Next, $\exp[(\alpha^2-\gamma^2)z^2]$ is expanded as a power series in z^2, which gives

$$\langle V(R)\rangle = 2\alpha^2\gamma\pi^{-\frac{1}{2}}\exp(+\alpha^2R^2)\sum_{n/2=0}^{\infty}\frac{(\alpha^2-\gamma^2)^{n/2}}{(n/2)!}I_n, \quad (48)$$

for even n, with

$$I_n=\int_{-\infty}^{+\infty} z^n\exp(-2\alpha^2Rz)dz\int_{|R-z|}^{\infty}\exp(-\alpha^2u^2)du. \quad (49)$$

When I_n is integrated by parts and only those terms which do not decrease exponentially with increasing R are retained, then the result is

$$I_n=\exp(-\alpha^2R^2)\sum_{p=0}^{n/2}\frac{n!}{(n-2p)!(2\alpha^2R)^{2p+1}} \times\int_{-R}^{+R}\exp(-\alpha^2z^2)dz. \quad (50)$$

Next we insert (50) into (48), rearrange the resulting double summation, and find, after some minor manipulations (again ignoring exponentially decreasing terms),

$$\langle V(R)\rangle=\sum_{p=0}^{\infty}\left(\frac{1}{\gamma^2}-\frac{1}{\alpha^2}\right)^p\frac{(2p)!}{2^{2p}p!R^{2p+1}}. \quad (51)$$

This result is just the same as that obtained from the multipole expression (26) for $\cos\theta=1$. Since we have not, in the present derivation, made use of a Taylor expansion for $V(R)$, we conclude that the divergent character of the first-order multipole series (26) is *not* induced by the use of a multipole Taylor expansion in regions of configuration space where it has no validity, but that it is a characteristic of the series in inverse powers of R. It follows that (26) is the asymptotic expansion of (51). The smallest term in the series will occur approximately for the integral value of n nearest to $2(\beta R)^2$. The order of this term is the higher the larger the value of R; the error involved is of the same order of magnitude as that of the last term retained.

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[27] H. Jeffreys and B. S. Jeffreys, *Methods of Mathematical Physics* (Cambridge University Press, New York, 1950), p. 500.

[28] Jeffreys and Jeffreys, reference 27, p. 502.

[29] J. Airey, Phil. Mag. **24**, 521 (1937); D. Shanks, J. Math. Phys. **34**, 1 (1955); Ph.D. thesis, University of Maryland, 1954 (unpublished).